Synthesis, mechanism studies of rhodium complexes and electrochemical oxidation, spectroscopic properties of phenol derivatives

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**NANYANG
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**Synthesis, Mechanism Studies of Rhodium
Complexes and Electrochemical Oxidation,
Spectroscopic Properties of Phenol Derivatives**

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Abbreviations

AC	aminochrome
Ar	aryl
α -TOA	α -Tocopherol acetate
α -TOH	α -tocopherol
ATR	attenuated total reflection
Bu	butyl
Cp*	1,2,3,4,5-Pentamethylcyclopentadienyl
CV	cyclic voltammetry
CPE	controlled potential electrolysis
DISP	disproportionation
DA	dopamine (4-(2-Aminoethyl)benzene-1,2-diol)
DAQ	dopamine <i>ortho</i> -quinone
DTBMP	2,6-di-tert-butyl-4-methoxyphenol
DOPP	di- <i>n</i> -octyl phenylphosphonate
DBS	di- <i>n</i> -butyl sebacate
DBP	di- <i>n</i> -butyl phthalate
ECE	electron transfer, Chemical reaction, Electron transfer.
Eq.	equivalents
Fc	ferrocene
FIM	fixed interference method
GC	glassy carbon

HBA	hydrogen-bonding acceptor
KSE	kinetic solvent effects
KTBPB	potassium tetrakis(4-biphenyl)borate
L-Dopa	L-3,4-dihydroxyphenylalanine
LAC	leucoaminochrome
MC	4-methylcatechol
NBD	norbornadiene
NPOE	2-nitrophenyl octyl ether
POH	phenol
PVC	poly vinyl chloride
Pt	Platinum
SSM	separate solution method
VT NMR	variable-temperature NMR
TBE	tert-butylethylene
TMP	2,4,6-trimethylphenol
TTBP	2,4,6-tri-tert-butylphenol

Summary

Part I

A series of rare five-coordinate organorhodium(III) intermediates $[\text{Rh}(\text{N}^{\wedge}\text{C})(\text{PAr}_3)_2\text{CH}=\text{CHR}]\text{PF}_6$ ($\text{N}^{\wedge}\text{C}$ = benzo[*h,f*]quinoline, benzo[*h*]quinoline, 2-phenylpyridine, R = *para*-Ph-(SO₂CF₃, CF₃, NO₂, Cl, F, H, CH₃, OCH₃), CH₂Ph, CH₂CH₂Ph, Ar = *para*-Ph-(OCH₃, CH₃, F)) and subsequent C–C coupling rhodium(I) complexes $[\text{Rh}(\text{N}^{\wedge}\text{C}-\text{CH}=\text{CHR})(\text{PAr}_3)_2]\text{PF}_6$ have been isolated and fully characterized. The total mechanism of C–H activation and subsequent C–C reductive elimination from the rhodium center has been proposed and the electronic effects of reactive ligands CH=CHAr and ancillary ligands PAr₃ on the rate of the C–C reductive elimination reactions from the five-coordinate intermediates were studied. The absolute rate of C–C reductive elimination has been measured and the rate decrease as the vinyl ligands with more electron-withdrawing groups and the ancillary ligands PAr₃ with more electron-donating groups. We also measured the kinetics in different solvents like CD₂Cl₂, THF-*d*₈ and acetone-*d*₆ in order to probe the impact of the solvent's polarity and donating ability on the rate of the reaction. The result shows that the coordinated solvent can accelerate the rate of reductive elimination step.

Chelation-assisted activation of C–X bonds (X = Cl, Br, and I) took place in the reaction of $[\text{Rh}(\text{PPh}_3)_2(\text{acetone})_2]\text{PF}_6$ and 2-(2-halophenyl)pyridine or 10-halobenzo[*h*]quinoline. A series of 16-electron five-coordinate cationic

rhodium(III) monohalide complexes was synthesized at room temperature. Neutral octahedral rhodium(III) dihalide complexes were obtained when the corresponding cationic monohalide complexes were further heated in acetone. Rhodium and iridium diiodides with these cyclometalation motifs could be alternatively synthesized from the reaction of the corresponding cyclometalated hydride complexes and I₂. X-ray crystal structures of representative monohalide and dihalide complexes are reported. Octahedral rhodium(III) dihalide complexes are active catalysts for the dimerization of terminal alkynes, while 16-electron cationic rhodium(III) monohalides are inactive.

Part II

Dopamine (and 4-methylcatechol) was electrochemically oxidised in aqueous solutions and in the organic solvents *N*, *N*-dimethylformamide and dimethyl sulfoxide containing varying amounts of supporting electrolyte and water, to form dopamine *o*-quinone. It was found that the electrochemical oxidation mechanism in water and in organic solvents was strongly influenced by the buffering properties of the supporting electrolyte. In aqueous solutions close to pH 7, where pH buffers were not used, the protons released during the oxidation process were able to sufficiently change the localized pH at the electrode surface, to reduce the deprotonation rate of dopamine *o*-quinone and thereby slow down the conversion into leucoaminochrome. In *N*, *N*-dimethylformamide and dimethyl sulfoxide solutions in the absence of buffers, dopamine was oxidized to dopamine *o*-quinone

that survived without further reaction for several minutes at 25 °C. The voltammetric data obtained in the organic solvents were made more complicated by the presence of HCl in commercial sources of dopamine that also underwent an oxidation process.

α -Tocopherol (Vitamin E) can be electrochemically oxidized in a $-2e^-/-H^+$ process to form a phenoxonium ion that is long-lived in dry organic solvents such as acetonitrile and dichloromethane. The cyclic voltammetry experiments demonstrated that α -tocopherol underwent hydrogen-bonding reactions with relatively low levels of water in the acetonitrile, but in the presence of relatively high levels of water quickly reacts to form a hemiketal. Several other phenols were examined which displayed similar voltammetric features to α -tocopherol, suggesting that hydrogen-bonding interactions of phenols with trace amounts of water was a common occurrence in organic solvents. The H-bonding interactions of α -tocopherol with other hydrogen acceptors such as DMSO and pyridine were also examined and the similar results were obtained.

Several phenols with structures similar to vitamin E were oxidised and the intermediate species produced were characterised by *in situ* infrared and UV-vis spectroscopies. The Fourier transform infrared (FTIR) measurements were performed by chemically oxidising the phenols with 2 mol equivalents of $NO^+SbF_6^-$ in CH_3CN and recording the spectra between 1900 – 1300 cm^{-1} with an attenuated total reflectance (ATR) probe utilising a fiber conduit and a diamond composite sensor. The compounds that formed long-lived phenoxonium cations

displayed two IR absorbances at $1665 (\pm 15) \text{ cm}^{-1}$ and one at $1600 (\pm 10) \text{ cm}^{-1}$ associated with the carbonyl, symmetric ring stretch and asymmetric ring stretch modes. The phenoxonium cations also displayed a very strong absorbance at $1500 (\pm 20) \text{ cm}^{-1}$ that is possibly associated with a C–O stretch. One long term stable products of the phenols oxidation are the *para*-quinones which display solution phase IR absorbances at $1650 (\pm 10) \text{ cm}^{-1}$. *In situ* electrochemical UV-vis experiments performed during the oxidation of the phenols led to the detection of bands due to the phenoxonium cations at $295 (\pm 5) \text{ nm}$ and $440 (\pm 15) \text{ nm}$ and due to the *para*-quinones at $260 (\pm 10) \text{ nm}$. The concentration of the substrate and the water content of the solvent had a major effect on the yields of the intermediates and products that were produced during the oxidation reactions.

The voltammetric properties of several substituted calix[4]arenes were examined in acetonitrile and dichloromethane. The compounds that contained one phenolic group in the macrocyclic cavity were able to be electrochemically oxidised at positive potentials. In acetonitrile, cyclic voltammetry experiments indicated that the phenolic compounds were oxidised in a two-electron (one-proton) chemically irreversible process, while in dichloromethane, the oxidation process occurred in a one-electron chemically reversible process to most likely form the radical cations. In both solvents, longer timescale (minutes to hours) electrolysis experiments indicated that the oxidation process occurred by two-electrons per molecule, to form reactive diamagnetic cations that could not be reduced back to the starting materials. The ion sensing properties of the

compounds were investigated in polymer membrane ion-selective electrodes and it was found that they responded reversibly in a Nernstian fashion to Groups IA and IIA metals and had the highest selectivity to the cesium cation.

Part I

Synthesis and Mechanism Investigation of C–H, C–X Activation and C–C Coupling *via* Rhodium Complexes

Chapter 1

Introduction of Reactions and Mechanism of Rhodium Complexes Involving C–H Activation and C–C Coupling

1. Introduction of history and development of rhodium chemistry

Transition metal-catalysts have been extensively applied to organic synthesis during the past several decades, which has played a dramatically important role in the advancement of modern science and technology by enabling the preparation of natural and target of chemicals, medicinal, biological, environmental, and materials. Among the reported examples, palladium, ruthenium and rhodium catalysts that are widely used for constructing new carbon–carbon or carbon–heteroatom bonds have attracted much attention for their amazing and powerful catalytic ability. Recently, these three noble transition metal catalysts were successfully introduced for the C–H bond direct functionalization reactions, which have the potential to emerge as one of the most efficient tools in organic synthesis. ^[1-3]

Organorhodium chemistry has a long history, which can date back to its emergence as the metal catalyst in carbonyl complex. Historically, commercial hydroformylation was carried out under a cobalt carbonyl complex catalyst. However, this catalyst was gradually replaced by a more active rhodium catalyst, which remains the one predominantly utilized today. An important example is the

Monsanto process, which is a rhodium-catalyzed carbonylation reaction developed in early 1970's for the preparation of acetic acid from methyl iodide.^[4] The discovery of Wilkinson's catalyst by Professor Wilkinson in the mid of 1960's proved to be the milestone of the development of modern organorhodium chemistry, since its discovery opened the new field of homogeneous hydrogenation.^[5] This development ultimately led to the remarkable process in asymmetric hydrogenation, as exemplified by the commercial production of L-Dopa by rhodium-catalyzed asymmetric hydrogenation developed in 1974 by Monsanto.^[6]

Although the early developments in hydroformylation and the discovery of Wilkinson's catalyst, progress in organorhodium chemistry seemed to be somewhat slower than that of organopalladium chemistry. Nonetheless, organorhodium chemistry is now rapidly developed in organic synthesis, a number of new rhodium-catalyzed reactions, offering unique synthetic methods that are often complimentary to those of palladium and ruthenium. These new reactions involve enantioselective hydrogenation (Zhang),^[7] hydroboration (Brown)^[8] reactions, C–C bond forming reactions such as cycloisomerization^[9] and cyclotrimerization (Tanaka),^[10] conjugate addition (Hayashi) ^[11] and other carbocyclizations and cycloadditions.^[3]

2. Introduction of organorhodium intermediates involved in chelation-assisted C–H activation and C–C formation.

2.1 Introduction of intermediates involved in Rh(I)-catalyzed C–H

activation and C–C formation reactions. In the field of C–C bond coupling reactions that proceed *via* direct C–H bond activation, rhodium catalysts stand out for their wide functional group tolerance and range of synthetic utility. Among various methods to activate the C–H bond with transition rhodium catalysts, a chelation-assisted system *via* cyclometalation is considered to be one of the most promising ways for high selectivity. Usually nitrogen, oxygen or phosphine atom is common as a chelator. In the past decade, lots of rhodium-catalyzed methods for chelation-assisted C–H activation and subsequent C–C formation have been reported.^[12] Although the field of the rhodium-catalyzed chelation-assisted C–H activation and C–C coupling reactions were extensively investigated in recent years, the scope and selectivity are still limited in some extent. The general profile of the mechanism is known, firstly the heteroatom (N, O, P) of the substrate coordinates to the electron rich rhodium center, then facile C–H bond activation provides a five-membered metallacyclic hydride organorhodium complex **2**, dissociation ancillary ligand L followed by alkene or alkyne coordination and hydride migratory to give intermediate **3** containing two Rh–C bonds. The last and most important step is reductive elimination from metal center to form C–C bond (scheme 1). However, the intermediates involved in the reactions are highly reactive and unstable, thus difficult to isolate and characterize these intermediates. Only a few examples of rhodium intermediates have ever been isolated and characterized.^[13] While the exact intermediates, the detailed mechanism and the controller effect are still not very clear. Therefore, investigation and understanding

of detailed mechanism involved in the reactions of C–H bond activation and C–C bond formation are very important to well design and control the reactions in organic synthesis.

Scheme 1. Mechanism of chelation-assisted C–H activation and C–C formation.

Rhodium hydride complexes *via* chelation-assisted C(sp²)–H bond activation have been investigated by several groups. In the late 1970's, Suggs reported that the chelation-assisted aldehydic C–H bond activation *via* the reaction of Rh(PPh₃)₃Cl complex with quinoline-8-carbaldehyde to form a five-membered metallacycle **2a**. **2a** are quite stable to prevent the decarbonylation reaction (eq.1).^[14]

Olefins or alkynes could react with the hydride intermediates undergoing the hydrometalation, following a reductive elimination from metal center to give the ketone products.^[15] The mechanism of this catalyzed process has been proposed by Jun and Kang.^[15d] The intermediate metallacycle **2b** has been isolated and characterized owing to its relative stability. However, the intermediate **3b** was not isolated or characterized by experiments due to its high reactivity, which only was proposed according to the catalytic products (Scheme 2).

Scheme 2. Mechanism of chelation-assisted hydroacylation of olefin catalyzed by Wilkinson's catalyst.

In the last two decades, Lim and Kang explored extensively and did pioneering work on the chelation-assisted alkylation and alkenylation of phenylpyridines *via* direct C–H activation by using rhodium(I) complexes.^[16] (eq. 3 and eq. 4). Although the mechanism has been proposed (Scheme 1), the analogous rhodium hydride complexes **2** and intermediates **3** were not isolated and characterized. In order to better understand the mechanism and disclose the steric and electronic effects of the phosphorous ligands on the rate of alkylation, different Tolman's cone angle (steric) and the pK_a (electronic) phosphorus(III) were chosen to study the effect of ligands toward the rhodium center. The results obtained are listed in Table 1.^[16] These results show that alkylation of 3-methyl-2-phenylpyridine with alkenes *via* aromatic C–H bond activation depends to a greater extent on the steric factor (cone angle) of phosphorus(III) ligands than on the electronic factor. The more bulky ligands on the rhodium center can accelerate the C–C coupling products removal from the metal center.

Table 1. The results of alkylation of 3-methyl-2-phenylpyridine by various phosphorous(III)

ligands ^a				
Run	Phosphine ligand	pK _a	Cone angle/ ^o	GC yield (%)
1	(EtO) ₃ P	3.31	109	4
2	Me ₃ P	8.65	118	21
3	(PhO) ₃ P	-2.00	128	6
4	Bu ₃ P	8.43	132	40
5	(<i>p</i> -Tolyl) ₃ P	3.84	145	70
6	Ph ₃ P	2.73	145	80
7	Cy ₃ P	9.70	170	92

^a1b: [(C₈H₁₄)₂RhCl]₂; L: Bu'CH=CH₂ = 1:0.05:0.3:5; 115 °C, 17 h, THF

In recent years, the imine group has attracted increasing attention and wider applications in C–H bond functionalization by Rh(I) catalysts. The rhodium-catalyzed alkylation and alkenylation of N-benzyl aryl ketimines have been reported by Jun and coworkers (eq. 5 and eq. 6).^[17, 18] This method can tolerate a broader scope of olefin than Ru-catalyzed alkylation of arene ketones. Both terminal alkynes and diphenylacetylene can afford the desired products in good yields. Mechanistically, rhodium hydride complex **2c** was generated *via ortho* C–H bond activation, following an insertion of olefin into the Rh–H bond providing the metallacycle intermediate **3c** which was stabilized by the coordinated carbonyl group (Scheme 3). It was speculated that the complex **2c** should be formed and be relatively stable. However, intermediates **2c** and **3c** were not isolated and characterized by the authors. To our best knowledge, only a few pincer-ligated other transition metal intermediates **3** have been reported to date^[13] and no rhodium intermediate **3** has been isolated and characterized yet.

Scheme 3. Intermediates **2c** and **3c** involved in alkylation of arene ketimines.

Very recently, in order to better understand the detailed mechanism about direct synthesis of dihydropyridines and pyridines by using imines and alkynes *via* C–H activation, Bergman and Ellman with co-workers synthesized (proposed) a rhodium hydride complex **2d** (Scheme 4),^[19] which firstly coordinates to the alkyne and subsequent a migratory insertion into the Rh–H bond providing the intermediate **3d**. At last reductive elimination provides the azatriene intermediate, which undergoes an electrocyclization to afford the dihydropyridine product. However, it is also very difficult to isolate **3d** complex during the catalytic process.

Scheme 4. Proposed mechanism of Wilkinson's complex catalyzed reaction of imines and

alkynes.

2.2 Intermediates involved in Rh(III)-catalyzed C–H activation and C–C formation. In 1987, Maitlis reported one cyclometallated benzoate complex obtained from the reaction of benzoic acid with $\text{Cp}^*\text{RhMe}_2(\text{Me}_2\text{SO})$ (Scheme 5).^[20] Further study for the mechanism of the reaction showed that a rhodium-benzonate complex **6a** could be detected at low temperature after an anionic ligand exchange. After dissociation of one mole of dimethyl sulphoxide, which followed by an *ortho* C–H activation of the aromatic ring and elimination of one mole of methane, a five-membered cyclometallated rhodium complex **8a** was obtained. The complex **8a** is quite stable and could be isolated and characterized at room temperature. The authors proposed that the process *via* rhodium-benzonate **6a** to five-membered cyclometallated rhodium complex **8a** probably first undergoes an oxidative addition of Rh(III) to generate the Rh(V) hydride **7a** intermediate and then undergoes a reductive elimination to give **8a**. The Rh(V) intermediate has not been detected yet and no detail studies about Rh(V) have ever been explored, although the oxidation state has been implicated in a number of reactions already.^[21]

Scheme 5. Mechanism of cyclometallation reaction of Rh(III) and benzoic acid.

There are two most likely mechanisms for the C–H activation in Cp*M(III) (M = Ir, Rh) system, electrophilic substitution and concerted oxidative addition (Scheme 6).^[22] These two different mechanisms have different requirements for electron density at the metal centers. Electrophilic substitution is favoured by electron deficient metal centers whilst oxidative addition prefers to occur at electron rich metal centers.

Scheme 6. Electrophilic substitution vs. oxidative addition mechanism in C–H activation

Recently, the reaction of Rh(III)-catalyzed insertion of alkynes into the cyclometallated rhodium intermediate **8** which followed a reductive elimination to give the isocoumarin products has been investigated (eq 7. Scheme 7).^[23] The co-catalyst Cu salt serves as the oxidant to regenerate Rh(I) back to Rh(III). The C–H activation step was proposed to undergo the concerted oxidative addition mechanism^[20] and there should be more detailed experimental investigation to support this mechanism.

Scheme 7. Proposed mechanism for Rh(III)-catalyzed isocoumarin synthesis.

Besides the carboxylate group can be used as a chelation-assisted group, N-containing group also can function as directing group in this system. Very Recently, Jones reported that benzylidenemethylamine, 2-phenylpyridine, and benzo[*h*]quinoline reacted with $[\text{Cp}^*\text{RhCl}_2]_2$ in dichloromethane at room temperature in the presence of NaOAc to provide metallacycles **8b**, **8c**, **8d** (Scheme 8). Insertion of alkynes into the Rh-C bond resulted in the formation of seven-membered metallacycles **9b**, **9c**, **9d**. At the end, these seven-membered metallacycles were mixed together with CuCl_2 in CH_2Cl_2 to give polycyclic isoquinolines in good yields. The mechanism of the reaction is similar with the proposed one as depicted in scheme 8.^[24a,b] Except the alkynes, Jones and co-workers found that alkenes could react with $[\text{RhCp}^*\text{Cl}_2]_2$ to give a six-membered rhodacycle, and the authors also investigated the regioselectivity and reactivity of the reaction.^[24c] The C-H activation step was proposed by the

author to undergo an electrophilic substitution process.^[22a]

Scheme 8. Synthesis of polycyclic isoquinoline salts by $[\text{RhCp}^*\text{Cl}_2]_2$.

In conclusion, a number of organorhodium intermediates involved in C–H bond activation and C–C bond formation reactions have been isolated and characterized. However, some important intermediates that possibly exist in the reactions, such as intermediate **3**, are still unavailable to isolate and characterize. Furthermore, the detailed mechanism and controller effects of the entire process are still not very clear, so it is important to investigate the intermediates and the detailed mechanism for extensive applications in synthesis and industry.

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Chapter 2

Mechanistic Study of Aryl–Vinyl Reductive Elimination from Rare Five-Coordinate Rh(III) Center

1. Introduction

Direct coupling of C–C bond *via* C–H bond activation and subsequent C–C reductive elimination from a transition metal complex has become one of the most important reactions in organometallic chemistry and has been widely applied in the organic synthesis in recent years.^[1-13] C–C reductive elimination is the critical and products release step in C–C coupling reactions. The importance of C–C coupling processes in homogeneous catalysis has prompted numerous studies of the mechanisms of C–H oxidative addition and C–C reductive elimination reactions. Experimental and computational study of C–C reductive elimination from palladium and platinum complexes have been explored considerably.^[14-18] But the mechanism and the controller effects of C–C reductive elimination from other transition metals (Ir, Rh, Ru, Os) are relatively less studied.^[19-25] In particular, the reported experiments and mechanism of the C–H activation and C–C reductive elimination from rhodium complexes are very rare.^[26,27] Despite this large research effort, however, it remains difficult to predict the detailed mechanistic pathways of these reactions.

We recently synthesized a series of stable rhodium(III) hydride complexes $[\text{Rh}(\text{N}^{\wedge}\text{C})(\text{PAr}_3)_2\text{H}(\text{acetone})]\text{PF}_6$ ($\text{N}^{\wedge}\text{C}$ = benzo[*h,f*]quinoliny, benzo[*h*]quinoliny,

2-phenylpyridinyl, Ar = *para*-Ph-(OCH₃, CH₃, F) through the reaction of [Rh(NBD)(PAr₃)₂][PF₆] with H₂ and tert-butylethylene and benzo[*h*]quinoline or 2-phenylpyridine.^[28] The dissociation of weakly coordinated acetone can make a vacant site for the coordination of alkenes or alkynes which can easily insert into the Rh–H bond. Therefore, the aryl–alkyl/vinyl coupling reaction probably takes place from the rhodium(III) center. We report here the studies of C–C coupling reaction of the rhodium hydride complexes with various alkynes. During the investigation of the mechanism of the total reaction involving C–H activation and subsequent C–C reductive elimination, we were so surprised to isolate rare five-coordinate organorhodium(III) complexes which only can be isolated in limited examples of pincer-ligated systems.^[20,25,29] Recently, the Goldman group reported a series of five-coordinate d₆ iridium complexes (PCP)Ir(R)(R)' (R = R' = Ph/Vi, Me/Me, Me/Vi, Me/CCPh, and Vi/CCPh, where Vi = *trans*-CH=CHPh)^[23,25] and explored the kinetics of elimination of different unsaturated organic ligands. As is known, C–C elimination from complexes with the common d₆ six-coordinate configuration generally proceeds *via* prior ligand loss, which greatly complicates any attempt to directly measure the rates of the specific elimination step.^[15,25] In our system, the intermediates were found to undergo C–C reductive elimination slowly at room temperature and obtain the stable C–C coupling Rh(I) complexes, thus offering an example of direct observation of reductive elimination from a five-coordinate d₆ metal center. The absolute rate of C–C reductive elimination and the electronic effects of different

reactive ligands and the ancillary ligands have also been measured and compared.

Scheme 1. The total reaction of C-H bond activation and C-C reductive elimination from Rh complexes.

Table 1. A series of intermediates and the coupling complexes

rhodium hydride complexes		five-coordinate intermediates	C-C coupling complexes
	1	2	3
	Ar	R	R
1A	1A-P ₁ : Ph	2A-P ₁ a: Ph	3A-P ₁ a: Ph
	1A-P ₂ : <i>p</i> -Ph-OCH ₃	b: <i>p</i> -PhSO ₂ CF ₃	b: <i>p</i> -PhSO ₂ CF ₃
	1A-P ₃ : <i>p</i> -Ph-CH ₃	c: <i>p</i> -PhCF ₃	c: <i>p</i> -PhCF ₃
	1A-P ₄ : <i>p</i> -Ph-F	d: <i>p</i> -PhNO ₂	d: <i>p</i> -PhNO ₂
		e: <i>o</i> -PhNO ₂	e: <i>o</i> -PhNO ₂
1B		f: <i>p</i> -PhCl	f: <i>p</i> -PhCl
		g: <i>p</i> -PhCH ₃	g: <i>p</i> -PhCH ₃
		h: <i>p</i> -PhOCH ₃	h: <i>p</i> -PhOCH ₃
		2A-P ₂ c: <i>p</i> -PhCF ₃	i: CH ₂ CH ₂ Ph
		2A-P ₃ c: <i>p</i> -PhCF ₃	j: CH ₂ Ph
1C		2A-P ₄ c: <i>p</i> -PhCF ₃	3A-P ₂ c: <i>p</i> -PhCF ₃
			3A-P ₃ c: <i>p</i> -PhCF ₃
			3A-P ₄ c: <i>p</i> -PhCF ₃
1D			
1B	1B-P ₁ : Ph	2B-P ₁ c: <i>p</i> -PhCF ₃	3B-P ₁ c: <i>p</i> -PhCF ₃
1C	1C-P ₁ : Ph	2C-P ₁ c: <i>p</i> -PhCF ₃	3C-P ₁ c: <i>p</i> -PhCF ₃
1D	1D-P ₁ : Ph	2D-P ₁ c: <i>p</i> -PhCF ₃	3D-P ₁ c: <i>p</i> -PhCF ₃

2. Results and Discussion

2.1 Synthesis of five-coordinate intermediates 2 $[Rh(N^{\wedge}C)(PAr_3)_2(CH=CHR)]PF_6$. All the procedures were performed under an argon atmosphere. The five-coordinate Rh(III) intermediates **2** $[Rh(N^{\wedge}C)(PAr_3)_2(CH=CHR)]PF_6$ were synthesized *via* the corresponding rhodium hydride complexes **1** $[Rh(N^{\wedge}C)(PAr_3)_2(acetone)H]PF_6$ with various terminal alkynes at $-20\text{ }^{\circ}C$ in anhydrous dichloromethane. The five-coordinate intermediates **2** in solution are unstable and undergo reductive elimination slowly at room temperature (Scheme 1). To isolate and identify the structure of the five-coordinate intermediates, the solvent dichloromethane was removed under salt ice bath at reduced pressure and then the residues were washed with diethyl ether to exclude the excessive alkynes, finally, orange precipitates were obtained in about 95% yield and were characterized by 1H , ^{13}C , and ^{31}P NMR spectroscopy (at $-20\text{ }^{\circ}C$) and elemental analysis. All the complexes that were synthesized including the starting materials, the five-coordinate intermediates and the coupling products are listed in Table 1.

In the 1H NMR spectrum of complex **2A-P1c** (Figure 1), a characteristic proton signal at $\delta 8.36$ (dt, $^3J_{HH} = 17.1\text{ Hz}$, $^3J_{PH} = 5.4\text{ Hz}$) is detected and assigned to H_1 on C_1 position of vinyl group $[Rh-CH_1=CH_2PhCF_3]$ due to its coupling with H_2 and phosphine atom. The other H_2 is detected at $\delta 5.13$ (d, $^3J_{HH} = 17.1\text{ Hz}$). The hydrogen coupling constant indicates the resulting vinyl group has a *trans* geometry. Signal 6.59 (d, $^3J_{HH} = 8.1\text{ Hz}$, 2H) is assigned to the H_3 on the phenyl group.

From the ^{13}C NMR spectrum of **2A-P₁f** (Figure 2), we can see there are two C atoms directly attached to the Rh and each C gives a triplet of doublets (td) at δ 145.53 (dt, $^2J_{\text{RhC}} = 40.2$ Hz, $^3J_{\text{PC}} = 9.6$ Hz) and δ 149.69 (dt, $^2J_{\text{RhC}} = 31.0$ Hz, $^3J_{\text{PC}} = 10.9$ Hz), the two signals can be distinguished by DEPT 135: one is a quaternary carbon and the other is a CH carbon. The quaternary carbon signal at δ 145.53 disappears in DEPT 135 spectrum. There are 4 high intensity peaks (*ipso*, *ortho*, *meta*, and *para*) for the 6 phenyl groups in the 2 PPh₃ ligands. One virtual coupling (virtual triplet) for the *ipso*-C of the phenyl groups in PPh₃ appears at δ 126.43 and the coupling constant is 24.3 Hz. In the ^{31}P NMR spectrum of **2A-P₁c** (Figure 3), a doublet signal (d, δ 23.7, $^1J_{\text{RhP}} = 112.4$ Hz) is observed for two equivalent phosphines, indicating their *trans* orientation.

Figure 1. ^1H NMR of **2A-P₁c** in CH_2Cl_2 .

Figure 2. ¹³C NMR of **2A-P1f** in CH₂Cl₂ at 255K.

Figure 3. ³¹P NMR of **2A-P1c** in CH₂Cl₂ at 255K.

and can be occupied by bubbling CO through the solution of dichloromethane at -20 °C (eq. 1). The six-coordinate Rh (III) complex **2A-P₁c-CO** [Rh(N[^]C)(PPh₃)₂-(CH=CHPhCF₃)(CO)]PF₆ (yellow) is relative stable at room temperature and the C–C reductive elimination can not occur which further indicate the five-coordinate intermediate prefers to undergo reductive elimination from the rhodium center.

2.2 Synthesis of complexes 3 [Rh(N[^]C–CH=CHR)(PAr₃)₂]PF₆. The aryl–vinyl coupling complexes **3** [Rh(N[^]C–CH=CHR)(PAr₃)₂]PF₆ were obtained *via* the corresponding five-coordinate rhodium intermediates **2** undergoing directly C–C reductive elimination at room temperature in anhydrous dichloromethane in 3-6 hours. All complexes **3** are stable at room temperature and have a good solubility in CH₂Cl₂, THF and acetone. The red precipitate complexes **3** were isolated quantitatively and were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy and elemental analysis. In the ¹H NMR spectrum of complex **3A-P₁a** (Ar = Ph, R = Ph) (Figure 5), two new doublet of doublets signals appear at δ 6.48 ppm and δ 5.50 ppm are assigned to the H₁ and H₂ on the vinyl group, according to the correlation showed in the spectra of HMQC and HMBC, the signal in high field is H₁. Their coupling constant (13.6 Hz) is slightly less than 16 Hz due to the change of the hybridization upon the alkene coordination, which can indicate that

the vinyl group connects with the aryl group.

From the ^{13}C NMR spectrum (Figure 6), we can see there are two C atoms of the vinyl group give a doublet of doublets at δ 78.6 (dd, $^2J_{\text{RhC}} = 19.9$ Hz, $^3J_{\text{PC}} = 6.2$ Hz) and a doublet at δ 85.0 (d, $^2J_{\text{RhC}} = 12.1$ Hz), the two signals can be distinguished by HMQE, the doublet signal δ 85.0 is correlated with the high field signal of H_1 . The two PPh_3 are different and have two sets of four relatively high intensity peaks (*ipso*, *ortho*, *meta*, and *para*) for the six phenyl groups ligands. The two *ipso*-C of the phenyl groups in PPh_3 appear as doublets at δ 130.6 and 130.9, the coupling constant being 45.8 Hz and 41.4 Hz.

Figure 5. ^1H NMR of **3A-P_{1a}** in CH_2Cl_2 at 295K.

Figure 6. ¹³C NMR of **3A-P₁a** in CH₂Cl₂ at 295K.

Figure 7. ³¹P NMR of **3A-P₁a** in CH₂Cl₂ at 295K.

In the ^{31}P NMR spectrum (Figure 7), two doublet of doublets signals 30.95 (dd, $^1J_{\text{RhP}} = 169.4$ Hz, $^2J_{\text{PP}} = 44.5$ Hz) and 36.21 (dd, $^1J_{\text{RhP}} = 155.6$ Hz, $^2J_{\text{PP}} = 43.0$ Hz) are observed for two different phosphine, indicating their *cis* orientation.

Single crystals of **3A-P_{1a}** (R = Ph) and **3A-P_{1i}** (R = CH₂CH₂Ph) suitable for X-ray crystallographic studies were obtained by the slow diffusion of diethyl ether into their dichloromethane solutions at room temperature (Table 2, Figure 8). In the crystal structure of **3A-P_{1a}** and **3A-P_{1i}**, the PPh₃ ligands are *cis* to each other and the small flexible two methylene groups enlarge the angle of other ligands.

3A-P_{1a}

3A-P₁i

Figure 8. Molecular structure (ORTEP) of the cation of **3A-P₁a** and **3A-P₁i** with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg) of **3A-P₁a**: Rh1-N1, 2.093(4); Rh1-C14, 2.158(5); Rh1-C15, 2.300(5); Rh1-P1, 2.3042(12); Rh1-P2, 2.3192(13); C14-C15, 1.427(7); N1-Rh1-C14, 87.63(17); N1-Rh1-C15, 77.94(16); C14-Rh1-C15, 37.16(18); N1-Rh1-P1, 168.90(11); C14-Rh1-P1, 99.18(13); C15-Rh1-P1, 102.22(12); N1-Rh1-P2, 87.51(11); C14-Rh1-P2, 131.52(13); C15-Rh1-P2, 161.16(13); P1-Rh1-P2, 94.37(5). Selected bond lengths (Å) and angles (deg) of **3A-P₁i**: Rh1-N1, 2.098(3); Rh1-C14, 2.127(5); Rh1-C15, 2.224(4); Rh1-P1, 2.2925(11); Rh1-P2, 2.3420(11); C14-C15, 1.405(7); N1-Rh1-C14, 87.42(17); N1-Rh1-C15, 79.50(15); C14-Rh1-C15, 37.59(17); N1-Rh1-P1, 167.70(11); C14-Rh1-P1, 97.29(14); C15-Rh1-P1, 97.30(12); N1-Rh1-P2, 88.21(10); C14-Rh1-P2, 130.15(13); C15-Rh1-P2, 162.41(13); P1-Rh1-P2, 97.

Table 2. Crystallographic Data for Complexes of 2A-P₁c, 3A-P₁a and 3A-P₁i.

	2A-P₁c .CH ₂ Cl ₂	3A-P₁a .2CH ₂ Cl ₂	3A-P₁i .(CH ₃ CH ₂) ₂ O
empirical formula	C ₅₉ H ₄₆ Cl ₂ F ₉ N P ₃ Rh	C ₅₉ H ₄₉ Cl ₄ F ₆ N P ₃ Rh	C ₆₅ H ₆₁ F ₆ N O ₂ P ₃ Rh
molecular weight (g mol ⁻¹)	1206. 69	1223.61	1197.97
radiation, λ		Mo K α , 0.71073 Å	
<i>T</i> (K)	223(2)	173(2)	173(2)
cryst syst	Monoclinic	monoclinic	Triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	13. 6534 (3)	12.3535(5)	10.8319(4)
<i>b</i> (Å)	25. 7008 (5)	28.8354(12)	13.2288(4)
<i>c</i> (Å)	15. 5862 (3)	15.2713(6)	22.0889(8)
β (deg)	93. 0920 (10)	99.472(2)	79.856(2)
<i>V</i> (Å ³)	5461. 29 (19)	5365.7(4)	2847.44(17)
<i>Z</i>	4	4	2
<i>D</i> _{calcd} (g cm ⁻³)	1. 468	1.515	1.397
μ (mm ⁻¹)	0.569	0.669	0.449
cryst size (mm)	0.30 x 0.28 x 0.26	0.20 x 0.15 x 0.10	0.30 x 0.15 x 0.12
total, unique no. of rflns	57442, 13106	43515, 10441	66048, 10559
<i>R</i> _{int}	0.0523	0.0619	0.0443
data, restraints, parameters	13106 / 259 / 741	10441 / 0 / 667	10559 / 117 / 742
<i>R</i> , <i>R</i> _w (all data)	0.0764, 0.1829	0.0830, 0.2067	0.0711, 0.1810
GOF	1.017	1.063	1.130
min., max. resid dens (eÅ ⁻³)	-0.658, 0.931	-0.833, 2.216	-1.349, 1.233

2.3 Mechanism studies. A probable mechanism of the total conversion can be proposed owing to the identity of five-coordinate intermediate (Scheme 2). Firstly, the weakly coordinated acetone easily dissociates from rhodium hydride complexes to give a vacant coordination site which is available for the coordination of alkynes. It is well-known that terminal alkynes insert into metal-hydride bond to form vinyl complexes. However, the mechanism behind this apparent insertion can be complex. At least three mechanisms have been proposed.^[6] A deuterium labeling experiment involving the rhodium hydride complex **1A-P₁** with 2 equivalent of PhC≡CD was performed at room temperature for 4 hours to obtain a coupling rhodium complex **3A-P_{1a-d}** (eq. 2).

Comparison of the ¹H NMR spectrum of **3A-P_{1a}** and **3A-P_{1a-d}**, the peak at 6.48 disappears for **3A-P_{1a-d}**, the peak at 5.50 slightly shifts to 5.55 ppm (in the same solvent). The peak at 5.55 now becomes a doublet, instead of a doublet of doublets. This is because the previous ³J_{HH} *trans* coupling is missing. The rest of the signals have no change. The deuterium experiment can directly indicate that the alkyne hydrogen PhC≡CH ends up in the H₁ position of the product and the hydride H₂ insert into the C₂ position, there is likely no breaking of alkyne C–H bond during this reaction. The mechanism indicate that the metal hydride insert directly into the alkyne to form the vinyl ligands. And then the aryl and vinyl

group reductive eliminate from the rare five-coordinate Rh(III) center at room temperature to form the final C–C coupling product. The five-coordinate intermediates and the stable coupling complexes obtained in our system offer a direct and efficient experimental method for exploring the kinetic and mechanism of the last reductive elimination step. The mechanism of C–C reductive elimination of alkyl, vinyl, aryl and acetylide reactive ligands from Pd, Pt, Ir and Rh complexes have been studied generally is three-center concerted elimination.^[14-25] We synthesized a series of complexes with different electronic properties of reactive ligands and ancillary ligands to investigate the electronic effect on the rate of C–C reductive elimination from rare five-coordinate Rh(III) intermediates by NMR spectroscopy analysis.

Scheme 2. A proposed total mechanism of C–H activation and C–C reductive elimination.

Five-coordinate intermediate **2A-P1c** (Ar = Ph, R = *p*-PhCF₃) underwent clean C–C elimination upon warming at various temperatures (monitored by ¹⁹F NMR) in CD₂Cl₂ with different rate. The reaction is first order reaction for Rh intermediate, the enthalpic and entropic contributions to the barrier energy have been determined experimentally and calculated by Eyring-Polanyi equation^[30] (eq.

3, Figure 9). The value of the $\Delta H^\ddagger$ is 20.9 kcal/mol and the $\Delta S^\ddagger$ is -6.1 eu, which is similar with the Ir(PCP)-(Vi)(Ph) system.^[25] The negative value of $\Delta S^\ddagger$ suggests that the transition state is more order than the ground state, which probably shows the three-center concerted reductive elimination mechanism (Scheme 3).^[14,25]

Scheme 3. Probable mechanism of C-C reductive elimination.

$$\ln \frac{k}{T} = \frac{-\Delta H^\ddagger}{R} \times \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (3)$$

T (K)	1/T	ln(k/T)	k (min ⁻¹)
287.67	0.003476	-11.766	0.002233
293.58	0.003406	-11.0392	0.004715
296.96	0.003367	-10.65	0.007038
305.3	0.003275	-9.6486	0.0197

Figure 9. The Eyring-polanyi Plot: $\ln(k/T)$ against $1/T$.

The electronic properties of reactive and ancillary ligands have a large impact on the rate and scope of reductive elimination reactions. Electronic effects of different vinyl reactive ligands and ancillary ligands have been measured (Scheme 4, σ_p substituent constant), the more electron-donating substituent on the phenyl group show relative high reactivity on reductive elimination, however, more donating ancillary ligands $P(Ar)_3$ make the metal center electron rich, and the electron-rich metal centers tend to undergo reductive processes more slowly than electron-poor metal centers. The reductive elimination activity trends in our system are consistent with the two baseline effects of electronics on three-center concerted reductive eliminations from palladium (II) complexes.^[14,16]

T = 293 K						
R	σ_p	$k(\text{min}^{-1})$	$\ln(10^4 \cdot K)$		R'	$k(\text{min}^{-1})$
-OMe	-0.268	0.0101	4.61		-OMe	0.0041
-H	0	0.0086	4.45		-H	0.0047
-F	0.062	0.0079	4.32		-F	0.0068
-CF ₃	0.54	0.0047	3.85			
-SO ₂ CF ₃	0.93	0.0026	3.26			

Scheme 4. Electronic effects of ligands on the rate of C-C reductive elimination.

We also investigated the effect of different conjugated aryl nitrogen-assisted reactive ligands (Scheme 5). From the data of rate constant we can conclude that the more extended conjugation aryl group with a rigid geometry structure which hinder the dissociation of nitrogen from Rh(III) center gives high rate. This trend of reactivity indicates that the reductive elimination involves no de-coordination of the chelating nitrogen atom. The rate of elimination is little different with different

conjugated heteroaryl substrates.

Scheme 5. The rate of elimination from different conjugated heteroaryl substrates.

Excess (4 equiv. and 8 equiv.) ancillary ligand PPh_3 were added into the solution of five-coordinate intermediate **2** in CD_2Cl_2 to conform if there is a dissociation of PPh_3 during the process of reductive elimination, the rates with 4 equiv. and 8 equiv (Scheme 6). PPh_3 on elimination are listed in Scheme 4, the rate dropped dramatically to $0.0028 \text{ min k}^{-1}$ when intermediate Rh(III) reacted with 4 equiv. PPh_3 . However, when 8 equiv. PPh_3 were added into the solution of the Rh(III) intermediate, the rate almost had no change. This probably shows that the PPh_3 de-coordinate reversibly from metal center during the process of elimination and it is not a simple first order reaction.

Scheme 6. The effect of the amount of PPh_3 on the rate of reductive elimination

The effect of solvent on the reductive elimination has also been measured and it was found that the weak coordinate solvent acetone- d_6 and THF- d_6 dramatically

improve the rate of elimination to 0.0231 min^{-1} and 0.0214 min^{-1} at 281K (Scheme 7). As we mentioned above, the strongly coordinate ligand CO can stabilize the five-coordinate intermediate and hinder the occurrence of elimination, the weakly coordinate solvent reversibly coordinate to the metal center to make the reactive ligand close to each other, and the reductive elimination still occurs at five-coordinate Rh(III) center. All of the solvents we chose are polar solvent, and CD_2Cl_2 is much more polar than others. Thus the improvement of rate of elimination is the effect of coordination of the solvent. The solvent effect on the rate of elimination further indicates the three-center concerted mechanism.

Scheme 7. Solvent effect on the rate of reductive elimination

3. Conclusion

We isolated and characterized a series of rare five-coordinate intermediates **2** $[\text{Rh}(\text{C}^{\wedge}\text{N})(\text{PAr}_3)_2(\text{CH}=\text{CHR})]\text{PF}_6$, which subsequently undergo reductive elimination to give stable C–C coupling Rh(I) complexes **3**. The absolute rates of reductive elimination have been measured and the enthalpic and entropic contributions to the barrier energy have been determined experimentally. The mechanism of the total conversion has been proposed and the reductive elimination is indicated to be the three-centre concerted mechanism by

experiments. The electronic effects of vinyl ligands and the ancillary ligands on reductive elimination and the solvent effect on elimination have been explored and rationalized.

4. Experiment section

4.1 General consideration. All manipulations were performed using standard Schlenk techniques and in glove box. All chemicals were used as received without any further purification unless otherwise mentioned. All solvent were degassed and dried by standard techniques. NMR spectra were obtained on a Bruker DPX 300, AMX 400 or 500 spectrometers. The sample temperature in VT NMR analysis was calibrated by 4 % methanol in methanol- d_4 . The chemical shift is given as dimensionless δ values and is frequency referenced relative to Me₄Si for ¹H and ¹³C NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. IR spectra were recorded on a Shimadzu IRPESTIGE-21 FTIR spectrometer from 4000 to 600 cm⁻¹ with 4 cm⁻¹ resolution.

4.2 General method for the synthesis of rhodium hydride 1. To a suspension of [Rh(NBD)(PAr₃)₂]PF₆ (Ar = Ph, *p*-PhOCH₃, *p*-PhF) (0.50 mmol) in acetone (8 mL) was bubbled H₂ for 15min at 0 °C, during which time the colour of the solution changed from red to pale yellow. *Tert*-Butylethylene (1.2 ml) and benzo[*h*]quinoline, 2-phenylpyridine or dibenzo[*f, h*]quinoline (0.60 mmol) were added to the solution and were refluxed at 65 °C for 5 h. The solvent was

concentrated to 0.5 ml under reduced pressure. The residue was put into the glove box and washed with diethyl ether 3×10 ml to give white powder rhodium hydride complexes **1**.

Yield: 454 mg (0.45 mmol, 92%). ^1H NMR (δ , 300 MHz, CD_3COCD_3 , 295 K): -12.29 (dt, $^1J_{\text{RhH}} = 16.6$ Hz, $^2J_{\text{PH}} = 11.0$ Hz, 1H, RhH), 2.06 (s, 6H, CH_3COCH_3), 6.96 (t, $^3J = 7.7$ Hz, 1H), 7.05-7.38 [m, 32H, 2H ($\text{C}_{13}\text{H}_8\text{N}$) + 30H (PPh_3)], 7.43 (d, $^3J = 7.7$ Hz, 1H), 7.57 (d, $^3J = 8.8$ Hz, 1H), 7.78 (dd, $^3J = 8.0$ Hz, $^3J = 5.0$ Hz, 1H), 8.16 (d, $^3J = 7.9$ Hz, 1H), 9.79 (d, $^3J = 4.9$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_3COCD_3 , 295 K): -143.56 (m, $^1J_{\text{FP}} = 704.0$ Hz, PF_6), 39.91 (d, $^1J_{\text{RHP}} = 114.3$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 100 MHz, CD_3COCD_3 , 295 K): 29.8 (s, CH_3), 120.52 (s), 122.44 (s), 122.83 (s), 126.83 (s), 127.31 (s), 128.08 (t, $J_{\text{PC}} = 4.7$ Hz, PPh_3), 128.60 (t, $^1J_{\text{PC}} = 23.0$ Hz, *ipso*- PPh_3), 130.30 (s, *p*- PPh_3), 133.36 (t, $J_{\text{PC}} = 5.6$ Hz, PPh_3), 134.73 (s), 135.73 (s), 138.44 (s), 139.65 (s), 148.19 (s), 150.71 (s), 153.08 (dt, $^1J_{\text{RhC}} = 31.0$ Hz, $^2J_{\text{PC}} = 11.2$ Hz, CRh), 205.26 (CO). Anal. Calcd. For $\text{C}_{54}\text{H}_{45}\text{F}_6\text{NOP}_3\text{Rh}$ (1009.74): C, 61.85; H, 4.49; N, 1.39. Found: C, 61.54; H, 4.95; N, 1.43.

Yield: 428 mg (0.44 mmol, 87%). ^1H NMR (δ , 300 MHz, CD_3COCD_3 , 295 K): -12.26 (dt, $^1J_{\text{RhH}} = 15.6$ Hz, $^2J_{\text{PH}} = 10.9$ Hz, 1H, RhH), 2.06 (s, 6H, CH_3COCH_3),

6.50 (t, $^3J = 6.7$ Hz, 1H), 6.87 (t, $^3J = 7.6$ Hz, 1H), 7.03 (d, $^3J = 7.7$ Hz, 1H), 7.12-7.42 [m, 33H, 3H ($C_{13}H_8N$) + 30H (PPh_3)], 7.62 (t, $^3J = 6.8$ Hz, 1H), 9.46 (d, $^3J = 5.5$ Hz, 1H); ^{31}P { 1H } NMR (δ , 121 MHz, CD_3COCD_3 , 295 K): -143.58 (m, $^1J_{FP} = 705.1$ Hz, PF_6), 39.91 (d, $^1J_{RhP} = 115.8$ Hz, PPh_3); ^{13}C { 1H } NMR (δ , 75 MHz, CD_3CN , 295 K): 119.31 (s), 121.99 (s), 122.22 (s), 124.64 (s), 128.54 (s), 128.16 (t, $J_{PC} = 4.9$ Hz, PPh_3), 129.93 (t, $^1J_{PC} = 23.4$ Hz, *ipso*- PPh_3), 130.30 (s, *p*- PPh_3), 133.39 (t, $J_{P-C} = 5.8$ Hz, PPh_3), 136.85 (s), 142.10 (s), 144.03 (s), 149.33 (s), 161.69 (s), 159.56 (dt, $^1J_{RhC} = 28.4$ Hz, $^2J_{PC} = 10.3$ Hz, CRh), 206.45 (CO).
 Anal. Calcd. For $C_{50}H_{45}F_6NOP_3Rh$ (985.72): C, 60.92; H, 4.60; N, 1.42. Found: C, 60.52; H, 4.96; N, 1.51.

Yield: 530 mg (0.45 mmol, 89%). 1H NMR (δ , 300 MHz, CD_3COCD_3 , 295 K): -12.49 (dt, $^1J_{RhH} = 17.6$ Hz, $^2J_{PH} = 10.9$ Hz, 1H, RhH), 3.75 (s, 18H, $PC_6H_4OCH_3$), 6.69 (d, $^3J = 8.5$ Hz, 12H, $PC_6H_4OCH_3$), 6.93-6.99 (m, 12H, $PC_6H_4OCH_3$), 7.06 (m, 1H), 7.29 (d, $^3J = 7.3$ Hz, 1H), 7.39-7.45 (m, 2H), 7.60 (d, $^3J = 8.8$ Hz, 1H), 7.78 (dd, $^3J = 7.9$ Hz, $^3J = 5.1$ Hz, 1H), 8.20 (d, $^3J = 7.8$ Hz, 1H), 9.76 (d, $^3J = 4.8$ Hz, 1H); ^{31}P { 1H } NMR (δ , 121 MHz, CD_3COCD_3 , 295 K): -143.54 (m, $^1J_{FP} = 704.8$ Hz, PF_6), 36.32 (d, $^1J_{RhP} = 112.8$ Hz, $PC_6H_4OCH_3$); ^{13}C { 1H } NMR (δ , 75 MHz, CD_3COCD_3 , 295 K): 26.17 (CD_3COCD_3), 55.67 ($PC_6H_4OCH_3$), 114.34 (t, $J_{PC} = 5.2$ Hz, $PC_6H_4OCH_3$), 120.99 (t, $^1J_{PC} = 25.4$ Hz, *ipso*- $PC_6H_4OCH_3$), 121.52 (s), 122.44 (s), 124.81 (s), 127.99 (s), 128.44 (s), 129.51 (s), 135.45 (s), 135.63 (t, J_{PC}

= 6.4 Hz, $\text{PC}_6\text{H}_4\text{OCH}_3$), 136.39 (s), 139.08 (s), 140.73 (s), 148.97 (s), 151.97 (s), 156.01 (dt, $^1J_{\text{RhC}} = 31.8$ Hz, $^2J_{\text{PC}} = 11.1$ Hz, CRh), 161.96 (s, *p*- $\text{PC}_6\text{H}_4\text{OCH}_3$), 206.20 (CO). Anal. Calcd. For $\text{C}_{58}\text{H}_{57}\text{F}_6\text{NO}_7\text{P}_3\text{Rh}$ (1189.89): C, 58.54; H, 4.83; N, 1.18. Found: C, 58.12; H, 4.97; N, 1.61.

Yield: 475 mg (0.43 mmol, 85%). ^1H NMR (δ , 300 MHz, CD_3COCD_3 , 295 K): -12.36 (dt, $^1J_{\text{RhH}} = 16.5$ Hz, $^2J_{\text{PH}} = 11.0$ Hz, 1H, RhH), 2.09 (s, 6H, CH_3COCH_3), 6.97 (m, 12H, $\text{PC}_6\text{H}_4\text{F}$), 7.04 (t, $^3J = 8.0$ Hz, 1H), 7.11-7.18 (m, 12H, $\text{PC}_6\text{H}_4\text{F}$), 7.31 (d, $^3J = 7.4$ Hz, 1H), 7.46-7.51 (m, 2H), 7.64 (d, $^3J = 8.8$, 1H), 7.85 (dd, $^3J = 8.0$ Hz, $^3J = 5.1$ Hz, 1H), 8.28 (d, $^3J = 7.9$ Hz, 1H), 9.83 (d, $^3J = 4.8$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_3COCD_3 , 295 K): -143.50 (m, $^1J_{\text{FP}} = 705.4$ Hz, PF_6), 38.47 (d, $^1J_{\text{Rhp}} = 115.5$ Hz, $\text{PC}_6\text{H}_4\text{F}$); ^{19}F { ^1H } NMR (δ , 282 MHz, CD_2Cl_2 , 295K): -109.11 (s, $\text{PC}_6\text{H}_4\text{F}$), -72.69 (d, $J_{\text{P-F}} = 709.9$ Hz, PF_6); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_3COCD_3 , 295 K): 116.28 (dt, $J_{\text{FC}} = 21.5$ Hz, $J_{\text{PC}} = 5.4$ Hz, $\text{PC}_6\text{H}_4\text{F}$), 122.35 (s), 123.24 (s), 125.03 (td, $^1J_{\text{PC}} = 24.4$ Hz, $^4J_{\text{FC}} = 3.4$ Hz, *ipso*- $\text{PC}_6\text{H}_4\text{F}$), 125.03 (s), 128.10 (s), 129.02 (s), 129.02 (s), 135.68 (s), 136.62 (dt, $J_{\text{FC}} = 8.4$ Hz, $J_{\text{PC}} = 6.7$ Hz, $\text{PC}_6\text{H}_4\text{F}$), 136.99 (s), 139.23 (s), 140.29 (s), 149.40 (s), 151.24 (s), 153.51 (dt, $^1J_{\text{RhC}} = 31.6$ Hz, $^2J_{\text{PC}} = 12.5$ Hz, CRh), 163.86 (d, $^1J_{\text{FC}} = 249.8$ Hz, *p*- $\text{PC}_6\text{H}_4\text{F}$), 206.11 (CO). Anal. Calcd. For $\text{C}_{52}\text{H}_{39}\text{F}_{12}\text{NOP}_3\text{Rh}$ (1117.11): C, 55.88; H, 3.52; N, 1.25. Found: C, 56.04; H, 3.23; N, 1.21.

Yield: 440 mg (0.42 mmol, 83%). ^1H NMR (δ , 400 MHz, CD_3CN , 295 K): -12.28 (dt, $^1J_{\text{RhH}} = 14.1$ Hz, $^2J_{\text{PH}} = 9.6$ Hz, 1H, RhH), 2.05 (s, 6H, CH_3COCH_3), 6.81 (t, $^3J = 7.7$ Hz, 1H), 7.04-7.18 [m, 31H, 30H (PPh_3) + 1H ($\text{C}_{17}\text{H}_{10}\text{N}$)], 7.40 (dd, $^3J = 8.0$ Hz, $^3J = 5.2$ Hz, 1H), 7.64 (m, 2H), 7.94 (d, $^3J = 8.0$ Hz, 1H), 8.38 (s, $^3J = 7.9$ Hz, 1H), 8.48 (d, $^3J = 7.9$ Hz, 1H), 8.63 (d, $^3J = 8.2$ Hz, 1H), 8.82 (d, $^3J = 4.8$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD_3CN , 295 K): -144.62 (m, $^1J_{\text{FP}} = 706.3$ Hz, PF_6), 40.18 (d, $^1J_{\text{RhP}} = 111.9$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 100 MHz, CD_3CN , 295K): 29.90 (CH_3COCH_3), 116.20 (s), 121.68 (s), 123.12 (s), 123.43 (s), 125.68 (s), 127.21 (s), 127.76 (s), 127.92 (t, $J_{\text{PC}} = 4.9$ Hz, PPh_3), 128.31 (s), 129.60 (t, $^1J_{\text{PC}} = 24.0$ Hz, *ipso*- PPh_3), 130.01 (s, *p*- PPh_3), 130.55 (s), 130.91 (s), 132.03 (s), 133.15 (t, $J_{\text{P-C}} = 5.8$ Hz, PPh_3), 138.61 (s), 140.45 (s), 148.51 (s), 151.78 (s), 157.46 (dt, $^1J_{\text{RhC}} = 27.9$ Hz, $^2J_{\text{PC}} = 11.4$ Hz, CRh), 206.49 (CO). Anal. Calcd. For $\text{C}_{56}\text{H}_{47}\text{F}_6\text{NOP}_3\text{Rh}$ (1059.80): C, 63.46; H, 4.47; N, 1.32. Found: C, 63.06; H, 4.45; N, 1.56.

Yield: 463 mg (0.43 mmol, 85%). ^1H NMR (δ , 300 MHz, CD_3COCD_3 , 295 K): -12.13 (dt, $^1J_{\text{RhH}} = 16.1$ Hz, $^2J_{\text{PH}} = 10.7$ Hz, 1H, RhH), 2.11 (s, 6H, CH_3COCH_3), 7.10-7.22 [m, 25H, 24H (PPh_3) + 1H ($\text{C}_{13}\text{H}_7\text{N}$)], 7.31-7.36 (m, 6H, PPh_3), 7.42 (d, $^3J = 7.4$ Hz, 1H), 7.69 (d, $^3J = 8.0$ Hz, 1H), 7.80 (s, 1H), 7.86 (dd, $^3J = 7.9$ Hz, $^3J =$

5.1 Hz, 1H), 8.19 (d, $^3J = 7.9$ Hz, 1H), 9.89 (d, $^3J = 4.1$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_3COCD_3 , 295 K): -143.48 (m, $^1J_{\text{FP}} = 705.2$ Hz, PF_6), 40.05 (d, $^1J_{\text{RhP}} = 113.1$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_3COCD_3 , 295 K): 120.52 (s), 122.44 (s), 122.82 (s), 126.83 (s), 127.31 (s), 128.08 (t, $J_{\text{P-C}} = 4.7$ Hz, PPh_3), 128.33 (t, $^1J_{\text{PC}} = 23.1$ Hz, *ipso*- PPh_3), 128.40 (s), 128.75 (s), 130.42 (s, *p*- PPh_3), 132.90 (s), 133.34 (t, $J_{\text{P-C}} = 5.7$ Hz, PPh_3), 135.12 (s), 139.55 (s), 148.90 (s), 150.02 (s), 154.48 (dt, $^1J_{\text{RhC}} = 31.9$ Hz, $^2J_{\text{PC}} = 11.3$ Hz, CRh), 205.32 (CO). Anal. Calcd. For $\text{C}_{52}\text{H}_{44}\text{BrF}_6\text{NOP}_3\text{Rh}$ (1089.63): C, 57.37; H, 4.07; N, 1.29. Found: C, 56.99; H, 3.65; N, 1.71.

4.3 General method for the synthesis of the five-coordinate rhodium intermediates 2. To a solution of the rhodium hydride complexes (0.1 mmol) in dichloromethane (3 ml) was added terminal alkynes (0.2 mmol) and then the solution was stirred for 2 h at -20°C . Then the solvent was removed under reduced pressure at -20°C and the residue was transferred into glove box and washed with diethyl ether 3×6 ml to give an orange powder. The five-coordinate complexes in solution are unstable and easily turn to C-C coupling rhodium complexes at room temperature, so the NMR is performed at -20°C .

Yield: 113 mg (0.09 mmol, 92%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 5.27 (d, $^3J_{\text{CH=CH}} = 17.2$ Hz, 1H, $\text{CH=CHC}_6\text{H}_4\text{SO}_2\text{CF}_3$), 6.74 (d, $^3J = 8.2$ Hz, 2H, $\text{CHC}_6\text{H}_4\text{SO}_2\text{CF}_3$), 6.90 (m, $^3J = 5.4$ Hz, 12H, PPh_3), 7.18 (t, $^3J = 7.1$ Hz, 12H,

*PPh*₃), 7.36-7.41 [m, 8H, 6H (*PPh*₃) + 2H (C₁₃H₈N)], 7.59 (t, ³*J* = 7.7 Hz, 1H), 7.69 (d, ³*J* = 7.1 Hz, 2H), 7.75 (d, ³*J* = 8.2 Hz, 2H, CHC₆H₄SO₂CF₃), 7.96 (d, ³*J* = 7.8 Hz, 2H), 8.72-8.78 [m, 2H, 1H (RhCH=CH)+1H (C₁₃H₈N)]; ³¹P {¹H} NMR (δ, 121 MHz, CD₂Cl₂, 255 K): -143.81 (m, ¹*J*_{FP} = 708.3 Hz, PF₆), 23.45 (d, ¹*J*_{RhP} = 110.6 Hz, *PPh*₃); ¹³C {¹H} NMR (δ, 75 MHz, CD₂Cl₂, 255 K): 119.74 (q, ¹*J*_{F-C} = 320.3 Hz, CF₃), 122.69 (s), 123.53 (s), 124.67 (s), 125.75 (s), 125.75 (t, ¹*J*_{PC} = 23.7 Hz, *ipso-PPh*₃), 127.20 (s), 128.68 (s), 128.87 (t, *J*_{PC} = 4.9 Hz, *PPh*₃), 131.04 (s), 131.15 (s), 131.36 (s), 131.52 (s, *p-PPh*₃), 132.91 (t, *J*_{PC} = 5.4 Hz, *PPh*₃), 133.53 (s), 134.23 (s), 136.43 (s), 136.54 (s), 144.80 (dt, ¹*J*_{RhC} = 43.5 Hz, ²*J*_{PC} = 9.0 Hz, CRh), 145.45 (s), 147.80 (s), 148.74 (s), 161.61 (dt, ¹*J*_{RhC} = 31.3 Hz, ²*J*_{PC} = 11.0 Hz, RhCH=CH).

Yield: 101 mg (0.09 mmol, 90%). ¹H NMR (δ, 300 MHz, CD₂Cl₂, 255 K): 5.14 (d, ³*J*_{CH=CH} = 17.0 Hz, 1H, CH=CHC₆H₄CF₃), 6.59 (d, ³*J* = 8.1, 2H, C₆H₄CF₃), 6.83-7.04 [m, 13H, 12H (*PPh*₃)+1H (C₁₃H₈N)], 7.18 (m, 12H, *PPh*₃), 7.32-7.42 [m, 9H, 6H (*PPh*₃) + 3H (C₁₃H₈N)], 7.57 (t, ³*J* = 7.7 Hz, 1H), 7.67-7.70 (m, 2H), 7.95 (d, ³*J* = 7.9, 2H, C₆H₄CF₃), 8.36 (dt, ³*J*_{CH=CH} = 17.0 Hz, ³*J*_{PH} = 5.5 Hz, 1H, RhCH=CH), 8.56 (d, ³*J* = 4.1, 1H); ³¹P {¹H} NMR (δ, 121 MHz, CD₂Cl₂, 255 K): -143.85 (m, ¹*J*_{FP} = 708.8 Hz, PF₆), 23.38 (d, ¹*J*_{RhP} = 112.1 Hz, *PPh*₃); ¹³C {¹H} NMR (δ, 75 MHz, CD₂Cl₂, 255 K): 122.85 (s), 123.69 (s), 124.83 (q, ¹*J*_{FC} = 271.1 Hz, CF₃), 124.94 (s), 125.24 (s), 125.44 (q, ³*J*_{FC} = 3.8 Hz, C₆H₄CF₃), 126.25 (t,

$^1J_{\text{PC}} = 24.0$ Hz, *ipso*- PPh_3), 127.05 (q, $^2J_{\text{FC}} = 31.7$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 127.47 (s), 128.97 (s), 129.11 (t, $J_{\text{P-C}} = 4.8$ Hz, PPh_3), 131.74 (s, *p*- PPh_3), 133.25 (t, $J_{\text{P-C}} = 5.4$ Hz, PPh_3), 134.48 (s), 136.73 (s), 141.49 (s), 145.08 (dt, $^1J_{\text{RhC}} = 42.9$ Hz, $^2J_{\text{PC}} = 9.2$ Hz, CRh), 148.08 (s), 148.95 (s), 153.65 (dt, $^1J_{\text{RhC}} = 32.2$ Hz, $^2J_{\text{PC}} = 10.7$ Hz, RhCH=CH).

Yield: 108 mg (0.10 mmol, 95%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 5.25 (d, $^3J_{\text{CH=CH}} = 17.0$ Hz, 1H, $\text{CH=CHC}_6\text{H}_4\text{NO}_2$), 6.62 (d, $^3J = 8.6$ Hz, 2H, $\text{CHC}_6\text{H}_4\text{NO}_2$), 6.91 (m, 12H, PPh_3), 7.16 (t, $^3J = 7.5$ Hz, 12H, PPh_3), 7.36-7.42 [m, 8H, 6H (PPh_3) + 2H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.60 (t, $^3J = 7.7$ Hz, 1H), 7.69 (d, $^3J = 8.5$ Hz, 2H, $\text{C}_6\text{H}_4\text{NO}_2$), 7.97 (m, 4H), 8.65 (dt, $^3J_{\text{CH=CH}} = 17.1$ Hz, $^3J_{\text{PH}} = 5.5$ Hz, 1H, RhCH=CH), 8.73 (d, $^3J = 4.9$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.81 (m, $^1J_{\text{FP}} = 708.8$ Hz, PF_6), 23.42 (d, $^1J_{\text{RhP}} = 110.7$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 122.64 (s), 123.50 (s), 123.64 (s), 123.91 (s), 124.65 (s), 125.49 (t, $^1J_{\text{PC}} = 24.1$ Hz, *ipso*- PPh_3), 127.19 (s), 128.67 (s), 128.84 (t, $J_{\text{P-C}} = 4.9$ Hz, PPh_3), 131.31(s), 131.49 (s, *p*- PPh_3), 132.92 (t, $J_{\text{PC}} = 5.5$ Hz, PPh_3), 134.22 (s), 136.38 (s), 136.52 (s), 143.72 (s), 144.77 (dt, $^1J_{\text{RhC}} = 42.7$ Hz, $^2J_{\text{PC}} = 9.2$ Hz, CRh), 145.05 (s), 147.77 (s), 148.75 (s), 159.38 (dt, $^1J_{\text{RhC}} = 31.3$ Hz, $^2J_{\text{PC}} = 11.4$ Hz, RhCH=CH).

Yield: 100 mg (0.09 mmol, 88%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 5.97 (d, $^3J_{\text{CH}=\text{CH}} = 16.9$ Hz, 1H, $\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$), 6.83 (d, $^3J = 7.8$ Hz, 1H), 6.89-6.99 (m, 12H, PPh_3), 7.13-7.21 [m, 13H, 12H (PPh_3) + 1H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.16-7.38 [m, 9H, 6H (PPh_3) + 3H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.57-7.69 (m, 4H), 7.93-7.99 (m, 2H), 8.41(dt, $^3J_{\text{CH}=\text{CH}} = 16.8$ Hz, $^3J_{\text{PH}} = 6.0$ Hz, 1H, $\text{RhCH}=\text{CH}$), 8.65 (d, $^3J = 4.8$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.88 (m, $^1J_{\text{FP}} = 707.7$ Hz, PF_6), 22.78 (d, $^1J_{\text{RhP}} = 111.2$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 122.47 (s), 123.39 (s), 123.99 (s), 124.61 (s), 124.77 (s), 125.90 (t, $^1J_{\text{PC}} = 24.0$ Hz, *ipso*- PPh_3), 126.09 (s), 126.77 (s), 127.11 (s), 127.26 (s), 128.72 (t, $J_{\text{PC}} = 4.8$ Hz, PPh_3), 131.39 (s, *p*- PPh_3), 131.63 (s), 132.58 (s), 132.96 (t, $J_{\text{P-C}} = 5.5$ Hz, PPh_3), 134.23 (s), 136.52 (s), 145.10 (dt, $^1J_{\text{RhC}} = 42.2$ Hz, $^2J_{\text{PC}} = 8.6$ Hz, CRh), 145.92 (s), 147.89 (s), 148.44 (s), 157.80 (dt, $^1J_{\text{RhC}} = 31.7$ Hz, $^2J_{\text{PC}} = 10.7$ Hz, $\text{RhCH}=\text{CH}$).

Yield: 102 mg (0.09 mmol, 90%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 5.12 (d, $^3J_{\text{CH}=\text{CH}} = 16.9$ Hz, 1H, $\text{CH}=\text{CHC}_6\text{H}_4\text{Cl}$), 6.48 (d, $^3J = 8.4$ Hz, 2H, $\text{CHC}_6\text{H}_4\text{Cl}$), 6.91-7.02 (m, 12H, PPh_3), 7.08-7.25 [m, 14H, 12H (PPh_3) + 2H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.34-7.39 [m, 8H, 6H (PPh_3) + 2H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.47 (t, $^3J = 8.4$ Hz, 1H), 7.56 (d, $^3J = 7.7$ Hz, 2H, $\text{CHC}_6\text{H}_4\text{Cl}$), 7.90-7.94 (m, 2H), 8.14 (dt, $^3J_{\text{CH}=\text{CH}} = 17.1$ Hz, $^3J_{\text{PH}} = 5.7$ Hz, 1H, $\text{RhCH}=\text{CH}$), 8.74 (d, $^3J = 4.8$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.84 (m, $^1J_{\text{FP}} = 708.9$ Hz, PF_6), 23.10 (d, $^1J_{\text{RhP}} =$

112.3 Hz, PPh_3); $^{13}C \{^1H\}$ NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 122.79 (s), 123.56 (s), 124.88 (s), 126.43 (t, $^1J_{PC} = 24.3$ Hz, *ipso*- PPh_3), 127.40 (s), 128.52 (s), 129.01 (t, $J_{PC} = 4.8$ Hz, PPh_3), 131.15(s), 131.61 (s, *p*- PPh_3), 131.95 (s); 133.30 (t, $J_{PC} = 5.4$ Hz, PPh_3), 133.69 (s), 133.77 (s), 133.83 (s), 134.43 (s), 136.64 (s), 136.95 (s), 145.53 (dt, $^1J_{RhC} = 40.2$ Hz, $^2J_{PC} = 9.6$ Hz, CRh), 148.26 (s), 148.92 (s), 149.69 (dt, $^1J_{RhC} = 31.0$ Hz, $^2J_{PC} = 10.9$ Hz, RhCH=CH).

Yield: 100 mg (0.09 mmol, 93%). 1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 5.15 (d, $^3J_{CH=CH} = 16.9$ Hz, 1H, CH=CHC₆H₄F), 6.45-6.50 (m, 2H, CHC₆H₄F), 6.77-6.93 [m, 15H, 12H (PPh_3) + 3H (C₁₃H₈N)], 7.11 (t, $^3J = 8.0$ Hz, 12H, PPh_3), 7.29-7.34 [m, 7H, 6H (PPh_3) + 1H (C₁₃H₈N)], 7.49 (t, $^3J = 7.7$ Hz, 1H), 7.61-7.64 (m, 2H), 7.84-7.89 (m, 2H), 7.95 (dt, $^3J_{CH=CH} = 17.2$ Hz, $^3J_{PH} = 5.6$ Hz, 1H, RhCH=CH), 8.70 (d, $^3J = 4.9$ Hz, 1H); $^{31}P \{^1H\}$ NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.87 (m, $^1J_{FP} = 709.0$ Hz, PF_6), 22.91 (d, $^1J_{RhP} = 112.4$ Hz, PPh_3); $^{13}C \{^1H\}$ NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 115.22 (d, $^2J_{FC} = 21.7$ Hz, C₆H₄F), 122.72 (s), 123.47 (s), 124.83 (s), 126.57 (t, $^1J_{PC} = 23.7$ Hz, *ipso*- PPh_3), 127.57 (d, $^3J_{FC} = 7.4$ Hz, C₆H₄F), 127.37 (s), 128.41 (s), 128.54 (s), 129.98 (t, $J_{PC} = 4.9$ Hz, PPh_3), 131.57 (s, *p*- PPh_3), 132.16 (s), 132.35 (s), 133.38 (t, $J_{PC} = 5.4$ Hz, PPh_3), 134.43 (s), 134.96 (s), 136.62 (s), 137.17 (s), 145.82 (dt, $^1J_{RhC} = 41.3$ Hz, $^2J_{PC} = 12.4$ Hz, CRh), 147.39 (dt, $^1J_{RhC} = 41.3$ Hz, $^2J_{PC} = 12.4$ Hz, RhCH=CH), 148.43 (s), 148.87 (s).

Yield: 95 mg (0.09 mmol, 90%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 5.10 (d, $^3J_{\text{CH}=\text{CH}} = 17.0$ Hz, 1H, $\text{CH}=\text{CHC}_6\text{H}_5$), 6.52 (d, $^3J = 7.1$ Hz, 2H, CHC_6H_5), 6.90-6.98 (m, 12H, PPh_3), 7.02-7.20 [m, 15H, 12H (PPh_3) + 1H ($\text{C}_{13}\text{H}_8\text{N}$) + 2H (CHC_6H_5)], 7.30-7.41 [m, 8H, 6H (PPh_3) + 2H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.55 (t, $^3J = 7.7$ Hz, 1H), 7.66-7.70 (m, 2H), 7.92-7.96 (m, 2H), 8.13 (dt, $^3J_{\text{CH}=\text{CH}} = 17.0$ Hz, $^3J_{\text{PH}} = 5.9$ Hz, 1H, $\text{RhCH}=\text{CH}$), 8.71 (d, $^3J = 4.9$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.88 (m, $^1J_{\text{FP}} = 707.6$ Hz, PF_6), 23.23 (d, $^1J_{\text{RhP}} = 112.5$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 122.41 (s), 123.24 (s), 124.58 (s), 124.78 (s), 124.96 (s), 126.12 (t, $^1J_{\text{PC}} = 24.0$ Hz, *ipso*- PPh_3), 127.10 (s), 127.97 (s), 128.11 (s), 128.22 (s), 128.71 (t, $J_{\text{PC}} = 4.9$ Hz, PPh_3), 131.33 (s, *p*- PPh_3), 131.49 (s), 132.07 (s), 133.00 (t, $J_{\text{PC}} = 5.5$ Hz, PPh_3), 134.13 (s), 136.32 (s), 136.44 (s), 138.00 (s), 144.95 (dt, $^1J_{\text{RhC}} = 42.0$ Hz, $^2J_{\text{PC}} = 9.4$ Hz, CRh), 147.76 (dt, $^1J_{\text{RhC}} = 31.0$ Hz, $^2J_{\text{PC}} = 11.3$ Hz, $\text{RhCH}=\text{CH}$), 147.82 (s), 148.53 (s).

Yield: 102 mg (0.09 mmol, 95%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 2.22 (s, 3H, PhCH_3), 5.02 (d, $^3J_{\text{CH}=\text{CH}} = 16.6$ Hz, 1H, $\text{CH}=\text{CHC}_6\text{H}_5$), 6.40 (d, $^3J = 7.2$ Hz, 2H, $\text{CHC}_6\text{H}_4\text{CH}_3$), 6.89-7.65 [m, 37H, 30H (PPh_3) + 5H ($\text{C}_{13}\text{H}_8\text{N}$) + 2H ($\text{C}_6\text{H}_4\text{CH}_3$)], 7.92 (m, 1H), 8.01 (dt, $^3J_{\text{CH}=\text{CH}} = 17.1$ Hz, $^3J_{\text{PH}} = 6.3$ Hz, 1H, $\text{RhCH}=\text{CH}$), 8.68 (d, $^3J = 3.8$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255

K): -143.88 (m, $^1J_{\text{FP}} = 708.2$ Hz, PF_6), 23.17 (d, $^1J_{\text{RhP}} = 113.1$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 20.86 (s, CH_3), 122.38 (s), 123.20 (s), 124.57 (s), 124.84 (s), 126.17 (t, $^1J_{\text{PC}} = 23.9$ Hz, *ipso*- PPh_3), 127.08 (s), 128.69 (t, $J_{\text{PC}} = 4.6$ Hz, PPh_3), 128.87 (s), 131.30 (s, *p*- PPh_3), 131.53 (s), 132.47 (s), 133.00 (t, $J_{\text{PC}} = 5.2$ Hz, PPh_3), 134.12 (s), 135.27 (s), 135.56 (s), 136.28 (s), 136.40 (s), 144.97 (dt, $^1J_{\text{RhC}} = 42.1$ Hz, $^2J_{\text{PC}} = 8.8$ Hz, CRh), 145.91 (dt, $^1J_{\text{RhC}} = 30.2$ Hz, $^2J_{\text{PC}} = 10.3$ Hz, RhCH=CH), 147.84 (s), 148.50 (s).

Yield: 102 mg (0.09 mmol, 94%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 3.74 (s, 3H, PhOCH_3), 5.02 (d, $^3J_{\text{CH=CH}} = 18.0$ Hz, 1H, $\text{CH=CHC}_6\text{H}_4\text{OCH}_3$), 6.45 (d, $^3J = 8.4$ Hz, 2H, $\text{CHC}_6\text{H}_4\text{OCH}_3$), 6.66 (d, $^3J = 8.4$ Hz, 2H, $\text{CHC}_6\text{H}_4\text{OCH}_3$), 6.93 (d, 12H, PPh_3), 7.17 (m, 12H, PPh_3), 7.30-7.40 [m, 8H, 6H (PPh_3) + 2H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.54 (s, 1H), 7.65-7.69 (m, 2H), 7.87 (dt, $^3J_{\text{CH=CH}} = 18.0$ Hz, $^3J_{\text{PH}} = 6.0$ Hz, 1H, RhCH=CH), 7.92 (d, $^3J = 7.7$ Hz, 2H), 8.71 (d, $^3J = 5.1$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.88 (m, $^1J_{\text{FP}} = 707.5$ Hz, PF_6), 23.09 (d, $^1J_{\text{RhP}} = 114.0$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 55.55 (s, OCH_3), 113.66 (s), 122.71 (s), 123.49 (s), 124.89 (s), 125.11 (s), 126.32 (s), 126.57 (t, $^1J_{\text{PC}} = 23.8$ Hz, *ipso*- PPh_3), 127.41 (s), 128.27 (s), 128.40 (s), 129.00 (t, $J_{\text{PC}} = 4.9$ Hz, PPh_3), 131.49 (s), 131.61 (s, *p*- PPh_3), 131.97 (s), 132.34 (s), 133.36 (t, $J_{\text{PC}} = 5.5$ Hz, PPh_3), 134.45 (s), 136.60 (s), 136.84 (s), 144.48 (dt, $^1J_{\text{RhC}} = 30.6$ Hz, $^2J_{\text{PC}} = 10.7$ Hz, RhCH=CH), 145.46 (dt, $^1J_{\text{RhC}} = 42.1$ Hz, $^2J_{\text{PC}} = 9.5$ Hz, CRh), 148.23 (s),

148.85 (s).

Yield: 103 mg (0.09 mmol, 88%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 295 K): 5.17 (d, $^3J_{\text{CH}=\text{CH}} = 16.8$ Hz, 1H, $\text{CH}=\text{CHC}_6\text{H}_4\text{CF}_3$), 6.62 (d, $^3J = 7.9$ Hz, 2H, $\text{C}_6\text{H}_4\text{CF}_3$), 6.95 (m, 12H, PPh_3), 7.13 [m, 13H, 12H (PPh_3) + 1H ($\text{C}_{17}\text{H}_{10}\text{N}$)], 7.37-7.29 [7H, 6H (PPh_3) + 1H ($\text{C}_{17}\text{H}_{10}\text{N}$)], 7.54 (t, $^3J = 8.9$ Hz, 1H), 7.84-7.73 (m, 3H), 8.38-8.22 (m, 3H), 8.67-8.54 (m, 3H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD_3CN , 295K): -143.69 (m, $^1J_{\text{FP}} = 707.6$ Hz, PF_6), 23.66 (d, $^1J_{\text{RhP}} = 112.4$ Hz, PPh_3); ^{19}F { ^1H } NMR (δ , 282 MHz, CD_3CN , 255 K): -72.76 (d, 6F, $^1J_{\text{PF}} = 710.6$ Hz, PF_6), -62.06 (s, 3F, CF_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 118.70 (s), 122.87 (s), 123.40 (s), 123.92 (s), 124.57 (q, $^1J_{\text{FC}} = 269.3$ Hz, CF_3), 124.95 (s), 125.19 (q, $^3J_{\text{FC}} = 3.0$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 125.93 (t, $^1J_{\text{PC}} = 24.0$ Hz, *ipso*- PPh_3), 126.61 (q, $^2J_{\text{FC}} = 33.0$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 127.29 (s), 128.28 (s), 128.79 (t, $J_{\text{PC}} = 4.6$ Hz, PPh_3), 129.12 (s), 129.58 (s), 131.38 (s, *p*- PPh_3), 131.73 (s), 131.94 (s), 132.32 (s), 132.63 (s), 133.09 (t, $J_{\text{PC}} = 5.4$ Hz, PPh_3), 135.56 (s), 141.24 (s), 147.26 (dt, $^1J_{\text{RhC}} = 39.3$ Hz, $^2J_{\text{PC}} = 9.3$ Hz, CRh), 148.38 (s), 148.60 (s), 153.76 (dt, $^1J_{\text{RhC}} = 30.5$ Hz, $^2J_{\text{PC}} = 11.4$ Hz, $\text{RhCH}=\text{CH}$).

Yield: 100 mg (0.08 mmol, 83%). ^1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 5.18 (d, $^3J_{\text{CH}=\text{CH}} = 17.1$ Hz, 1H, $\text{CH}=\text{CHC}_6\text{H}_4\text{CF}_3$), 6.62 (d, $^3J = 7.1$ Hz, 2H,

$C_6H_4CF_3$), 6.85 [m, 14 H 12H (PPh_3) + 1 H ($C_{13}H_7N$)], 7.11-7.16 [m, 13H, 12H (PPh_3) + 1H ($C_{13}H_7N$)], 7.32-7.37 [m, 8H, 6H (PPh_3) + 2H ($C_{13}H_7N$)], 7.60 (t, $^3J = 7.1$ Hz, 1H), 7.71 (s, 1H), 7.76 (d, $^3J = 10.3$ Hz, 1H), 7.90 (t, $^3J = 10.3$ Hz, 1H), 8.27 (dt, $^3J_{CH=CH} = 16.1$ Hz, $^3J_{PH} = 6.1$ Hz, 1H, RhCH=CH), 8.54 (d, $^3J = 4.5$ Hz, 1H); ^{31}P { 1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.84 (m, $^1J_{FP} = 708.0$ Hz, PF_6), 23.11 (d, $^1J_{RhP} = 110.7$ Hz, PPh_3); ^{19}F { 1H } NMR (δ , 282 MHz, CD_2Cl_2 , 255 K): -72.79 (d, $^1J_{PF} = 710.4$ Hz, 6F, PF_6), -62.22 (s, CF_3); ^{13}C { 1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 123.07 (s), 124.54 (q, $^1J_{FC} = 268.5$ Hz, CF_3), 124.97 (s), 125.19 (q, $^3J_{FC} = 2.3$ Hz, $C_6H_4CF_3$), 125.83 (t, $^1J_{PC} = 24.8$ Hz, *ipso*- PPh_3), 126.68 (q, $^2J_{FC} = 30.0$ Hz, $C_6H_4CF_3$), 126.73 (s), 127.59 (s), 128.26 (s), 128.79 (t, $J_{PC} = 5.3$ Hz, PPh_3), 129.21 (s), 131.43 (s, *p*- PPh_3), 131.97 (s), 132.55 (s), 132.97 (t, $J_{PC} = 6.8$ Hz, PPh_3), 135.49 (s), 136.98 (s), 141.08 (s), 145.65 (dt, $^1J_{RhC} = 41.3$ Hz, $^2J_{PC} = 9.8$ Hz, CRh), 147.41 (s), 149.18 (s), 152.61 (dt, $^1J_{RhC} = 32.3$ Hz, $^2J_{PC} = 9.0$ Hz, RhCH=CH).

Yield: 98 mg (0.09 mmol, 89%). 1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 5.07 (d, 1H, $^3J_{CH=CH} = 17.2$ Hz, CH=CH $C_6H_4CF_3$), 6.50 (d, $^3J = 7.8$ Hz, 2H, $C_6H_4CF_3$), 6.99-7.03 [m, 13H, 12H (PPh_3) + 1H ($C_{11}H_8N$)], 7.13-7.17 (m, 3H), 7.26-7.37 [m, 15H, 12H (PPh_3) + 3H ($C_{11}H_8N$)], 7.44-7.53 [m, 7H, 6H (PPh_3) + 1H ($C_{11}H_8N$)], 7.60 (m, 1H), 8.03 [dt, $^3J_{CH=CH} = 17.2$ Hz, $^2J_{PH} = 5.4$ Hz, 1H, RhCH=CH), 8.34 (d, $^2J_{PH} = 5.0$ Hz, 1H); ^{31}P { 1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.96 (m, $^1J_{FP}$

= 708.8 Hz, PF_6), 23.68 (d, $^1J_{RhP}$ = 112.9 Hz, PPh_3); ^{19}F { 1H } NMR (δ , 282 MHz, CD_2Cl_2 , 255 K): -72.95 (d, $^1J_{PF}$ = 710.4 Hz, 6F, PF_6), -62.12 (s, 3F, CF_3); ^{13}C { 1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 120.33 (s), 123.35 (s), 124.53 (q, $^1J_{FC}$ = 269.7 Hz, CF_3), 124.91 (s), 125.00 (s), 125.08 (q, $^3J_{FC}$ = 3.6 Hz, $C_6H_4CF_3$), 125.33 (s), 126.13 (t, $^1J_{PC}$ = 23.9 Hz, *ipso*- PPh_3), 126.59 (q, $^2J_{FC}$ = 31.5 Hz, $C_6H_4CF_3$), 129.07 (t, J_{PC} = 4.8 Hz, PPh_3), 130.19(s), 131.51 (s, *p*- PPh_3), 132.35 (s), 133.28 (t, J_{PC} = 5.3 Hz, PPh_3), 134.49 (s), 138.21 (s), 141.25 (s), 141.35 (s), 148.92 (s), 149.20 (dt, $^1J_{RhC}$ = 40.7 Hz, $^2J_{PC}$ = 8.7 Hz, CRh), 149.85 (s), 154.22 (dt, $^1J_{RhC}$ = 31.1 Hz, $^2J_{PC}$ = 10.5 Hz, RhCH=CH).

Yield: 110 mg (0.08 mmol, 84%). 1H NMR (δ , 300 MHz, CD_2Cl_2 , 255 K): 3.56 (s, 18H, OCH_3), 5.36 (d, $^3J_{CH=CH}$ = 16.8 Hz, 1H, CH=CH $C_6H_4CF_3$), 6.64 (d, 12H, $PC_6H_4OCH_3$), 6.72-6.79 [m, 14H, 12 ($PC_6H_4OCH_3$) + 2H ($C_6H_4CF_3$)], 7.39-7.45 [m, 4H, 2H ($C_{13}H_8N$) + 2H ($C_6H_4CF_3$)], 7.56 (t, 3J = 7.7 Hz, 1H), 7.69 (m, 2H), 7.93 (d, 3J = 7.6 Hz, 1H), 8.00 (d, 3J = 7.9 Hz, 1H), 8.44 (dt, 1H, $^3J_{CH=CH}$ = 17.1 Hz, $^3J_{PH}$ = 5.6 Hz, RhCH=CH), 8.71 (d, 3J = 4.7 Hz, 1H); ^{31}P { 1H } NMR (δ , 121 MHz, CD_2Cl_2 , 255 K): -143.88 (m, $^1J_{FP}$ = 708.9 Hz, PF_6), 21.03 (d, $^1J_{RhP}$ = 110.4 Hz, PPh_3); ^{19}F { 1H } NMR (δ , 282 MHz, CD_2Cl_2 , 255 K): -72.99 (d, $^1J_{PF}$ = 710.3 Hz, 6F, PF_6), -62.18 (s, CF_3); ^{13}C { 1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 55.56 (s, OCH_3), 114.14 (t, J_{PC} = 5.3 Hz, PPh_3), 117.30 (t, $^1J_{PC}$ = 26.5 Hz, *ipso*- $PC_6H_4OCH_3$), 122.56 (s), 122.99 (s), 124.30 (s), 124.61 (q, $^1J_{FC}$ = 269.6 Hz,

CF₃), 124.96 (s), 125.11 (q, ³J_{FC} = 3.8 Hz, C₆H₄CF₃), 126.55 (q, ²J_{FC} = 31.7 Hz, C₆H₄CF₃), 127.05 (s), 128.50 (s), 128.77 (s), 131.06 (s), 131.33 (s), 134.12 (s), 134.36 (t, J_{PC} = 6.1 Hz, PC₆H₄OCH₃), 136.01 (s), 136.71 (s), 141.51 (s), 145.91 (dt, ¹J_{RhC} = 43.1 Hz, ²J_{PC} = 9.5 Hz, CRh), 147.98 (s), 148.77 (s), 155.87 (dt, ¹J_{RhC} = 32.4 Hz, ²J_{PC} = 11.1 Hz, RhCH=CH), 161.56 (s, *p*-PC₆H₄OCH₃).

Yield: 113 mg (0.09 mmol, 92%). ¹H NMR (δ, 300 MHz, CD₂Cl₂, 255 K): 5.20 (d, 1H, ³J_{CH=CH} = 17.1 Hz, CH=CHC₆H₄CF₃), 6.89-6.91 [m, 25H, 24H (PC₆H₄F) + 1H (C₁₃H₈N)], 6.47-7.64 [m, 5H, 2H (C₆H₄CF₃) + 3H (C₁₃H₈N)], 7.72-7.79 [m, 3H, 1 H (C₁₃H₈N) + 2H (C₆H₄CF₃)], 8.04 (d, ³J = 7.9 Hz, 1H), 8.33 (dt, 1H, ³J_{CH=CH} = 17.0 Hz, ³J_{PH} = 5.1 Hz, RhCH=CH), 9.04 (d, ³J = 4.9 Hz, 1H); ³¹P {¹H} NMR (δ, 121 MHz, CD₂Cl₂, 255 K): -143.65 (m, ¹J_{FP} = 709.1 Hz, PF₆), 22.58 (d, ¹J_{RhP} = 113.2 Hz, PPh₃); ¹⁹F {¹H} NMR (δ, 282 MHz, CD₂Cl₂, 255 K): -72.99 (d, 6F, ¹J_{PF} = 710.3 Hz, PF₆), -62.18 (s, CF₃); ¹³C {¹H} NMR (δ, 75 MHz, CD₂Cl₂, 255 K): 116.57 (dt, ²J_{F-C} = 21.4 Hz, ³J_{P-C} = 5.2 Hz, PC₆H₄F), 121.94 (td, ¹J_{PC} = 25.1 Hz, ⁴J_{FC} = 3.1 Hz, *ipso*-PC₆H₄F), 123.65 (s), 124.00 (s), 124.82 (q, ¹J_{FC} = 269.8 Hz, CF₃), 124.96 (s), 125.20 (s), 125.83 (q, ³J_{FC} = 3.8 Hz, C₆H₄CF₃), 127.27 (s), 127.51 (q, ²J_{FC} = 36.5 Hz, C₆H₄CF₃), 129.10 (s), 129.27 (s), 132.33 (s), 132.73 (s), 134.47 (s), 135.60 (dt, ³J_{FC} = 8.2 Hz, ²J_{PC} = 6.5 Hz, PC₆H₄F), 136.70 (s), 137.32 (s), 140.91 (s), 145.25 (dt, ¹J_{RhC} = 41.9 Hz, ²J_{PC} = 11.0 Hz, CRh), 148.16 (s), 149.84 (s), 151.60 (dt, ¹J_{RhC} = 31.7 Hz, ²J_{PC} = 12.8 Hz, RhCH=CH),

164.58 (d, $^1J_{\text{CF}} = 252.7$ Hz, $\text{PC}_6\text{H}_4\text{F}$).

To the solution of the five-coordinate intermediate **2** in CD_2Cl_2 in NMR tube was bubbled CO at 0 °C for 15 min, during which time the color of the solution turned from orange to yellow, and then obtained the six-coordinate complexes. Yield: 103 mg (0.09 mmol, 90%). ^1H NMR (δ , 400 MHz, CD_2Cl_2 , 295 K): 6.47 (d, 1H, $^3J_{\text{CH}=\text{CH}} = 16.3$ Hz, $\text{CH}=\text{CHC}_6\text{H}_4\text{CF}_3$), 6.82-6.86 (m, 12H, PPh_3), 7.02-7.11 [m, 14H, 12H (PPh_3) + 2H ($\text{C}_6\text{H}_4\text{CF}_3$)], 7.25-7.33 [m, 8H, 6H (PPh_3) + 2H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.41-7.49 [m, 2H, 1H ($\text{C}_{13}\text{H}_8\text{N}$) + 1H ($\text{CH}=\text{CHC}_6\text{H}_4\text{CF}_3$)], 7.55-7.58 [m, 3H, 1H ($\text{C}_{13}\text{H}_8\text{N}$) + 2H ($\text{C}_6\text{H}_4\text{CF}_3$)], 7.73 (d, $^3J = 8.8$ Hz, 1H), 7.78 (d, $^3J = 7.6$ Hz, 1H), 7.95 (d, $^3J = 7.9$ Hz, 1H), 9.01 (d, $^3J = 4.9$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD_2Cl_2 , 295 K): -144.27 (m, $^1J_{\text{FP}} = 709.8$ Hz, PF_6), 19.00 (d, $^1J_{\text{RhP}} = 99.2$ Hz, PPh_3); ^{19}F { ^1H } NMR (δ , 282 MHz, CD_2Cl_2 , 295 K): -73.18 (d, $^1J_{\text{PF}} = 709.7$ Hz, 6F, PF_6), -62.50 (s, CF_3); ^{13}C { ^1H } NMR (δ , 100 MHz, CD_2Cl_2 , 295 K): 123.13 (s), 124.34 (s), 124.61 (s), 125.17 (s), 125.56 (q, $^3J_{\text{CF}} = 3.9$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 126.32 (s), 127.75 (s), 127.80 (t, $^1J_{\text{P-C}} = 25.2$ Hz, *ipso*- PPh_3), 127.86 (s), 128.05 (t, $^4J_{\text{P-C}} = 3.0$ Hz, PPh_3), 129.42 (s), 129.49 (s), 131.04 (s, *p*- PPh_3), 133.45 (t, $J_{\text{PC}} = 5.0$ Hz, PPh_3), 134.63 (s), 135.60 (s), 137.08 (s), 140.90 (s), 141.76 (s), 142.00 (s), 142.24 (dt, $^1J_{\text{RhC}} = 25.9$ Hz, $^2J_{\text{PC}} = 9.3$ Hz, $\text{RhCH}=\text{CH}$), 150.77 (s), 151.71 (s), 159.01 (dt, $^1J_{\text{RhC}} = 22.2$ Hz, $^2J_{\text{PC}} = 11.1$ Hz, CRh), 188.90 (dt, $^1J_{\text{RhC}} = 44.4$ Hz, $^2J_{\text{PC}} = 9.2$ Hz, RhCO). Anal. Calcd. For $\text{C}_{59}\text{H}_{44}\text{F}_9\text{NOP}_3\text{Rh}$ (1149.80): C, 61.63; H, 3.86; N, 1.22.

Found: C, 61.40; H, 3.49; N, 1.96.

4.4 General method for synthesis rhodium C–C coupling products 3. To a solution of the rhodium hydride complexes **1** (0.1 mmol) in dichloromethane (3 ml) was added terminal alkynes (0.2 mmol) and then the solution was stirred for 5 h at 0 °C. Then the solvent was removed under reduced pressure at room temperature and the residue was transferred into the glove box and washed with diethyl ether 3 × 6 ml to give a red powder.

Yield: 96 mg (0.09 mmol, 91%). ^1H NMR (δ , 500 MHz, CD_2Cl_2 , 295 K): 5.50 (dd, $^3J_{\text{CH=CH}} = 13.8$ Hz, $^3J_{\text{RhH}} = 6.7$ Hz, 1H, CH=CH-Ph), 6.48 (dd, $^3J_{\text{CH=CH}} = 14.0$ Hz, $^3J_{\text{RhH}} = 2.9$ Hz, 1H, CH=CH-Ph), 6.61 (d, $^3J = 7.2$ Hz, 2H, CH- C_6H_5), 6.77 (m, 2H), 6.83 (t, $^3J = 7.0$ Hz, 1H), 6.94 (m, 6H, PPh_3), 7.01 (t, $^3J = 7.9$ Hz, 6H, PPh_3), 7.15-7.17 [m, 10H, 9H (PPh_3) + 1H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.25 (t, $^3J = 8.5$ Hz, 6H, PPh_3), 7.35 [m, 4H, 3H (PPh_3) + 1H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.60 (dd, $^3J = 7.9$ Hz, $^3J = 5.4$ Hz, 1H), 7.79 (d, $^3J = 8.6$ Hz, 1H), 7.96 (t, $^3J = 7.3$ Hz, 1H), 8.01 (m, 2H), 8.17 (d, $^3J = 7.0$ Hz, 1H), 9.48 (m, 1H); ^{31}P { ^1H } NMR (δ , 202 MHz, CD_2Cl_2 , 298 K): -144.35 (m, $^1J_{\text{FP}} = 708.4$ Hz, PF_6), 30.95 (dd, $^1J_{\text{RhP}} = 169.4$ Hz, $^2J_{\text{PP}} = 44.5$ Hz, PPh_3), 36.21 (dd, $^1J_{\text{RhP}} = 155.6$ Hz, $^2J_{\text{PP}} = 43.0$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 125 MHz, CD_2Cl_2 , 295 K): 78.62 (dd, $^1J_{\text{RhC}} = 19.9$ Hz, $^2J_{\text{PC}} = 6.2$ Hz, CH=CH-Ph), 85.00 (d, $^1J_{\text{RhC}} = 12.1$ Hz, CH=CH-Ph), 123.75 (s), 124.93 (s), 126.29 (s), 126.34 (s), 127.93 (s), 127.98 (d, $J_{\text{PC}} = 10.1$ Hz, PPh_3), 128.05 (d, $J_{\text{PC}} = 9.8$ Hz, PPh_3), 128.30 (s), 129.10

(s), 129.7 (s), 130.08 (s), 130.29 (s, *p*-PPh₃), 130.62 (d, ¹J_{PC} = 45.8 Hz, *ipso*-PPh₃), 130.81 (s), 130.86 (d, ¹J_{PC} = 41.4 Hz, *ipso*-PPh₃), 132.84 (d, J_{PC} = 12.2 Hz, PPh₃), 134.72 (d, J_{PC} = 10.4 Hz, PPh₃), 136.37 (s), 136.67 (s), 137.64 (s), 137.74 (s), 143.22 (s), 147.83 (s). Anal. Calcd. For C₅₇H₄₅F₆NP₃Rh•1.5CH₂Cl₂ (1181.19): C, 59.48; H, 4.10; N, 1.19. Found: C, 59.11; H, 4.02; N, 1.23.

Complex was synthesized by following the procedure of the above method.

Yield: 98 mg (0.09 mmol, 92%). ¹H NMR (δ, 400 MHz, CD₂Cl₂, 295 K): 2.10-2.17 (t, ³J = 10.9 Hz, 1H, CH₂), 3.24 (dt, ³J = 13.8 Hz, ²J = 3.9 Hz, 1H, CH₂), 4.15-4.23 (m, 1H, CH=CH-CH₂-Ph), 5.82 (dd, ³J = 13.2 Hz, ³J_{PH} = 4.4 Hz, 1H, CH=CH-CH₂Ph), 6.42 (d, ³J = 7.7 Hz, 2H, C₆H₅), 6.90-7.02 [m, 15H, 12H (PPh₃) + 2H (C₆H₅) + 1H (C₁₃H₈N)], 7.17 (m, 3H, PPh₃), 7.26-7.33 [m, 7H, 6H (PPh₃) + 1H (C₁₃H₈N)], 7.43-7.46 [m, 4H, 3H (PPh₃) + 1H (C₁₃H₈N)], 7.50 (dd, ³J = 8.2 Hz, ³J = 5.2 Hz, 1H, C₁₃H₈N), 7.60 (m, 6H, PPh₃), 7.69 (d, ³J = 8.8 Hz, 1H), 7.84-7.94 (m, 4H, C₁₃H₈N), 9.35 (m, 1H); ³¹P {¹H} NMR (δ, 121 MHz, CD₂Cl₂, 295 K): -143.75 (m, ¹J_{FP} = 707.7 Hz, PF₆), 29.32 (dd, ¹J_{RhP} = 160.9 Hz, ²J_{PP} = 41.4 Hz, PPh₃), 36.98 (dd, ¹J_{RhP} = 155.9 Hz, ²J_{PP} = 41.9 Hz, PPh₃); ¹³C {¹H} NMR (δ, 75 MHz, CD₂Cl₂, 295 K): 40.27 (s, CH₂), 76.10 (dd, ¹J_{RhC} = 22.7 Hz, ²J_{PC} = 7.5 Hz, CH=CH-CH₂Ph), 91.99 (d, ¹J_{RhC} = 12.0 Hz, CH=CH-CH₂Ph), 123.75 (s), 125.08 (s), 126.32 (s), 126.41 (s), 128.09 (s), 128.41 (d, J_{PC} = 10.2 Hz, PPh₃), 128.66 (s, CH₂C₆H₅), 128.93 (d, J = 9.8 Hz, PPh₃), 129.38 (s), 129.92 (s), 131.02 (s), 130.45

(s), 131.16 (d, $^4J_{\text{PC}} = 2.0$ Hz, *p*-PPh₃), 131.29 (d, $^1J_{\text{PC}} = 40.2$ Hz, *ipso*-PPh₃), 131.78 (dd, $^1J_{\text{PC}} = 45.0$ Hz, $^2J_{\text{RhC}} = 2.0$ Hz, PPh₃), 133.25 (d, $J_{\text{PC}} = 12.4$ Hz, PPh₃), 135.08 (d, $J_{\text{PC}} = 10.4$ Hz, PPh₃), 136.97 (s), 137.21 (s), 137.89 (s), 141.42 (s), 143.32 (s), 148.11 (s). Anal. Calcd. For C₅₈H₄₇F₆NP₃Rh (1067.82): C, 65.24; H, 4.44; N, 1.31. Found: C, 65.07; H, 4.42; N, 1.52.

Complex was synthesized by following the procedure of the above method.

Yield: 95 mg (0.09 mmol, 89%). ^1H NMR (δ , 300 MHz, CD₂Cl₂, 295 K): 1.01-1.17 (m, 1H, CH₂CH₂Ph), 1.90-2.00 (m, 1H, CH₂CH₂Ph), 2.35-2.43 (m, 2H, CH₂CH₂Ph), 3.89-3.99 (m, 1H, CH=CH-CH₂CH₂Ph), 5.21 (dd, $^3J_{\text{CH=CH}} = 13.2$ Hz, $^2J_{\text{RhH}} = 4.8$ Hz, 1H, CH=CH-CH₂-Ph), 6.19 (d, $^3J = 7.2$ Hz, 2H, CH₂-C₆H₅), 6.81-7.03 [m, 15H, 12H (PPh₃) + 3H (C₁₃H₈N)], 7.11-7.16 (m, 3H, PPh₃), 7.24-7.35 [m, 8H, 6H (PPh₃) + 2H (C₁₃H₈N)], 7.41-7.54 [m, 10H, 6H (PPh₃) + 3H (PPh₃) + 1H (C₁₃H₈N)], 7.70-7.75 (m, 2H, C₁₃H₈N), 7.90 (d, $^3J = 7.7$ Hz, 1H), 7.97 (d, $^3J = 7.9$ Hz, 1H), 9.30-9.32 (m, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD₂Cl₂, 295 K): -143.36 (m, $^1J_{\text{FP}} = 710.3$ Hz, PF₆), 28.87 (dd, $^1J_{\text{RhP}} = 161.5$ Hz, $^2J_{\text{PP}} = 41.4$ Hz, PPh₃), 39.22 (dd, $^1J_{\text{RhP}} = 156.3$ Hz, $^2J_{\text{PP}} = 41.4$ Hz, PPh₃); ^{13}C { ^1H } NMR (δ , 75 MHz, CD₂Cl₂, 295 K): 35.92 (s, CH₂CH₂Ph), 37.42 (d, $^2J_{\text{RhC}} = 6.0$ Hz, CH₂CH₂Ph), 75.65 (dd, $^1J_{\text{RhC}} = 22.8$ Hz, $^2J_{\text{PC}} = 7.5$ Hz, CH=CH-CH₂CH₂Ph), 93.30 (d, $^1J_{\text{RhC}} = 12.1$ Hz, CH=CH-CH₂Ph), 123.62 (s), 124.83 (s), 125.81 (s), 126.47 (s), 126.77 (s), 127.98 (s), 128.33 (d, $J_{\text{PC}} = 10.0$ Hz, PPh₃), 128.47 (s,

CH₂-C₆H₅), 128.85 (d, $J_{\text{PC}} = 9.8$ Hz, *PPh*₃), 129.08 (s), 129.37 (s), 130.00 (s), 130.33 (d, $J_{\text{PC}} = 2.2$ Hz, *p-PPh*₃), 130.87 (s), 131.00 (d, $J_{\text{PC}} = 2.2$ Hz, *p-PPh*₃), 131.50 (d, $^1J_{\text{PC}} = 40.2$ Hz, *ipso-PPh*₃), 131.78 (dd, $^1J_{\text{PC}} = 45.1$ Hz, *ipso-PPh*₃), 132.71 (d, $J_{\text{PC}} = 12.4$ Hz, *PPh*₃), 135.09 (d, $J_{\text{PC}} = 10.4$ Hz, *PPh*₃), 136.74 (s), 137.19 (s), 137.80 (s), 140.66 (s), 143.29 (s), 147.95 (s). Anal. Calcd. For C₅₉H₄₉F₆NP₃Rh (1081.84): C, 65.50; H, 4.57; N, 1.29. Found: C, 65.05; H, 4.37; N, 1.56.

4.5 Direct conversion of intermediates 2 into C-C coupling products 3 in CD₂Cl₂ NMR tube. The following C-C coupling products were obtained by slowly converting from five-coordinate intermediates **2** at room temperature for several hours. All of five-coordinate intermediates totally converted into coupling products.

^1H NMR (δ , 300 MHz, CD₂Cl₂, 295 K): 5.26 (dd, $^3J_{\text{CH=CH}} = 13.5$ Hz, $^2J_{\text{RhH}} = 7.5$ Hz, 1H, CH=CHC₆H₄SO₂CF₃), 6.48 (dd, $^3J_{\text{CH=CH}} = 13.5$ Hz, $^2J_{\text{RhH}} = 4.5$ Hz, 1H, CH=CHC₆H₄SO₂CF₃), 6.78-6.80 (m, 2H, CH-C₆H₄SO₂CF₃), 6.94-6.97 (m, 12H, *PPh*₃), 7.20-7.40 [m, 21 H, 12H (*PPh*₃) + 6H (*PPh*₃) + 2H (C₆H₄SO₂CF₃) + 1H (C₁₃H₈N)], 7.74-7.80 (m, 2H), 7.97 (t, $^3J = 7.5$ Hz, 1H), 8.07 (m, 2H), 8.26 (d, $^3J = 6.9$ Hz, 1H), 9.59 (m, 1H); ^{31}P { ^1H } NMR (δ , 121 MHz, CD₂Cl₂, 295 K): -143.56 (m, $^1J_{\text{FP}} = 708.7$ Hz, PF₆), 31.71 (dd, $^1J_{\text{RhP}} = 167.1$ Hz, $^2J_{\text{PP}} = 43.1$ Hz, *PPh*₃), 34.43 (dd, $^1J_{\text{RhP}} = 153.1$ Hz, $^2J_{\text{PP}} = 43.0$ Hz, *PPh*₃); ^{19}F { ^1H } NMR (δ , 282 MHz,

CD₂Cl₂, 295 K): -79.23 (s, SO₂CF₃), -72.92 (d, ¹J_{PF} = 710.1 Hz, PF₆); ¹³C {¹H} NMR (δ, 75 MHz, CD₂Cl₂, 298 K): 69.90 (dd, ¹J_{RhC} = 23.2 Hz, ²J_{PC} = 6.8 Hz, CH=CH-PhSO₂CF₃), 82.03 (d, ¹J_{RhC} = 13.3 Hz, CH=CH-PhSO₂CF₃), 119.50 (q, ¹J_{FC} = 323.85 Hz, CF₃), 124.30 (s), 124.62 (s), 126.16 (s), 126.56 (s), 126.73 (s), 128.16 (d, J_{PC} = 10.3 Hz, PPh₃), 128.34 (d, J_{PC} = 9.9 Hz, PPh₃), 128.53 (s), 128.63 (s), 129.42 (s), 129.58 (dd, ¹J_{PC} = 46.1 Hz, ³J_{RhC} = 2.6 Hz, *ipso*-PPh₃), 129.42 (s), 129.68 (s), 130.28 (d, ¹J_{PC} = 42.5 Hz, *ipso*-PPh₃), 130.34 (d, ⁴J_{PC} = 2.2 Hz, *p*-PPh₃), 130.43 (s), 130.87 (s, *p*-PPh₃), 132.75 (d, J_{PC} = 12.0 Hz, PPh₃), 134.65 (d, J_{PC} = 10.4 Hz, PPh₃), 136.05 (s), 136.79 (s), 138.03 (s), 142.47 (s), 147.69 (s), 148.59 (s).
 Anal. Calcd. For C₅₈H₄₄F₉NO₂P₃RhS•0.5CH₂Cl₂ (1228.32): C, 57.20; H, 3.69; N, 1.18; S, 2.61. Found: C, 57.15; H, 3.53; N, 1.40; S, 2.38.

¹H NMR (δ, 300 MHz, CD₂Cl₂, 295 K): 5.32 (dd, ³J_{CH=CH} = 13.5 Hz, ²J_{Rh-H} = 6.9 Hz, 1H, CH=CH-C₆H₄CF₃), 6.46 (dd, ³J_{CH=CH} = 13.5 Hz, ²J_{Rh-H} = 4.8 Hz, 1H, CH=CH-C₆H₄CF₃), 6.72 (d, ³J = 6.0 Hz, 2H, C₆H₄CF₃), 6.91-7.00 [m, 14H, 12H (PPh₃) + 2H (C₁₃H₈N)], 7.14-7.26 [m, 15H, 12H (PPh₃) + 3H (PPh₃)], 7.32-7.38 [m, 4H, 3H (PPh₃) + 1H (C₁₃H₈N)], 7.67 (dd, ³J = 8.0 Hz, ³J = 5.2 Hz, 1H), 7.77 (d, ³J = 8.8 Hz, 1H), 7.95 (t, ³J = 7.2 Hz, 1H), 8.01-8.04 (m, 2H), 8.20 (d, ³J = 6.8 Hz, 1H), 9.53 (m, 1H); ³¹P {¹H} NMR (δ, 121 MHz, CD₂Cl₂, 295 K): -143.53 (m, ¹J_{F-P} = 707.6 Hz, PF₆), 31.07 (dd, ¹J_{Rh-P} = 166.8 Hz, ²J_{P-P} = 43.0 Hz, PPh₃), 35.81 (dd, ¹J_{Rh-P} = 153.7 Hz, ²J_{P-P} = 42.8 Hz, PPh₃); ¹³C {¹H} NMR (δ, 100 MHz,

CD₂Cl₂, 295 K): 74.05 (dd, $^1J_{\text{Rh-C}} = 21.8$ Hz, $^2J_{\text{P-C}} = 6.3$ Hz, CH=CH-C₆H₄CF₃), 84.05 (d, $^1J_{\text{Rh-C}} = 12.6$ Hz, CH=CH-C₆H₄CF₃), 124.42 (s), 124.60 (q, $^1J_{\text{F-C}} = 270.1$ Hz, CF₃), 125.14 (s), 125.38 (q, $^3J_{\text{F-C}} = 3.6$ Hz, C₆H₄CF₃), 126.87 (s), 126.92 (s), 127.53 (q, $^2J_{\text{F-C}} = 33.1$ Hz, C₆H₄CF₃), 128.31 (s), 128.48 (d, $J_{\text{P-C}} = 10.4$ Hz, PPh₃), 128.59 (d, $J_{\text{P-C}} = 10.1$ Hz, PPh₃), 128.68 (s), 129.63 (s), 130.05 (s), 130.66 (d, $^1J_{\text{P-C}} = 46.1$ Hz, *ipso*-PPh₃), 130.57 (d, $^4J_{\text{P-C}} = 2.1$ Hz, *p*-PPh₃), 130.89 (d, $^4J_{\text{P-C}} = 1.9$ Hz, *p*-PPh₃), 131.00 (d, $^1J_{\text{P-C}} = 42.6$ Hz, *ipso*-PPh₃), 133.22 (d, $J_{\text{P-C}} = 12.10$ Hz, PPh₃), 134.99 (d, $J_{\text{P-C}} = 10.4$ Hz, PPh₃), 136.60 (s), 137.11 (s), 138.22 (s), 142.84 (s), 143.23 (s), 148.28 (s). Anal. Calcd. For C₅₈H₄₄F₉NP₃Rh (1121.79): C, 62.10; H, 3.95, N, 1.25. Found: C, 61.94; H, 4.30; N, 1.15.

^1H NMR (δ , 400 MHz, CD₂Cl₂, 295 K): 5.69 (dd, $^3J_{\text{CH=CH}} = 13.3$ Hz, $^2J_{\text{RhH}} = 6.9$ Hz, 1H, CH=CH-C₆H₄NO₂), 5.95 (d, $^3J = 7.9$ Hz, 1H, C₆H₄NO₂), 6.54 (dd, $^3J_{\text{CH=CH}} = 13.2$ Hz, $^2J_{\text{RhH}} = 5.1$ Hz, 1H, CH=CH-C₆H₄NO₂), 6.72 (t, $^3J = 7.6$ Hz, 1H, C₆H₄NO₂), 6.94-6.97 (m, 12H, PPh₃), 7.01 (t, $^3J = 7.7$ Hz, 1H, C₆H₄NO₂), 7.14-7.21 (m, 9H, PPh₃), 7.27 (t, $^3J = 7.7$ Hz, 6H, PPh₃), 7.35-7.41 [m, 4H, 3H (PPh₃) + 1H (C₆H₄NO₂)], 7.59 (q, $^3J = 8.0$ Hz, $^3J = 5.4$ Hz, 1H), 7.81 (t, $^3J = 8.6$ Hz, 2H), 7.98 (t, $^3J = 7.4$ Hz, 1H), 8.03-8.08 (m, 2H), 8.21 (d, $^3J = 7.1$ Hz, 1H), 9.56 (m, $^3J = 3.9$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD₂Cl₂, 298 K): -144.42 (m, $^1J_{\text{FP}} = 710.3$ Hz, PF₆), 29.78 (dd, $^1J_{\text{RhP}} = 165.6$ Hz, $^2J_{\text{PP}} = 43.6$ Hz, PPh₃),

35.44 (dd, $^1J_{\text{RhP}} = 153.9$ Hz, $^2J_{\text{PP}} = 43.7$ Hz, PPh_3); ^{13}C $\{^1\text{H}\}$ NMR (δ , 100 MHz, CD_2Cl_2 , 295 K): 68.33 (dd, $^1J_{\text{RhC}} = 23.0$ Hz, $^2J_{\text{PC}} = 7.0$ Hz, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{NO}_2$), 81.34 (d, $^1J_{\text{RhC}} = 13.0$ Hz, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{NO}_2$), 122.77 (s), 124.71 (s), 125.85 (s), 126.31 (s), 126.35 (s), 126.65 (s), 126.97 (s), 126.99 (s), 128.09 (d, $J_{\text{PC}} = 10.1$ Hz, PPh_3), 128.31 (d, $J_{\text{PC}} = 9.90$ Hz, PPh_3), 128.51 (s), 129.08 (s), 129.58 (s), 130.30 (d, $^4J_{\text{PC}} = 2.0$ Hz, $p\text{-PPh}_3$), 130.31 (d, $^1J_{\text{PC}} = 42.0$ Hz, $ipso\text{-PPh}_3$), 130.42 (dd, $^1J_{\text{PC}} = 47.0$ Hz, $ipso\text{-PPh}_3$), 130.65 (d, $^4J_{\text{PC}} = 3.0$ Hz, $p\text{-PPh}_3$), 130.80 (s), 132.91 (d, $J_{\text{PC}} = 12.0$ Hz, PPh_3), 133.83 (s), 134.42 (d, $J_{\text{PC}} = 10.0$ Hz, PPh_3), 135.03 (d, $J_{\text{PC}} = 5$ Hz, PPh_3), 136.40 (s), 136.85 (s), 138.01 (s). Anal. Calcd. For $\text{C}_{57}\text{H}_{44}\text{F}_6\text{N}_2\text{O}_2\text{P}_3\text{Rh}\cdot 0.5\text{CH}_2\text{Cl}_2$ (1141.25): C, 60.51; H, 3.97; N, 2.45. Found: C, 60.73; H, 3.82; N, 2.80.

^1H NMR (δ , 300 MHz, CD_2Cl_2 , 295 K): 5.29 (dd, $^3J_{\text{CH}=\text{CH}} = 13.5$ Hz, $^2J_{\text{RhH}} = 7.2$ Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{NO}_2$), 6.51 (dd, $^3J_{\text{CH}=\text{CH}} = 13.5$ Hz, $^2J_{\text{RhH}} = 4.8$ Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{NO}_2$), 6.72 (d, $^3J = 7.6$ Hz, 2H, $\text{CH}-\text{C}_6\text{H}_4\text{NO}_2$), 6.94-6.98 (m, 12H, PPh_3), 7.16-7.28 (m, 15H, PPh_3), 7.35-7.41 [m, 4H, 3H (PPh_3) + 1H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.53 (d, $^3J = 8.8$ Hz, 2H, $\text{CH}-\text{C}_6\text{H}_4\text{NO}_2$), 7.75-7.80 (m, 2H), 8.01 (t, $^3J = 6.8$ Hz, 1H), 8.10 (m, 2H), 8.29 (d, $^3J = 6.7$ Hz, 1H), 9.61 (m, 1H); ^{31}P $\{^1\text{H}\}$ NMR (δ , 121 MHz, CD_2Cl_2 , 295 K): -143.55 (m, $^1J_{\text{FP}} = 708.7$ Hz, PF_6), 31.40 (dd, $^1J_{\text{RhP}} = 167.4$ Hz, $^2J_{\text{PP}} = 42.6$ Hz, PPh_3), 34.96 (dd, $^1J_{\text{RhP}} = 153.1$ Hz, $^2J_{\text{PP}} = 42.5$ Hz, PPh_3); ^{13}C $\{^1\text{H}\}$ NMR (δ , 75 MHz, CD_2Cl_2 , 295 K): 68.49 (dd, $^1J_{\text{RhC}} = 22.8$ Hz,

$^2J_{\text{PC}} = 6.9$ Hz, CH=CH-C₆H₄NO₂), 82.56 (d, $^1J_{\text{RhC}} = 12.9$ Hz, CH=CH-C₆H₄NO₂), 123.27 (s), 124.16 (s), 124.61 (s), 124.96 (s), 126.56 (s), 126.65 (s), 128.12 (d, $J_{\text{PC}} = 10.2$ Hz, *PPh*₃), 128.33 (d, $J_{\text{PC}} = 9.92$ Hz, *PPh*₃), 128.50 (s), 129.35 (s), 129.67 (s), 129.91 (d, $^1J_{\text{PC}} = 45.8$ Hz, *ipso-PPh*₃), 130.42 (d, $^1J_{\text{PC}} = 41.5$ Hz, *ipso-PPh*₃), 130.84 (s), 132.77 (d, $J_{\text{PC}} = 11.6$ Hz, *PPh*₃), 134.58 (d, $J_{\text{PC}} = 10.4$ Hz, *PPh*₃), 136.18 (s), 136.75 (s), 137.95 (s), 142.89 (s), 144.77 (s), 146.41 (s), 146.47 (s), 147.77 (s). Anal. Calcd. For C₅₇H₄₄F₆N₂O₂ P₃Rh•0.5CH₂Cl₂ (1141.25): C, 60.51; H, 3.97; N, 2.45. Found: C, 60.90; H, 3.71; N, 2.88.

^1H NMR (δ , 400 MHz, CD₂Cl₂, 295K): 5.44 (dd, $^3J_{\text{CH=CH}} = 13.0$ Hz, $^2J_{\text{RhH}} = 6.9$ Hz, 1H, CH=CH-C₆H₄F), 6.40-6.49 [m, 3H, 1H (CH=CH-C₆H₄F) + 2H (C₆H₄F)], 6.60-6.62 (m, 2H, CH-C₆H₄F), 6.92-7.02 (m, 12H, *PPh*₃), 7.18-7.20 (m, 9H, *PPh*₃), 7.25-7.28 (m, 6H, *PPh*₃), 7.35-7.38 [m, 4H, 3H (*PPh*₃) + 1H (C₁₃H₈N)], 7.60 (m, 1H), 7.80 (d, $^3J = 8.6$ Hz, 1H), 7.94-8.03 (m, 3H), 8.17 (d, $^3J = 7.0$ Hz, 1H), 9.47 (m, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD₂Cl₂, 295 K): -144.38 (m, $^1J_{\text{FP}} = 711.2$ Hz, PF₆), 30.60 (dd, $^1J_{\text{RhC}} = 168.6$ Hz, $^2J_{\text{PC}} = 44.2$ Hz, *PPh*₃), 36.11 (dd, $^1J_{\text{RhC}} = 155.7$ Hz, $^2J_{\text{PC}} = 43.0$ Hz, *PPh*₃). No ^{13}C NMR spectra could be obtained with acceptable signal to noise ratio. Anal. Calcd. For C₅₇H₄₄F₇NP₃Rh•2CH₂Cl₂ (1241.65): C, 57.07; H, 3.90; N, 1.13. Found: C, 57.09; H, 3.37; N, 1.35

^1H NMR (δ , 400 MHz, CD_2Cl_2 , 295 K): 5.36 (dd, $^3J_{\text{CH}=\text{CH}} = 13.6$ Hz, $^2J_{\text{RhH}} = 6.8$ Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{Cl}$), 6.41 (dd, $^3J_{\text{CH}=\text{CH}} = 13.6$ Hz, $^2J_{\text{RhH}} = 4.8$ Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{Cl}$), 6.56(d, $^3J = 7.8$ Hz, 2H, $\text{CH}-\text{C}_6\text{H}_4\text{Cl}$), 6.71 (d, $^3J = 8.0$ Hz, 2H, $\text{CH}-\text{C}_6\text{H}_4\text{Cl}$), 6.92-7.01 (m, 12H, PPh_3), 7.15-7.21 (m, 9H, PPh_3), 7.24-7.29 (m, 6H, PPh_3), 7.35-7.38 [m, 4H, 3H (PPh_3) + 1H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.63 (dd, $^3J = 8$ Hz, $^3J = 5.6$ Hz, 1H), 7.79 (d, $^3J = 8.8$ Hz, 1H), 7.93-8.03 (m, 3H, $\text{C}_{13}\text{H}_8\text{N}$), 8.17 (d, $^3J = 7.2$ Hz, 1H), 9.49 (m, $^3J = 6.8$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 161 MHz, CD_2Cl_2 , 295 K): -144.29 (m, $^1J_{\text{FP}} = 711.5$ Hz, PF_6), 30.47 (dd, $^1J_{\text{RhP}} = 172.3$ Hz, $^2J_{\text{PP}} = 44.8$ Hz, PPh_3), 35.77 (dd, $^1J_{\text{RhP}} = 160.3$ Hz, $^2J_{\text{PP}} = 45.5$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_2Cl_2 , 295 K): 76.03 (dd, $^1J_{\text{RhC}} = 21.4$ Hz, $^2J_{\text{PC}} = 6.2$ Hz, $\text{CH}=\text{CH}-\text{C}_6\text{H}_5\text{Cl}$), 84.70 (d, $^1J_{\text{RhC}} = 12.9$ Hz, $\text{CH}=\text{CH}-\text{Ph}$), 124.33 (s), 125.23 (s), 126.76 (s), 126.84 (s), 128.44 (d, $J_{\text{PC}} = 10.0$ Hz, PPh_3), 128.50 (d, $J_{\text{PC}} = 9.8$ Hz, PPh_3), 128.77 (s), 128.93 (s), 129.53 (s), 130.04 (s), 130.52 (s), 130.83 (d, $J_{\text{PC}} = 2.3$ Hz, $p\text{-PPh}_3$), 130.92 (d, $^1J_{\text{PC}} = 46.4$ Hz, $ipso\text{-PPh}_3$), 131.17 (d, $^1J_{\text{PC}} = 41.7$ Hz, $ipso\text{-PPh}_3$), 131.21 (s), 131.85 (s), 132.12 (s), 133.36 (d, $J_{\text{PC}} = 12.2$ Hz, PPh_3), 135.07 (d, $J_{\text{PC}} = 10.4$ Hz, PPh_3), 136.63 (s), 137.07 (s), 137.23 (s), 138.13 (s), 143.40 (s), 148.38 (s). Anal. Calcd. For $\text{C}_{57}\text{H}_{44}\text{ClF}_6\text{NP}_3\text{Rh}\cdot 2\text{CH}_2\text{Cl}_2$ (1130.70): C, 61.08; H, 4.01; N, 1.24. Found: C, 61.26; H, 4.61; N, 1.39.

^1H NMR (δ , 400 MHz, CD_2Cl_2 , 295 K): 5.55 (dd, $^3J_{\text{CH}=\text{CH}} = 13.9$ Hz, $^3J_{\text{RhH}} = 6.2$ Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{CH}_3$), 6.41 (dd, $^3J_{\text{CH}=\text{CH}} = 14.0$ Hz, $^2J_{\text{RhH}} = 4.8$ Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{CH}_3$), 6.53 (d, 2H, $\text{CH}-\text{C}_6\text{H}_4\text{CH}_3$), 6.59 (d, $^3J = 7.9$ Hz, 2H, $\text{CH}-\text{C}_6\text{H}_4\text{CH}_3$), 6.93 (t, 6H, PPh_3), 7.01 (m, 6H, PPh_3), 7.13-7.18 (m, 9H, PPh_3), 7.25 (m, 6H, PPh_3), 7.31-7.36 [m, 4H, 3H (PPh_3) + 1H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.55 (dd, $^3J = 7.6$ Hz, $^3J = 5.2$ Hz, 1H), 7.79 (d, $^3J = 8.8$ Hz, 1H), 7.93-8.01 (m, 3H, CHN), 8.12 (d, $^3J = 7.2$ Hz, 1H), 9.44 (m, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD_2Cl_2 , 295 K): -144.35 (m, $^1J_{\text{F-P}} = 709.5$ Hz, PF_6), 31.12 (dd, $^1J_{\text{Rh-P}} = 169.5$ Hz, $^2J_{\text{P-P}} = 43.7$ Hz, PPh_3), 36.44 (dd, $^1J_{\text{Rh-P}} = 156.9$ Hz, $^2J_{\text{P-P}} = 44.7$ Hz PPh_3); ^{13}C { ^1H } NMR (δ , 100 MHz, CD_2Cl_2 , 295 K): 20.74 (s, CH_3), 80.64 (dd, $^1J_{\text{Rh-C}} = 18.8$ Hz, $^2J_{\text{P-C}} = 6.0$ Hz, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{CH}_3$), 85.38 (d, $^1J_{\text{Rh-C}} = 12.0$ Hz, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{CH}_3$), 123.68 (s), 125.00 (s), 126.25 (s), 127.68 (s), 127.80 (s), 127.94 (d, $J_{\text{P-C}} = 9.7$ Hz, PPh_3), 127.97 (d, $J_{\text{P-C}} = 10.1$ Hz, PPh_3), 129.01 (s), 129.66 (s), 130.03 (d, $^4J_{\text{P-C}} = 1.8$ Hz, $p\text{-PPh}_3$), 130.14 (d, $J_{\text{P-C}} = 1.7$ Hz, $p\text{-PPh}_3$), 130.77 (s), 130.89 (dd, $^1J_{\text{P-C}} = 45.9$ Hz, $ipso\text{-PPh}_3$), 130.93 (d, $^1J_{\text{P-C}} = 41.2$ Hz, $ipso\text{-PPh}_3$), 132.88 (d, $J_{\text{P-C}} = 12.2$ Hz, PPh_3), 134.70 (d, $J_{\text{P-C}} = 10.4$ Hz, PPh_3), 136.25 (s), 136.63 (s), 136.70 (s), 137.57 (s), 143.37 (s), 148.06 (s). Anal. Calcd. For $\text{C}_{58}\text{H}_{47}\text{F}_6\text{NP}_3\text{Rh}$ (1067.82): C, 65.24; H, 4.44; N, 1.31. Found: C, 64.73; H, 4.27; N, 1.16.

^1H NMR (δ , 400 MHz, CD_2Cl_2 , 295 K): 5.59 (dd, $^3J_{\text{CH}=\text{CH}} = 14.1$ Hz, $^2J_{\text{Rh-H}} = 6.3$ Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{OCH}_3$), 6.32 [m, 3H, 2H ($\text{CH}-\text{C}_6\text{H}_4\text{OCH}_3$) + 1H

(CH=CH-C₆H₄OCH₃)], 6.36 (dd, ³J_{CH=CH} = 15.3 Hz, ²J_{Rh-H} = 4.8 Hz, 1H, CH=CH-C₆H₄CH₃), 6.58 (d, ³J = 8.0 Hz, 2H, CH-C₆H₄CH₃), 6.90-7.05(m, 12H, PPh₃), 7.14-7.19 (m, 9H, PPh₃), 7.25-7.36 [m, 10H, 9H (PPh₃) + 1H (C₁₃H₈N)], 7.56 (dd, ³J = 8 Hz, ³J = 5.2 Hz, 1H), 7.78 (d, ³J = 8.8 Hz, 1H), 7.92-7.99 (m, 3H, CHN), 8.11 (d, ³J = 6.8 Hz, 1H), 9.47 (m, 1H); ³¹P {¹H} NMR (δ, 121 MHz, CD₂Cl₂, 295 K): -143.66 (m, ¹J_{F-P} = 708.3 Hz, PF₆), 31.79 (dd, ¹J_{Rh-P} = 169.5 Hz, ²J_{P-P} = 44.3 Hz, PPh₃), 37.40 (dd, ¹J_{Rh-P} = 157.7 Hz, ²J_{P-P} = 44.4 Hz, PPh₃); ¹³C {¹H} NMR (δ, 75 MHz, CD₂Cl₂, 295 K): 55.17 (s, OCH₃), 81.15 (dd, ¹J_{Rh-C} = 18.5 Hz, ²J_{P-C} = 5.9 Hz, CH=CH-C₆H₄OCH₃), 85.60 (d, ¹J_{Rh-C} = 9.8 Hz, CH=CH-C₆H₄OCH₃), 113.81 (s), 123.74 (s), 124.99 (s), 126.17 (s), 126.22 (s), 127.70 (s), 127.95 (d, J_{P-C} = 10.1 Hz, PPh₃), 127.97 (d, J_{P-C} = 9.8 Hz, PPh₃), 128.94 (s), 129.15 (s), 129.60 (s), 129.92 (s), 129.99 (d, ⁴J_{P-C} = 2.2 Hz, *p*-PPh₃), 130.16 (d, ⁴J_{P-C} = 2.2 Hz, *p*-PPh₃), 130.96 (dd, ¹J_{P-C} = 44.3 Hz, *ipso*-PPh₃), 131.02 (d, ¹J_{P-C} = 40.1 Hz, *ipso*-PPh₃), 132.88 (d, J_{P-C} = 12.2 Hz, PPh₃), 134.74 (d, J_{P-C} = 10.4 Hz, PPh₃), 136.20 (s), 136.58 (s), 137.52 (s), 143.36 (s), 148.26 (s), 158.54 (s). Anal. Calcd. For C₅₈H₄₇F₆NOP₃Rh•CH₂Cl₂ (1168.75): C, 60.63; H, 4.23; N, 1.20. Found: C, 60.20; H, 4.17; N, 1.21.

¹H NMR (δ, 400 MHz, CD₂Cl₂, 295 K): 5.48 (dd, ³J_{CH=CH} = 14.0 Hz, ²J_{RhH} = 6.8 Hz, 1H, CH=CH-C₆H₄CF₃), 6.42 (dd, ³J_{CH=CH} = 13.2 Hz, ²J_{RhH} = 2.4 Hz, 1H, CH=CH-C₆H₄CF₃), 6.74 (m, 6H, PC₆H₄F), 6.86 (m, 2H, C₆H₄CF₃), 6.89-7.07 [m,

14H, 12H ($\text{PC}_6\text{H}_4\text{F}$) + 2H ($\text{C}_6\text{H}_4\text{CF}_3$)], 7.18-7.24 (m, 6H, $\text{PC}_6\text{H}_4\text{F}$), 7.49 (d, $^3J = 8.4$ Hz, 1H), 7.82-7.86 (m, 2H), 8.00 (t, $^3J = 7.2$ Hz, 1H), 8.07 (d, $^3J = 8.0$ Hz, 1H), 8.12 (d, $^3J = 6.8$ Hz, 1H), 8.21 (d, $^3J = 6.9$ Hz, 1H), 9.67 (m, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD_2Cl_2 , 295 K): -143.99 (m, $^1J_{\text{FP}} = 711.2$ Hz, PF_6), 28.28 (dd, $^1J_{\text{RhP}} = 170.0$ Hz, $^2J_{\text{PP}} = 43.6$ Hz, $\text{PC}_6\text{H}_4\text{F}$), 34.55 (dd, $^1J_{\text{RhP}} = 156.4$ Hz, $^2J_{\text{PP}} = 43.6$ Hz, $\text{PC}_6\text{H}_4\text{F}$); ^{13}C { ^1H } NMR (δ , 100 MHz, CD_2Cl_2 , 295 K): 75.46 (dd, $^1J_{\text{RhC}} = 21.7$ Hz, $^2J_{\text{PC}} = 6.6$ Hz, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{CF}_3$), 85.20 (d, $^1J_{\text{RhC}} = 12.5$ Hz, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{CF}_3$), 115.69 (dd, $J_{\text{FC}} = 21.9$ Hz, $J_{\text{PC}} = 11.4$ Hz, $\text{PC}_6\text{H}_4\text{F}$), 115.90 (dd, $J_{\text{FC}} = 21.9$ Hz, $J_{\text{PC}} = 11.0$ Hz, $\text{PC}_6\text{H}_4\text{F}$), 124.06 (q, $^1J_{\text{FC}} = 270.0$ Hz, CF_3), 124.66 (s), 124.76 (s), 125.15 (q, $^3J_{\text{FC}} = 3.5$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 126.01 (d, $^1J_{\text{PC}} = 47.9$ Hz, *ipso*- $\text{PC}_6\text{H}_4\text{F}$), 126.18 (d, $^1J_{\text{PC}} = 40.5$ Hz, *ipso*- $\text{PC}_6\text{H}_4\text{F}$), 126.38 (s), 126.74 (s), 128.02 (s), 125.15 (q, $^4J_{\text{FC}} = 3.5$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 127.86 (q, $^2J_{\text{FC}} = 32.7$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 128.01 (s), 128.67 (s), 129.32 (s), 129.63 (s), 131.09 (s), 134.74 (dd, $J_{\text{FC}} = 11.9$ Hz, $J_{\text{PC}} = 8.6$ Hz, $\text{PC}_6\text{H}_4\text{F}$), 136.68 (s), 137.97 (s), 142.03 (s), 142.57 (s), 148.68 (s), 163.83 (d, $^1J_{\text{FC}} = 252.4$ Hz, *p*- $\text{PC}_6\text{H}_4\text{F}$), 164.07 (d, $^1J_{\text{FC}} = 252.4$ Hz, *p*- $\text{PC}_6\text{H}_4\text{F}$). Anal. Calcd. For $\text{C}_{58}\text{H}_{38}\text{F}_{15}\text{NP}_3\text{Rh}$ (1229.73): C, 56.65; H, 3.11; N, 1.14. Found: C, 57.02; H, 3.29; N, 1.08.

^1H NMR (δ , 400 MHz, CD_2Cl_2 , 295 K): 3.74 (s, 9H, OCH_3), 3.83 (s, 9H, OCH_3), 5.20 (dd, $^3J_{\text{CH}=\text{CH}} = 12.0$ Hz, $^2J_{\text{RhH}} = 4.4$ Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{CF}_3$), 6.45-6.47 (m, 6H, $\text{PC}_6\text{H}_4\text{OCH}_3$), 6.63-6.73 [m, 9H, 6H ($\text{PC}_6\text{H}_4\text{OCH}_3$) + 1H

(CH=CHC₆H₄CF₃) + 2H (C₆H₄CF₃)], 6.87 (m, 6H, PC₆H₄OCH₃), 7.00 (d, ³J = 6.8 Hz, 2H, C₆H₄CF₃), 7.16 (m, 6H, PC₆H₄OCH₃), 7.42(d, ³J = 8.0 Hz, 1H), 7. 67 (m, 1H), 7.78 (d, ³J = 8.0 Hz, 1H), 7.95-7.99 (m, 2H), 8.09 (d, ³J = 7.2 Hz, 1H), 8.23 (d, ³J = 5.6 Hz, 1H), 9.48 (m, 1H); ³¹P {¹H} NMR (δ, 162 MHz, CD₂Cl₂, 295 K): -144.19 (m, ¹J_{FP} = 711.2 Hz, PF₆), 27.50 (dd, ¹J_{RhP} = 169.2 Hz, ²J_{PP} = 43.4 Hz, PPh₃), 31.74 (dd, ¹J_{RhP} = 155.2 Hz, ²J_{PP} = 43.1 Hz, PPh₃); ¹³C {¹H} NMR (δ, 100 MHz, CD₂Cl₂, 295 K): 55.75 (s, OCH₃), 55.78 (s, OCH₃), 72.39 (dd, ¹J_{RhC} = 22.3 Hz, ²J_{PC} = 6.5 Hz, CH=CH-C₆H₄CF₃), 82.76 (d, ¹J_{RhC} = 12.7 Hz, CH=CH-C₆H₄CF₃), 113.54 (d, J_{PC} = 11.1 Hz, PC₆H₄OCH₃), 113.59 (d, J_{PC} = 10.9 Hz, PC₆H₄OCH₃), 121.86 (d, ¹J_{PC} = 49.9 Hz, *ipso*-PC₆H₄OCH₃), 124.35 (¹J_{PC} = 46.9 Hz, *ipso*-P-C₆H₄OCH₃), 123.56 (s), 124.35 (q, ¹J_{FC} = 270.0 Hz, CF₃), 124.86 (q, ³J_{FC} = 3.6 Hz, C₆H₄CF₃), 126.12 (s), 126.30 (s), 126.72 (q, ²J_{FC} = 31.0 Hz, C₆H₄CF₃), 127.74 (s), 127.86 (s), 129.22 (s), 129.49 (s), 130.83 (s), 134.09 (d, J_{PC} = 13.4 Hz, PC₆H₄OCH₃), 135.89 (d, J_{PC} = 11.7 Hz, PC₆H₄OCH₃), 136.65 (s), 136.69 (s), 137.53 (s), 143.09 (s), 143.16 (s), 147.76 (s), 160.88 (d, ⁴J_{PC} = 1.8 Hz, *p*-PC₆H₄OCH₃), 161.15 (d, ⁴J_{PC} = 1.9 Hz, *p*-PC₆H₄OCH₃). Anal. Calcd. For C₆₄H₅₆F₉NO₆P₃Rh (1301.95): C, 59.04; H, 4.34; N, 1.08. Found: C, 58.80; H, 3.66; N, 1.44.

¹H NMR (δ, 400 MHz, CD₂Cl₂, 295 K): 5.25 (dd, ³J_{CH=CH} = 13.7 Hz, ²J_{RhH} = 6.9 Hz, 1H, CH=CH-C₆H₄CF₃), 6.41 (d, ³J = 13.6 Hz, 1H, CH=CH-C₆H₄CF₃),

6.72 (d, $^3J = 6.5$ Hz, 2H, $C_6H_4CF_3$), 6.87-6.90 (m, 6H, PPh_3), 6.94-6.97 [m, 10H, 9H (PPh_3) + 1H ($C_{17}H_8N$)], 7.10-7.25 [m, 13H, 12H (PPh_3) + 1H ($C_{17}H_{10}N$)], 7.33-7.37 (m, 3H, PPh_3), 7.71 (t, $^3J = 7.3$ Hz, 1H), 7.76-7.81 [m, 3H, 2H ($C_6H_4CF_3$) + 1H ($C_{17}H_{10}N$)], 8.04 (t, $^3J = 7.9$ Hz, 1H), 8.15 (d, $^3J = 7.3$ Hz, 1H), 8.33 (d, $^3J = 7.2$ Hz, 1H), 8.59 (d, $^3J = 8.2$ Hz, 1H), 8.74 (d, $^3J = 8.2$ Hz, 1H), 9.55 (m, 1H); ^{31}P { 1H } NMR (δ , 162 MHz, CD_2Cl_2 , 295 K): -144.23 (m, $^1J_{FP} = 709.9$ Hz, PF_6), 30.88 (dd, $^1J_{RhP} = 169.7$ Hz, $^2J_{PP} = 43.0$ Hz, PPh_3), 35.71 (dd, $^1J_{RhP} = 156.2$ Hz, $^2J_{PP} = 44.0$ Hz, PPh_3); ^{13}C { 1H } NMR (δ , 75 MHz, CD_2Cl_2 , 295 K): 75.33 (dd, $^1J_{RhC} = 21.9$ Hz, $^2J_{PC} = 6.3$ Hz, $CH=CH-C_6H_4CF_3$), 84.53 (d, $^2J_{RhC} = 12.0$ Hz, $CH=CH-C_6H_4CF_3$), 122.41 (s), 122.94 (s), 123.75 (s), 124.49 (s), 125.06 (q, $^3J_{FC} = 3.7$ Hz, $C_6H_4CF_3$), 125.07 (d, $^1J_{FC} = 134.3$ Hz, CF_3), 126.80 (s), 127.31 (q, $^2J_{FC} = 31.1$ Hz, $C_6H_4CF_3$), 127.85 (s), 127.91 (s), 128.06 (d, $J_{PC} = 9.7$ Hz, PPh_3), 128.18 (d, $J_{PC} = 9.0$ Hz, PPh_3), 128.40 (s), 128.73 (s), 129.49 (s), 129.61 (s), 130.00 (d, $^4J_{PC} = 2.2$ Hz, $p-PPh_3$), 130.18 (dd, $^1J_{PC} = 45.8$ Hz, $ipso-PPh_3$), 130.32 (s), 130.49 (d, $^4J_{PC} = 2.0$ Hz, $p-PPh_3$), 130.60 (d, $^1J_{PC} = 42.1$ Hz, $ipso-PPh_3$), 131.46 (s), 132.39 (s), 132.83 (d, $J_{PC} = 12.1$ Hz, PPh_3), 134.57 (d, $J_{PC} = 10.5$ Hz, PPh_3), 135.29 (s), 136.28 (s), 142.24 (s), 143.38 (s), 147.12 (s). Anal. Calcd. For $C_{62}H_{46}F_9NP_3Rh$ (1171.85): C, 63.55; H, 3.96; N, 1.20. Found: C, 63.15; H, 4.32; N, 1.35.

1H NMR (δ , 500 MHz, CD_2Cl_2 , 295 K): 5.28 (dd, $^3J_{CH=CH} = 14.0$ Hz, $^2J_{Rh-H} =$

7.4 Hz, 1H, CH=CH-C₆H₄CF₃), 6.48 (d, ³J_{CH=CH} = 12.7 Hz, 1H, CH=CH-C₆H₄CF₃), 6.87-6.90 (m, 2H, C₆H₄CF₃), 6.95-6.97 (m, 6H, PPh₃), 6.95-6.97 [m, 14H, 12H (PPh₃) + 2H (C₆H₄CF₃)], 7.19-7.24 (m, 15H, PPh₃), 7.34-7.37 (m, 3H, PPh₃), 7.73-7.77 (m, 2H), 7.98 (d, ³J = 7.9 Hz, 1H), 8.06 (t, ³J = 7.6 Hz, 1H), 8.28 (d, ³J = 7.2 Hz, 1H), 8.49 (d, ³J = 8.2 Hz, 1H), 9.60 (m, 1H); ³¹P {¹H} NMR (δ, 202 MHz, CD₂Cl₂, 295 K): -144.19 (m, ¹J_{FP} = 709.4 Hz, PF₆), 30.39 (dd, ¹J_{RhP} = 167.9 Hz, ²J_{PP} = 43.1 Hz, PPh₃), 34.82 (dd, ¹J_{RhP} = 154.0 Hz, ²J_{PP} = 42.8 Hz, PPh₃); ¹³C {¹H} NMR (δ, 125 MHz, CD₂Cl₂, 295 K): 73.85 (dd, ¹J_{RhC} = 20.8 Hz, ²J_{PC} = 6.5 Hz, CH=CH-C₆H₄CF₃), 82.90 (d, ¹J_{RhC} = 12.6 Hz, CH=CH-C₆H₄CF₃), 124.18 (q, ¹J_{FC} = 270.1 Hz, CF₃), 124.35 (s), 124.77 (s), 125.03 (q, ³J_{FC} = 3.1 Hz, C₆H₄CF₃), 125.83 (s), 127.23 (q, ²J_{FC} = 33.0 Hz, C₆H₄CF₃), 127.11 (s), 127.41 (s), 127.98 (s), 128.18 (d, J_{PC} = 12.4 Hz, PPh₃), 128.27 (d, J_{PC} = 10.3 Hz, PPh₃), 129.05 (s), 129.89 (s), 130.19 (d, ¹J_{PC} = 48.5 Hz, *ipso*-PPh₃), 130.22 (s), 130.59 (s, *p*-PPh₃), 130.55 (d, ¹J_{PC} = 42.1 Hz, *ipso*-PPh₃), 131.67 (s), 132.81 (d, J_{PC} = 12.0 Hz, PPh₃), 134.54 (d, J_{PC} = 10.3 Hz, PPh₃), 135.07 (s), 136.53 (s), 136.87 (s), 142.16 (s), 148.34 (s). Anal. Calcd. For C₅₈H₄₃BrF₉NP₃Rh (1200.69): C, 58.02; H, 3.61; N, 1.17. Found: C, 58.45; H, 3.84; N, 1.30.

¹H NMR (δ, 400 MHz, CD₂Cl₂, 295 K): 4.78 (d, ³J_{CH=CH} = 14.0 Hz, 1H, CH=CH-C₆H₄CF₃), 6.02 (d, ³J_{CH=CH} = 14.2 Hz, 1H, CH=CH-C₆H₄CF₃), 6.68 (d,

$^3J_{\text{CH=CH}} = 7.2$ Hz, 2H, $\text{C}_6\text{H}_4\text{CF}_3$), 6.94 (d, $^3J = 7.6$ Hz, 1H), 7.02-7.12 [m, 25H, 24 H (PPh_3) + 1H ($\text{C}_{11}\text{H}_8\text{N}$)], 7.32 [m, 7H, 6H (PPh_3) + 1H ($\text{C}_{11}\text{H}_8\text{N}$)], 7.43-7.55 [m, 4H, 2H ($\text{C}_6\text{H}_4\text{CF}_3$) + 2H ($\text{C}_{11}\text{H}_8\text{N}$)], 7.75-7.82 (m, 2H), 9.00 (d, $^3J = 4.7$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD_2Cl_2 , 295 K): -144.31 (m, $^1J_{\text{FP}} = 711.6$ Hz, PF_6), 30.91 (dd, $^1J_{\text{RhP}} = 171.3$ Hz, $^2J_{\text{PP}} = 41.2$ Hz, PPh_3), 35.48 (dd, $^1J_{\text{RhP}} = 156.2$ Hz, $^2J_{\text{PP}} = 41.8$ Hz PPh_3); ^{13}C { ^1H } NMR (δ , 75 MHz, CD_2Cl_2 , 255 K): 81.90 (dd, $^1J_{\text{RhC}} = 18.1$ Hz, $^2J_{\text{PC}} = 5.8$ Hz, $\text{CH=CH-C}_6\text{H}_4\text{CF}_3$), 87.67 (d, $^1J_{\text{RhC}} = 10.1$ Hz, $\text{CH=CH-C}_6\text{H}_4\text{CF}_3$), 124.40 (q, $^1J_{\text{FC}} = 270.2$ Hz, CF_3), 125.53 (q, $^3J_{\text{FC}} = 3.5$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 125.72 (s), 125.80 (s), 127.89 (q, $^2J_{\text{FC}} = 32.0$ Hz, $\text{C}_6\text{H}_4\text{CF}_3$), 128.03 (s), 128.12 (s), 128.35 (d, $J_{\text{PC}} = 9.8$ Hz, PPh_3), 128.70 (d, $J_{\text{PC}} = 10.3$ Hz, PPh_3), 128.93 (s), 129.10 (s), 130.69 (s, $p\text{-PPh}_3$), 130.81 (d, $^1J_{\text{PC}} = 44.3$ Hz, ipso-PPh_3), 131.13 (d, $^1J_{\text{PC}} = 43.7$ Hz, ipso-PPh_3), 132.14 (s), 132.29 (s), 133.30 (s), 133.64 (d, $J_{\text{PC}} = 12.0$ Hz, PPh_3), 134.65 (s), 134.86 (d, $J_{\text{PC}} = 10.4$ Hz, PPh_3), 135.98 (s), 139.39 (s), 141.94 (s), 149.88 (s), 156.28 (s), 162.65 (s). Anal. Calcd. For $\text{C}_{56}\text{H}_{44}\text{F}_9\text{NP}_3\text{Rh}\cdot\text{CH}_2\text{Cl}_2$ (1182.70): C, 57.89; H, 3.92; N, 1.18. Found: C, 58.28; H, 3.94; N, 1.37.

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Chapter 3

Chelation-Assisted Carbon–Halogen Bond Activation by a Rhodium(I) Complex

1. Introduction

Haloarenes are ubiquitously used as organic substrates in catalysis. The interactions between aryl halides and low-valent transition metals often entail carbon-halide bond oxidative addition, which is a key step in transition-metal-catalyzed cross coupling reactions involving haloarenes.^[1] Oxidative addition reactions of aryl halides have been studied mostly for group 10 metals, particularly for Pd(0).^[2,3] Catalytic functionalization of C_{aryl}–Cl bonds has also been achieved in cross-coupling reactions, although C_{aryl}–Cl bonds have relatively high dissociation energy.^[4,5] As a contrast to the ample examples of carbon-halogen oxidative addition to Pd(0), C_{aryl}–halogen oxidative addition is less common for Co(I), Rh(I), and Ir(I) complexes.^[6-16] The generation of such group 9 metal aryl species followed by further functionalization entails synthetically important rhodium-catalyzed C–C coupling reactions,^[17] which is typically achievable with Pd(0) complexes. Recent examples of C_{aryl}–Cl oxidative addition for rhodium and iridium are almost limited to (PNP)M,^[7] [Ir(CO)(PPh₃)₂]⁺,^[8] (Phebox)Rh(H₂O)Cl₂,^[9] RhCl₃(Py)₃,^[10] Rh(PCy₃)₂(H)(Cl)₂,^[11] Rh(diimine)(COD),^[12] Rh(PPh₃)₃F,^[13] [Rh(coe)₂Cl]₂,^[14] (NNN)RhX,^[15] cyclometalated phosphinimine rhodium(I) complexes,^[16] and a low-coordinate

Rh(I) phosphine system.^[18] Weller and co-workers^[18] have recently reported intermolecular C_{aryl}–Cl activation that took place on [Rh(P^{*i*}Bu₃)₂L₂]BAr₄F (BAr₄F = [B(3,5-C₆H₃(CF₃)₂)₄]) (L: weakly coordinating ligands or solvent molecules), which is generated in situ from the 14-electron [Rh(H)₂(P^{*i*}Bu₃)₂]BAr₄F precursor. The high reactivity of this system likely results from the electron-rich character of the metal and the readily accessible coordination sites.

It has been recently reported that [Rh(PPh₃)₂(acetone)₂]⁺, [Rh(H)₂(PPh₃)₂(acetone)₂]⁺, and [Ir(H)₂(PPh₃)₂(acetone)₂]⁺ could mediate the intramolecular C–H activation of heteroarenes by our group, provided there is sufficient chelation assistance from chelating groups such as imines.^[19,20] In this consideration, we are interested in the [Rh(PPh₃)₂(acetone)₂]⁺ system for the activation of C_{aryl}–halogen bonds. This rhodium(I) system might also achieve this goal owing to the low valence of this rhodium complex and high lability of acetone ligands. It is also important to investigate the selectivity of C_{aryl}–H versus C_{aryl}–X activation when these bonds are both accessible. Selective C–H activation in the presence of C_{aryl}–Cl or C_{aryl}–Br bonds has been reported for Pd, Rh, Ir, and Au systems.^[7,21] Activation of C_{aryl}–X (X = Cl, Br, and I) bonds by [Rh(PPh₃)₂(acetone)₂]⁺ under mild conditions by oxidative addition assisted by prior substrate coordination has been achieved. Different rhodium(III) halide products were obtained under different reaction conditions.

2. Results and Discussion

The [Rh(PPh₃)₂(acetone)₂]⁺ complex is the dehydrogenation product of

$[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{acetone})_2]^+$, which could be synthesized by bubbling H_2 through a suspension of $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$ (NBD = norbornadiene) in acetone.^[22] No attempt was made to isolate the dihydride product due to its poor stability. On the basis of related iridium dihydride chemistry,^[7,23] the addition of a hydrogen acceptor such as *tert*-butylethylene (TBE) to this rhodium(III) dihydride should reversibly strip the hydride ligands and afford the proposed $[\text{Rh}(\text{PPh}_3)_2(\text{acetone})_2]^+$ complex in situ.

Attempts to activate the C–X bonds in iodobenzene or 2-bromopyridine by reacting it with $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{acetone})_2]\text{PF}_6$ and TBE in acetone resulted in a mixture of unidentifiable species. Thus, we focused on C–X activation with chelation assistance. Stirring a mixture of 10-chlorobenzo[*h*]quinoline (**1A-Cl**), TBE (20 equiv), and $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{acetone})_2]\text{PF}_6$ in acetone slowly led to a yellow precipitate (**2A-Cl**) at ambient temperature (Scheme1). The resulting complex **2A-Cl** was isolated in 89% yield and was characterized by ^1H , ^{13}C , and ^{31}P NMR spectroscopy and elemental analysis. In the ^1H NMR spectrum, neither hydride resonance signal nor any signal of ligated acetone could be detected. In the ^{13}C NMR spectrum, a characteristic quaternary carbon signal at δ 154.2 (dt, $^1J_{\text{RhC}} = 27.7$ Hz, $^2J_{\text{PC}} = 9.5$ Hz) is detected and assigned to Rh-C, suggestive of the metalation of the ligand, likely at the C₁₀ position facilitated by chelation assistance. In the ^{31}P NMR spectrum, a doublet signal (δ 13.87, $^1J_{\text{RhP}} = 95.0$ Hz) is observed for two equivalent phosphines, indicating their *trans* orientation. The haloarene starting materials can be extended to the bromo analogue (**1A-Br**) and

2-(2-halophenyl)pyridines (**1B-Br** and **1B-I**), and the corresponding monohalide products were isolated in 86-92% yield. All of these rhodium monohalide complexes are soluble in CH₂Cl₂ and CH₃CN but are sparingly soluble in acetone. Complexes **2A-Br**, **2B-Br**, and **2B-I** are relatively stable in CH₃CN, but they decompose slowly in CH₂Cl₂ solutions to give dihalide complexes among other products (vide infra).

Scheme 1. Synthesis of five-coordinate Rh(III) halide complexes.

Single crystals of **2A-Br** and **2B-I** suitable for X-ray crystallographic studies were obtained by the slow diffusion of diethyl ether into their dichloromethane solutions at -20°C. X-ray crystallography unambiguously confirmed the identity of **2A-Br** and **2B-I** as rather rare five-coordinate rhodium(III) halide complexes (Table 1 and Figures 1 and 2). In the crystal structures of **2A-Br** and **2B-I**, the PPh₃ ligands are *trans* to each other and the coordination sphere involves five regular bonds, while the sixth coordination site is empty and is *trans* to the high trans-effect aryl ligand. This type of five-coordinate binding mode has been observed mostly for Rh, Ir, and Ru pincer complexes.^[7,18,24] The Rh–N[2.047(2) Å] and Rh–C [1.991(3) Å] distances in the metalacycles of **2A-Br** are nearly identical

to the corresponding ones in **2B-I**. The phenyl and the pyridyl rings in **2B-I** are essentially coplanar so that there is negligible difference between the N(1)-Rh(1)-C(19) angle of these two complexes [81.43(3)° for **2A-Br** and 79.49(9)° for **2B-I**]. The C(19)-Rh(1)-Br(1) angle in **2A-Br** [105.59(8)°] deviates significantly from 90°, and this is even more pronounced for **2B-I** [C(19)-Rh(1)-I(1) = 114.44(7)°], which is possibly due to the steric repulsion caused by the bulky iodide ligand.

Figure 1. Molecular structure (ORTEP) of the cation of **2A-Br** with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Rh1-Br1, 2.4465(3); Rh1-C19, 1.991(3); Rh1-N1, 2.047(2); Rh1-P1, 2.3675(7); Rh1-P2, 2.3737(7); P1-Rh1-P2, 177.01(3); N1-Rh1-C19, 81.43(3); C19-Rh1-Br1, 105.59(8).

Figure 2. Molecular structure (ORTEP) of the cation of **2B-I**·0.5CH₂Cl₂ with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Rh1-I1, 2.6399(2); Rh1-C19, 1.990(2); Rh1-N1, 2.053(2); Rh1-P1, 2.3605(7); Rh1-P2, 2.3747(7); P1-Rh1-P2, 176.97(2); N1-Rh1-C19, 79.49(9); C19-Rh1-I1, 114.44(7).

Table 1. Crystallographic Data for Complexes **2A-Br**, **2B-I**·0.5CH₂Cl₂, and

	4A-Br₂·0.5MeCN·Et₂O		
	2A-Br	2B-I ·0.5CH ₂ Cl ₂	4A-Br₂·0.5MeCN·Et₂O
empirical formula	C ₄₈ H ₃₈ BrF ₆ NP ₃ Rh	C _{47.5} H ₃₉ ClF ₆ INP ₃ Rh	C ₅₄ H _{49.5} Br ₂ N _{1.5} OP ₂ Rh
molecular weight (g mol ⁻¹)	1030.54	1095.97	1060.12
radiation, λ		Mo K α , 0.71073 Å	
<i>T</i> (K)		173(2)	
cryst syst	orthorhombic	monoclinic	monoclinic
space group	<i>P</i> _{bca}	<i>P</i> ₂₁ / <i>n</i>	<i>P</i> ₂₁ / <i>c</i>
<i>a</i> (Å)	19.7286(5)	12.6321(3)	12.0657(3)
<i>b</i> (Å)	19.7688(6)	20.3275(4)	18.4792(4)
<i>c</i> (Å)	22.2111(7)	17.1309(4)	20.7142(5)
β (deg)	90	91.5330(10)	96.1040(10) ^o
<i>V</i> (Å ³)	8662.6(4)	4397.28(17)	4592.35(19)
<i>Z</i>	4	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.580	1.655	1.533
μ (mm ⁻¹)	1.490	1.321	2.223
cryst size (mm)	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.05	0.20 × 0.16 × 0.10
total, unique no. of rflns	473175, 13285	106611, 13627	60594, 14723
<i>R</i> _{int}	0.0864	0.0467	0.0720
data, restraints, parameters	13285, 0, 550	13627, 0, 550	14723, 0, 561
<i>R</i> , <i>R</i> _w (all data)	0.0361, 0.0900	0.0555, 0.1044	0.1106, 0.1568
GOF	1.128	1.122	1.052
min., max. resid dens (eÅ ⁻³)	-1.283, 1.098	-1.264, 1.060	-1.377, 1.059

We noted that both *ortho*-C-X and *ortho*-C-H bonds in **1B-Br** or **1B-I** can be potentially activated. However, only the C-X activation was observed. To explore the activation of C-H bonds, benzo[*h*]quinoline and 2-phenylpyridine were allowed to react with $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{acetone})_2]^+$. The activation of C-H bonds in these heteroaryl substrates did proceed, but only at elevated temperatures (>50 °C), to afford isolable hydride complexes **3A** and **3B** in 86% and 87% yields, respectively (Scheme 2), which have been fully characterized. In the ^1H NMR spectrum of **3A**, the hydride resonates at δ -12.29 (dt, $^1J_{\text{RhH}} = 16.6$ Hz, $^2J_{\text{PH}} = 11.0$ Hz), and the ligated acetone is also detected. These results indicate that the activation of the *ortho* C-H bonds in **1B-Br** and **1B-I** likely has a higher barrier. The differences between the coordination numbers of **2A-Cl** and **2A-Br** (or **2B-Br**, **2B-I**) and **3A** (or **3B**) seem accountable to steric effects: since electronically one would predict that complexes **2A-Cl** and **2A-Br** (or **2B-Br**, **2B-I**) should be more electrophilic than **3A** (or **3B**) and should have a stronger tendency of acetone binding.

Scheme 2. Synthesis of rhodium hydride complexes.

Heating an acetone solution of **1A-Br** (1.2 equiv), $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{acetone})_2]^+$,

and TBE (20 equiv) under reflux, however, afforded a precipitate, and product **4A-Br₂** was isolated in analytically pure form in 40% yield (Scheme 3). Complex **4A-Br₂** could also be obtained in similar yield by heating an acetone suspension of **2A-Br**. These results indicate that **2A-Br** is an intermediate leading to the decomposition product **4A-Br₂**. ³¹P NMR analysis of the acetone solution from which **4A-Br₂** precipitated shows a major peak at δ 25.2 (d, ²J_{RhP} = 100 Hz), and the ESI-MS spectrum of this acetone solution gives a peak of *m/e* = 391.62. Both this *m/e* value and the isotopic pattern agree with a structure of [(N[^]C)Rh(PPh₃)₂]²⁺ in mass spectrometry. The corresponding species in acetone solution is tentatively assigned to [(N[^]C)Rh(PPh₃)₂(acetone)]²⁺. However, no such analytically pure product could be isolated. We propose that **2A-Br** reversibly dimerizes to a dicationic bridging bromide intermediate which undergoes an irreversible ligand redistribution process to give these two products as a major decomposition pathway (Scheme 4). Similar reactions of the shifting of two bridging halide ligands to one metal center have been reported for Rh, Ir, and Pd.^[25]

Scheme 3. Synthesis of 18-electron rhodium dihalide complexes.

Scheme 4. Formation of complex **4A-Br₂**

Complex **4A-Br₂** has been unambiguously identified by NMR spectroscopy, X-ray crystallography, and elemental analysis. In the ^{31}P or ^{19}F NMR spectrum, no resonance signal of PF_6^- could be detected, indicating that **4A-Br₂** is a neutral complex. The ^{31}P NMR spectrum (CD_2Cl_2) shows that the PPh_3 ligands are equivalent (δ 14.6, d, $^1J_{\text{RhP}} = 91.6$ Hz). Analogously, neutral rhodium(III) dihalides **4B-Br₂** and **4B-I₂** could be synthesized from **1B-Br** and **1B-I** with 38% and 42% yields, respectively (Scheme 3). These dihalide complexes have poor solubility in common organic solvents and are sparingly soluble in CH_2Cl_2 and CH_3CN .

Alternatively, rhodium(III) diiodide complexes (such as **4B-I₂**) could be synthesized from the reaction of the corresponding rhodium hydride (such as **3B**) and I_2 in THF (eq. 1), and the products obtained *via* these two routes have identical spectroscopic data. The scope of this reaction could also be extended to its iridium analogue (complex **5**, eq. 2). One possible mechanism to account for this transformation is that I_2 proceeds by oxidative addition to the metal center to give a rhodium(V) or iridium(V) hydride diiodide complex, followed by proton abstraction. Conversion of transition metal hydrides to metal halides has been reported using various halogenating reagents.^[26]

Single crystals of complex **4A-Br₂** were obtained by the slow diffusion of diethyl ether into its acetonitrile solution. One equivalent of ether and half an equivalent of acetonitrile cocrystallized with **4A-Br₂**. X-ray crystallography unambiguously confirmed the identity of this complex (Figure 3 and Table 1). The Rh(1)–C(1) distance [2.028(4) Å] here is slightly longer than the corresponding one in **2A-Br** [1.991(3) Å]. In complex **4A-Br₂**, the Rh(1)–Br(1) length is significantly longer (ca. 0.1 Å longer) than that of the Rh(1)–Br(2) bond, undoubtedly due to the significantly high trans influence of the aryl ligand compared with the quinoline N atom. Either of the Rh–Br bonds in **4A-Br₂** is at least 0.05 Å longer than the Rh–Br bond in **2A-Br**. In contrast to complex **2A-Br**, the C(1)–Rh(1)–Br(2) angle [90.13(12)°] in **4A-Br₂** is essentially 90°.

Figure 3. Molecular structure (ORTEP) of **4A-Br₂·0.5MeCN·C₄H₁₀O** with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Rh1-Br1, 2.6022(5); Rh1-Br2, 2.5053(5); Rh1-C1, 2.028(4); Rh1-N1, 2.061(3); Rh1-P1, 2.3725(10); Rh1-P2, 2.3913(11); P1-Rh1-P2, 179.49(4); N1-Rh1-C1, 81.85(15); C1-Rh1-Br2, 90.13(12).

Rhodium complexes have been widely used in the dimerization of terminal alkynes, and the most common dimerization products are *trans*-enynes, although *cis*- or *gem*-enynes are also known.^[27] Our investigations of the application of these rhodium monohalide and dihalide complexes started from the catalytic dimerization of phenylacetylene (eq. 3). Both rhodium monohalide and dihalide complexes have been screened with 1 mol % loading under refluxing conditions, and the results are given in Table 2.

Table 2. Screening of rhodium catalysts for the dimerization of phenylacetylene^a

entry	catalyst	solvent	temp (°C)	Selectivity (<i>trans</i> : <i>gem</i>)	NMR yield of <i>trans</i> product (%) ^b
1	4A-Br₂	acetone	56	72:28	40
2	4A-Br₂	CH ₂ Cl ₂	40	82:18	56
3	4A-I₂	CH ₂ Cl ₂	40	90:10	69
4	4B-Br₂	CH ₂ Cl ₂	40	77:23	49
5	4B-I₂	CH ₂ Cl ₂	40	90:10	70
6	4B-I₂	CH ₃ COCH ₃	56	70:30	48
7	4B-I₂	CH ₂ ClCH ₂ Cl	83	65:35	31
8	2A-Br	CH ₂ Cl ₂	40	-	<5
9	4A-Br₂ /NaBAR ₄ ^F	CH ₂ Cl ₂	40	-	<5
10	2B-I	CH ₂ Cl ₂	40	-	<5
11	4B-I₂ /PPh ₃ (1:6)	CH ₂ Cl ₂	40	-	<5

^a Conditions: 0.8 mmol phenylacetylene, 0.008 mmol rhodium catalyst, 4 mL solvent, 12 h, reflux. ^b NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

The 18-electron neutral rhodium dihalide complexes are active to different extents in catalyzing the dimerization of phenylacetylene, and in all cases the *trans*-enyne is the major product and the *gem*-enyne is the only minor product based on ¹H NMR analysis. Catalyst screening in different solvents under refluxing conditions indicates that dichloromethane seems to be the optimal solvent (Table 2). Screening of rhodium catalysts with the same metallacycle entity but with different dihalides shows that diiodide complexes give higher activity and selectivity than dibromides (entry 2 vs entry 3; entry 4 vs entry 5). The activity and selectivity are essentially the same for rhodium catalysts with the same dihalides but with a different metallacyclic motif (entry 3 vs entry 5; entry 2 vs entry 4). The highest NMR yield obtained for the *trans*-enyne is 70%. To our surprise, 16-electron ionic monohalide complexes **2A-Br** and **2B-I** showed very poor NMR yields (entries 8 and 10). This is in consistent with the result obtained when a

combination of **4A-Br₂** and NaBAR₄F was used in a 1 to 1.2 ratio (entry 9). Here, the addition of NaBAR₄F inhibits this reaction, and this system is in fact equivalent to the cation of **2A-Br** generated in situ: the bromide *trans* to the aryl ligand should be readily removed under these conditions. We also noted that this dimerization reaction is inhibited by the addition of PPh₃ (entry 11, Table 2).

Complex **4B-I₂** was then retained to further study the scope of this type of catalytic reaction (eq. 4) in CH₂Cl₂, and NMR yields are given in Table 3. Terminal alkyne substrates with electron-rich or electron-poor aryl substituents all dimerize, with the lowest *trans* to *gem* selectivity (87:13) observed for *para*-NO₂(C₆H₄)C≡CH (entry 5). Alkynes with electron-poor aryl groups tend to have low reactivity but still give yields comparable to that of phenylacetylene (entries 4-5). For EtOC(O)C≡CH, the dimerization is highly selective, although only 65% NMR yield was obtained (entry 6).

Table 3. Dimerization of terminal alkynes catalyzed by complex **4B-I₂**^a

entry	R	time (h)	selectivity (<i>trans</i> : <i>gem</i>)	NMR yield of <i>trans</i> product (%) ^b
1	Ph-	12	90:10	70
2	<i>p</i> -CH ₃ (C ₆ H ₄)-	12	91:9	88
3	<i>p</i> -CH ₃ O(C ₆ H ₄)-	12	94:6	94
4	<i>p</i> -CF ₃ (C ₆ H ₄)-	24	98:2	71
5	<i>p</i> -NO ₂ (C ₆ H ₄)-	24	87:13	70
6	EtO(O)C-	12	100:0	65

^a Conditions: 0.8 mmol alkyne, 0.008 mmol rhodium catalyst, 4 mL solvent, 12 h, reflux.

^b NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

Scheme 5. Proposed mechanism of alkyne dimerization.

Compared with other representative systems of catalytic alkyne dimerization,^[16] the rhodium dihalides show lower catalytic activity. This is likely due to the 18-electron structures of these complexes with active species. Instead, a vacant coordination site should be generated to accommodate an incoming alkyne substrate. This could be achieved by (i) the dissociation of a halide ligand, particularly the labile halide that is *trans* to the aryl ligand, (ii) dechelation of the nitrogen arm, or (iii) dissociation of one of the phosphine ligands. Dissociation of a labile halide ligand (such as in **4A-Br₂**) seems unlikely since the resulting 16-electron cationic species is in fact the cation part of the corresponding rhodium monohalide (such as **2A-Br**), which proved to be inactive in catalysis (entries 8-9, Table 2). The likelihood of the dissociation of the nitrogen arm of the chelating ligand can be evaluated by comparing the activity of rhodium complexes with different cyclometalated motifs. It is known that dissociation of the nitrogen arm in a flexible chelating system (such as in 2-phenylpyridyl) should have a lower barrier than that in a rigid one (such as in benzo[*h*]quinoly).^[28] In fact, both activity and selectivity are essentially the same^[29] for rhodium catalysts with

different metalacyclic motifs (entries 3 and 5, Table 2), which indicates that nitrogen arm dissociation is unlikely. The proposed mechanism of alkyne dimerization is shown in scheme 5.

To examine the likelihood of phosphine dissociation, we then compared complexes **2B-I** and **4B-I₂** for phosphine exchange reactions. In two separate reactions, **2B-I** or equimolar **4B-I₂** was allowed to react with 10 equivalent of tris(*p*-fluorophenyl) phosphine in CH₂Cl₂ for 1 h (Scheme 6). The ratios of starting materials, monophosphine substitution products, and diphosphine substitution products were analyzed by ³¹P NMR spectroscopy and are given in Scheme 6. The phosphine substitution reaction of **4B-I₂** is significantly faster than that of **2B-I**. The correlation between rates of phosphine substitution and catalytic activity of complexes **2B-I** and **4B-I₂** agrees with the hypothesis that the five-coordinate species derived from the dissociation of a PPh₃ ligand is the most likely active catalyst. This hypothesis is also consistent with the fact that rhodium diiodides possess higher catalytic activity than rhodium dibromides (entries 4 and 5, Table 2), the dissociation of a PPh₃ ligand from a rhodium diiodide complex is favored for both electronic and steric reasons. Electronically, the metal center is relatively more electron-rich for diiodide complexes. Sterically, the large bulk of iodides provides steric repulsion to facilitate the departure of a phosphine ligand. Both of these factors will favor the dissociation of a phosphine ligand to generate an active 16-electron intermediate.

Scheme 6

3. Conclusions

We have achieved nitrogen coordination-assisted activation of C–X bonds (X = Cl, Br, and I) in the reaction of 2-(2-halophenyl)pyridine or 10-halobenzo[*h*]quinoline and $[\text{Rh}(\text{PPh}_3)_2(\text{acetone})_2]^+$. A series of rather rare five-coordinate 16-electron cationic rhodium(III) monohalide intermediates has been synthesized under mild conditions. However, reactions of these haloarenes and $[\text{Rh}(\text{PPh}_3)_2(\text{acetone})_2]^+$ in acetone under reflux afforded neutral octahedral rhodium(III) dihalide complexes. Alternatively, rhodium and iridium diiodides with these cyclometalation motifs could be synthesized from the corresponding hydride complexes *via* hydride-iodide exchange. X-ray crystal structures of representative mono- and dihalide complexes have been reported. The aryl ligands are *trans* to vacant coordination sites in these five-coordinate monohalide complexes. The catalytic activity of these rhodium(III) halide complexes has been assessed for the dimerization of terminal alkynes. The 18-electron rhodium dihalides are much more active catalysts, while cationic rhodium monohalide

complexes are essentially inactive. Screening of catalysts shows that such rhodium diiodide complexes possess higher catalytic activity than the dibromide complexes. A five-coordinate phosphine dissociation product of a dihalide complex has been proposed as the active species in the catalytic cycle.

4. Experimental Section

4.1 General considerations. All manipulations were carried out using standard Schlenk techniques. All chemicals were used as received without any further purification unless otherwise specified. All solvents were degassed and dried by standard techniques. NMR spectra were obtained on a Bruker DPX 300, AMX 400, 500, or JEOL ECA 400 spectrometer. The chemical shift is given as dimensionless δ values and is referenced relative to SiMe₄ for ¹H and ¹³C NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer.

4.2 Synthesis and characterization Compounds **1A-Cl**, **1A-Br**, **1B-Br**, **1B-I** were prepared based on a recent report.^[29] Some of the ¹³C NMR spectra of dihalide complexes could not be obtained with acceptable signal to noise ratio due to their poor solubility in common solvents.

Compound 2A-Cl. To a suspension of [Rh(NBD)(PPh₃)₂]⁺PF₆⁻ (100 mg, 0.116 mmol) in acetone (5 ml) was bubbled H₂ for 15 min at 0 °C, during which time the color of the solution changed from red to yellow. *tert*-Butylethylene (0.5 ml) and 10-chlorobenzo[*h*]quinoline (30 mg, 0.139 mmol) were then added to the

solution and were stirred at room temperature for 2 h. The resulting precipitate was then filtered and washed with diethyl ether 2×20 ml to give a yellow powder **2A-Cl**. Yield: 102 mg (0.103 mmol, 89%). ^1H NMR (δ , 400 MHz, CD_3CN , 298 K): 6.85 (dd, $^3J = 8.0$ Hz, $^3J = 5.6$ Hz, 1H), 7.05-7.09 (m, 12H, PPh_3), 7.12-7.21 [m, 13H, 12H (PPh_3) + 1H ($\text{C}_{13}\text{H}_8\text{N}$)], 7.26 (m, 6H, PPh_3), 7.33 (d, $^3J = 8.0$ Hz, 1H), 7.58 (d, $^3J = 7.8$ Hz, 1H), 7.71-7.74 (m, 2H), 7.80 (d, $^3J = 8.0$ Hz, 1H), 8.15 (d, $^3J = 5.5$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD_3CN , 298 K): -144.62 (m, $^1J_{\text{F-P}} = 706.5$ Hz, PF_6), 13.87 (d, $^1J_{\text{Rh-P}} = 95.0$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 100 MHz, CD_3CN , 298 K): 122.08 (s), 122.38 (s), 123.64 (s), 127.02 (s), 127.90 (t, $J_{\text{P-C}} = 4.8$ Hz, PPh_3), 128.70 (t, $^1J_{\text{P-C}} = 23.9$ Hz, *ipso*- PPh_3), 128.81 (s), 129.43 (s), 130.48 (s, *p*- PPh_3), 133.29 (s), 133.74 (t, $J_{\text{P-C}} = 4.8$ Hz, PPh_3), 136.25 (s), 137.55 (s), 139.27 (s), 150.03 (s), 152.56 (s), 154.18 (dt, $^1J_{\text{Rh-C}} = 27.7$ Hz, $^2J_{\text{P-C}} = 9.5$ Hz, CRh). Anal. Calcd. For $\text{C}_{49}\text{H}_{38}\text{ClF}_6\text{NP}_3\text{Rh}$ (986.10): C, 59.68; H, 3.88; N, 1.42. Found: C, 59.66; H, 3.50; N, 1.73.

Compound 2A-Br. **2A-Br** was synthesized by directly following the procedure for the preparation of **2A-Cl**. The reaction of $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+\text{PF}_6^-$ (500 mg, 0.578 mmol) and 10-bromobenzo[*h*]quinoline (179 mg, 0.694 mmol) gave a yellow powder **2A-Br**. Yield: 513 mg (0.497 mmol, 86%). ^1H NMR (δ , 400 MHz, CD_3CN , 298 K): 6.91 (dd, $^3J = 8.0$ Hz, $^3J = 5.6$ Hz, 1H), 7.05-7.12 (m, 24H, PPh_3), 7.21 (t, $^3J = 7.8$ Hz, 1H), 7.25-7.29 (m, 6H, PPh_3), 7.36 (d, $^3J = 8.8$ Hz, 1H), 7.63 (d, $^3J = 7.6$ Hz, 1H), 7.78 (m, 2H), 7.85 (d, $^3J = 8.0$ Hz, 1H), 8.19 (d, $^3J = 5.2$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD_3CN , 298 K): -144.62 (m, $^1J_{\text{F-P}} =$

706.7 Hz, PF₆), 14.62 (d, ¹J_{Rh-P} = 94.6 Hz, PPh₃); ¹³C {¹H} NMR (δ, 100 MHz, CD₃CN, 298 K): 122.09 (s), 122.98 (s), 123.63 (s), 127.17 (s), 127.75 (t, J_{P-C} = 4.88 Hz, PPh₃), 128.77 (t, ¹J_{P-C} = 23.8 Hz, *ipso*-PPh₃), 128.79 (s), 129.82 (s), 130.41 (s, *p*-PPh₃), 133.31 (s), 133.93 (t, J_{P-C} = 5.0 Hz, PPh₃), 136.29 (s), 138.96 (s), 138.44 (s), 139.31 (s), 149.82 (s), 152.48 (s), 154.38 (dt, ¹J_{Rh-C} = 27.8 Hz, ²J_{P-C} = 10.5 Hz, CRh). Anal. Calcd. For C₄₉H₃₈BrF₆NP₃Rh (1030.55): C, 57.11; H, 3.72; N, 1.36. Found: C, 57.19; H, 3.27; N, 1.31.

Compound 2B-Br. **2B-Br** was synthesized by directly following the procedure for the preparation of **2A-Cl**. The reaction of [Rh(NBD)(PPh₃)₂]⁺PF₆⁻ (100 mg, 0.116 mmol) and 2-(2-bromophenyl)pyridine (32 mg, 0.139 mmol) gave **2B-Br** as a yellow powder. Yield: 107 mg (0.107 mmol, 92%). ¹H NMR (δ, 400 MHz, CD₃CN, 298 K): 6.52 (t, ³J = 6.6 Hz, 1H), 6.72 (t, ³J = 7.6 Hz, 1H), 7.08 (t, ³J = 7.6 Hz, 2H), 7.16-7.19 (m, 12H, PPh₃), 7.23-7.25 [m, 13H, 12H (PPh₃) + 1H (C₁₁H₈N)], 7.26 (m, 6H, PPh₃), 7.30 (d, ³J = 8.0 Hz, 1H), 7.35 (d, ³J = 8.0 Hz, 1H), 7.88 (d, ³J = 6.0 Hz, 1H); ³¹P {¹H} NMR (δ, 162 MHz, CD₃CN, 298 K): -144.62 (m, ¹J_{F-P} = 705.8 Hz, PF₆), 14.95 (d, ¹J_{Rh-P} = 95.8 Hz, PPh₃); ¹³C {¹H} NMR (δ, 100 MHz, CD₃CN, 298 K): 119.92 (s), 123.64 (s), 123.82 (s), 124.12 (s), 128.00 (t, J_{P-C} = 4.8 Hz, PPh₃), 129.06 (t, ¹J_{P-C} = 23.9 Hz, *ipso*-PPh₃), 130.51 (s, *p*-PPh₃), 130.85 (s), 131.54 (s), 134.28 (t, J_{P-C} = 4.8 Hz, PPh₃), 137.96 (s), 140.92 (s), 143.73 (s), 150.56 (s), 157.93 (dt, ¹J_{Rh-C} = 26.7 Hz, ²J_{P-C} = 9.5 Hz, CRh). Anal. Calcd. For C₄₇H₃₈BrF₆NP₃Rh (1006.53): C, 56.08; H, 3.81; N, 1.39. Found: C, 56.48; H, 4.22; N, 1.42.

Compound 2B-I. **2B-I** was synthesized by directly following the procedure for the preparation of **2A-Cl**. The reaction of $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+\text{PF}_6^-$ (500 mg, 0.578 mmol) and 2-(2-iodophenyl)pyridine (195 mg, 0.694 mmol) gave **2B-I** as an orange powder. Yield: 548 mg (0.520 mmol, 90%). ^1H NMR (δ , 300 MHz, CD_3CN , 298 K): 6.60 (t, $^3J = 6.4$ Hz, 1H), 6.72 (t, $^3J = 8.5$ Hz, 1H), 7.13-7.24 [m, 26H, 24H (PPh_3)+2H ($\text{C}_{11}\text{H}_8\text{N}$)], 7.31-7.40 [m, 7H, 6H (PPh_3)+1H ($\text{C}_{11}\text{H}_8\text{N}$)], 7.45 (d, $^3J = 9.2$ Hz, 1H), 7.74 (d, $^3J = 8.5$ Hz, 1H), 7.94 (d, $^3J = 6.4$ Hz, 1H); ^{31}P { ^1H } NMR (δ , 162 MHz, CD_3CN , 298 K): -143.99 (m, $^1J_{\text{F-P}} = 703.5$ Hz, PF_6), 16.15 (d, $^1J_{\text{Rh-P}} = 94.0$ Hz, PPh_3); ^{13}C { ^1H } NMR (δ , 100 MHz, CD_3CN , 298 K): 120.19 (s), 123.76 (s), 123.95 (s), 124.05 (s), 127.85 (t, $J_{\text{P-C}} = 4.8$ Hz, PPh_3), 129.56 (t, $^1J_{\text{P-C}} = 23.95$ Hz, *ipso*- PPh_3), 130.48 (s, *p*- PPh_3), 131.39 (s), 134.59 (t, $J_{\text{P-C}} = 5.8$ Hz, PPh_3), 138.06 (s), 143.77 (s), 144.11 (s), 150.10 (s), 158.06 (dt, $^1J_{\text{Rh-C}} = 26.8$ Hz, $^2J_{\text{P-C}} = 10.5$ Hz, CRh), 163.61 (s). Anal. Calcd. For $\text{C}_{47}\text{H}_{38}\text{IF}_6\text{NP}_3\text{Rh}$ (1053.53): C, 53.58; H, 3.64; N, 1.33. Found: C, 53.17; H, 3.86; N, 1.44.

Complex 3A. To a suspension of $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+\text{PF}_6^-$ (500 mg, 0.578 mmol) in acetone (8 ml) was bubbled H_2 for 15 min at 0 °C, during which time the color of the solution changed from red to light yellow. *tert*-Butylethylene (0.8 ml) and benzo[*h*]quinoline (124 mg, 0.694 mmol) were then added to the solution and the mixture was refluxed for 5 h. The solution was concentrated to 0.5 ml under reduced pressure. The residue was washed with diethyl ether (2×20 ml) to give **3A** as a white powder. Yield: 502 mg (0.497 mmol, 86%). ^1H NMR (δ , 300 MHz, CD_3COCD_3 , 295 K): -12.29 (dt, $^1J_{\text{Rh-H}} = 16.6$ Hz, $^2J_{\text{P-H}} = 11.0$ Hz, 1H, RhH), 2.06

(s, 6H, acetone), 6.96 (t, $^3J = 7.7$ Hz, 1H), 7.05-7.38 [m, 32H, 2H ($C_{13}H_8N$)+30H (PPh_3)], 7.43 (d, $^3J = 7.7$ Hz, 1H), 7.57 (d, $^3J = 8.8$ Hz, 1H), 7.78 (dd, $^3J = 8.0$ Hz, $^3J = 5.0$ Hz, 1H), 8.16 (d, $^3J = 7.9$ Hz, 1H), 9.79 (d, $^3J = 4.9$ Hz, 1H); ^{31}P { 1H } NMR (δ , 121 MHz, CD_3COCD_3 , 295 K): -143.56 (m, $^1J_{F-P} = 704.0$ Hz, PF_6), 39.91 (d, $^1J_{Rh-P} = 114.3$ Hz, PPh_3); ^{13}C { 1H } NMR (δ , 100 MHz, CD_3COCD_3 , 295 K): 120.52 (s), 122.44 (s), 122.83 (s), 126.83 (s), 127.31 (s), 128.08 (t, $J_{P-C} = 4.7$ Hz, PPh_3), 128.60 (t, $^1J_{P-C} = 23.0$ Hz, *ipso*- PPh_3), 130.30 (s, *p*- PPh_3), 133.36 (t, $J_{P-C} = 5.6$ Hz, PPh_3), 134.73 (s), 135.73 (s), 138.44 (s), 139.65 (s), 148.19 (s), 150.71 (s), 153.08 (dt, $^1J_{Rh-C} = 31.0$ Hz, $^2J_{P-C} = 11.2$ Hz, CRh), 205.26 (CO). Anal. Calcd. For $C_{54}H_{45}F_6NOP_3Rh$ (1009.74): C, 61.85; H, 4.49; N, 1.39. Found: C, 61.54; H, 4.95; N, 1.43.

Complex 3B. Complex **3B** was obtained as a white powder by directly following the synthesis of **3A**. Yield: 428 mg (0.44 mmol, 87%). 1H NMR (δ , 300 MHz, CD_3COCD_3 , 295 K): -12.26 (dt, 1H, $^1J_{Rh-H} = 15.6$ Hz, $^2J_{P-H} = 10.9$ Hz, Rh-H), 2.06 (s, 6H, acetone), 6.50 (t, $^3J = 6.7$ Hz, 1H), 6.87 (t, $^3J = 7.6$ Hz, 1H), 7.03 (d, $^3J = 7.7$ Hz, 1H), 7.12-7.42 [m, 33H, 3H ($C_{11}H_8N$) + 30H (PPh_3)], 7.62 (t, $^3J = 6.8$ Hz, 1H), 9.46 (d, $^3J = 5.5$ Hz, 1H); ^{31}P { 1H } NMR (δ , 121 MHz, CD_3COCD_3 , 295 K): -143.58 (m, $^1J_{F-P} = 705.1$ Hz, PF_6), 39.91 (d, $^1J_{Rh-P} = 115.8$ Hz, PPh_3); ^{13}C { 1H } NMR (δ , 75 MHz, CD_3CN , 295 K): 119.31 (s), 121.99 (s), 122.22 (s), 124.64 (s), 128.54 (s), 128.16 (t, $J_{P-C} = 4.9$ Hz, PPh_3), 129.93 (t, $^1J_{P-C} = 23.4$ Hz, *ipso*- PPh_3), 130.30 (s, *p*- PPh_3), 133.39 (t, $J_{P-C} = 5.8$ Hz, PPh_3), 136.85 (s), 142.10 (s), 144.03 (s), 149.33 (s), 161.69 (s), 159.56 (dt, $^1J_{Rh-C} = 28.4$ Hz, $^2J_{P-C} = 10.3$ Hz, Rh-C),

206.45 (CO). Anal. Calcd. For $C_{50}H_{45}F_6NOP_3Rh$ (985.72): C, 60.92; H, 4.60; N, 1.42. Found: C, 60.52; H, 4.96; N, 1.51.

Compound 4A-Br₂. To a suspension of $[Rh(NBD)(PPh_3)_2]^+PF_6^-$ (100 mg, 0.116 mmol) in acetone (5 ml) was bubbled H_2 for 15 min at 0 °C, during which time the color of the solution changed from red to yellow, *tert*-Butylethylene (0.5 ml) and 10-bromobenzo[*h*]quinoline (60 mg, 0.231 mmol) were then added to the solution and were refluxed for 10 h. The precipitate was then filtered, washed with acetone, cold CH_2Cl_2 , and then diethyl ether to give **4A-Br₂** as a yellow powder. Yield: 45.6 mg (0.047 mmol, 41%). 1H NMR (δ , 400 MHz, CD_2Cl_2 , 298 K): 6.53 (dd, $^3J = 8.0$ Hz, $^3J = 5.7$ Hz, 1H), 6.87 (t, $^3J = 7.5$ Hz, 1H), 6.94-6.97 (m, 12H, PPh_3), 7.14 (t, $^3J = 7.4$ Hz, 6H, PPh_3), 7.19-7.24 (m, 12H, PPh_3), 7.41 (d, $^3J = 8.4$ Hz, 2H), 7.56 (d, $^3J = 7.7$ Hz, 1H), 7.69 (d, $^3J = 8.0$ Hz, 1H), 7.74 (d, $^3J = 8.7$ Hz, 1H), 9.02 (d, $^3J = 5.4$ Hz, 1H); ^{31}P { 1H } NMR (δ , 162 MHz, CD_3CN , 298 K): 13.25 (d, $^1J_{Rh-P} = 96.9$ Hz, PPh_3). No ^{13}C NMR spectra could be obtained with acceptable signal to noise ratio due to the poor solubility in common NMR solvents. Single crystals of **4A-Br₂** could be obtained by the diffusion of diethyl ether into a dilute solution of **4A-Br₂** in CH_2Cl_2 or MeCN. Anal. Calcd. For $C_{49}H_{38}Br_2NP_2Rh$ (965.49): C, 60.96; H, 3.97; N, 1.45. Found: C, 60.69; H, 4.01; N, 1.47.

Compound 4A-I₂. To a suspension of rhodium hydride **3A** (100 mg, 0.116 mmol) in THF was added I_2 (50 mg, 0.231 mmol) and the mixture was stirred at 0 °C for 4 h. The precipitate was then filtered and was washed with diethyl ether 2

$\times 20$ ml to give **4A-I₂** as an orange powder. Analytically pure **4A-I₂** could be obtained after recrystallization from the diffusion of diethyl ether into a dilute of **4A-I₂** in CH₂Cl₂. Yield: 87 mg (0.084 mmol, 73%). ¹H NMR (δ , 400 MHz, CD₂Cl₂, 298 K): 6.55 (dd, ³*J* = 7.6 Hz, ³*J* = 5.8 Hz, 1H), 6.85 (t, ³*J* = 7.6 Hz, 1H), 6.90-6.93 (m, 12H, *PPh*₃), 7.10-7.16 (m, 18H, *PPh*₃), 7.42 (d, ³*J* = 8.7 Hz, 1H), 7.50 (d, ³*J* = 7.9 Hz, 1H), 7.70 (d, ³*J* = 7.7 Hz, 1H), 7.75 (d, ³*J* = 7.9 Hz, 1H), 7.78 (d, ³*J* = 8.8 Hz, 1H), 9.32 (d, ³*J* = 5.5 Hz, 1H); ³¹P {¹H} NMR (δ , 162 MHz, CD₂Cl₂, 298 K): 11.98 (d, ¹*J*_{Rh-P} = 94.9 Hz, *PPh*₃). No ¹³C NMR spectra could be obtained with acceptable signal to noise ratio due to its poor solubility in common NMR solvents. Anal. Calcd. For C₄₉H₃₈I₂NP₂Rh (1035.47): C, 55.55; H, 3.62; N, 1.32. Found: C, 55.53; H, 3.86; N, 1.40.

Compound 4B-I₂. **4B-I₂** was synthesized by either following the procedure for **4A-Br₂** or that for **4A-I₂**. The reaction of [Rh(NBD)(PPh₃)₂]⁺PF₆⁻ (100 mg, 0.116 mmol) and 2-(2-iodophenyl)pyridine (65 mg, 0.232 mmol) gave **4B-I₂** as an orange powder. Yield: 50 mg (0.049 mmol, 42%). ¹H NMR (δ , 300 MHz, CD₂Cl₂, 298 K): 6.17 (t, ³*J* = 6.0 Hz, 1H), 6.38 (t, ³*J* = 8.0 Hz, 1H), 6.92-7.04 (m, 12H, *PPh*₃), 7.13-7.25 [m, 9H, 6H (*PPh*₃)+3H (C₁₁H₈N)], 7.35-7.44 [13H, 12H (*PPh*₃)+1H (C₁₁H₈N)], 7.53 (d, ³*J* = 8.4 Hz, 1H), 9.16 (d, ³*J* = 5.8 Hz, 1H); ³¹P {¹H} NMR (δ , 162 MHz, CD₂Cl₂, 298 K): 12.23 (d, ¹*J*_{Rh-P} = 95.7 Hz, *PPh*₃). No ¹³C NMR spectra could be obtained with acceptable signal to noise ratio due to its poor solubility in common NMR solvents. Anal. Calcd. for C₄₇H₃₈I₂NP₂Rh (1035.47): C, 54.52; H, 3.70; N, 1.35. Found: C, 54.09; H, 4.04; N, 1.37.

Compound 4B-Br₂. **4B-Br₂** could be synthesized by directly following the procedure for the preparation of **4A-Br₂**. The reaction of [Rh(NBD)(PPh₃)₂]⁺PF₆⁻ (100 mg, 0.116 mmol) and 2-(2-bromophenyl)pyridine (54 mg, 0.232 mmol) gave **4B-Br₂** as a yellow powder. Yield: 41 mg (0.044 mmol, 38%). ¹H NMR (δ, 300 MHz, CD₂Cl₂, 298 K): 6.17 (t, ³J = 7.6 Hz, 1H), 6.41 (t, ³J = 7.3 Hz, 1H), 6.89 (t, ³J = 7.2 Hz, 1H), 7.01- 7.06 (m, 12H, PPh₃), 7.16-7.21 [m, 7H, 6H (PPh₃)+1H (C₁₁H₈N)], 7.26-7.33 (m, 2H), 7.37-7.45 [13H, 12H (PPh₃)+1H (C₁₁H₈N)], 8.92 (d, ³J = 5.9 Hz, 1H); ³¹P {¹H} NMR (δ, 121 MHz, CD₂Cl₂, 298 K): 13.66 (d, ¹J_{Rh-P} = 96.2 Hz, PPh₃). No ¹³C NMR spectra could be obtained with acceptable signal to noise ratio due to the poor solubility in common NMR solvents. Anal. Calcd. for C₄₇H₃₈Br₂NP₂Rh (941.47): C, 59.96; H, 4.07; N, 1.49. Found: C, 59.99; H, 4.06; N, 1.39.

Compound 5. Iridium compound **5** was synthesized by directly following the procedure for the preparation of **4A-I₂**. The reaction of Iridium hydride (100 mg, 0.091 mmol) and I₂ (99 mg, 0.182 mmol) gave **5** as a yellow powder. Yield: 88 mg (0.077 mmol, 85%). ¹H NMR (δ, 400 MHz, CD₂Cl₂, 298 K): 6.52 (dd, ³J = 7.7 Hz, ³J = 5.8 Hz, 1H), 6.89 (t, ³J = 7.8 Hz, 1H), 6.93-6.97 (m, 12H, PPh₃), 7.14-7.17 (m, 18H, PPh₃), 7.41 (d, ³J = 8.7 Hz, 1H), 7.49 (d, ³J = 7.7 Hz, 1H), 7.62 (m, 2H), 7.80 (d, ³J = 8.7 Hz, 1H), 9.26 (d, ³J = 5.6 Hz, 1H); ³¹P {¹H} NMR (δ, 162 MHz, CD₂Cl₂, 298 K): -26.54 (s, PPh₃); ¹³C {¹H} NMR (δ, 100 MHz, CD₂Cl₂, 298 K): 120.14 (s), 122.04 (s), 122.92 (s), 126.38 (s), 126.68 (t, J_{P-C} = 4.8 Hz, PPh₃), 128.77 (s), 129.25 (s, *p*-PPh₃), 130.63 (t, ¹J_{P-C} = 26.7 Hz, *ipso*-PPh₃), 131.19 (s),

133.21 (s), 135.12 (t, $J_{\text{P-C}} = 4.8$ Hz, PPh_3), 138.08 (s), 140.66 (t, $^2J_{\text{P-C}} = 8.4$ Hz, Ir-C), 153.51 (s), 155.94 (s). One CH resonance signal is missing due to signal overlapping. Anal. Calcd. for $\text{C}_{49}\text{H}_{38}\text{I}_2\text{IrNP}_2$ (1148.81): C, 51.23; H, 3.33; N, 1.22. Found: C, 51.08; H, 3.76; N, 1.25.

4.3 General method for alkyne dimerization. Rhodium catalyst (0.01 mmol, 1 mol %) was added to a dichloromethane solution (3 mL) of an alkyne (1 mmol) in a Schlenk flask and the mixture was then heated under reflux for 12 h. The reaction mixture was cooled to room temperature and all volatiles were removed under reduced pressure to give a residue, which was then chromatographed on silica gel to give the enyne product. The ratio of the *trans*- to *gem*-enyne was analyzed by ^1H NMR spectroscopy for the crude product. The *trans*- to *gem*-enyne ratios and the isolated yields of the major products are listed in Table 3. The identities of the dimerization products of entries 1^[30], 2^[26b], 3^[30], 4^[30], and 5^[30] were confirmed by comparisons with reported NMR data.

Dimerization product of $\text{EtOC(O)C}\equiv\text{CH}$ (entry 6, Table 3). ^1H NMR (δ , 400 MHz, CDCl_3 , 298 K): 1.27 (t, $^3J = 7.1$ Hz, 3H, CH_3), 1.29 (t, $^3J = 7.2$ Hz, 3H, CH_3), 4.20 (q, $^3J = 7.1$ Hz, 2H, CH_2), 4.24 (q, $^3J = 7.1$ Hz, 2H, CH_2), 6.42 (d, $^3J = 16$ Hz, 1H), 6.74 (d, $^3J = 16$ Hz, 1H). ^{13}C { ^1H } NMR (δ , 100 MHz, CDCl_3 , 298 K): 13.99 (s, CH_3), 14.13 (s, CH_3), 61.34 (s, CH_2), 62.49 (s, CH_2), 81.50 (s, $\text{C}\equiv\text{C}$), 87.02 (s, $\text{C}\equiv\text{C}$), 121.54 (s, $\text{C}=\text{C}$), 135.42 (s, $\text{C}=\text{C}$), 153.15 (s, CO), 164.72 (s, CO). Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_4$ (196.2): C, 61.21; H, 6.16. Found: C, 61.38; H, 6.31.

4.4 Crystallographic Analysis. X-ray quality single crystals of complexes

2A-Br, **2B-I**, and **4A-Br₂** were obtained by the slow diffusion of diethyl ether into their dichloromethane or MeCN solutions. Complex **2B-I** co-crystalized with half an equiv of ether. Complex **4A-Br₂** co-crystalized with half an equiv of MeCN and one equivalent of Et₂O. Crystal data were collected on a Bruker X8 Kappa CCD diffractometer at 173 K using graphite monochromated Mo K α radiation (λ = 0.71073Å). APEX2 Software Suite (Bruker, 2005) was used for data acquisition, structure solution, and refinement. Absorption corrections were applied using SADABS. The structure was solved by direct method and refined by full-matrix least-squares method on F^2 using Xshell.

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Part II

Electrochemical Oxidation and Spectroscopic Properties of Phenol Derivatives

Chapter 4

Introduction of Electrochemical Oxidation of Phenols

1. Electrochemical oxidation of phenols at different pH and in non-aqueous media.

The oxidation reactions of phenols play a very important role in many diverse fields: such as in biological systems^[1] and in synthetic antioxidants in foodstuffs.^[2] There are numerous chemical and electrochemical syntheses based on phenol oxidation.^[3] The complex mechanisms and species involved in the electrochemical oxidation of phenols have been investigated extensively over the last several decades.^[4-14] The primary electrochemical oxidation process of phenols can be described in a square-scheme mechanism (Scheme 1).^[15] The different species involved are linked by electron and proton transfers. At different electrode potentials, different pH values and in different solvent-electrolyte systems, a variable range of oxidative intermediates are present. In sufficiently acidic non-aqueous media, phenols **1** can be electrochemically oxidized by one-electron to form the cation radical **2**. For some phenols the equilibrium of the following proton loss reaction is shifted to the side of the cation radical **2** under strong acid conditions. At more positive potentials ($E_2 > E_1$) the cation radical **2** can be oxidized by one-electron to form the dication **3**, which is a very strong acid and loses a proton immediately to form a phenoxonium cation **6** even in strong acid conditions (EEC mechanism).

In organic solvents such as CH_3CN or CH_2Cl_2 in the absence of acids or bases, phenol **1** is oxidized at E_1 to give the cation radical **2** by in a one-electron transfer, The intermediate **2** immediately deprotonates to form the neutral phenoxyl radical **5**, which is further oxidized at the applied potential to give the phenoxonium cation **6**. Because $E_4 < E_1$, one two-electron oxidation peak is observed (ECE mechanism or ECE-DISP mechanism).

In the presence of a strong organic soluble base (such as Et_4NOH), the phenol is deprotonated to form the phenolate anion **4**, which is oxidized by one-electron at a much more negative potential than the starting phenol to form the phenoxyl radical **5**. At a more positive potential, radical **5** is further oxidized in a one-electron transfer to form the phenoxonium ion **6** (CEE mechanism). **6** is itself not generally stable towards base, so it is desirable to use an equal molar amount of base in the initial generation of the phenolate anion.

Scheme 1. Square scheme of phenol oxidation; only one resonance structure of the species **1-6** is shown.

For example, Webster and co-workers reported the oxidative behavior of α -tocopherol which is the most naturally abundant, fully methylated, and biologically active of the four (α , β , γ , δ) structurally related phenolic (PhOH) compounds that are labeled vitamin E in different pure organic solvents and dry acidic and basic organic solvents (Scheme 2).^[16-18] In the absence of water or other nucleophiles, the stability of the oxidized species can be dramatically improved. The phenoxonium cation (α -TO⁺) is one of the only several stable phenoxonium cations that have been spectroscopically characterized.^[19]

In acetonitrile in the absence of added acid or base, α -TOH can be voltammetrically oxidized at approximately +0.5 V vs Fc/Fc⁺ (Fc = ferrocene) by one electron at solid electrodes to form the cation radical (α -TOH^{•+}). The cation radical quickly dissociates into α -TO[•] and a proton, then the radical is immediately further oxidized at the electrode surface by one-electron to form the brightly orange/red-colored phenoxonium cation (α -TO⁺) (Scheme 2, pathway 2). The radical is easier to be oxidized than α -TOH at about +0.2 V, thus the cyclic voltammogram shows one two-electron oxidation peak (Figure 1, green line). α -TO⁺ is relative stable for several hours in absence of water or other nucleophiles and can be reduced back to α -TOH on cyclic voltammetry and controlled potential electrolysis time scales.

Scheme 2. Electrochemical oxidation of α -tocopherol in dry CH_3CN or CH_2Cl_2 .

When $\text{CF}_3\text{SO}_3\text{H}$ is added to the α -TOH solution in CH_3CN or CH_2Cl_2 , α -TOH is oxidized at +0.6 V vs. Fc/Fc^+ by one-electron to form the cation radical. In acidic conditions, the equilibrium constant of the deprotonation step of the hydroxyl group is shifted towards the cation radical, thus cation radical ($\alpha\text{-TOH}^{\bullet+}$) has a substantial lifetime (at least several minutes). The cation radical can be further oxidized at about +1.4 V vs. Fc/Fc^+ by losing one electron to form dication ($\alpha\text{-TOH}^{2+}$) (red line in Figure 1). Cyclic voltammetry, electrolysis and spectroelectrochemical experiments have indicated that the dication is not stable for more than a few seconds and immediately deprotonates to form $\alpha\text{-TO}^+$ which is stable in acidic conditions. $\alpha\text{-TO}^+$ can be reduced back to the radical $\alpha\text{-TO}^\bullet$, which

in acidic conditions is immediately protonated to form the cation radical, which is further reduced back to the starting material (Figure 1, red line; Scheme 2, pathway 1).

The addition of an equimolar amount of organic soluble base (Et_4NOH) to CH_3CN solutions of $\alpha\text{-TOH}$ immediately induces the formation of the phenolate anion ($\alpha\text{-TO}^-$) which can be oxidized at -0.9 V to form $\alpha\text{-TO}^\bullet$ and then at about $+0.2\text{ V}$ to form the cation (Scheme 2, pathway 3). $\alpha\text{-TO}^-$ is easier to oxidize than $\alpha\text{-TOH}$ by approximately -1.5 V , resulting in a substantial shift in potential of the voltammetric process and a decrease in anodic peak current due to a change from a two- to a one-electron oxidation process (Figure 1, blue line). The radical ($\alpha\text{-TO}^\bullet$) in basic condition is relative unstable and easily form other species (mainly *via* a dimerization process), so the oxidation peak of the radical is more complicated.^[20]

Figure 1. Cyclic voltammograms of 2 mM $\alpha\text{-TOH}$ and 0.5 M Bu_4NPF_6 in acidic CH_3CN (—), pure CH_3CN (—), basic CH_3CN (—)

2. Reactions of oxidized species with each other and with other reagents

Although the electron transfer reactions in Scheme 2 are given as

heterogenous steps, the true experiment steps may be more complicated, because some species may react with each other through electron transfers steps (a disproportionation mechanism). For example, the radical cation **2** can react with radical **5** to give phenol **1** and phenoxonium cation **6** (eq. 1).

Furthermore, some other side reactions could take place such as dimerization of the radicals or electrophilic attack of the cations on nucleophiles.^[15] Radical **5** and phenoxonium cation **6** can be stabilized through three resonances (Scheme 3. **a**, **b**, **c**). The products obtained from radical **5** with radical X range from *ortho*- or *para*- substitute quinolide structures **8** and **9** to aromatic ether **7** according to the properties of substitute R, R₁ and radical X.^[21-26] Radical X may be halogen atom,^[21] oxygen radical ($\cdot\text{OOtBu}$, $\cdot\text{O-N=CR}_2$),^[20,21] nitrogen radical ($\cdot\text{NO}$,^[23] $\cdot\text{NO}_2$,^[24] $\cdot\text{NHR}$ ^[25]), or carbon radical ($\cdot\text{CH}_2\text{Ph}$).^[26] The quinolide products are easily formed compared to the ether, and the ether product is obtained from a carbon radical.^[26] When the radical X is another phenoxyl radical **5**, with the exception of the O-O coupling aromatic peroxides, all C-O and C-C coupled species have been found,^[3,12,27] the type of coupling is dependent on the steric and electronic effects of the substituents R and R₁.

Scheme 3. Reaction pathway of phenoxyl radicals **5** and phenoxonium cation **6**.

Phenoxonium cation **6** react with nucleophiles HX (HOH, ROH, ROOH, and RCOOH etc) and quinolide products **8**, **9** can also be obtained.^[28-30] The electronic and steric nature of substitute R and R₁ can dramatically affect the product. Thus, if R₁ is electron-donating, **9** is favored; if R₁ is electron-withdrawing, **8** predominates.

The possible products obtained from the phenoxonium cation **6** may be divided into two groups depending on the reaction pathway shown in Scheme 4. When the substituent Z or Y is OH group (hydroquinone or catechol), the process of oxidation involves losing two electrons and two protons. *Para*- or *ortho*-benzoquinone derivatives are formed, the *para*-benzoquinone **A1** is relative stable, while the *ortho*-benzoquinone **A2** is highly reactive to form dimerizations or other side reactions products in the absence of trapping reagents.^[31-33]

Scheme 4. The reaction pathways of phenoxonium cation with nucleophile.

If substitute Y contains a nucleophile group in **A2**, a cyclization reaction may occur. Such as 4-(2-Aminoethyl)benzene-1,2-diol (dopamine) which is produced in the brain and functions as a neurotransmitter and neurohormone^[34] can be oxidized in aqueous solution relatively easily in a two-electron and two-proton process transforming into the *ortho*-quinone, then the amino group attacks the quinone to form leucoaminochrome which is more easily oxidized to form aminochrome (eq. 2).^[35]

When the phenoxonium cation substitution involves *para*- or *ortho*-alkyl groups with hydrogen atom alpha to the aromatic ring, highly reactive *para*- or *ortho*-benzoquinone methides may be obtained (**A3** or **A4**).^[8,36-38] In pathway B

(Scheme 4), the *para*- or *ortho*-alkoxyphenoxonium cation can be attacked by nucleophiles in the position of the alkoxy group to form dienones (**B1** or **B2**), since the alkoxy is an electron donating group. If the nucleophile is water, *para*- or *ortho*-benzoquinone will be formed. For example, α -tocopherol, the fully methylated form of vitamin E, shows a two-electron oxidation wave during cyclic voltammetry in acetonitrile to form the phenoxonium cation. If the acetonitrile contains water, the water undergoes nucleophile attack at the *para*-carbon to form a hemiketal and then slowly turns to a more stable *para*-benzoquinone. (eq. 3).^[18,20]

In conclusion, phenols and derivatives undergo a series of electron- and proton-transfers to form many species such as radical cations, neutral radicals, diamagnetic cations and dications. These species are very important and extensively investigated and applied in the biological chemistry as antioxidants, signaling molecules and in organic synthesis. The naturally occurring important biological molecules dopamine and vitamin E and other phenol derivatives will be discussed in the following chapters.

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Chapter 5

The Effect of the Supporting Electrolyte on the Electrochemical Oxidation of Dopamine in Water and Organic Solvents

1. Introduction

4-(2-Aminoethyl)benzene-1,2-diol (dopamine) is produced in the brain and functions as a neurotransmitter and neurohormone.^[1] Due to its catechol (*o*-hydroquinone) structure,^[2-4] it can be oxidised in aqueous solution relatively easily in a two-electron and two-proton process transforming into the *o*-quinone, which survives for at least several minutes at pH 1 (Scheme 1, reaction 1). The reaction in Scheme 1 is written as a $-2e^-/-2H^+$ process (concerted mechanism), but the individual electron transfer steps could occur separately to the proton transfer reactions (consecutive mechanism). At low pH, the amine group on dopamine ($pK_a = 8.92$) and dopamine *o*-quinone is protonated; however, as the pH increases the amine exists in its unprotonated form and dopamine *o*-quinone undergoes a cyclisation reaction to form leucoaminochrome (Scheme 1, reaction 2).^[5,6] Leucoaminochrome is oxidized at a less positive potential than dopamine; therefore, it reacts immediately with dopamine *o*-quinone to form aminochrome and dopamine (Scheme 1, reaction 3)^[5,6]. Aminochrome is itself not long-lived and ultimately reacts to form neuromelanin, a polymeric material.

Scheme 1. Oxidation mechanism for dopamine.

Detailed electrochemical experiments have established that the electrochemical behaviour of dopamine is greatly influenced by the, (i) electrode material and surface activity, (ii) pH, (iii) solvent system, and (iv) supporting electrolyte.^[5-15] Because of dopamine's key involvement in neural processes, there is keen interest in *in vivo* voltammetric monitoring of dopamine in mammalian brains.^[16] The voltammetric mechanism involves an adsorption/desorption process at carbon^[17-24] and metallic electrodes,^[21,25-28] which aids in the voltammetric detection limits. Pure carbon fibers give excellent detection limits,^[17-21] and there have been extensive studies that use surface modified electrodes to improve the detection of dopamine and reduce the interference from other biological molecules that are easily oxidised, such as ascorbic acid.^[29-49] The oxidation of dopamine at the interface between aqueous and non-aqueous solvents has also been examined using liquid-liquid electrochemical techniques and 4-electrode potentiostats.^[50-52]

The majority of electrochemical studies on dopamine have been performed in buffered aqueous systems due to its low solubility in most organic solvents and because it exists biologically in an aqueous phase environment rather than within bilayer lipid membranes. It has recently been shown that the buffering capacity of the electrolyte has a large effect on the electrochemical properties of dopamine, due to the protons released during the oxidation reaction effecting the environment at the electrode surface.^[13] In this study we were interested in examining how the aprotic non-aqueous solvents *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) affected the oxidation mechanism of dopamine, and whether the organic solvents could stabilise the dopamine *o*-quinone against the cyclisation reaction.

2. Results and Discussion

2.1. Electrochemistry in buffered aqueous solutions. Figure 1 shows CV data obtained in buffered aqueous solutions at pH 1 and pH 7 during the oxidation of dopamine (DA). At pH 1, dopamine is oxidised in a chemically reversible two-electron, two-proton process to form dopamine *o*-quinone (DAQ) (Scheme 1, reaction 1). As the pH increases, the lifetime of dopamine *o*-quinone decreases due to the cyclisation reaction of the amine group. At slow scan rates ($\nu = 0.05 \text{ V s}^{-1}$) at pH 7, dopamine is observed to undergo oxidation to dopamine *o*-quinone which quickly reacts to form leucoaminochrome (Scheme 1, reaction 2). Because leucoaminochrome is more easily oxidized than dopamine, it is immediately oxidised to aminochrome (AC) which can then be detected as a reduction process

on the reverse scan.^[5,6] Aminochrome's structure is closer to that of a zwitterionic *p*-quinoneimine, than an *o*-quinone, which accounts for the large shift in reduction potential between aminochrome and dopamine *o*-quinone.^[1] At pH 7, as the scan rate is increased to 0.7 V s^{-1} , the cyclisation reaction of dopamine *o*-quinone is outrun and a reversible two-electron, two-proton process is observed, similar to observed at $\nu = 0.05 \text{ V s}^{-1}$ at pH 1. The rate constant for the cyclisation reaction in pH 7 buffered solutions has been estimated by variable scan rate CV experiments to be approximately 0.2 s^{-1} at 25°C .^[5,6]

Figure 1. Cyclic voltammograms of dopamine in aqueous buffered solutions at pH 1 and pH 7 recorded at $22 \pm 2^\circ\text{C}$ at a 3 mm diameter GC electrode and with a starting and finishing potential of 0 V vs. Ag/AgCl. The scan is commenced in the positive potential direction.

It can be seen in Figure 1 that the oxidation process of dopamine shifts to more negative potentials as the pH increases. The observed oxidation potential (E_{obs}) of the process can be estimated from the mid-point of the oxidative (E_{p}^{ox}) and reductive ($E_{\text{p}}^{\text{red}}$) peaks, which vary according to the pH because protons are involved in the reduction reaction.^[53-56] Hence, the measured E_{obs} is shifted from the formal potential (E_{f}^0) according to the Nernst equation;^[57] where n is the

$$E_{\text{obs}} = E_{\text{f}}^0 + \frac{RT}{nF} \times \ln \frac{[\text{DAQ}][\text{H}^+]^2}{[\text{DA}]} \quad (1)$$

number of electrons transferred (2), R is the gas constant ($8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (in K) and F is the Faraday constant (96485 C mol^{-1}). When $[\text{DA}] = [\text{DAQ}]$, then $E_{\text{obs}} = E_{1/2}^{\text{r}}$ (the reversible half-wave potential).^[57] According to eq 1, at 25°C the $E_{1/2}^{\text{r}}$ optimally shifts by -59.2 mV per unit increase in pH (providing the E_{f}^0 does not significantly vary with the change in pH). Equation 1 is valid for pH values between 1–7, while in more basic conditions the acid dissociation constants of all the protonated compounds need to be incorporated into the Nernst equation.^[54-56]

2.2. Electrochemistry in pure DMF and DMSO. Figure 2 show cyclic voltammograms of dopamine and 4-methylcatechol in DMF and DMSO. 4-Methylcatechol has a structure similar to dopamine but has a methyl group in place of the propylamine group, therefore, cannot undergo the cyclisation reaction that dopamine *o*-quinone undergoes. The cyclic voltammetric results for dopamine obtained in the two solvents were similar but showed additional processes to those

observed in aqueous solutions and small variations in the data were observed between the Pt and GC electrode surfaces. Both dopamine and 4-methylcatechol displayed an oxidation process at approximately +0.8 V vs. Ag wire and a reverse reduction process at approximately 0 V vs. Ag wire when the scan direction is reversed. The reduction process at 0 V vs. Ag wire was only evident if the scan was first performed in the positive potential direction, and is therefore associated reduction of with *o*-quinone that forms *via* the $-2e^-/-2H^+$ oxidation process (Scheme 1).

Figure 2. Cyclic voltammograms of 1 mM dopamine (DA) and 4-methylcatechol (MC) in DMF and DMSO with 0.2 M Bu_4NPF_6 recorded at 22 ± 2 °C at a 1 mm diameter GC electrode with a scan rate of 0.1 V s^{-1} . The starting and finishing potential is 0 V vs. Ag wire (0.5 M Bu_4NPF_6 in CH_3CN) with the scan commenced in the positive potential direction.

DMF and DMSO solutions containing dopamine displayed an additional oxidation process at approximately +1.1 V, which solutions containing

4-methylcatechol did not show (Figure 2). The process at +1.1 V was determined to be due to the oxidation of HCl, which was confirmed by a comparison of a cyclic voltammogram of a solution containing pure HCl in DMF and DMSO. Many compounds used for medicinal purposes are commercially available combined with HCl because the hydrochloric acid is used to aid the adsorption of molecules *in vivo*. HCl is less dissociated in organic solvents (compared to in water) resulting in a number of complicated equilibria between the dissociated and non-dissociated forms.^[58] A detailed electrochemical study found that the electrochemical oxidation of HCl in DMSO involves the oxidised form reacting with the solvent.^[58] At a Pt electrode, DMSO or DMF solutions containing HCl displayed an additional reduction process at negative potentials that was not observed on GC and is due to a surface based process associated with the initial oxidation reaction. The HCl present in the dopamine solutions could partially be removed by adding an equal molar amount of AgSbF₆ to the dopamine solutions, thereby causing the Cl⁻ to precipitate as AgCl.

There is a very wide separation between the forward ($E_p^{ox} = +0.8$ V vs. Ag wire) and reverse ($E_p^{red} = 0$ V vs. Ag wire) processes in DMF and DMSO associated with dopamine and 4-methylcatechol converting into their respective *o*-quinones (Figure 2). There is no evidence in the case of dopamine of formation of the leucoaminochrome reaction product after the initial oxidation, as occurs in pH 7 buffered aqueous solutions (Figure 1). Thus, the protons released during the oxidation process are sufficiently labile in DMF and DMSO to decrease the pH at

the electrode surface and reprotonate the quinone during the reduction cycle and so regenerate the hydroquinone. The reason for the large separation between the oxidation and reduction peaks most likely relates to the individual electron transfer steps occurring in a consecutive manner, with each electron transfer step having a unique redox potential. Scheme 2 shows the theoretical series of electron transfer and proton transfer reactions that are involved in the electrochemically induced conversion of the hydroquinone (QH_2) into the quinone (Q), where the oxidation and reduction reactions occur *via* different pathways. In addition to the consecutive electron transfer and proton transfer steps, a concerted mechanism where the electron and proton transfer simultaneously is also possible and would occur by diagonal arrows in Scheme 2. The large potential separation between the forward and reverse processes in organic solvents has also been reported for the reversible $-2\text{e}^-/-\text{H}^+$ electrochemical transformations of the phenolic compound vitamin E.^[59]

Scheme 2. Electrochemical square-scheme mechanism showing series of possible consecutive electron-transfer and proton-transfer reactions associated with the reversible transformation between *o*-hydroquinones (QH₂) and *o*-quinones (Q) in acidic conditions. Species “QH₂” represents any *o*-hydroquinone, including dopamine (DA) and 4-methylcatechol (MC).

An alternative reason for the wide separation between the oxidation and reduction processes in DMF and DMSO based on resistance effects of the solutions is not supported by electrochemical experiments on other compounds. For example, the oxidation of ferrocene in DMF or DMSO under the same conditions as the experiments on dopamine resulted in the measured potential separation between the forward and reverse processes of 70 mV, close to that theoretically expected for a electrochemically reversible transfer one-electron transfer^[57] and considerably less than observed for dopamine and 4-methylcatechol (~800 mV).

DMF and DMSO are both very hygroscopic solvents, thus the initial water concentrations of both solvents (containing 0.2 M Bu₄NPF₆) were calculated to be 25 ± 5 mM, based on the published experimental procedure where values of $|E_1 - E_2|$ for a quinone are correlated with the amount of water present (E_1 and E_2 are the first and second reduction potentials of vitamin K₁).^[55,56] Cyclic voltammetric experiments were also performed on 4-methylcatechol and dopamine in DMF in the presence of 3 Å molecular sieves, where the water content could be lowered to 2.5 mM. It was found that the voltammetric behavior was the same as observed at the higher water concentration shown in Figure 2, thus it is not believed that trace

water has a large effect of the voltammetric properties of dopamine in DMF or DMSO.

2.3. *In situ* UV-vis spectroscopy of oxidation reaction. Since dopamine *o*-quinone is known to be relatively short-lived in pH 7 buffered solutions (Figure 1), we were interested in comparing how long-lived the quinone was in pure DMF and DMSO solutions (containing Bu₄NPF₆), since the timescale of the cyclic voltammetric experiments shown in Figure 2 only indicate that it has a lifetime of at least a few seconds. Figure 3 shows the *in situ* electrochemical UV-vis spectra obtained during the oxidation of dopamine in an OSTLE cell^[57] at pH 1 in aqueous solution and in DMSO and DMF. At pH 1, the oxidised product shows a broad absorbance band at approximately 385 nm, which is associated with the two-electron oxidation product, dopamine *o*-quinone.^[60] In both DMSO and DMF, the oxidised product also displays a broad absorbance band at 385 nm, similar to that observed in aqueous solutions at low pH. Previous UV-vis experiments on oxidised products of dopamine in aqueous solutions at pH ≥ 7 have indicated that aminochrome has an absorbance maxima at higher wavelength (475 nm),^[60, 61] and it can be observed to form as a reaction product after the initial formation of dopamine *o*-quinone at 385 nm.^[60] Therefore, the UV-vis spectroscopic experiments in DMSO and DMF are consistent with the formation of dopamine *o*-quinone as a moderately stable product over the longer electrolysis timescales.

Figure 3. *In situ* electrochemical UV-vis spectra obtained in an OSTLE cell during the oxidation of dopamine and reduction of the oxidised product at 22 ± 2 °C. Experiments in aqueous solution at pH 1 used sulfuric acid as the electrolyte, while 0.2 M Bu₄NPF₆ was used for experiments in DMSO and DMF.

The UV-vis data in Figure 3 indicate that the dopamine *o*-quinone can be reduced back to dopamine under electrolysis conditions, although the reaction is not completely chemically reversible and the UV-vis spectra show residual absorbances above 300 nm possible due to the formation of the polymeric reaction compound, neuromelanin.^[60, 61] Nevertheless, since the UV-vis spectra shown in Figure 3 were performed over a period of 1.5 hours, the partially reversible nature of the UV-vis spectra indicate that the dopamine *o*-quinone survives for many

minutes in DMSO and DMF, much longer than in pH 7 buffered aqueous solutions.

2.4. Electrochemistry of dopamine in mixed aqueous/organics solvents containing buffers. Figure 4 (bottom to top) shows the results that were obtained when water containing pH 7 buffer were added to DMF solutions containing dopamine. The non-aqueous reference electrode was used throughout the measurements in order to provide a better comparison with the potentials obtained in DMF and in DMF-water mixture, although a junction potential will unavoidably occur (it was found that the potential difference between the aqueous and non-aqueous reference electrodes was < 100 mV).

At a DMF:Water (buffer) ratio of 100:1, the reductive peak for the dopamine *o*-quinone (formed by initial oxidation of dopamine) decreased in intensity, and, when a ratio of 100:5 was reached, the peak for the reduction of dopamine *o*-quinone could not be detected. Furthermore, as soon as the aqueous buffer was added to the DMF solution, a new oxidative process was detected at between +0.2 to +0.4 V, and the oxidation process at +0.9 V diminished in intensity. As more aqueous buffer was added to the solution the process at +0.9 V progressively decreased in intensity, so that at a DMF:Water (buffer) ratio of 100:30, only the oxidation process at +0.2 to +0.4 V was observed.

Figure 4. Cyclic voltammograms of 2 mM dopamine (solid lines) or 4-methylcatechol (dotted lines) recorded at $22 \pm 2^\circ\text{C}$ at a 1 mm diameter GC electrode at a scan rate of 0.1 V s^{-1} and with a starting and finishing potential of 0 V vs. Ag wire (0.5 M Bu_4NPF_6 in CH_3CN). Voltammograms in pure DMF contained 0.2 M Bu_4NPF_6 while voltammograms in pure water contained pH 7 buffer. Voltammograms of mixed solutions of DMF and water were obtained by adding water (containing pH 7 buffer) to DMF solutions (containing 0.2 M Bu_4NPF_6) in the given volume ratio.

The results in Figure 4 can be interpreted based on the presence of the buffer in the aqueous solution neutralizing (or partially neutralizing) the protons released during the oxidation process and causing a shift in the redox potential towards

more negative potentials according to equation 1. The observation that both the new oxidation peaks (at +0.2 to +0.4 V) and initial oxidation process (at +0.9 V) are evident at intermediate buffer ratios implies that the interactions with the buffer are complicated and a minimum concentration of buffer is needed in order to fully stabilise the localised pH at the electrode surface. As the DMF:Water (buffer) ratio increased above 100:10, a new reductive peak became evident at approximately -0.4 V, which is likely associated with the formation of aminochrome, due to the buffer modifying the acid concentration at the electrode surface to allow the deprotonation of the dopamine *o*-quinone.

2.5. Electrochemistry of dopamine in mixed aqueous/organics solvents containing inert electrolyte, LiClO_4 . Figure 5 (from bottom to top) shows cyclic voltammograms of dopamine in DMF containing 0.2 M Bu_4NPF_6 as increasing ratios (v/v) of aqueous solutions of 0.2 M LiClO_4 were added. As water (containing LiClO_4) was successively added to the DMF solution, the voltammograms in Figure 5 show that the potential gap between the E_p^{ox} and E_p^{red} peaks narrowed. Furthermore, the addition of water to the DMF solutions resulted in the oxidation process for HCl moving to increasingly more positive potentials, so that at a DMF:Water (LiClO_4) ratio of 100:30, the oxidation peak of HCl was not detected within the potential window examined.

Figure 5. Cyclic voltammograms of 2 mM dopamine (solid lines) or of 4-methylcatechol (dotted lines) recorded at 22 ± 2 °C at a 1 mm diameter GC electrode at a scan rate of 0.1 V s^{-1} and with a starting and finishing potential of 0 V vs. Ag wire (0.5 M Bu_4NPF_6 in CH_3CN). Voltammograms in pure DMF contained 0.2 M Bu_4NPF_6 while voltammograms in pure water contained 0.2 M LiClO_4 . Voltammograms of mixed solutions of DMF and water were obtained by adding water (containing 0.2 M LiClO_4) to DMF solutions (containing 0.2 M Bu_4NPF_6) in the given volume ratio.

Figure 5 (top) show voltammograms of dopamine and 4-methylcatechol in pure water containing LiClO_4 , which had a measured pH of approximately 7. Where the forward process consisted of one peak (similar to in pure DMF or

DMSO), in water containing 0.2 M LiClO₄, the reverse reductive process was split into two processes, which is likely due to the electron transfer steps in the reduction reaction occurring sequentially. In addition, the reductive peak at approximately +0.1 V associated with the cyclised reaction product, aminochrome, was much smaller than observed in pH 7 buffered aqueous solution (compare Figure 1), indicating that the rate of the cyclisation reaction was slower in aqueous solutions containing LiClO₄ compared to pH 7 buffered solutions (even though the pH values of the bulk solution were the same). The reason for the difference between the different aqueous electrolyte solutions relates to the buffering properties of the electrolytes, since in non-buffered solutions the protons released during the oxidation reaction are able to decrease the pH at the electrode surface and thereby reduce the rate of the cyclisation reaction of dopamine *o*-quinone.

The data in Figures 4 and 5 indicate that the addition of water to organic solvents has a much smaller effect on the electrochemistry of dopamine, compared to the buffering properties of the electrolyte. It can also be observed in Figures 4 and 5 that there is a substantial shift in the oxidation peak potential (E_p^{ox}) of dopamine in aqueous solutions containing LiClO₄ (Figure 5) and aqueous solutions containing the pH 7 buffer (Figure 4), even though the pH of the bulk solutions are the same. The cyclic voltammogram of dopamine in water containing 0.2 M LiClO₄ had an $E_p^{ox} = +0.8$ V vs. Ag wire compared to dopamine in pH 7 buffered water with $E_p^{ox} = +0.4$ V vs. Ag wire. The shift to more positive potentials of dopamine in water containing 0.2 M LiClO₄ implies that dopamine

experiences a more acidic environment at the electrode surface compared to the buffered solution.

3. Conclusions

Dopamine is electrochemically oxidised in DMF or DMSO (containing an inert electrolyte such as Bu_4NPF_6 or LiClO_4) in a chemically reversible $-2\text{e}^-/-2\text{H}^+$ process to form dopamine *o*-quinone. The separation between the forward (E_p^{ox}) and reverse (E_p^{red}) peaks is very wide, approximately 0.8 – 0.9 V, significantly greater than observed in aqueous solutions. *In situ* electrochemical-UV-vis spectroscopy confirms that dopamine *o*-quinone survives for at least several minutes in DMSO and DMF at 22 ± 2 °C (with Bu_4NPF_6), compared to in pH 7 buffered aqueous solutions where the half-life is several seconds. While the addition of water (containing LiClO_4) to the DMF or DMSO solutions had a relatively small effect on the voltammetric behavior, the addition of pH 7 buffered water to the DMF or DMSO solutions resulted in a shift in the oxidation peak to more negative potentials and a loss in the reduction process associated with dopamine *o*-quinone.

The electrochemical oxidation of dopamine in unbuffered aqueous solutions at pH 7 resulted in the formation of dopamine *o*-quinone, which survived longer than in pH 7 buffered solutions. The reason for the increased lifetime of the dopamine *o*-quinone in pH 7 unbuffered solutions most likely relates to the protons released during the oxidation process changing the pH in the vicinity of the electrode and thereby, stabilizing the dopamine *o*-quinone against deprotonation (and slowing

the following reaction to form leucoaminochrome). Therefore, the lifetime of dopamine *o*-quinone in a biological medium (should it occur naturally) may be significantly longer than in ideally buffered pH 7 solutions under laboratory conditions.

4. Experimental Section

4.1. Chemicals. 3-Hydroxytyramine hydrochloride (dopamine-HCl) (> 98.5%) was obtained from Fluka and 4-methylcatchol (96%) was from Alfa Aesar. ACS grade DMSO and DMF (Tedia) were used as received. Bu_4NPF_6 was prepared by reacting equal molar amounts of aqueous solutions of Bu_4NOH (40%, Alfa Aesar) and HPF_6 (65%, Fluka), washing the precipitate with hot water, recrystallizing 3 times from hot ethanol followed by drying under vacuum at 160 °C for 24 hours and storing under vacuum. Lithium perchlorate (anhydrous, 99%) was from Alfa Aesar and is often give explosive mixtures with organic compounds. Water, with a resistivity $\geq 18 \text{ M}\Omega \text{ cm}$ from an ELGA Purelab Option-Q was used for experiments at different pH-values. Sulfuric acid was used for experiments at pH 1. Citric acid–phosphate buffered solution (pH 7) was prepared from disodium hydrogen phosphate (Merck) and citric acid (Amresco).

4.2. Electrochemical measurements. Cyclic voltammetry (CV) experiments were conducted with a computer controlled Eco Chemie $\mu\text{Autolab III}$ potentiostat. Working electrodes were 1 mm and 3 mm diameter planar Pt or glassy carbon (GC) disks, used in conjunction with a Pt auxiliary electrode. For non-aqueous experiments, an Ag wire reference electrode was connected to the test solution *via*

a salt bridge containing 0.5 M Bu_4NPF_6 in CH_3CN . An Ag/AgCl reference electrode containing 3 M KCl was used for experiments in aqueous systems..

4.3. *In situ UV-vis spectroscopy.* A Perkin-Elmer Lambda 750 spectrophotometer was used in conjunction with an optically semi-transparent thin layer electrochemical (OSTLE) cell (pathlength = 0.05 cm) using a Pt mesh working electrode.^[62,63] The cavity of the spectrometer was purged from the atmosphere with a high volume flow of nitrogen gas.

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Chapter 6

The role of hydrogen-bonding on the electrochemical oxidation of α -tocopherol and other phenols with proton acceptors in acetonitrile

1. Introduction

Many naturally occurring phenols have specific functions in biological systems, either in a harmful way such as acting as endocrine disruptive chemicals, or in a beneficial role such as acting as antioxidants and preventing free radical damage of cell membranes.^[1,3,4] In both scenarios the oxidative properties of the compounds are important, thus electrochemistry is a useful technique for examining the oxidation of phenolic compounds.^[5,6] In this work we have used electrochemistry to investigate the role that low levels of water and other hydrogen-bonding acceptors has on the oxidative behavior of phenols. Since many naturally occurring phenols exist within bilayer membranes in a low water environment, the effects of low levels of water on the oxidative behavior may affect their oxidative or antioxidant properties.

Vitamin E is a lipid soluble phenolic compound whose exact function has taken on a degree of controversy in recent years.^[4,7] The majority of studies have argued that its sole function is as a chain breaking antioxidant (essentially a sacrificial compound)^[2-4] while other reports have proposed that the antioxidant properties are actually a side-function to its main function as a cellular signaling

molecule.^[7-10] It is a general property of all phenolic compounds that they are able to act as antioxidants, by virtue of their labile hydroxyl hydrogen atom, which can be donated to reactive free radicals, thereby terminating radical propagation reactions. α -Tocopherol (α -TOH) the most biologically active form of vitamin E, displays some other unusual electrochemical properties that are not shared by most other phenols,^[11-21] and it has been proposed that these properties may be important in a non-antioxidant biological function (should they really occur).^[15,17]

α -TOH is initially oxidized by one-electron to form a radical cation, α -TOH^{•+}. α -TOH^{•+} rapidly loses a proton to form the neutral radical (α -TO[•]), which is then immediately further oxidized by one-electron to form the phenoxonium ion (α -TO⁺) (Scheme 1).^[11-21] It is known that the initial one-electron oxidation to form the radical cation occurs by a consecutive mechanism in dry acetonitrile or dichloromethane, because the radical cation has been positively identified by a range of spectroscopic techniques.^[13,15,22] When hydrogen-bonding acceptors are present as the substrates, a proton-coupled electron transfer (concerted mechanism) has been shown to occur for a number of phenols.^[23-31] It is uncertain whether the second electron transfer step occurs heterogeneously at the electrode surface as drawn in Scheme 1 for an ECE process, or whether it occurs by a homogeneous disproportionation reaction.^[19,28] For either scenario, the oxidation reaction is completely chemically reversible on the cyclic voltammetry (< seconds) and electrolysis (> hours) timescale, provided the solvent contains low levels of water.^[13,14,16,18] As the water content of the organic solvent is increased, α -TO⁺ is

known to undergo a hydrolysis reaction with water to most likely form a hemiketal, which further reacts to convert a quinone.^[18-21] The difference between α -TOH and most other phenols is that its phenoxonium ion (α -TO⁺) is long-lived and reacts relatively slowly with water. There are only a few other examples of phenols that can form long-lived phenoxonium cations,^[32-36] with most reacting on the μ S timescales.^[37-43]

Scheme1. Electrochemically induced transformations of α -tocopherol in CH_3CN or CH_2Cl_2 .^[13] One resonance structure is displayed for each compound. The counter ions for the charged species are the supporting electrolyte anion $[\text{PF}_6^-]$, and the " H^+ " ions likely exist coordinated to the organic solvent (or with trace water).

It was discovered during the course of the experiments that α -TOH itself undergoes hydrogen bonding interactions with low levels of water in the solvent. The experimental results from α -TOH were compared with voltammetric data from other phenols in order to determine whether hydrogen-bonding with trace water (and other hydrogen-bonding acceptors) was a common occurrence for phenols in non-aqueous solvents. It was found that some unusual features in the voltammetric data could be linked to interactions of the phenols with trace levels of water or other hydrogen-bonding acceptors.

2. Results and Discussion

2.1. Cyclic voltammetry measurements at variable water concentrations (0.013 M – 0.56 M). The electrochemical reaction mechanism for α -TOH in CH_3CN containing varying amounts of water is given in Scheme 2. When the water content of the CH_3CN is $< \sim 50 \times 10^{-3} \text{ M}$, there is no voltammetric evidence of the hemiketal ($\alpha\text{-TO(OH)}$) that can form *via* reaction of $\alpha\text{-TO}^+$ with water, since the reaction occurs too slowly to be detected on the CV time-scale. As the water content of the solvent increases, the lifetime of the $\alpha\text{-TO}^+$ decreases; thus the presence of the hemiketal becomes evident as a reductive peak at $\sim -0.4 \text{ V vs. Fc/Fc}^+$ when the scan is first performed in the positive potential direction so as to oxidize $\alpha\text{-TOH}$ to $\alpha\text{-TO}^+$. Figure 1 shows cyclic voltammograms obtained at a scan rate of 0.1 V s^{-1} when increasing amounts of water are added to the solution. It can be observed in Figure 1 that as more water is added, the peak for the reduction of the $\alpha\text{-TO}^+$ back to $\alpha\text{-TOH}$ at $\sim +0.2 \text{ V vs. Fc/Fc}^+$ diminishes in size, while concomitantly the peak associated with the reduction of the hemiketal at $\sim -0.4 \text{ V vs. Fc/Fc}^+$ becomes larger.

Scheme 2. Electrochemical oxidation mechanism of α -tocopherol in CH_3CN containing water. $\text{R} = (\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3))_3\text{CH}_3$.

It is difficult to obtain spectroscopic data to confirm the existence of hemiketal shown in Scheme 2 because such compounds are difficult to isolate from solution and rapidly convert to the quinones (α -TOQ) in the presence of small amounts of acid.^[44-49] The assignment of the process at ~ -0.4 V vs. Fc/Fc⁺ as due to the hemiketal was based on previous electrolysis experiments.^[18,21] Controlled potential electrolysis of α -TOH and several other phenols with similar structures in CH₃CN containing $\sim 0.05 - 0.1$ M H₂O resulted in the formation of the species at -0.4 V vs. Fc/Fc⁺ that survived in the bulk solution for several minutes.^[18] It was found that applying a reductive potential (> -0.4 V vs. Fc/Fc⁺) resulted in the oxidized species partly converting back to the starting material. Thus, it was reasoned that the most likely compound for the process at -0.4 V vs. Fc/Fc⁺ was the hemiketal, since any ring-opened structure (such as the quinone (α -TOQ)) was unlikely to be able to be converted back to the ring-closed form simply by applying a reducing potential.

The CVs in Figure 1 demonstrate that the potential of the oxidation peak (E_p^{ox}) shifts to more negative potentials as increasing concentrations of water were added to the solvent. This effect is believed to be caused by hydrogen-bonding interactions between α -TOH/ α -TOH⁺ and water molecules and is illustrated in Scheme 2. The model predicts that there is an equilibrium reaction between the hydrogen-bonded and non-hydrogen-bonded forms, each with different oxidation potentials. Therefore, as the water content of the solvent changes, there is a shift in the oxidation potential. A similar effect is observed during the reduction of

quinones in non-aqueous solvents which display a large shift in potential (especially for the second one-electron transfer), due to hydrogen bonding between the anion radical and dianion with trace water.^[50-52]

Figure 1. CVs of $2 \times 10^{-3} \text{ M}$ α -TOH in CH_3CN containing 0.2 M Bu_4NPF_6 at $22 \pm 2^\circ\text{C}$ recorded at a 1 mm diameter Pt electrode at scan rate (v) of 0.1 V s^{-1} in the presence of varying amounts of water. Current data were scaled by multiplying by $v^{-0.5}$. Positive current is in the upwards direction. The starting potential is -1 V vs. Fc/Fc^+ and the finishing potential is -1 V vs. Fc/Fc^+ on the second scan.

The hydrolysis reaction between $\alpha\text{-TO}^+$ and H_2O is to form the hemiketal

(α -TOH(OH)) is given in two steps in Scheme 2. The first step is the reaction of water at the aromatic ether carbon followed by the loss of a proton to form the hemiketal. The voltammetric data cannot presently be used to discriminate between the two steps, thus the slower process was arbitrarily assigned to the addition of water. The rate determining step for the reaction of α -TO⁺ with water was estimated to be approximately 11 L mol⁻¹ s⁻¹ (by digital simulation techniques), which is approximately 5 × slower than estimated for the reaction between γ -TO⁺ and δ -TO⁺ with water in acetonitrile.^[19]

2.2. Cyclic voltammetry of α -TOH in the presence of weak bases and coordinating solvents.

It was expected that the hydrogen bonding of α -TOH with other weakly coordinating solvents (in addition to H₂O) would also be voltammetrically detectable *via* the shift in the potential of the oxidation process. Figure 2 shows CVs that were obtained when dimethyl sulfoxide (DMSO) and pyridine were added to α -TOH in CH₃CN. In the case of DMSO (Figure 2a) the CV response was observed to change immediately a small amount of DMSO (0.002 M) was added to the solution. The E_p^{ox} -value continued shifted to more negative potentials as more DMSO was added to the solution and the reverse reductive peak at +0.2 V *vs.* Fc/Fc⁺ decreased in intensity and a new reductive peak appears at -0.6 V *vs.* Fc/Fc⁺ due to the reaction of α -TO⁺ with DMSO. DMSO is often considered to be similar to CH₃CN when used as a solvent during electrochemical measurements (both being aprotic solvents with similar dielectric constants).^[6] However, in this instance the DMSO appears more reactive, since the

decrease in current magnitude of the reductive peak at +0.2 V vs. Fc/Fc^+ as DMSO is added to the solution indicates that $\alpha\text{-TO}^+$ undergoes a reaction with the DMSO.

Figure 2. CVs of 2×10^{-3} M $\alpha\text{-TOH}$ in CH_3CN containing 0.2 M Bu_4NPF_6 at 22 ± 2 °C recorded at a 1 mm diameter Pt electrode at scan rate (v) of 0.1 V s^{-1} in the presence of varying amounts of (a) DMSO and, (b) pyridine. Positive current is in the upwards direction.

The addition of an equal molar amount of pyridine to a solution of $\alpha\text{-TOH}$ in

CH₃CN resulted in a large shift in potential of the oxidation peak to more negative potentials (Figure 2b). The large shift in E_p^{ox} (compared to the addition of DMSO) could be due to stronger hydrogen bonding between the pyridine and the phenoxyl proton on α -TOH. The lack of chemical reversibility of the oxidation process is likely caused by a reaction between the pyridine and α -TO⁺. When a very strong base, such as Et₄NOH, is added to the solvent, α -TOH undergoes complete deprotonation to form the phenolate anion, α -TO⁻, which is easily oxidized at approximately -0.9 V vs. Fc/Fc⁺.^[12]

2.3. Cyclic voltammetry of other phenols in CH₃CN with variable water concentrations. The electrochemical properties of several other compounds were examined in CH₃CN containing variable amounts of H₂O (Figure 3). α -Tocopherol acetate (α -TOA) contains an acetate group in place of the phenolic hydrogen atom and undergoes a one-electron chemically reversible oxidation in CH₃CN to form a cation radical that survives for at least several minutes at room temperature.^[31] The CV in Figure 3 demonstrates that the E_p^{ox} -value of α -TOA does not shift when water is added to solution, which was the expected result because α -TOA lacks the hydroxyl group and so should not undergo strong hydrogen-bonding interactions with water. The i_p^{ox} -value for α -TOA does increase when water is added to solution (similar to observed for α -TOH and the other phenols), and the i_p^{red} -value for the reverse reductive process decreases, due to chemical instability of the cation radical in the presence of water. The CV results that were obtained for α -TOA rule out the possibilities that changes observed in the oxidation peak

potential for α -TOH as water was added to the solution were due to large changes in the junction potential of the reference electrode, or due to solution resistance effects. Instead the results support the change in potential being due to hydrogen bonding effects, since they are specific to compounds with the phenolic hydrogen atoms and involve relatively small amounts of water.

Figure 3. CVs of 2×10^{-3} M analytes in CH_3CN containing 0.2 M Bu_4NPF_6 at $22 \pm 2^\circ\text{C}$ recorded at a 1 mm diameter Pt electrode at scan rate (v) of 0.1 V s^{-1} . (—) 0.013 M H_2O . (---) 0.123 M H_2O . Positive current is in the upwards direction.

Figure 3 shows CVs obtained for 2,4,6-trimethylphenol (TMP), 2,4,6-tri-*tert*-butylphenol (TTBP) and 2,6-di-*tert*-butyl-4-methoxyphenol (DTBMP), which all show a shift in E_p^{ox} -value as water is added to the solution. The shift in the E_p^{ox} -value was greater for TMP than for TTBP or DTBMP, which may be caused by the bulky *tert*-butyl groups in the 2, 6-positions reducing the hydrogen bonding

reactions with H₂O. The CVs in Figures 1 and 3 demonstrate that the presence of relative small amounts of water in the solvent is sufficient to shift the peak potential of the oxidation process. Therefore, when reporting the oxidative behavior of phenols in organic solvents, the accurate water content of the solvent should also be reported.

2.4. UV-vis and NMR spectroscopic experiments of α -TOH in CH₃CN with variable concentrations of water and coordinating solvents. Spectroscopic experiments were conducted on α -TOH in order to obtain additional evidence for the hydrogen bonding interactions. UV-vis spectra for α -TOH in the presence of several coordinating solvents are shown in Figure 4. The UV-vis spectrum of α -TOH displays a λ max at approximately 290 nm with an ϵ -value of 3.4×10^3 L mol⁻¹ cm⁻¹. When H₂O, DMSO or pyridine were added to the solution, no change was observed in the position or intensity of the absorbance band associated with α -TOH, indicating that the hydrogen bonding interactions were weak (pyridine itself has an absorbance band at approximately 250 nm). When an equal molar amount of Bu₄NOH was added to the solution, the UV-vis data confirmed that the phenolate anion was immediately formed by deprotonation of the phenol, resulting in a shift in the λ max to 325 nm (Figure 4).

NMR spectra obtained during the addition of bases to α -TOH in CD₃CN showed a shift in the frequency of the hydroxyl proton resonance due to hydrogen-bonding interactions (Figure 5-7). The NMR chemical shifts (δ) of the hydroxyl proton are given in Table 1. The largest shift of the resonance frequency

of the hydroxyl proton was observed when pyridine was added, followed by DMSO then D₂O, which is similar to the trend in shifts in E_p^{ox} -values observed by voltammetry, which supports hydrogen bonding interactions between the hydroxyl proton and the hydrogen bonding acceptor.

Figure 4. UV-vis spectra of 2×10^{-3} M α -TOH in CH₃CN in a 0.5 – 1 mm pathlength quartz cuvette at 22 ± 2 °C in the absence and presence of DMSO, pyridine and Bu₄NOH.

Table 1. 400-MHz ^1H NMR chemical shifts (δ) of the hydroxyl proton in 80 mM α -TOH in dried CD_3CN with different ratios of hydrogen-bonding acceptors (HBA) (D_2O , DMSO and pyridine).

α -TOH : HBA	1 : 0	1 : 1	1 : 5	1 : 10
	$\delta(\text{OH})/\text{ppm}$			
α -TOH : D_2O	5.34	5.37	5.45	5.57
α -TOH : $\text{DMSO-}d_6$	5.34	5.44	5.75	6.04
α -TOH : Pyridine	5.34	5.44	5.80	6.13

Figure 5. ^1H NMR of α -TOH with D_2O

Figure 6. ^1H NMR of α -TOH with DMSO

Figure 6. ^1H NMR of α -TOH with Pyridine

3. Conclusions

α -TOH is electrochemically oxidized in CH₃CN to form the diamagnetic cation, α -TO⁺, in a chemically reversible $-2e^-/-H^+$ process. CV and spectroscopic experiments on α -TOH and other phenols in CH₃CN in the presence of varying concentrations of water indicated that the phenols undergoing hydrogen-bonding interactions with H₂O, resulting in the E_p^{ox} -values shifting to more negative potentials as water or other bases were added to the solvent. Therefore, when interpreting the electrochemical behavior of phenols in non-aqueous solvents, in some circumstances it may be beneficial to know the precise trace water content of the solvent. Furthermore, the antioxidant activity of phenols has been found to be influenced by kinetic solvent effects (KSE) where hydrogen bonding of the phenol with the solvent alters the rate of reaction of the phenol with reactive free radicals.^[3,53,54] Thus, as well as the solvent, the trace water content of the solvent may also be important in determining the antioxidant properties of phenols.

4. Experimental Section.

4.1. Chemicals. ($\pm$)- α -TOH (97%) was obtained from Aldrich and stored in the dark under nitrogen. Molecular sieves of the form 1/16" rods with 3 Å pore size (CAS: 308080-99-1) were obtained from Fluka and all solvents were HPLC or analytical grade and used directly from the bottles (after drying over 3 Å molecular sieves). Purified water, with a resistivity ≥ 18 M Ω cm was obtained from an ELGA Purelab Option-Q system.

4.2. Voltammetry. Cyclic voltammetry (CV) experiments were conducted

with a computer controlled Metrohm Autolab PGSTAT302N potentiostat. The working electrode was a 1 mm Pt disk (Cypress Systems), used in conjunction with a Pt auxiliary electrode (Metrohm) and an Ag wire miniature reference electrode (Cypress Systems) connected to the test solution via a salt bridge containing 0.5 M Bu₄NPF₆ in CH₃CN. The internal filling solution of the reference electrode was prepared immediately prior to use to reduce the amount of contamination from water in the reference electrode filling solution. Accurate potentials were obtained using ferrocene as an internal standard.

4.3. Spectrometers. UV-vis spectra were obtained with a Perkin-Elmer Lambda 750 Spectrophotometer and NMR experiments were conducted with a Bruker Avance 400-MHz (¹H) spectrometer.

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Chapter 7

Infrared and UV-vis Spectra of Phenoxonium Cations Produced during the Oxidation of Phenols

1. Introduction

Phenolic compounds have an important function in many biological processes; either in a complementary fashion such as acting as antioxidants, or in a negative role such as acting as endocrine disruptive chemicals.^[1] In both scenarios the oxidative behavior of the compounds is important; thus electrochemical studies have been used extensively to study and characterise the oxidation reactions.^[2-5] The initial electrochemical oxidation of phenols can be considered to occur through a series of electron transfer and proton transfer reactions that can be represented in a “square-scheme” mechanism, with the lifetimes of the oxidized compounds varying considerably depending on the structure of the phenols.^[4, 5]

The tocopherols (TOH) are a series of naturally occurring phenolic compounds consisting of several structurally related forms (α , β , γ , δ) that differ in the degree of methylation of the aromatic ring. It has been found that α -TOH (the most methylated tocopherol) undergoes an electrochemical $-2e^-/-H^+$ process to form a phenoxonium cation ($\alpha\text{-TO}^+$), which is surprisingly long-lived in acetonitrile and dichloromethane solutions.^[6-16] The reaction is chemically reversible on the milliseconds and hours time-scales, providing the moisture content of the solvent is low, and the phenol can be regenerated in 100 % yield.^[8, 9]

The phenoxonium cations of the other forms of the tocopherols have lifetimes considerably less than $\alpha\text{-TO}^+$.^[10] There are presently only a few examples of compounds that are known to form long-lived phenoxonium cations,^[17-21] so it is interesting that one derived from a natural compound is long-lived, which has led to speculation that it may have some biological importance.^[10,12]

A recent electrochemical study examined a number of phenolic compounds with structures similar to $\alpha\text{-TOH}$ and identified several compounds whose associated phenoxonium cations survived for at least several minutes in acetonitrile solutions at room temperature. It was proposed (based on processes detected during voltammetric and electrolysis experiments) that the phenoxonium cations reacted with water in the solvent to form *para*-quinone hemiketals, which in some cases could also be electrochemically reduced back to the parent phenols. The aim of this study is to provide spectroscopic characterization of the phenoxonium cations, which can also be produced as very short-lived species during flash photolysis experiments in aqueous solutions.^[22-29] Under transient conditions the identity of intermediate species can be difficult to determine, thus characteristic spectroscopic data from compounds with relatively long lifetimes can be useful in identifying compounds under conditions where they are likely to be considerably more reactive (such as in biological conditions or in aqueous environments).

2. Results and Discussion

2.1. Electrochemical mechanism. Scheme 1 shows the general mechanism for the electrochemical oxidation in CH₃CN or CH₂Cl₂ of the class of phenols (POH) used in this study that have a five- or six-membered ring containing an ether group, with the ether oxygen in the *para*-position to the hydroxyl group.^[13] In CH₃CN containing Bu₄NPF₆ as the supporting electrolyte, the electrochemical mechanism is similar for all the compounds and involves the initial one-electron oxidation of POH at approximately +0.5 V vs. Fc/Fc⁺ (where Fc = ferrocene) to form the radical cation (POH^{•+}). POH^{•+} rapidly dissociates *via* the loss of the hydroxyl proton to form the phenoxyl neutral radical (PO[•]), which is then immediately further oxidised at the electrode surface by one-electron to form the phenoxonium cation (PO⁺).^[13] A homogeneous disproportionation mechanism may alternatively account for the second electron transfer step.^[16] Although the expression “phenoxonium” is used to describe the cations, molecular orbital calculations and NMR experiments on the model phenoxonium cation of α -tocopherol (compound **1b**) indicated that most of the positive charge is located on the carbon atom adjacent to the ether oxygen atom, rather than on the oxygen atom.^[9]

Scheme 1. Oxidation mechanism for the phenols.

Figure 1. Representative cyclic voltammograms recorded at a scan rate of 100 mV s^{-1} in CH_3CN containing $0.2 \text{ M Bu}_4\text{NPF}_6$ for 5 mM of the phenols and related compounds at $22 (\pm 2)^\circ\text{C}$

°C. (—) Chemically reversible $-2e^-/-H^+$ transformation of phenol into phenoxonium ion. (····) Reduction ($+2e^-/+2H^+/-H_2O$) of *para*-quinone hemiketal back to phenol. (----) Chemically reversible $+1e^-$ transformation of *para*-quinone into semiquinone. Data modified from reference 13.

The lifetime of PO^+ depends on the substituents in the R_1 – R_5 positions (Scheme 1), as well as the temperature and solvent composition.^[13] Some phenoxonium cations have been found to be long-lived (for at least several minutes) and can be reversibly reduced back to the starting materials. A typical cyclic voltammogram of a compound that forms a phenoxonium ion that survives for at least the voltammetric time-scale (a few seconds) is shown in Figure 1 (solid line) where a forward oxidation peak (E_p^{ox}) is observed at approximately +0.5 V vs. Fc/Fc^+ and a reverse reduction peak (E_p^{red}) is detected at approximately +0.2 V vs. Fc/Fc^+ . Both the forward and reverse processes correspond to the transfer of two electrons and one proton. The wide separation between the E_p^{ox} and E_p^{red} peaks (ΔE_{pp}) is due to the electron transfer reactions occurring sequentially in two one-electron steps at different potentials.^[8-16] The voltammograms in Figure 1 are representative of a general reaction scheme of phenols; however, not all of the processes may be detectable for all compounds. For example, the phenoxonium cations of many phenols are not long-lived, therefore, the peak for the reduction of the phenoxonium back to the phenol at +0.2 – +0.4 V is often not observed (especially at slow scan rates).

Most PO^+ compounds react quickly with water (or other nucleophiles) in the solvent to form the *para*-quinone hemiketals ($Q(OH)$) as a major product, which

can convert into the *para*-quinones (Q), although the reaction is concentration dependant and also involves the formation of other unidentified products (Scheme 1).^[13] Evidence for the *para*-quinone hemiketal intermediates came from the observation that during electrolysis experiments new species were produced with reductive peaks at approximately -0.4 V vs. Fc/Fc⁺ for some of the compounds (Figure 1, dotted line).^[13] The reduction potential of the intermediate occurred between that observed for the phenoxonium ion (solid line) and that observed for the stable *para*-quinone (dashed line). Applying a potential more negative than -0.4 V vs. Fc/Fc⁺ allowed the intermediate compound be reduced back to the starting material indicating that it was unlikely to be a ring-opened structure such as the *para*-quinone (which cannot be reduced back to the starting materials under the mild conditions used for electrochemistry), and supporting the formation of the *para*-quinone hemiketal. The *para*-quinone hemiketals convert slowly *via* tautomerism into the *para*-quinones which can be reduced at approximately -1 V vs. Fc/Fc⁺ in a one-electron chemically reversible process.^[13] Experiments on solid state samples of α -tocopherol attached to an electrode surface indicated that the phenol is immediately converted to the quinone in high yield when the oxidation occurs in aqueous solutions,^[16] but in non-aqueous solvents the yields of the quinones (from the phenols) are low.^[31]

2.2. Infrared spectroscopy. Figure 2 shows *in situ* background subtracted ATR-FTIR spectroscopic data that were obtained by chemically oxidising a range of phenols in CH₃CN with 2 mol equivalents of NOSbF₆. The dotted lines in

Figure 2 are the initial spectra of the phenols and the solid lines are the spectra of their associated phenoxonium cations. The phenols in Figure 2 were chosen based on previous controlled potential electrolysis experiments that indicated that their associated phenoxonium cations had lifetimes of at least several minutes.^[13] CH₃CN is the preferred solvent for the oxidation experiments because it affords the greatest life-times of the phenoxonium ions and because it has few bands in the infrared region that interfere with the FTIR detection of the phenoxonium cations. NO⁺ was used as the oxidant because the chemical oxidation occurs much more rapidly than electrochemical oxidation, because its reduction potential is sufficiently positive to oxidise many phenols and because it is cleanly reduced to NO(g) which is easily removed from solution.^[9]

The ATR probe used for the *in situ* FTIR experiments has a usable range between approximately 1900 – 650 cm⁻¹,^[35, 36] although it is the carbonyl region (1800 – 1600 cm⁻¹) that is the most useful in characterising the phenoxonium ions.^[8-10] The sensitivity limits of the ATR-FTIR probe require relatively high concentrations of substrates, therefore; all experiments were conducted with 0.1 M concentrations of the phenols.

Figure 2. Background subtracted *in situ* ATR-FTIR spectra obtained by oxidising 0.1 M of the phenols in CH₃CN with 2 mol equivalents of NOSbF₆ 22 (±2) °C. The spectra represent 256 scans recorded with 4 cm⁻¹ resolution. (.....) Starting phenols. (—) Immediately after oxidation, except for **1d**, which is a pure compound.

The infrared spectra of the oxidised forms of the phenols in Figure 2 appear similar and show three characteristic bands between 1663 – 1600 cm⁻¹. Compounds **1b** and **2b** mainly differ in that they contain a 6-membered heterocyclic ring while compounds **3b** and **4b** contain a 5-membered heterocyclic ring. Molecular orbital calculations on compound **1b** predict that two of the bands are associated with the symmetric and asymmetric ring stretching modes and one band is associated with the carbonyl stretching mode, although in each case other

coupled vibrations within the molecules contribute to the modes.^[9] The absorbance at close to 1600 cm^{-1} is predicted to be associated with the asymmetric ring stretching mode.^[9] The two bands that occur at 1663 cm^{-1} and 1650 cm^{-1} are predicted to be due to the carbonyl stretch and symmetrical ring stretch, respectively.^[9] The molecular orbital calculations predict the carbonyl band to be at the higher wavenumber, which, if correct, means that it is weaker in intensity than the symmetric ring stretching mode. The spectrum of the quinone of the α -tocopherol model compound (**1d**) is provided in Figure 2 as a comparison to the phenoxonium cations, and shows one strong band in the carbonyl region at 1645 cm^{-1} , possibly because the C=O stretch and symmetric ring stretching modes are overlapping.

The spectra of all the phenoxonium cations in Figure 2 also show a strong absorbance at close to 1500 cm^{-1} , which is the strongest absorbance between $1900 - 1300\text{ cm}^{-1}$. Molecular orbital calculations on compound **1b** predicted several absorbances close to 1500 cm^{-1} that coincide with the C–O stretch coupled with bending modes of the methyl groups on the quaternary carbon.^[9] The C–O stretching modes in ethers normally occur between $1300 - 1000\text{ cm}^{-1}$.^[37] Nevertheless, an X-ray crystallographic study on compound **1b** showed that the quinoid like carbon-oxygen ether bond in the phenoxonium cation is shorter than a normal C–O bond,^[11] which could account for the shift in the absorbance of the C–O bond to higher wavenumbers in the cation.

The lifetime of the phenoxonium cations is partly determined by how reactive they are with nucleophiles, such as water, in the solvent.^[10] In an ultra-dry environment it has been found that the phenoxonium cation of the model compound of α -tocopherol (**1b**) can survive for at least several weeks at $-27\text{ }^{\circ}\text{C}$.^[9] ^[11] Since water is always present in organic solvents, the phenoxonium cations may be longer-lived at higher concentrations where the effects of trace water are less, providing they do not react in a dimerisation or related processes. The water concentration of the CH_3CN inside the reaction vessel was calculated to be $25 (\pm 5)$ mM, based on the published experimental procedure where values of $|E_1 - E_2|$ for a quinone are correlated with the amount of water present (E_1 and E_2 are the first and second reduction potentials of vitamin K_1).^[38, 39] The high humidity of the local environment combined with the cell used for the *in situ* spectroscopic analysis make it difficult to completely exclude the water from the solvent.

Figure 3 shows infrared spectra that were obtained before and after the oxidation of compound **5a** with 2 mol equivalents of NO^+ . The spectrum obtained immediately after the oxidation of **5a** showed absorbances in the carbonyl region typical of the phenoxonium cation at 1660 , 1651 and 1605 cm^{-1} , and with a strong absorbance close to 1500 cm^{-1} . The phenoxonium cation of compound **5a** (**5b**) is known to be more reactive with water than compounds **1b** – **4b**,^[13] thus when an equal molar amount of water was added to the solution, the spectrum of **5b** immediately diminished in intensity to most likely form **5c** (the *para*-quinone hemiketal) (Figure 3). There are several reports on the existence of *para*-quinone

hemiketals related to the tocopherols, although the compounds are difficult to obtain in pure form and rapidly convert in the presence of acid to the quinones.^[31,40-44] The infrared stretching frequency of the carbonyl group of the *para*-quinone hemiketals of the tocopherols have been assigned between 1680 – 1630 cm⁻¹,^[40-44] although there is some ambiguity whether this may be a strong ring stretching mode, as is observed in the phenoxonium cations.

Figure 3. Background subtracted *in situ* ATR-FTIR spectra obtained by oxidising 0.1 M **5a** in CH₃CN with 2 mol equivalents of NOSbF₆ 22 (±2) °C. The spectra represent 256 scans recorded with 4 cm⁻¹ resolution. (.....) **5a**. (—) The spectrum of **5b** was obtained immediately after oxidation and the spectrum of **5c** was obtained from **5b** after the addition of 0.1 M of water.

The band that was present in the spectrum of **5b** at 1651 cm⁻¹ appears to shift to 1647 cm⁻¹ in the spectrum of **5c**. The band at 1647 cm⁻¹ for **5c** could be due to either a carbonyl stretch or ring stretching mode (or an overlap of both). Although

the band at 1647 cm^{-1} occurs at a similar wavenumber to that observed for a quinone, such as **1d** in Figure 2, it is unlikely that **5b** converts so rapidly and quantitatively to the quinone in the presence of an equal molar amount of water. Normally the conversion of phenols to quinones in non-aqueous solvents is a relatively low yield reaction with numerous side products.^[13,31] The broad band that occurs at approximately $1710 - 1720\text{ cm}^{-1}$ in the spectrum of **5c** is due to water.

2.3. In situ electrochemical UV-vis spectroscopy. Figure 4 shows *in situ* electrochemical UV-vis experiments that were conducted on compounds **1a**, **2a** and **3a** which are known to form relatively long-lived phenoxonium cations.^[13] The spectroscopic experiments were performed over a time-scale of around 30 minutes and needed to be performed at low concentrations ($< 1\text{ mM}$) to avoid overloading the instrument detector. There is a disparity in the concentration of the phenolic compounds used in the infrared and UV-vis spectroscopic experiments because of the infrared experiments requiring very high concentrations in order to obtain acceptable signal-to-noise ratios. The low concentration of analytes used for the UV-vis measurements leads to there being a substantially higher ratio of water present that favours the formation of the *para*-quinone hemiketals or *para*-quinones over the phenoxonium cations. Nevertheless, the spectra obtained during the oxidation of the phenolic compounds shown in Figure 5 are consistent with the formation of the phenoxonium cations.^[8-10]

Figure 4. *In situ* electrochemical UV-vis spectra obtained in CH_3CN containing 0.2 M Bu_4NPF_6 during the oxidation of approximately 1 mM of the phenols at -20°C . (.....) Starting phenols. (—) Intermediate scans. (—) Final scan.

At 25°C the starting phenols showed an absorption band at approximately 295 nm with $\epsilon \approx 3000 \text{ L cm}^{-1} \text{ mol}^{-1}$.^[45,46] As the temperature decreased the band narrowed and appeared to split into two closely spaced absorbances that could not be completely resolved at -40°C .^[8] During the *in situ* oxidation of the phenols at -20°C , an intense band was observed at 293 – 296 nm ($\epsilon \approx 11000 \text{ L cm}^{-1} \text{ mol}^{-1}$) and a less intense very broad band at 432 – 452 nm ($\epsilon \approx 700 \text{ L cm}^{-1} \text{ mol}^{-1}$) (the ϵ -values supersede the previously reported values).^[10,15] The spectra are very similar to those obtained of the phenoxonium cations of the α - and

β -tocopherols.^[10] In each case the spectrum of the starting material could be regenerated by applying a reducing potential to the electrode, indicating that the oxidised compounds were long-lived.

Figure 5 shows the UV-vis spectra obtained during the electrolysis of compounds **4a**, **6a** and **7a**. In this instance the phenoxonium cations (**4b**, **6b** and **7b**), formed by electrochemical oxidation were known to be more reactive than compounds **1b**, **2b** and **3b**.^[13] The initial oxidation of the phenols did produce the phenoxonium cations, as evidenced by the initial increase in intensity of the bands at approximately 300 nm and 436 – 452 nm. However, as the electrolysis progressed, these bands diminished in intensity again and a strong band (or pair of bands) was detected at 254 – 264 nm. The band detected at 254 – 264 nm is very similar to that observed in the UV-vis spectra of the quinones shown in Figure 6. Therefore, it appears that in the low analyte concentration UV-vis measurements there is a greater tendency of the oxidised compounds to react to form the quinones as the final products. It was found that the spectra of the starting phenols could not be regenerated by applying a reducing potential after the oxidation of compounds **4a**, **6a** and **7a**.

Figure 5. *In situ* electrochemical UV-vis spectra obtained in CH_3CN containing 0.2 M Bu_4NPF_6 during the oxidation of approximately 1 mM of the phenols at -20°C . (.....) Starting phenols. (---) Intermediate scans. (—) Final scan.

Figure 6. UV-vis spectra of approximately 1 mM of the quinones obtained in CH₃CN at 22 (±2) °C.

The FTIR spectra obtained during the chemical oxidation of **6a** and **7a** at high concentrations with NOSbF₆ were complicated and showed a number of bands in the carbonyl region that were weak in intensity suggesting that a number of products were formed (in addition to the phenoxonium cations or quinones) and were difficult to interpret. Therefore, although Scheme 1 and Figure 1 represent a general reaction pathway, it is likely that in many cases other reactions can occur making it difficult to fully characterize the FTIR and UV-vis spectra of the phenoxonium cations, hemiketals and quinones associated with all phenolic compounds.

3. Conclusions

Infrared spectroscopic measurements made during the oxidation of several phenols led to the detection of a range of products depending on the lifetimes of the oxidised compounds. The compounds that formed long-lived phenoxonium cations showed infrared absorbances at 1685 – 1650 cm⁻¹ due to the carbonyl stretching and symmetric ring stretching modes and a band at approximately 1600 cm⁻¹ due to the asymmetric ring stretching. The phenoxonium cations also showed a very intense band at approximately 1500 cm⁻¹, which is possibly associated with a C–O single bond mode. The solution phase spectra of the ring opened quinones showed a single strong infrared band in the carbonyl region at approximately 1650 cm⁻¹. The UV-vis spectra of phenoxonium cations showed intense bands at 293 –

296 nm and relatively less intense bands at 434 – 460 nm, compared to the long-term *para*-quinone oxidation products that showed bands at 256 – 264 nm.

4. Experimental Section

4.1. Chemicals. HPLC grade CH₃CN (Tedia) was dried over 3 Å molecular sieves and Bu₄NPF₆ was prepared and purified by standard methods.^[30] NOSbF₆ (99%) used for chemical oxidation experiments was obtained from Sigma-Aldrich. The synthesis of the phenols and quinones used for analysis have been described previously.^[13, 31]

4.2. Voltammetry and Spectrometers. Bulk oxidation experiments were performed in a divided controlled potential electrolysis (CPE) cell separated with a porosity no. 5 (1.0 – 1.7 μm) sintered glass frit.^[32] *In situ* UV-vis spectra were obtained with a Perkin-Elmer Lambda 750 spectrophotometer in an optically semi-transparent thin layer electrochemical (OSTLE) cell (pathlength = 0.05 cm) using a Pt mesh working electrode.^[33, 34] Solution phase background subtracted *in situ* FTIR experiments were conducted with a Mettler Toledo iC10 spectrometer utilizing a diamond composite ATR fiber conduit probe.^[35, 36]

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Chapter 8

The Electrochemistry and Ion Sensing Properties of Calix[4]arene Derivatives

1. Introduction

The supramolecular sensing properties of calixarenes towards ions or neutral molecules have been studied extensively over the last two decades.^[1-3] The weak and reversible interactions with Groups IA and IIA metals have made them ideal for use in potentiometric chemical sensors and in optical sensors.^[1-3] Considerable attention has focused on new synthetic strategies to modify the calixarene structures to improve or diversify the recognition properties.^[4-6] In this work we discuss the sensing properties of some recently synthesised calix[4]arenes where one aromatic group contains a hydroxyl (phenolic) or quinone based functionality (Scheme 1, compounds **1a**, **1b**, **2a**, **5a**, **5b** and **5c**).^[7,8]

In addition to the ion-sensing properties of the calix[4]arenes, the electrochemical properties were also examined. Calixarenes often display complicated electrochemical properties due to the presence of several phenolic groups resulting in multiple electron transfer oxidative processes, and because of adsorption processes affecting the shape of the voltammograms.^[9] However, compounds **1a**, **5a**, **5b** and **5c** contain only one electroactive phenolic group, and so were expected to show simpler electrochemical properties. Phenolic compounds are known to undergo a number of proton and electron transfer reactions in an

electrochemical “square-scheme” mechanism, where the lifetimes of the oxidised species depend on their structures and particularly on the substituents in the 2, 4 and 6 positions.^[10-13] Recent studies have demonstrated that some phenolic compounds can be oxidized to form relatively long-lived diamagnetic cations (phenoxonium ions) in a two-electron and one-proton process.^[14-23] We were particular interested in determining whether the macrocyclic structure of the calix[4]arenes could impact improved lifetimes on the oxidized forms of the compounds.

Scheme 1. Structure of compounds and synthetic pathways.

2. Results and Discussion

2.1. Electrochemistry of 1a, 5a, 5b and 5c. Figure 1a shows CVs of **5a** in CH₃CN at a variety of scan rates at a GC electrode. The compound shows a chemically irreversible oxidation process with an anodic peak potential (E_p^{ox}) at $\sim +0.6$ V vs. Fc/Fc⁺. The oxidation process remained chemically irreversible in the

sense that the anodic (i_p^{ox}) to cathodic (i_p^{red}) peak current ratio ($i_p^{\text{ox}}/i_p^{\text{red}}$) was $\gg 1$ at all measured scan rates (Figure 1a). In contrast, the CV data obtained in CH_2Cl_2 shows that the $i_p^{\text{ox}}/i_p^{\text{red}}$ -ratio for the first oxidation process approaches unity as the scan rate is increased to 5 V s^{-1} (Figure 2a).

The oxidation of phenols (POH) typically occurs by two-electrons per molecule *via* an electrochemical ECE mechanism^[10-23] (or possibly a disproportionation mechanism that also involves two-electrons per molecule) (Scheme 2).^[21] The first electron transfer step produces the cation radical ($\text{POH}^{+\bullet}$), which loses a proton to form a neutral phenoxyl radical ($\text{PO}^\bullet$). Because the phenoxyl radicals are easier to oxidise than their associated phenols, they immediately undergo further oxidation to form the diamagnetic cation (PO^+). Normally the diamagnetic cations are short-lived and undergo rapid hydrolysis reactions with trace water or other nucleophiles in the solvent.^[10-23]

Scheme 2. Oxidation mechanism for phenols.^[10-23]

Figure 1. Voltammetric and coulometric data of 1 mM **5a** in CH₃CN with 0.2 M Bu₄NPF₆. (a) CVs recorded at 20 °C at variable scan rates with a 1 mm diameter GC electrode. Current data were scaled by multiplying by $\nu^{0.5}$. (b) CVs recorded at -20 °C at a 1 mm diameter Pt electrode (solid line) prior to the bulk oxidation of **5a**, and (dotted line) after the exhaustive oxidation of **5a** at an applied potential of +0.8 V vs. Fc/Fc⁺. Current data were scaled by multiplying by $\nu^{0.5}$. (c) Current/coulometry vs. time data obtained during the exhaustive oxidation of **5a** at +0.8 V vs. Fc/Fc⁺ at -20 °C.

Figure 2. Voltammetric and coulometric data of 1 mM **5a** in CH_2Cl_2 with 0.2 M Bu_4NPF_6 . (a) CVs recorded at 20 °C at variable scan rates with a 1 mm diameter GC electrode. Current data were scaled by multiplying by $\nu^{-0.5}$. (b) CVs recorded at -20 °C at a 1 mm diameter Pt electrode (solid line) prior to the bulk oxidation of **5a**, and (dotted line) after the exhaustive oxidation of **5a** at an applied potential of +0.8 V vs. Fc/Fc^+ . Current data were scaled by multiplying by $\nu^{-0.5}$. (c) Current/coulometry vs. time data obtained during the exhaustive oxidation of **5a** at +0.8 V vs. Fc/Fc^+ at -20 °C

The chemically irreversible voltammetric process that is observed in acetonitrile (Figure 1a) is consistent with what is expected for most phenols, where the oxidation mechanism occurs by two-electrons per molecule in a chemically irreversible process. However, the voltammograms that are observed in CH_2Cl_2 (Figure 2a) are similar in appearance to what is expected for a one-electron transfer. Therefore, it is likely that the difference in the CVs observed in the two solvents is due to a different number of electrons transferred on the short voltammetric timescale (seconds). It was previously observed that the cation radical of the phenolic compound α -tocopherol had an increased lifetime in CH_2Cl_2 compared to in CH_3CN , due to a change in the equilibrium constant for the deprotonation step of the cation radical (K_{eq} in Scheme 2).^[15-20,29] This can be rationalised by the phenolic radical cations being less acidic in low dielectric constant solvents. It is likely that the same situation applies to **5a**, so that the cation radical formed by initial one-electron oxidation has a longer lifetime in CH_2Cl_2 compared to CH_3CN . The CVs obtained of **5a** in CH_2Cl_2 display lower peak currents than those obtained for equivalent concentrations in CH_3CN , which supports the assignment of the one-electron oxidation in CH_2Cl_2 (assuming similar diffusion coefficient values between the different solvents).

An alternative mechanism where **5a** undergoes a chemically reversible two-electron transfer to the diamagnetic cation (as seen for α -tocopherol^[15-20]) is less likely. In situations where a diamagnetic cation has been voltammetrically detected, the E_{p}^{ox} to $E_{\text{p}}^{\text{red}}$ separations (ΔE_{pp}) are usually very wide ($\sim 300 - 400$

mV) due to the wide potential separation between the formal potentials (E°_f) of the phenol and phenoxyl ion oxidation steps (E_1 and E_2 in Scheme 2). The ΔE_{pp} -values observed in Figure 2a are similar to those observed for one-electron transfers, taking into account the resistance effects of the low dielectric constant solvent.

Although the cyclic voltammograms in CH_2Cl_2 (Figure 2a) show signs of chemical reversibility, the observation that scan rates $\gg 0.1 \text{ V s}^{-1}$ are needed to obtain $i_p^{\text{ox}}/i_p^{\text{red}}$ -ratios approaching unity, indicates that the lifetime of the one-electron oxidized species is still only a few seconds. Controlled potential electrolysis of **5a** in both CH_3CN (Figure 1c) and CH_2Cl_2 (Figure 2c) occurred by the transfer of close to two-electrons per molecule. Therefore, the longer timescale electrolysis experiments in CH_2Cl_2 allow time for the intermediate cation radical to undergo deprotonation and then be further oxidised, resulting in an increase in the number of electrons transferred compared to the faster timescale CV experiments. It was also observed that in both exhaustively electrolysed solutions, the two-electron oxidized compound had reacted to form a new product that showed a reduction process at approximately -0.4 to $-0.6 \text{ V vs. Fc/Fc}^+$ (Figures 1b and 2b), indicating that the diamagnetic cation (if formed) was not long-lived under electrolysis conditions. During the electrolysis reaction the solution was observed to change to a pale yellow-green colour, possibly due to the appearance of the intermediate radical cation present in small amounts.

The voltammetric data obtained for **1a**, **5b** and **5c** were similar to that obtained for **5a**, although there were some differences in the observed potential of

the oxidation processes and the degree of chemical reversibility in CH₂Cl₂. A comparison of the voltammetry for each compound in CH₃CN and CH₂Cl₂ is given in Figure 3. In each case, the voltammetry appeared more chemically reversible in CH₂Cl₂ compared to in CH₃CN. As the scan rate was increased, the voltammetry observed in CH₂Cl₂ became more chemically reversible and appeared to approach a one-electron chemically reversible reaction indicating that the cation radicals had an observable lifetime. In contrast, in CH₃CN, the voltammetry appeared chemically irreversible at all scan rates measured (up to 50 V s⁻¹), indicating that the cation radicals formed by the initial one-electron oxidation were relatively short-lived. Furthermore, in each case the i_p^{ox} -values measured in CH₃CN were significantly larger than those measured in CH₂Cl₂ suggested a greater number of electrons were transferred in CH₃CN, at least on the short CV timescale. However, longer timescale electrolysis experiments on **5b** in CH₂Cl₂ and CH₃CN at -20 °C, indicated in both solvents that the oxidation processes occurred by two-electrons per molecule to form a final product that could not be reduced back to the starting material by applying a reductive potential (similar to the results obtained for **5a**).

Figure 3. Cyclic voltammograms obtained at $T = 20\text{ }^{\circ}\text{C}$ of 1 mM solutions of analytes recorded at a 1 mm diameter GC working electrode at $\nu = 0.1\text{ V s}^{-1}$ in CH_3CN or CH_2Cl_2 with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte. Current data were scaled by multiplying by $\nu^{-0.5}$. (a) **5b**, (b) **5a**, (c) **5c**, (d) **1a**.

2.2. Electrochemistry of 2a. **2a** is thought to convert to compounds **5a**, **5b** and **5c** in an oxidation mechanism involving the diamagnetic cationic intermediate, **3** (Scheme 1).^[8] Therefore, we were interested in determining whether the intermediate, **3**, could be voltammetrically detected during the oxidation of **2a** with AgSbF_6 . **2a** is poorly soluble in CH_3CN but dissolves completely in CH_2Cl_2 . A cyclic voltammogram of **2a** in CH_2Cl_2 at $20\text{ }^{\circ}\text{C}$ is shown in Figure 4a, which displays a reduction process at approximately $-1.6\text{ V vs. Fc/Fc}^+$ and a number of

oxidation processes at potentials $> +0.9$ V vs. Fc/Fc^+ . Neither the reduction nor oxidation processes show any evidence of chemical reversibility at scan rates up to 50 V s^{-1} , indicating that the oxidised and reduced forms of **2a** were chemically short-lived.

Figure 4. Cyclic voltammograms of 1 mM **2a** recorded at a GC working electrode at $\nu = 0.1 \text{ V s}^{-1}$ in CH_2Cl_2 with 0.2 M $n\text{-Bu}_4\text{NPF}_6$. Current data were scaled by multiplying by $\nu^{0.5}$. (a) $T = 20^\circ\text{C}$. (b) $T = -25^\circ\text{C}$. Dotted trace was obtained after the addition of 0.8 mM of AgSbF_6 .

The solid line in Figure 4b shows a CV of 1 mM **2a** at -25°C and the dotted line shows a CV obtained in the same solution immediately after the addition of 0.8 mM of AgSbF_6 . The dotted line CV shows a new species with an oxidation process at $\sim +0.4$ to $+0.5$ V vs. Fc/Fc^+ . A white precipitate (of AgBr) was observed as soon as the AgSbF_6 was added to the solution, indicating that Br^- was being removed from **2a**. However, the solution remained uncoloured and no new

reduction processes were observed, indicating that the cation, **3**, was not voltammetrically detectable, should it indeed be formed. The new species that could be voltammetrically oxidized at +0.4 – 0.5 V vs. Fc/Fc⁺ (dotted line) appears to be a stable product and its voltammetric response remained unchanged as the temperature was increased to 20 °C.

Experiments were also performed at a higher concentration of **2a**. When 10 mM of AgSbF₆ was added to 10 mM **2a** at –20 °C, the solution turned a yellow/orange colour and the AgBr precipitate was observed, and a new product was detected with an oxidation potential at ~ +0.4 to +0.5 V vs. Fc/Fc⁺. Similar to the low concentration experiments, the voltammetry did not show any clear evidence of the presence of an intermediate or semi-stable cation (**3**) that should form *via* loss of the Br[–] from the starting material. It is possible that **3** does form, but it is in substantially less than 100% yield, so it is difficult to detect voltammetrically.

2.3. Electrochemistry of 1b. **1b** can be reduced in two one-electron steps at approximately –1.2 and –2.0 V vs. Fc/Fc⁺ (Fc = ferrocene) (Figure 5), to form the monoanion radical and dianion, respectively. The first reduction process at –1.2 V vs. Fc/Fc⁺ is chemically reversible where the anodic (i_p^{ox}) and cathodic (i_p^{red}) peak current ratio ($i_p^{\text{ox}} / i_p^{\text{red}}$) is close to unity. The second electron transfer process at –2.0 V vs. Fc/Fc⁺ only displays a forward reduction step (E_p^{red}) with no detectable oxidation peak (E_p^{ox}) when the scan direction is reversed, and can therefore, be considered to be chemically irreversible (at a scan rate of 100 mV s^{–1}). The

i_p^{ox} -value for the second electron transfer process is much less than the first process, possibly due to a slow rate of heterogeneous electron transfer or due to a complexation reaction between the dianion and starting material that is sometimes detected during the reduction of quinones.^[30] The electrochemical results obtained for **1b** are similar to what are observed for most quinoid compounds in aprotic non-aqueous solvents, which display two one-electron reduction processes at negative potentials.^[30-34]

Figure 5. Cyclic voltammogram of 1 mM **1b** recorded at a scan rate of 100 mV s⁻¹ at a 1 mm diameter GC electrode in CH₃CN containing 0.2 M Bu₄NPF₆ at 22 °C.

2.4. Ion sensing properties. The sensing properties of the compounds were tested for Groups IA and IIA ions by incorporating the molecules into polymer membrane ion selective electrodes (see Experimental Section). The membrane composition consisted (by mass) of PVC (33%), several different types of plasticizers (65%), potassium tetrakis-(4-biphenyl)borate as the counter ion (1%) and the calix[4]arene (1%). A total ionic strength adjustment buffer was not used for the measurements because of strong interference from the Groups IA and IIA metals commonly used in buffers.

The membranes containing the sensing compounds were all found to display a potential dependent response except for the membrane containing **2a**, which showed no change in potential as the concentration of ions was varied. It is possible that the combination of a bromide and *tert*-butyl group bonded to the same carbon in compound **2a** hindered the ions entering the calix[4]arene cavity, thereby preventing weak bonding interactions. Membranes containing compound **1b**, with the *para*-quinone moiety, were found to reversibly vary in potential as the concentration of ions were varied, indicating that the presence of a phenolic group was not essential for a reversible response.

It was found that the compounds that displayed a potential response showed the highest selectivity for Cs^+ , compared to the other metal ions. There have been a number of reports where calix[4]arenes or calix[6]arenes have been found to be selective for Cs^+ when incorporated into the polymer membranes of ion selective electrodes.^[35-43] Table 1 provides a summary of the sensing results obtained for the different compounds in the presence of different Group IA ions as well as with different plasticizers in the membranes. In most instances the slopes were close to +59 mV (except for Na^+ and Li^+) and the linear region of the response was between 10^{-6} M to 10^{-2} M. The best result (in terms of the Nernstian slope) was obtained using NPOE as the plasticizer.

Table 1. Results from polymer membrane ion-selective electrode experiments with varying membrane compositions and Group IA ions.

Ion (<i>i</i>)	Membrane Composition	Slope of plot of E vs. $\log a_i$ / mV	Linear concentration range / M
Cs ⁺	1a ,KTBPB, PVC/NPOE	59.3	4.6×10^{-6} to 3.6×10^{-2}
Cs ⁺	1a , KTBPB, PVC/DBS	56.0	5.5×10^{-6} to 4.0×10^{-2}
Cs ⁺	1a , KTBPB, PVC/DOPP	52.9	4.5×10^{-6} to 1.1×10^{-2}
Cs ⁺	1a , KTBPB, PVC/DBP	56.0	3.6×10^{-6} to 4.0×10^{-2}
K ⁺	1a , KTBPB, PVC/NPOE	55.6	3.2×10^{-6} to 3.3×10^{-2}
Na ⁺	1a , KTBPB, PVC/NPOE	46.0	7.6×10^{-6} to 9.1×10^{-2}
Li ⁺	1a , KTBPB, PVC/NPOE	46.0	1.7×10^{-6} to 7.3×10^{-2}
Cs ⁺	1b , KTBPB, PVC/NPOE	56.9	4.6×10^{-6} to 4.0×10^{-2}
Cs ⁺	5a , KTBPB, PVC/NPOE	56.7	5.0×10^{-6} to 4.2×10^{-2}
Cs ⁺	5b , KTBPB, PVC/NPOE	59.9	5.0×10^{-6} to 4.3×10^{-2}
Cs ⁺	5c , KTBPB, PVC/NPOE	58.6	4.9×10^{-6} to 4.1×10^{-2}

Table 2. Ion selectivity coefficient measurements for Cs⁺ as the primary ion (*i*) in the presence of interfering ions (*j*) for a membrane composition of **1a**/KTBPB/PVC/NPOE.

Interfering ion (<i>j</i>)	$\log_{10}$ Selectivity Coefficient ($\log_{10} K_{Cs,j}^{pot}$)	
	SSM (from eq 2)	FIM (from eq 3)
Rb ⁺	-0.19	-0.58
K ⁺	-0.86	-1.65
NH ₄ ⁺	-1.26	-2.05
Na ⁺	-2.07	-2.65
Li ⁺	-2.64	-2.86
Ca ²⁺	-4.01	-3.81
Mg ²⁺	-4.49	-4.12

Table 2 gives selectivity coefficient results that were obtained from **1a** in the presence of a range of Groups IA and IIA ions using the SSM and FIM methods.^[28] Variations were obtained for the absolute selectivity coefficient values for the different ions obtained with the different methods (FIM and SSM) but the trends were similar. It can be observed from the results in Table 2 the ISE containing **1a** is more selective in the order Cs⁺ (0.25) > Rb⁺ (0.25) > K⁺ (0.3) > NH₄⁺ (0.25) >

Na^+ (0.43) > Li^+ (0.6) > Ca^{2+} (0.6) > Mg^{2+} (0.8), which closely follows the order of hydrated ion size given in parenthesis (in nm).^[44]

3. Conclusions

The electrochemical oxidation of compounds **1a**, **5a**, **5b** and **5c** that contain a phenolic group in the macrocyclic structure occurred by one electron per molecule in dichloromethane on short voltammetric timescales (seconds) to most likely form cation radicals. In acetonitrile, and over the longer timescales (minutes to hours) of controlled potential electrolysis experiments, the cation radicals deprotonate to form neutral radicals which are further oxidised to diamagnetic cations in an ECE mechanism. Compound **1b**, containing a quinone group in the macrocyclic structure displayed electrochemical properties similar to other quinones, that is, could be electrochemically reduced in two one-electron reduction process.

With the exception of **2a**, all of the compounds displayed ion sensing properties for Groups IA and IIA metals, with the highest selectivity shown for the Cs^+ ion. The reason that **2a** did not potentiometrically respond to the cations most likely relates to steric effects introduced by having a *tert*-butyl and bromide group bonded to the same carbon on the *upper* or *wide* (or *exo*) ring, thereby hindering entrance of the ions into the macrocyclic ring. There appeared to be little change to the sensing properties by changing the quinone (**1b**) to a phenol (**1a**, **5a**, **5b** and **5c**) functionality, suggesting that the size of the macrocyclic structure was the most important factor in determining the sensing properties. Correspondingly, the order

of selectivity of the Groups IA and IIA ions (and NH_4^+) calculated according to both the separate solution and fixed interference methods, were found correlate with the order of the hydrated ion size.

4. Experimental Section

4.1. Chemicals and reagents. HPLC grade CH_3CN (Tedia) and CH_2Cl_2 (J. T. Baker) were dried over 3 Å molecular sieves and HPLC grade tetrahydrofuran (THF) was used directly from the bottle. High molecular weight poly(vinyl chloride), 2-nitrophenyl octyl ether (NPOE) and potassium tetrakis(4-biphenyl)borate (KTBPB) were obtained from Fluka. Di-*n*-octyl phenylphosphonate (DOPP), di-*n*-butyl sebacate (DBS), di-*n*-butyl phthalate (DBP) were obtained from Alfa Aesar. LiCl, NaCl, KCl, CsCl, CaCl_2 , NH_4Cl , MgSO_4 salts were obtained from Goodrich Chemical Enterprise (GCE). Rb standard solution (1000 $\mu\text{g/ml}$ in 2 % HNO_3) was obtained from Certified standards. All sample solutions for analysis were prepared with water, with a resistivity $\geq 18 \text{ M}\Omega \text{ cm}$ from an ELGA Purelab Option-Q. The synthesis of compounds **1a**, **1b**, **2a**, **5a**, **5b** and **5c** have been described previously.^[7, 8]

4.2. Voltammetry. Cyclic voltammetry (CV) experiments were conducted with a computer controlled Eco Chemie $\mu\text{Autolab III}$ potentiostat. Working electrodes were 1 mm diameter planar Pt and glassy carbon (GC) disks (Cyress Systems), used in conjunction with a Pt auxiliary electrode (Metrohm) and an Ag wire miniature reference electrode (Cyress Systems) connected to the test solution *via* a salt bridge containing 0.5 M Bu_4NPF_6 in CH_3CN . Accurate

potentials were obtained using ferrocene as an internal standard, which was added to the test solution at the end of the measurements.

4.3. Controlled potential electrolysis. Bulk electrolysis experiments were performed in a divided controlled potential electrolysis (CPE) cell separated with a porosity no. 5 (1.0 – 1.7 μm) sintered glass frit.^[24] The working and auxiliary electrodes were identically sized Pt mesh plates symmetrically arranged with respect to each other with an Ag wire reference electrode (isolated by a salt bridge) positioned to within 2 mm of the surface of the working electrode. The volumes of both the working and auxiliary electrode compartments were approximately 20 mL each. The solution in the working electrode compartment was simultaneously deoxygenated and stirred using bubbles of argon gas. The number of electrons (n) transferred during the bulk oxidation process was calculated from

$$N = Q/nF \quad (1)$$

where N = no. of moles of starting compound, Q = charge (coulombs) and F is the Faraday constant (96485 C mol⁻¹).

4.4. Preparation of polymer membrane ion-selective electrodes. The PVC-based membranes were prepared by mixing the calix[4]arenes (1 mg), KTBPB (1 mg), plasticizers (65 mg), and PVC (33 mg) in THF (2 ml). After the mixture had completely dissolved in the THF, the clear solution was poured into a 5 cm diameter Petri dish and the THF was allowed to evaporate for approximately 24 hours at room temperature. A 5 mm diameter circular piece of the membrane

was cut out and attached to the end of a commercial electrode (Selectophore Fluka). The inner filling solution of the ISE electrode contained 0.1 M of the ions that the electrode was tested with, and the electrode/membrane was conditioned for 2 days in a 0.5 M solution of the particular ion.

4.5. Selectivity coefficients measurements. Selectivity coefficients (K_{ij}^{pot}) were determined using cesium as the primary ion (i) and other Groups IA and IIA metals as interfering ions (j) using both the fixed interference method (FIM) and separate solution method (SSM).^[25-28] In the SSM, the solution of 0.01M NaCl served as the internal filling solution and the electrodes were conditioned in 0.01M NaCl solution for at least 48 hours before measuring other 0.01 M interfering ions and 0.01 M primary cesium ion. The selectivity coefficient was calculated by equation 2, where E_i is the cell potential of the solution containing only the primary ion, E_j is the cell potential of the solution containing both the primary ion and interfering ion, Z_i and Z_j are the charges on the primary and interfering ions respectively, a_i is the activity of the primary ion calculated by Debye-Hückel theory, R is the gas constant ($8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (in K) and F is the Faraday constant (96485 C mol^{-1}).

$$\log K_{ij}^{\text{pot}} = \frac{E_j - E_i}{(2.303RT)/(Z_i F)} + \left(1 - \frac{Z_i}{Z_j}\right) \log a_i \quad (2)$$

For the FIM, the concentration of the interfering ion was kept at 0.01M, whereas the Cs^+ ion was varied from 1.0×10^{-7} to 1.0×10^{-1} M. Before taking any potential measurements, the membranes were equilibrated in 0.5 M Cs^+ solution for 48 h, and the inner solution consisted of 0.1 M CsCl. The selectivity

coefficients was calculated by equation 3, where DL (detection limit) and BG (background) were obtained graphically from readings of the primary ion in the presence of the interfering ion.^[28]

$$\log K_{ij}^{\text{pot}} = \log \frac{a_i(\text{DL})}{a_j(\text{BG})^{Z_i/Z_j}} \quad (3)$$

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Publications Accepted

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- 2) Chelation-assisted Rhodium Hydride-catalyzed Regioselective H/D Exchange in Arenes

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- 3) Hydrogen Bonding-assisted Tautomerization of Pyridine Moieties in the Coordination Sphere of an Ir(I) Complex

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- 4) Electrochemistry and Ion-sensing Properties of Calix[4]arene Derivatives

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Publications being prepared

- 8) Mechanistic Study of Aryl-Vinyl Reductive Elimination from Rare five-coordinate Rh(III) center

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