Diyne and bisalkynyl complexes of pentamethylcyclopentadienyliridium

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**Diyne and Bisalkynyl Complexes of
Pentamethylcyclopentadienyliridium**

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**SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY**

2015

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Abstract

The reductive elimination of $[\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})_2]$ to $[\text{Cp}^*\text{Ir}(\text{CO})(\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh})]$ has been investigated. This reaction proceeds at an accelerated rates in protic solvents, and the reaction pathway has been examined computationally and experimentally. The effects of substitution at the phenyl ring and of the ancillary ligand have also been examined.

The reactivity of both bis(alkynyl) complexes $[\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CAr})_2]$ and diyne complexes $[\text{Cp}^*\text{Ir}(\text{CO})(\text{ArC}\equiv\text{C}-\text{C}\equiv\text{CAr})]$ have also been investigated. The diyne complex reacted with two electron-donors L to form the 4-membered metallacycles $[\text{Cp}^*\text{Ir}(\text{L})\{\text{C}(\text{C}\equiv\text{CAr})=\text{C}(\text{Ar})\text{C}=\text{O}\}]$ by an intramolecular cycloaddition reaction. The kinetics of the reaction has been measured and the reaction pathway studied computationally. The photochemical reaction of the diyne complex with 3-hexyne afforded an allyl complex, its reaction with phenylacetylene afforded the unstable iridapentadiene species $[\text{Cp}^*\text{Ir}(\text{CO})\{\text{CH}=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{C}(\text{C}\equiv\text{CPh})\}]$, and acid-catalysed hydrolysis yielded the iridacyclopentenone $[\text{Cp}^*\text{Ir}(\text{CO})\{\text{C}(\text{Ph})=\text{CHC}(=\text{O})\text{CHPh}\}]$.

The bisalkynyl complexes $[\text{Cp}^*\text{Ir}(\text{L})(\text{C}\equiv\text{CAr})_2]$ were found to undergo acid-catalysed aerobic oxidation to form the iridaindenes $[\text{Cp}^*\text{Ir}(\text{L})\{\text{C}_6\text{H}_4\text{-}1,2\text{-CH}=\text{CC}(=\text{O})\text{C}(=\text{O})\text{Ar}\}]$. They also undergo an Arbuzov-type reaction with $\text{P}(\text{OMe})_3$ in the presence of CH_3COOH to give the iridacyclic phosphates $[\text{Cp}^*\text{Ir}(\text{L})\{\text{C}(\text{Ar})=\text{C}[\text{P}(=\text{O})(\text{OMe})_2]\text{C}=\text{CHAr}\}]$. Reaction pathways for both reactions have been proposed.

Compound numbering scheme

Formula

- 1a** $[\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2]$
1b $[\text{Cp}^*\text{Ir}(\text{P}(\text{OMe})_3)\text{Cl}_2]$
1c $[\text{Cp}^*\text{Ir}(\text{P}(\text{OPh})_3)\text{Cl}_2]$
1d $[\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{Cl}_2]$
1e $[\text{Cp}^*\text{Ir}(\text{PPh}_3)\text{Cl}_2]$
1f $[\text{Cp}^*\text{Ir}(\text{C}_6\text{H}_5\text{CH}_2\text{NCNCH}_2\text{C}_6\text{H}_5\text{CH}=\text{CH})\text{Cl}_2]$
1g $[\text{Cp}^*\text{Ir}(\text{CH}_3\text{NCNCH}_3\text{C}_6\text{H}_4)\text{Cl}_2]$

Structure

- 1a**, L=CO
1b, L=P(OMe)₃
1c, L=P(OPh)₃
1d, L=PMe₃
1e, L=PPh₃

- 2-H** $\text{PhC}\equiv\text{CLi}$
2-OMe $4\text{-OMeC}_6\text{H}_4\text{C}\equiv\text{CLi}$
2-Cl $4\text{-ClC}_6\text{H}_4\text{C}\equiv\text{CLi}$
2-Me $4\text{-MeC}_6\text{H}_4\text{C}\equiv\text{CLi}$
2-F $4\text{-FC}_6\text{H}_4\text{C}\equiv\text{CLi}$
2k $\text{C}_6\text{F}_5\text{C}\equiv\text{CLi}$

2-X, X=H, OMe, Cl, Me, F

2k, X=F

- 3a-H** $[\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})_2]$
3a-^tBu $[\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{C}^t\text{Bu})_2]$
3b-H $[\text{Cp}^*\text{Ir}(\text{P}(\text{OMe})_3)(\text{C}\equiv\text{CPh})_2]$
3c-H $[\text{Cp}^*\text{Ir}(\text{P}(\text{OPh})_3)(\text{C}\equiv\text{CPh})_2]$
3d-H $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}\equiv\text{CPh})_2]$
3e-H $[\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{C}\equiv\text{CPh})_2]$
3f-H $[\text{Cp}^*\text{Ir}(\text{C}_6\text{H}_5\text{CH}_2\text{NCNCH}_2\text{C}_6\text{H}_5\text{CH}=\text{CH})(\text{C}\equiv\text{CPh})_2]$
3g-H $[\text{Cp}^*\text{Ir}(\text{CH}_3\text{NCNCH}_3\text{C}_6\text{H}_4)(\text{C}\equiv\text{CPh})_2]$

3h-H [$\text{Cp}^*\text{Ir}(\text{PH}_3)(\text{C}\equiv\text{CPh})_2$]

3a-H, $\text{L}=\text{CO}$

3b-H, $\text{L}=\text{P}(\text{OMe})_3$

3c-H, $\text{L}=\text{P}(\text{OPh})_3$

3d-H, $\text{L}=\text{PMe}_3$

3e-H, $\text{L}=\text{PPh}_3$

3h-H, $\text{L}=\text{PH}_3$

3a-OMe, $\text{X}=\text{Y}=\text{OMe}$

3a-Cl, $\text{X}=\text{Y}=\text{Cl}$

3a-Me, $\text{X}=\text{Y}=\text{Me}$

3a-F, $\text{X}=\text{Y}=\text{F}$

3i, $\text{X}=\text{F}$, $\text{Y}=\text{Me}$

3j, $\text{X}=\text{C}_6\text{F}_5$, $\text{Y}=\text{OMe}$

3k, $\text{X}=\text{Y}=\text{C}_6\text{H}_5$

3a-OMe [$\text{Cp}^*\text{Ir}(\text{CO})(4\text{-OMePhC}\equiv\text{C})_2$]

3a-Cl [$\text{Cp}^*\text{Ir}(\text{CO})(4\text{-ClPhC}\equiv\text{C})_2$]

3a-Me [$\text{Cp}^*\text{Ir}(\text{CO})(4\text{-MePhC}\equiv\text{C})_2$]

3a-F [$\text{Cp}^*\text{Ir}(\text{CO})(4\text{-FPhC}\equiv\text{C})_2$]

3i [$\text{Cp}^*\text{Ir}(\text{CO})(4\text{-FPhC}\equiv\text{C})(4\text{-MePhC}\equiv\text{C})$]

3j [$\text{Cp}^*\text{Ir}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{C})(4\text{-OMePhC}\equiv\text{C})$]

3k [$\text{Cp}^*\text{Ir}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{C})_2$]

3d-OMe [$\text{Cp}^*\text{Ir}(\text{PMe}_3)(4\text{-OMePhC}\equiv\text{C})_2$]

3d-Me [$\text{Cp}^*\text{Ir}(\text{PMe}_3)(4\text{-MePhC}\equiv\text{C})_2$]

3d-Cl [$\text{Cp}^*\text{Ir}(\text{PMe}_3)(4\text{-ClPhC}\equiv\text{C})_2$]

3d-F [$\text{Cp}^*\text{Ir}(\text{PMe}_3)(4\text{-FPhC}\equiv\text{C})_2$]

3d-X, X=OMe, Me, Cl, F

4a-H [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})$]

4a-OMe [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-4-OMePhC}\equiv\text{CC}\equiv\text{CPh4-OMe})$]

4a-Cl [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-4-ClPhC}\equiv\text{CC}\equiv\text{CPh4-Cl})$]

4a-Me [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-4-MePhC}\equiv\text{CC}\equiv\text{CPh4-Me})$]

4a-F [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-4-FPhC}\equiv\text{CC}\equiv\text{CPh4-F})$]

4i [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-4-F-C}_6\text{H}_4\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{-4-Me})$]

4i' [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-4-Me-C}_6\text{H}_4\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{-4-F})$]

4j [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-C}_6\text{F}_5\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{-4-OMe})$]

4j' [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-4-OMeC}_6\text{H}_4\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{F}_5)$]

4k [$\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-C}_6\text{F}_5\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{F}_5)$]

4a-H, X=Y=H

4a-OMe, X=Y=OMe

4a-Cl, X=Y=Cl

4a-Me, X=Y=Me

4a-F, X=Y=F

4i, X=F, Y=Me

4i', X=Me, Y=F

4j, X=C₆F₅, Y=OMe

4j', X=OMe, Y=C₆F₅

4k, X=Y=C₆F₅

5a CO

5b *t*-BuNC

5c PPh₃

5d PMePh₂

5e PBu₃

5f PMe₃

5g P(OPh)₃

5h P(OMe)₃

6a-H [$\text{Cp}^*\text{Ir}(\text{CO})\{\text{C}(\text{C}\equiv\text{CC}_6\text{H}_5)=\text{C}(\text{C}_6\text{H}_5)\text{C}=\text{O}\}$]

6b-H [$\text{Cp}^*\text{Ir}(t\text{-BuNC})\{\text{C}(\text{C}\equiv\text{CC}_6\text{H}_5)=\text{C}(\text{C}_6\text{H}_5)\text{C}=\text{O}\}$]

6c-H [$\text{Cp}^*\text{Ir}(\text{PPh}_3)\{\text{C}(\text{C}\equiv\text{CC}_6\text{H}_5)=\text{C}(\text{C}_6\text{H}_5)\text{C}=\text{O}\}$]

6d-H [$\text{Cp}^*\text{Ir}(\text{PMePh}_2)\{\text{C}(\text{C}\equiv\text{CC}_6\text{H}_5)=\text{C}(\text{C}_6\text{H}_5)\text{C}=\text{O}\}$]

9a-X X=H, CH₃, Cl

10

11

12a, R=Ph

12a-^tBu, R=^tBu

13d-Me [Cp*Ir(PMe₃)₃]{4-Me-C₆H₃-1,2-

CH=CC(=O)C(=O)C₆H₄-4-Me}]

13d-Cl [Cp*Ir(PMe₃)₃]{4-Cl-C₆H₃-1,2-

CH=CC(=O)C(=O)C₆H₄-4-Cl}]

13d-F [Cp*Ir(PMe₃)₃]{4-F-C₆H₃-1,2-CH=CC(=O)C(=O)C₆H₄-4-F}]

13b-H, L=P(OMe)₃, X=H

13c-H, L=P(OPh)₃, X=H

13d-H, L=PMe₃, X=H

13e-H, L=PPh₃, X=H

13d-OMe, L=PMe₃, X=OMe

13d-Me, L=PMe₃, X=Me

13d-Cl, L=PMe₃, X=Cl

13d-F, L=PMe₃, X=F

14b-H

[Cp*Ir(P(OMe)₃)₃]{C(C₆H₅)=C[P(=O)(OMe)₂]C=CHC₆H₅}]

14d-H

[Cp*Ir(PMe₃)₃]{C(C₆H₅)=C[P(=O)(OMe)₂]C=CHC₆H₅}]

14e-H

[Cp*Ir(PPh₃)₃]{C(C₆H₅)=C[P(=O)(OMe)₂]C=CHC₆H₅}]

14f [Cp*Ir(P(OMe)₃)₃]{C(C₆H₅)=C[P(=O)(OEt)₂]C=CHC₆H₅}]

14b-OMe

[Cp*Ir(P(OMe)₃)₃]{C(4-OMe-C₆H₄)=C[P(=O)(OMe)₂]C=CHC₆H₄-4-OMe}]

14b-F [Cp*Ir(P(OMe)₃)₃]{C(4-F-C₆H₄)=C[P(=O)(OMe)₂]C=CHC₆H₄-4-F}]

15

[Cp*Ir(P(OMe)₃)₃]{(C₆H₅)C=C[P(=O)(OMe)₂]CH=C(C₆H₅)}]

14b-H, L=P(OMe)₃, X=H, R=Me

14d-H, L=PMe₃, X=H, R=Me

14e-H, L=PPh₃, X=H, R=Me

14f, L=P(OMe)₃, X=H, R=Et

14b-OMe, L=P(OMe)₃, X=OMe, R=Me

14b-F, L=P(OMe)₃, X=F, R=Me

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Abbreviations and Nomenclature

Standard abbreviations and IUPAC nomenclature are used throughout this thesis. Less common usages are as follows:

Cp*	pentamethylcyclopentadiene
dcm	dichloromethane
hex	hexane
thf	tetrahydrofuran
tol	toluene
TLC	Thin layer chromatography

Infrared (IR) spectroscopy

ν_{CO}	Stretching frequency in the carbonyl region ($1800\text{--}2200\text{ cm}^{-1}$)
vw	very weak
w	weak
m	medium
s	strong
vs	very strong
sh	shoulder
br	broad

Nuclear Magnetic Resonance (NMR) Spectroscopy

δ	chemical shift
J	coupling constant
s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet
VT	variable temperature

Mass Spectrometry (MS)

EI	electrom impact
ESI	electrospray ionization
FAB	Fast atom bombardment
m/z	Mass to charge ratio

Chapter 1: Alkyne and alkynyl metal complexes

The activation of alkynes by transition metal (TM) complexes is one of the most important group of transition metal catalysed reactions (Scheme 1.1).¹ The important first step is the formation of a π -alkyne complex (complex **1** in Figure 1.1). With terminal alkynes, this may be followed by the formation of a hydrido-alkynyl complex (**2**) via oxidative addition and both of these complexes may undergo subsequent rearrangement to a vinylidene complex (**3**).

Scheme1.1

Figure 1.1. Three common structures from the activation of alkynes by metal.

Complex **2** is a representative of the broader class of transition metal alkynyl complexes. In the reaction scheme above, the final step is a reductive

elimination to form a new alkyne. Alkynyl complexes are thus related to π -alkyne complexes via a reductive elimination. In this chapter, an examination of π -alkyne complexes, alkynyl complexes, and reductive elimination (particularly that involving C-C bond formation) will be made.

1.1 Alkyne metal complexes

Coordination of an alkyne via its π electrons to a metal centre comprises two primary bonding components: (1) σ -donation from a filled π -bonding orbital of the alkyne to an appropriate acceptor orbital of the metal, and (2) π back-donation from a filled d-orbital of the metal into the π^* orbital of the alkyne (Figure 1.2).

Figure 1.2. Dewar-Chatt model for alkyne metal complexes.

The binding of the alkyne to the metal centre generally leads to a net loss of electron density from the alkyne. This leads naturally to an enhancement towards nucleophilic attack, and reduced susceptibility towards electrophilic attack, compared to the free alkyne.

A metal-bound alkyne can undergo reactions with nucleophiles, typically leading to the formation of vinyl-metal complexes (Scheme 1.2). Direct attack of the nucleophile at the alkyne to form *trans*-adducts (M relative to Nu) is typically observed in coordinatively saturated, non-labile complexes (pathway A). The formation of *cis* adducts proceeds probably via initial attack at the metal, followed by subsequent migration to the alkyne (pathway B) (Scheme 1.2).

Scheme 1.2

Pathway B in Scheme 1.2 represents a broader reaction type, alkyne insertion. An example of alkyne insertion is the reaction of L_2PtClMe with electrophilic alkynes (Scheme 1.3).² Such reactions are key step in many metal-catalyzed alkyne reactions (Scheme 1.4).³

Scheme 1.3

Scheme 1.4

Although metal-bound alkynes are typically less electrophilic than free alkynes, nevertheless, the complex $\text{NbCl}_3(\text{THF})_2(\text{alkyne})$ reacted with 1,2-aryldialdehydes to form 2,3-disubstituted-1-naphthols regioselectively, via an electrophilic addition (Scheme 1.5).⁴

Scheme 1.5

The binding of an alkyne onto a metal centre not only serves to activate the alkyne but the metal centre also acts as a template, bringing two or more unsaturated molecules into close proximity for coupling to occur. Some examples of such coupling reactions are depicted in Scheme 1.6.

Scheme 1.6

The formation of cyclopentenone, also known as the Pauson-Khand reaction, is formally a [2+2+1] cycloaddition. Complexes of the group 9 transition metals,⁵ but also of other metals like titanium, tungsten, ruthenium and palladium, can catalyse this reaction.⁶ The typical catalyst for the reaction is a cobalt complex, and joins an alkyne, an alkene, and carbon monoxide regioselectively, tending to place a large alkyne substituent adjacent to the CO (Scheme 1.7).

Scheme 1.7

The formation of metallacyclobutene complexes can be illustrated by the cycloaddition reactions of $[Co(\eta^5-C_5H_5)(PPh_3)(R^1C=R^2)]$ ($R^1 = H, Me, \text{ or } Ph$; $R^2 = Ph, CO_2Me, \text{ or } CN$) with isocyanides R^3NC ($R^3 = Ph, p\text{-}MeC_6H_4, \text{ or } 2,6\text{-}Me_2C_6H_3$) to give cobaltacyclobutene complexes (Scheme 1.8).⁷

Scheme 1.8

In general, the reaction of a metal-alkyne complex with another alkyne leads to the formation of metallacyclopentadienes. The regioselectivity of the reaction is primarily controlled by steric rather than electronic effects. For example, in the formation of cobaltacyclopentadiene, the α -position is substituted by the bulkier group (Scheme 1.9).⁸

Scheme 1.9

1.2 Alkynyl metal complexes

Besides their relevance to transition metal-catalysed processes involving alkynes, metal alkynyl complexes have also found applications in materials science in themselves. An example is as precursors or monomers for metal-containing conjugated alkynyl polymers, which have been shown to exhibit a range of new properties, such as, electronic conduction,⁹ luminescence, nonlinear optical effects,¹⁰ photoconductivity,¹¹ and liquid crystallinity.¹²

In general metal alkynyl complexes are obtained by ligand (L) substitution reactions of terminal alkynes with alkynyl groups in the presence of base, or by direct oxidative addition of alkynes to metals (Scheme 1.10).¹³

Scheme 1.10

Metal alkynyl complexes can be regarded as complexes of the $\text{HC}\equiv\text{C}^-$ ligand, which is isoelectronic with CN^- , CO , and N_2 . The bonding description is thus similar and comprises two interactions: (1) σ -donation from lone pair of alkynyl to d_σ orbital of the metal, and (2) π back-donation from a filled d_π orbital of the metal into the π^* orbital of the alkynyl (Figure 1.3).

Figure 1.3. Dewar-Chatt model for alkynyl metal complexes.

Compared to other ligands, the alkynyl ligand is a good σ donor but poor π acceptor. This tends to lead to a δ^+ charge on the α -carbon and hence should make it susceptible to nucleophilic attack. On the other hand, the $\text{C}\equiv\text{C}$ bond retains much of its π -electron density and is hence susceptible to attack by electrophiles, much like those of organic alkynes. As a result, direct nucleophilic attack at α -carbon of alkynyl metal complexes are rarely observed and usually some activation is involved. For example, the coupling of the alkyl and alkynyl ligands in $\text{Ir}(\text{CO})(\text{CH}_3)\text{L}_2(\text{C}\equiv\text{CR})(\text{CH}=\text{CHNEt}_3)^+$ to form the *cis*-bis(alkenyl) complex $\text{Ir}(\text{CO})(\text{CH}_3)\text{L}_2(\text{CH}_3\text{C}=\text{CHR})(\text{CH}=\text{CHNEt}_3)^+$ involves a formal intramolecular CH_3^- attack and is mediated by protons (Scheme 1.11).¹⁴

Scheme 1.11

More commonly, metal alkynyl complexes act as nucleophiles, for example, in their reactions with a second transition metal to afford heterobimetallic complexes;¹⁵ this is illustrated by the reaction of *cis*-dialkynyl platinum(II) complex, Pt(C≡CPh)₂(dppe), with Ru₃(CO)₁₂ (Scheme 1.12).¹⁶

Scheme 1.12

1.3 Reductive elimination in metal complexes

As has already been mentioned above, reductive elimination (RE) and its reverse, oxidative addition (OA), are important processes in many catalytic cycles. For example, the generalised catalytic cycle for Negishi and Suzuki coupling is depicted in Scheme 1.13. The initial step is an OA and the final step, during which the product is eliminated, is a RE.

Catalytic cycle of the Negishi and Suzuki coupling

Scheme 1.13

In spite of its great importance, RE is less well studied than OA because complexes that undergo RE are generally less stable. The reaction is most often seen in complexes with high oxidation states and which are sterically hindered. The formal oxidation state of the metal is reduced by two units (Figure 1.4), and is especially efficient for the d^6 (Pd(IV), Pt(IV), Rh(III) and Ir(III)) and d^8 (Ni(II), Pd(II) and Au(III)) metals. Reductive elimination forming R-H, R-R, R-SiMe₃, R-COR and H-COR bonds are often favoured for thermodynamic reasons, as the C-X (X = H, C or Si) bond energies are usually greater than that for the sum of the M-X and M-C bonds.¹⁷ In the following discussion, focus will be on reductive elimination leading to the formation of H-H, C-H, C-X and, in particular, the C-C bond.

Figure 1.4. Typical reductive elimination reaction.

1.3.1 H-H and C-H reductive elimination

A number of examples studied for C-H reductive elimination from Pt(IV) alkyl hydrides were found to proceed via prior dissociation of a ligand. An example of direct reductive elimination is that in the Pt(IV) complexes $\text{P}_2\text{PtMe}_3\text{H}$; where $\text{P}_2 = \text{dppe}$ or dppbz (Scheme 1.14).¹⁸

Scheme 1.14

The mechanism for H-H and C-H reductive elimination can be looked at through its reverse reaction, i.e., oxidative addition of the H-H bond (H_2 activation) and of the C-H bond (C-H bond activation). The transition states involved thus correspond to the σ complexes or π -complexes (Scheme 1.15).

Scheme 1.15

A number of studies have shown that the kinetic barrier for these reductive eliminations is affected by the nature of the bond being formed, and the hybridisation of the carbon atom, and the activation energy increases in the order: $H-H < H-C(sp^2) < H-C(sp^3)$. Thus Low, et. al., found that the intrinsic barrier for H-H bond formation is very small (1.55 kcal/mol) compared to that for C-H coupling (10.4 kcal/mol). Compared to breaking M-H bonds to form H-H bonds, the directionality of the sp^3 hybrid orbital of a methyl group makes it more difficult to convert from an M-C to a C-H bond during reductive elimination (Scheme 1.16).¹⁹

intrinsic barrier $\Delta E^\ddagger = 1.55$ kcal/mol

intrinsic barrier $\Delta E^\ddagger = 10.4$ kcal/mol

Scheme 1.16

Similarly, a DFT study on the reductive elimination of H-H and C-H (H-Csp², H-Csp³) bonds from both neutral *cis*-[AuPPh₃(R₁R₂)Cl] and cationic *cis*-[Au(PH₃)₂(R₁R₂)]⁺ show that the activation energy increases in the order: H-H < H-C(sp²) < H-C(sp³) (Scheme 1.17).²⁰

Scheme 1.17

1.3.2 C-X reductive elimination

Detailed studies on C-X (where X = halogen, N, O, I, etc.) reductive elimination are more limited as the instability of precursor complexes makes direct observation difficult. C-X (X=O, N, I) reductive elimination have been observed with low-valent, d⁸ metal centers (Ni(II) Pd(II)) involving acyl and aryl groups,²¹ and in high-valent, d⁶ metal centers (Pt(IV), Pd(IV),²² Ir(III),²³ Rh(III)).²⁴ An example each involving low and high-valent metal centers are shown below (Schemes 1.18 and 1.19, respectively).

L=Bulky Phosphine ($t\text{Bu}_3\text{P}$)
X=Cl, Br, I

Scheme 1.18

Scheme 1.19

In a series of studies on the reductive elimination of $\text{C}(\text{sp}^3)\text{-O}$,²⁵ $\text{C}(\text{sp}^3)\text{-I}$,²⁶ and $\text{C}(\text{sp}^3)\text{-N}$ bonds,²⁷ in Pt(IV) complexes, Goldberg concluded that the general mechanism of the reductive elimination of $\text{C}(\text{sp}^3)\text{-X}$ at a high-valent d^6 five-coordinate alkyl species involved in nucleophilic attack of the heteroatom group, which can be viewed as the reverse step of the $\text{S}_{\text{N}}2$ oxidative addition (Scheme 1.20).²⁸ However, the $\text{C}(\text{sp}^2 \text{ or } \text{sp})\text{-X}$ reductive elimination is less favourable than $\text{C}(\text{sp}^3)\text{-X}$ reductive elimination.²⁹

Scheme 1.20

1.3.3 C-C reductive elimination

There are three general mechanistic pathways for C-C reductive elimination (Scheme 1.21):

(A) Radical or intermolecular pathway,³⁰

(B) Direct reductive elimination, and

(C) With prior ligand dissociation.¹⁹

Scheme 1.21

To avoid the effects of prior ligand loss on mechanistic studies, most kinetic studies have been on metal complexes that undergo direct reductive elimination.³¹ It has been found the activation barrier of C-C reductive elimination is affected by:

- 1) The nature of the metal centre.
- 2) Directionality of the M-C bond.
- 3) The ancillary ligands.
- 4) Steric effects.

In a detailed DFT study on the bis- σ -vinyl complexes $[M(CH=CH_2)_2X_n]$, it was concluded that the propensity towards vinyl-vinyl reductive elimination increased in the order: Pd(IV), Pd(II) < Pt(IV), Pt(II), Rh(III) < Ir(III), Ru(II), Os(II) (Scheme 1.22).³² The effects of different ligands X were examined for both the palladium and platinum complexes, which showed that the activation barrier followed the order: X: Cl < Br, NH_3 < I < PH_3 . The stereoselectivity can be controlled by substituents on the vinyl groups, and the asymmetric nature of vinyl-vinyl coupling can also be adjusted by changing the structural parameters.

Scheme 1.22

In another theoretical study, on C-C reductive elimination of unsaturated organic ligands from complexes of the type $(PH_3)_2M(R)(R')$ (where M = Pd, Pt and R, R' = methyl, vinyl, phenyl, and ethynyl), it was concluded that the kinetic barrier was dependent on the thermodynamics of the elimination and directionality of the M-C bond, as determined by the hybridization of the C atoms involved in bond-formation, and it follows the order: $sp > sp^2 > sp^3$ (Scheme 1.23).³³ This is an extension of the directionality principle used by Goddard to rationalize the less facile addition/elimination of C-C versus C-H bonds.³⁴

Scheme 1.23

The pincer-ligated species (PCP)Ir, where PCP = κ^3 -C₆H₃-2,6-(CH₂P^tBu₂)₂, was found to promote the dimerization of phenylacetylene to give the enyne complex (PCP)Ir(*trans*-1,4-phenyl-but-3-ene-1-yne) (Scheme 1.24).³⁵ The reaction proceeded through three steps: (1) addition of the alkynyl C-H bond to iridium, (2) insertion of a second phenylacetylene molecule into the resulting Ir-H bond, and (3) reductive elimination of vinylacetylene. Each of these steps has been investigated experimentally and computationally. DFT calculations showed that the C-C elimination transition state for the alkynyl-vinyl bond formation involved the vinyl group π -system; the vinyl group had to be rotated around the Ir-C bond by ca. 90° to achieve an appropriate orientation. This rotation was severely inhibited by steric crowding, particularly when the vinyl group had an R-substituent.

Scheme 1.24

In an extension to that study, the absolute rates of C-C elimination in the complexes (tBuPCP)Ir(R)(R'), where R and R' are Me, Ph, and (phenyl-substituted) vinyl and alkynyl groups, were measured (Scheme 1.25). In general, the elimination rate decreased (activation barrier increased) in the order: acetylide < vinyl ~ Me < Ph. The underlying factors behind this order were studied by DFT calculations. A similar conclusion as above was made, i.e., the

slow rate of elimination for the vinyl and phenyl complexes can be attributed to the need to rotate the aryl or vinyl group around the Ir-C bond in the transition state prior to C-C elimination, so that the group with which it couples can add to the face of the aryl or vinyl group (Figure 1.5).³⁶

Scheme 1.25

Figure 1.5. Ground-state structures for **1**-(Me)(Ph), **1**-(Me)(Vi) (left two), and transition-state structures for **1**-(Me)(Ph), **1**-(Me)(Vi) (right two). Three-dimensional models are shown with H atoms omitted (other than those on hydrocarbyl ligands). Atoms are depicted at 75% van der Waals radii.

1.4 Aim and objectives of this project

Some time ago, we found that the reaction of Cp*Ir(CO)Cl₂ with two equivalents of phenylacetylide afforded the bis(alkynyl) iridium complex

$\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})_2$ and its C-C bond reductive elimination product $\text{Cp}^*\text{Ir}(\text{CO})(\text{PhC}\equiv\text{CC}\equiv\text{CPh})$ (Scheme 1.26).

Scheme 1.26

Given the importance of C-C bond forming reductive elimination, and the scarcity of examples known of the reductive elimination of alkynyl iridium complexes, we became interested in studying the kinetics involved in this system. In those few reports on experimental and computational studies, the direct reductive elimination from the $\text{M}(\text{R})(\text{R}')$ moiety was not directly observed; only the free reductive elimination product $\text{R}-\text{R}'$ was obtained. This meant that the kinetic measurements were of the reductive elimination plus elimination of the $\text{R}-\text{R}'$ product from the metal centre; the intermediate π -complexes were not observed. In our system, however, the π -complexes are the major product and are very stable. This provides an opportunity to directly observe the reductive elimination process.

In contrast to the many examples of the reaction of metal-alkyne complexes with alkynes or nucleophiles,³⁷ examples from transition metal-diyne complexes like $\text{Cp}^*\text{Ir}(\text{CO})(\text{PhC}\equiv\text{CC}\equiv\text{CPh})$ are scarce; the few examples include pyridine exchange in $(\text{TTP})\text{Ti}(\eta^2-\text{PhC}\equiv\text{CC}\equiv\text{CPh})$ (where $\text{TPP} = \text{meso-5,10,15,20-tetraphenylporphyrinato dianion}$) to form $(\text{TTP})\text{Ti}(\text{py})_2$,³⁸ and the reaction of $\text{Pt}(\eta^2-\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh})(\text{PPh}_3)_2$ with $\text{Fe}(\text{CO})_5$ to give the bimetallic complex $[\text{FePt}(\mu_3-\eta^1:\eta^2-\text{COC}_4\text{Ph}_2)(\text{CO})_3(\text{PPh}_3)_2]$ (Scheme 1.27).³⁹ An advantage associated with the complexes $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})_2$ and $\text{Cp}^*\text{Ir}(\text{CO})(\text{PhC}\equiv\text{CC}\equiv\text{CPh})$ is the Cp^* ligand. This is a bulky, stable and strongly electron-donating ligand, and tends to impart stability to its complexes.

Scheme 1.27

In this project, therefore, the aim is to study the reductive elimination of $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})_2$ to $\text{Cp}^*\text{Ir}(\text{CO})(\text{PhC}\equiv\text{CC}\equiv\text{CPh})$, and the chemistry of the two species. Specifically, the following are to be carried out:

1. Measurement of the kinetics of the reductive elimination.
2. Study the mechanism for the reductive elimination.
3. Examine the effects of the ancillary ligand and of substituents on the alkynyl.
4. Explore the reactivity of diyne iridium complexes.

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Chapter 2: Reductive Elimination in $\text{Cp}^*\text{Ir}^{\text{III}}(\text{L})(\text{C}\equiv\text{CAr})(\text{C}\equiv\text{CAr}')$

2.1 Reaction of $\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2$ with PhCCLi

As mentioned in chapter 1, it has been found that the reaction of the iridium(III) complex $[\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2]$ (**1a**) with three equivalents of lithium phenylacetylide PhCCLi (**2-H**) in THF afforded a mixture of the bis(alkynyl) iridium(III) complex $[\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})_2]$ (**3a-H**) and the diyne complex $[\text{Cp}^*\text{Ir}(\text{CO})(\text{PhC}\equiv\text{CC}\equiv\text{CPh})]$ (**4a-H**) at -78°C (Scheme 2.1).

Scheme 2.1

The products **3a-H** and **4a-H** have been characterised spectroscopically and analytically. Their ^1H NMR spectra showed a resonance for the Cp^* ligand (at 2.14 ppm and 2.06 ppm for **3a-H** and **4a-H**, respectively), and multiplets for ten aromatic protons. The IR spectra showed a weak $\text{C}\equiv\text{C}$ stretch (at 2139 cm^{-1} and 2165 cm^{-1} for **3a-H** and **4a-H**, respectively) and a strong CO stretch (at 2045 cm^{-1} and 1970 cm^{-1} for **3a-H** and **4a-H**, respectively). Their MS spectra showed a molecular ion corresponding to the formulation $\text{Cp}^*\text{Ir}(\text{CO})(\text{CCPh})_2$. Although diffraction-quality crystals of **3a-H** were not obtained, the single crystal X-ray crystallographic study of an analogue in which the CO ligand has been substituted by a PPh_3 ligand (**3e-H**) has been carried out (see below), and the ORTEP plot depicting its molecular structure, together with selected bond parameters, is given in Figure 2.1. The structure of **4a-H**, on the other hand, has been confirmed by a single crystal X-ray diffraction study; the ORTEP plot

showing its molecular structure, together with selected bond parameters, is given in Figure 2.2.

The Ir-C bond lengths in **4a-H** are longer than those in **3e-H** (2.084(5) and 2.112(5) Å vs 1.992(3) and 1.997(3) Å, respectively), consistent with η^2 -alkyne vs alkynyl bonding.¹ The C12-C13 bond length in **4a-H** (1.295(7) Å) is also in agreement with that for a typical C(sp)=C(sp) double bond (1.28 Å), compared to the C(sp)≡C(sp) triple bonds in **3e-H** (C11-C12 and C20-C21 bond lengths are 1.203(4) and 1.208(4) Å, respectively).² Binding of the alkyne to the Ir centre also results in the phenyl and C≡CPh groups bending away from linearity.

Figure 2.1. ORTEP plot (50% probability thermal ellipsoids) showing the molecular structure of **3e-H**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1-C20 = 1.992(3); Ir1-C11 = 1.997(3); Ir1-P1 = 2.2705(7); C11-C12 = 1.203(4); C12-C13 = 1.439(4); C20-C21 = 1.208(4); C21-C22 = 1.432(4); C20-Ir1-C11 = 92.39(11); C21-C20-Ir1 = 172.2(2); C20-C21-C22 = 171.3(3); C12-C11-Ir1 = 172.3(3); C11-C12-C13 = 175.5(3).

Figure 2.2. ORTEP plot (50% probability thermal ellipsoids) showing the molecular structure of **4a-H**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1-C11 = 1.816(5); Ir1-C12 = 2.084(5); Ir1-C13 = 2.112(5); C12-C13 = 1.295(7); C12-C22 = 1.435(6); C13-C14 = 1.376(7); C14-C15 = 1.205(7); C15-C16 = 1.438(7); C12-Ir1-C13 = 35.95(18); C13-C12-Ir1 = 73.2(3); C12-C13-Ir1 = 70.8(3); C13-C12-C22 = 146.2(5); C12-C13-C14 = 153.3(5).

This conversion of **3a-H** to **4a-H** represents a rare opportunity to study a reductive elimination step leading to the formation of a C(sp)-C(sp) bond. There are a number of reported investigations on different metals to examine the activation barrier for C(sp³)-C(sp³), C(sp²)-C(sp²), and C(sp)-C(sp) bond formation. In those reports, however, reductive elimination of a bis(alkynyl) complex to the diyne complex was not directly observed experimentally; only the free diyne was obtained and hence the kinetic studies were of the reductive elimination plus elimination of the diyne from the metal centre (Table 2.1).

Table 2.1. Comparison of reductive elimination studies to form C-C bond.

Reductive elimination complexes	R or R'	Products	Result
$M(PH_3)_2R_2$ (M=Pd, Pt) ³	CH ₃ , C≡CH, C ₆ H ₅ , CH ₂ =CH ₂	$M(PH_3)_2+R-R$	C-C bond: Vin-Vin > Ph-Ph > Eth-Eth > Me-Me.
<i>cis</i> - [AuPPh ₃ RR'Cl] ⁴	R/R'=Ph/Ph, CH=CH ₂ /CH=C H ₂ , CH ₃ /CH ₃	AuPPh ₃ Cl+ R-R'	Activation energy: Csp ² (vinyl)- Csp ² (vinyl)<Csp ² (ar yl) - Csp ² (aryl)<Csp ² (ary l)-Csp ³ <Csp ³ -Csp ³ .
Ir(PCP)RR' ⁵	R/R'=Ph/Ph, Ph/Me, Ph/CCPh	Ir(PCP)+R- R'	Activation barrier: C≡CPh < CH=CHPh ~ Me < Ph.
Cp*IrLR ₂	C≡CPh	Cp*IrL(R- R)	?

2.2 Reductive elimination of **3a-H** to **4a-H** in MeOH

Solutions of **3a-H** in d₈-THF or C₆D₆ failed to convert to **4a-H**; monitoring the solutions by ¹H NMR spectroscopy at room temperature and at 80 °C, with 1,3,5-trimethoxybenzene as internal standard, showed that **3a-H** mostly decomposed to other products (Figure 2.3). A solution of **4a-H** in C₆D₆ heated at 80 °C for 2 days showed little change, ruling out the decomposition of **4a-H** immediately after its formation from **3a-H**. Interestingly, a solution of **3a-H** in CD₃OD showed that it converted cleanly to **4a-H**; their ¹H resonances were observed at δ 2.15 and 2.05 ppm, respectively (Figure 2.4).

Figure 2.3. Mass balance for a solution of **3a-H** in C_6D_6 at 353K.

Figure 2.4. 1H NMR spectral overlay for the conversion of **3a-H** to **4a-H** in CD_3OD at 296 K.

The reductive elimination of **3a-H** to **4a-H** in methanol was thus studied by following the conversion with ^1H NMR spectroscopy. If the solvent was involved in the reaction, then it was expected to follow pseudo first order kinetics, and hence a plot of $\ln[\mathbf{3a-H}]$ versus time would be linear (Figure 2.5). Linearity for the plot are around 0.94-0.98, indicating there is a little decomposition of **3a-H**, the observed activation barrier become slightly lower than that in theoretical studies. An Eyring plot with the rate constants obtained gave: $\Delta H^\ddagger = +53(8) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -171(24) \text{ J K}^{-1} \text{ mol}^{-1}$, and hence $\Delta G^\ddagger_{298 \text{ K}} = +104(7) \text{ kJ mol}^{-1}$ (Figure A2.2).

Figure 2.5. Plot of $\ln[\mathbf{3a-H}]$ vs time for the conversion of **3a-H** to **4a-H**. Graphs have been normalised to reflect the difference in gradients and for the unmediated reaction, has been truncated to within comparable time range with the others.

2.3 Computational study on the reductive elimination

2.3.1 Mechanism based on direct reductive elimination

We initially explored a mechanism resembling that reported for the system $[\text{Ir}(\text{PCP})(\text{C}\equiv\text{CPh})_2]\cdot\text{Li}^+ \rightarrow \text{Ir}(\text{PCP}) + \text{PhC}\equiv\text{CC}\equiv\text{CPh} + \text{LiI}$.^{3c} Complex **4a-H** was equivalent to their computed, but unobserved, π -complex (Scheme 2.2). That **4a-H** could be isolated may be attributed to the fact that dissociation of the diyne ligand is thermodynamically unfavourable; ΔG° for its decomposition into $[\text{Cp}^*\text{Ir}(\text{CO})]$ and $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$ was computed to be $+148 \text{ kJ mol}^{-1}$.

Scheme 2.2

Computation for the gas-phase reaction was carried out with density functional theory (DFT), using the B3LYP density functional (the basis set used was the LANL2DZ (Los Alamos Effective Core Potential Double- ζ) augmented with an f polarization function for the iridium atom,⁶ and 6-311+G(2d,p) for the light atoms). The pathway involves the formation of a σ -complex intermediate (**INT**), and the two associated transition states (**TS1** and **TS2**) have also been located (Figure 2.6); the values indicated are the computed free energies (in kJ mol^{-1}) with respect to **3a-H**.

Figure 2.6. Computed free energy changes for the reductive elimination from **3a-H** to **4a-H** without solvent effect. Figures given are the free energies (in kJ mol⁻¹) with respect to **3a-H**.

With this pathway, the kinetic barrier for the formation of **4a-H** is associated with **TS2**. Although the computed barrier of $\Delta G^\ddagger = +124 \text{ kJ mol}^{-1}$ is fairly close to the experimental value ($\Delta G^\ddagger_{298 \text{ K}} = +104(7) \text{ kJ mol}^{-1}$), however, there are significant discrepancies between the experimental and computed $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values (Table 2.2). While the computed values suggest that the kinetic barrier should be determined almost completely by the enthalpy term, we have found experimentally that the entropy contribution is very large and negative while the enthalpy contribution is much reduced. Calculations in the solvated phase (PCM model, solvent = MeOH) for **3a-H** and **TS2** gave even larger $\Delta H^\ddagger$ and $\Delta G^\ddagger$ values. Indeed, the large and negative experimental value for $\Delta S^\ddagger$

strongly suggests that the solvent plays a role other than simply to affect the dielectric constant.

Table 2.2. Computed and experimental data for the reaction **3a-H** → **4a-H** at 298 K.

3a-H → 4a-H	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
Experimental	53(8)	-171(24)	104(7)
Calculated (gas)	124	0	124
Calculated (MeOH)	141	-10	144

2.3.2 Proposed mechanism for reductive elimination in MeOH

The role of the solvent was investigated by adding various amounts of the solvent to **3a-H** (Table 2.3). Compared to a near-quantitative conversion of **3a-H** to **4a-H** at 70 °C with methanol, it was 35% conversion with 2-propanol. With acetic acid, there was decomposition; with 20 equivalents (wrt **3a-H**) of the acid, an 18% conversion was obtained at 23 °C, although prolonged reaction also led to decomposition. These results suggested that the reaction rate was correlated to the pK_a of the solvent, in the order: CH₃COOH > MeOH > 2-isopropanol > benzene ~ THF. The possibility of proton catalysis was excluded by an experiment in which one equivalent of HCl (in dioxane) was added to a solution in d₈-THF; no **4a-H**, but a number of other products, was observed. The latter observation also accounted for the complex mixture of products observed on prolonged reaction in the presence of acetic acid.

Table 2.3. Reductive elimination of **3a-H** in different solvents. In each reaction, 0.005 mmol of **3a-H** in 0.4 ml of solvent was used, with 1,3,5-trimethoxybenzene as internal standard.

Solvent	T (°C)	Conversion (%)	Completion time (h)	p <i>K</i> _a
CD ₃ OD	70	88	5	15
2-isopropanol	70	35	5	17
Acetic acid*	23	18	5	5
C ₆ D ₆	70	–	>24	43
d-THF	70	–	>24	>50

*A solution of acetic acid (6 mL, 20 equivalents) in CDCl₃ was used.

The observations above suggested that the reductive elimination of **3a-H** is probably catalysed by an RO[–] (R = alkyl, CH₃C=O) from the solvent; in the case of methanol, this would be the methoxide (OMe[–]) ion. A natural bond orbital (NBO) analysis on **3a-H** shows that the carbon atom of the CO ligand is positively charged (+0.78), while the iridium metal centre carries a slight negative charge (–0.25) (Figure A2.3). It is therefore proposed that low levels of OMe[–] ions from the dissociation of methanol attacks the carbonyl ligand of **3a-H** to form a metallocarboxylic acid complex [Cp*Ir{C(=O)OCH₃}(C≡CPh)₂][–] (**INT1**) which then undergoes reductive elimination to the corresponding diyne complex [Cp*Ir{C(=O)OCH₃}(PhC≡CC≡CPh)] (**INT2**), followed by dissociation of the methoxide to afford **4a-H** (Scheme 2.3).

Scheme 2.3

The free energy profile for the proposed reaction pathway has been studied computationally in the solvated state (PCM model, solvent = MeOH). The Gibbs' free energies of the various species, including two of the transition states, **TS2** (which connects **INT1** and **INT2**) and **TS3** (which connects **INT2** and **4a-H**), are given wrt **3a-H** (Figure 2.7). That the calculations here show that **4a-H** is more stable than **3a-H** by only 2 kJ mol⁻¹, as opposed to 38 kJ mol⁻¹ in Figure 2.6 can be attributed to the use of the PCM model (solvent = MeOH) here; **3a-H** has a larger dipole moment than **4a-H** (7.4 and 4.3 Debye, respectively, in the gas phase) and thus the polar solvent, methanol, should stabilize it more. Alternatives to **INT1** were also explored, including the result of OMe^- at the iridium or the alkynyl ligand, but both optimisations failed to converge. The computed values show that **TS3**, which represents the kinetic barrier from **INT2** to **4a-H**, is only +38 kJ mol⁻¹ and lies below **TS2**. The rate-determining step should therefore be represented by **TS2**. The computed overall kinetic barrier ($\Delta G^\ddagger_{298} = 112$ kJ mol⁻¹, $\Delta H^\ddagger = 42$ kJ mol⁻¹ and $\Delta S^\ddagger = -235$ J K⁻¹mol⁻¹) is reasonably close to the experimental data ($\Delta G^\ddagger_{298} = 104(7)$ kJ mol⁻¹, $\Delta H^\ddagger = 53(8)$ kJ mol⁻¹ and $\Delta S^\ddagger = -171(24)$ J K⁻¹mol⁻¹).

Figure 2.7. Computed free energy profile for the reductive elimination from **3a-H** to **4a-H** in MeOH. Figures given are the free energies (in kJ mol^{-1}) with respect to **3a-H**.

The computationally optimised structures of **INT1** and **INT2**, together with selected bond parameters, are depicted in Figure 2.8. The intermediate **INT1** lies $+8 \text{ kJ mol}^{-1}$ above the reactants. The C-OCH₃ bond length is $1.38 \text{ \AA}$, indicative of a bond between them; an NBO analysis gave a Wiberg bond index of 0.75. There is otherwise no significant structural difference with **3a-H**, although the Ir atom carries a reduced negative charge (-0.14 compared to -0.25 in **3a-H**) (Figure A2.4), which may be the driving force for the reductive elimination. Similarly, **INT2**, which lies $+50 \text{ kJ mol}^{-1}$ above the reactants, shows

a C-OCH₃ of 1.40 Å and a Wiberg bond index of 0.93. The Ir atom charge is reduced further to −0.06, consistent with reduction of the Ir(III) in **3a-H** towards an Ir(I) in **4a-H**.

Figure 2.8. Computationally optimised molecular structure, and selected bond lengths (Å), of **INT1** (left) and **INT2** (right).

The optimised structure of the rate-determining transition state **TS2** is depicted in Figure 2.9, together with selected bond parameters. This transition state connects the intermediates **INT1** and **INT2**, and it resembles structurally the latter more closely. This is in agreement with the Hammond postulate.⁷ For example, the C-C bond lengths associated with the four central carbon atoms closely resemble that of a diyne. In the proposals above, it may be expected that the transition state would more closely resemble a σ -complex, in which the C-C bond being formed is interacting with the Ir centre. In **TS2**, however, the central

C-C bond length of 1.43 Å is more typical for a C(sp²)-C(sp) than a C(sp)-C(sp) single bond (1.43 and 1.38 Å, respectively).⁸ The Ir-C distances to the two central carbon atoms are also very asymmetrical, at 2.09 and 2.24 Å; the latter is just beyond the sum of the van der Waals radii (2.22 Å).⁹ These suggest, therefore, that the interaction between the Ir and the hydrocarbon moiety is primarily through a single Ir-C bond. The C≡C bond length of 1.28 Å adjacent to this Ir-C bond is and longer than that of the more remote C≡C bond (1.23 Å), and is consistent with an allene moiety (1.30 Å). Such a bonding structure implies electron delocalization from Ir to the allene through to the phenyl ring, with a zwitterionic form in which the Ir carries a positive charge; there is indeed an occupied orbital (HOMO-24) showing this delocalisation, and the Ir atom does carry a slightly more positive charge than **INT2** (0.02 and -0.14, respectively).

Figure 2.9. (Top) Computationally optimised molecular structure, and selected bond lengths (Å), and (bottom) the HOMO-24, of **TS2**.

2.4 The effect of added salt on the reductive elimination in MeOH

The proposed mechanism suggested that added OMe^- may accelerate the reductive elimination further, and the addition of salts may have a similar effect. It was found, however, that the addition of NaOMe gave rise to a complex mixture. On the other hand, the addition of one equivalent of $[\text{Me}_4\text{N}]\text{Cl}$ led to the complete conversion of **3a-H** to **4a-H** within 4 h at ambient temperature, compared to 3-4 days in the absence of the salt. A similar rate acceleration was observed with LiCl, LiBr and $[\text{PPN}]\text{Cl}$, the last having a non-coordinating cation and thus ruling out the cation as a factor. No acceleration was observed with $[\text{Bu}_4\text{N}]\text{F}$ and $[\text{Bu}_4\text{N}]\text{I}$, and $[\text{NMe}_4]\text{OH}$ or BF_4^- (as the Li^+ and Na^+ salts) afforded as-yet unidentified products but no **4a-H** (Table 2.4). $[\text{Bu}_4\text{N}]\text{F}$, $[\text{Bu}_4\text{N}]\text{I}$, and $[\text{Me}_4\text{N}]\text{OH}$ are all very soluble in MeOH, but not accelerate the reductive elimination, ruling out solubility issues associated with the added salt.

Table 2.4. Reaction completion time for the reductive elimination of **3a-H** to **4a-H** in the presence of a salt.

Entry	salt	Amount (equivalents)	Temperature (°C)	Reaction completion time
1	LiCl	10	23	4 h
2	LiBr	10	23	18 h
3	$[\text{Bu}_4\text{N}]\text{F}$	10	23	—
4	$[\text{Bu}_4\text{N}]\text{I}$	10	23	—
5	$\text{Li}[\text{BF}_4]$	10	23	—
6	NaBF_4	10	23	—
7	$[\text{Me}_4\text{N}]\text{OH}$	10	23	—
8	$[\text{Me}_4\text{N}]\text{Cl}$	1	23	4 h
9	$[\text{Me}_4\text{N}]\text{Cl}$	3	23	1 h
10	$[\text{PPN}]\text{Cl}$	10	23	30 min
11	—	—	23	~3 d
12	—	—	70	5 h

The rates for various concentrations of $[\text{Me}_4\text{N}]\text{Cl}$ added were determined and showed saturation around 10 or 20 molar equivalents of Cl^- (Figure 2.10 left). This suggests that the Cl^- is not directly involved in the reductive elimination through attack at the carbonyl ligand, as that should lead to a monotonic increase in reaction rate with chloride concentration. Furthermore, an Arrhenius plot for the reaction in the presence of 0.2 equivalent of Cl^- gave ΔE_a (298 K) = +51(3) kJ mol^{-1} , which is very close to the +56(8) kJ mol^{-1} for the reaction in the absence of chloride (Figure A2.12-2.13).

Figure 2.10. Plot of k_{obs} vs $[\text{Cl}^-]$ at 298 K (left). Possible general base catalyst role of chloride ions (right).

The exact role of the Cl^- and Br^- ions are unclear at this stage but it is possible that they may have accelerated the reductive elimination by increasing the dissociation of methanol to OMe^- ions through a general base catalysis mechanism (Figure 2.10 right).

2.5 The formation of **4a-H** in THF

The foregoing brings out an apparent contradiction: The reductive elimination of **3a-H** to **4a-H** occurred readily only in protic solvents such as MeOH but not in non-protic solvents such as THF, yet in the reaction of **1a** with **2-H** which was carried out in THF, the isolated product was mainly **3a-H** if the reaction temperature was kept at $-78\text{ }^{\circ}\text{C}$, but **4a-H** was the sole product from a room temperature reaction. This has been confirmed by two separate experiments involving a 1:3 ratio of **1a** and **2-H**: (i) if the reaction was maintained at $-80\text{ }^{\circ}\text{C}$ for 30 min and then the solvent removed, the NMR spectrum of the residue showed the presence of **3a-H** and some unidentified side products but no **4a-H**, and TLC separation afforded **3a-H** in ~40% yield; (ii) but if after stirring at $-80\text{ }^{\circ}\text{C}$ for 30 min the reaction mixture was allowed to warm up to room temperatures before the removal of solvent, then the NMR spectrum of the residue showed that only **4a-H** was formed, with little side-products. Attempts to directly monitor the reaction at $-80\text{ }^{\circ}\text{C}$ by NMR spectroscopy was unsuccessful as it was found that **2-H** had very low solubility at that temperature.

The above experiments also ruled out the possibility that excess phenylacetylide could have catalysed the conversion of **3a-H** to **4a-H**. The involvement of LiCl formed from the reaction was also excluded; a solution of **3a-H** in d_8 -THF failed to react with 20 equivalents of LiCl. These results all suggest that **3a-H** is not the precursor to **4a-H**. If **3a-H** results from **B**, then the reaction of **3a-H** with excess LiCl should lead to more **B** and eventually **4a-H**. The observations contradict this, indicating that **B** cannot be the precursor of **3a-H**. It is therefore proposed that the reaction pathway involves the intermediary of the monoalkynyl complex $[\text{Cp}^*\text{Ir}(\text{CO})(\text{Cl})(\text{C}\equiv\text{CPh})]$ (**A**) and the formation of **3a-H** and **4a-H** follow different pathways from here; the free energy changes (kJ mol^{-1}) involved have also been computed in the gas phase (Scheme 2.4). The formation of **4a-H** from **B** presumably involves a pathway similar to that proposed in Scheme 2.3.

Scheme 2.4

Both pathways are highly exergonic ($\Delta G^\ddagger = -141$ and -129 kJ mol⁻¹, respectively). From **A**, alkynide displacement of chloride can lead either directly to **3a-H**, or to an ionic complex $[\text{Cp}^*\text{Ir}(\text{COCl})(\text{C}\equiv\text{CPh})_2]^- \text{Li}^+$ (**B**) together with a chloride migration to the carbonyl to form a chloroacyl ligand. This latter pathway which leads eventually to **4a-H** has been proposed in analogy to that for the conversion of **3a-H** to **4a-H** in MeOH described above; intermediate **B** is the analogue of **INT1** in Figure 2.7 in which the OMe has been replaced by Cl. Accordingly, therefore, it may be expected to involve a similar high kinetic barrier. Thus although **4a-H** is the thermodynamic product, **3a-H** is the kinetic product. This is in accord with observations that at low temperatures, **3a-H** is formed preferentially, although the solubility of **2-H** limited the amount of it formed; at higher temperatures, more of **2-H** goes into solution but the higher temperature also favours the formation of **4a-H**. An attempt to verify this pathway via a reaction of **1a** and **2-H** in the presence of excess LiCl (1:3:20 ratio) afforded only unreacted **1a**; presumably, the common salt effect had further reduced the solubility of **2-H**.

The computationally optimised structures of **A** and **B**, together with selected bond parameters, are depicted in Figure 2.11. The C-Cl bond length in **B** is 2.03 Å, which is elongated compared to a typical C(sp²)-Cl bond length of 1.734 Å,¹⁰ but an NBO analysis gave a Wiberg bond index of 0.71, indicative of a bond between them.

Figure 2.11. Computationally optimised molecular structures, and selected bond lengths (Å), of **A** (left) and **B** (right).

2.6 Substitution effects on the reductive elimination

Two structural aspects of the reductive elimination were examined:

1. Effect of the ancillary ligand
2. Effect of substitution at the alkynyl ligand

2.6.1 Effect of the ancillary ligand

Analogues of **3a-H** with a number of different ligands L in place of the carbonyl can be obtained from the reaction of **1x** with **2-H** (Scheme 2.5). The complexes **3b-H-3g-H** have been characterised spectroscopically and analytically. No reductive elimination of **3b-H-3g-H** to their corresponding diyne complexes was observed, even after heating at 80 °C for 3 d in methanol; decomposition to other products was observed in some cases, which will be discussed in Chapter 4. For those with a phosphane as the ancillary ligand, the presence of the free ligand did not lead to reductive elimination, nor did the presence of added *1,4*-diphenylbutadiyne. These ruled out the likelihood that a diyne complex was formed but which rapidly decomposed. The results also point to the important role of CO as the ligand in the reductive elimination observed for **3a-H**.

Scheme 2.5

2.6.2 Substitution at the alkynyl

The effect of substitution at the phenyl rings of the alkynyl was investigated with the analogues $[\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CC}_6\text{H}_4\text{X-}p)_2]$ (**3a-X**), where X = OMe, Cl, Me or F. These were prepared from the reaction of **1a** with three equivalents of the corresponding lithium alkynide at -78 °C, and quenched at -78

°C and isolated by TLC plates; on warming up to room temperature, the corresponding diyne complexes **4a-X** were obtained (Scheme 2.6).

Scheme 2.6

As for **3a-H**, the kinetics for the reductive elimination of **3a-OMe** and **3a-Cl** in CD₃OD were also measured by ¹H NMR spectroscopy (Figure A2.5-2.9); the kinetic parameters are compared with those for **3a-H** in Table 2.5. The results show that there is little electronic effect from the ring substituents on the kinetic barrier.

Table 2.5. Kinetic data for the reaction **3a-X** → **4a-X** (X= OMe, Cl) at 298 K.

Reaction	Substitution on Phenyl	Experimental		
		$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
3a-H → 4a-H	H	53(8)	-171(24)	104(7)
3a-OMe → 4a-OMe	OMe	46(3)	-186(9)	102(3)
3a-Cl → 4a-Cl	Cl	46(4)	-196(13)	104(4)

2.7 Regioselectivity of the reductive elimination

The regioselectivity of the reductive elimination was examined through the sequential reaction of **1a** with lithium 4-fluorophenylacetylide (**2-F**) and 4-tolylacetylide (**2-Me**) (Scheme 2.7). The ¹H NMR spectrum of the resulting diyne product showed two methyl resonances in a 3:2 ratio; only one Cp* resonance was observed. The ¹⁹F NMR spectrum, on the other hand, showed four resonances (-111.2, -111.6, -112.8 and -113.2 ppm) in a 1:1:2:1 ratio (Figure 2.12).

Scheme 2.7

These data could be ascribed to the presence of a mixture of the two regioisomers, *viz.*, **4i** and **4i'**, and the two homocoupled products **4-CH₃** and **4-F** in a 2:1:1:1 molar ratio. A computational study on the regioisomers suggests that **4i**, with the iridium bonded to the 4-fluorophenylalkynyl moiety, is 0.5 kJ mol⁻¹ lower in energy. This corresponds to an equilibrium constant (K) of 1.2 in its favour, which compares favourably with the experimental value of 2. Similarly, the reaction involving **2-OMe** and lithium pentafluorophenylacetylide also gave a 4:2:5 molar ratio of the two regioisomers **4j**, **4j'** and the homocoupled C₆F₅-diyne product **4k**; the corresponding homocoupled OMe-diyne **4-OMe** was not observed. A computational study also suggests that the isomer **4j**, with the iridium bonded to the pentafluorophenylalkynyl moiety, lies 0.8 kJ mol⁻¹ in energy than the other regioisomer, corresponding to K ~ 1.7 in its favour (Table 2.6). The more electron-deficient alkyne is thus preferentially bound to the iridium metal centre.¹¹ This has been attributed to an increase π -back donation from iridium metal centre to electron deficient alkynes, since in late transition

metal with low oxidation state like iridium, π -back donation from iridium to alkyne is more significant than σ -donation from alkyne to iridium.

Figure 2.12. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of mixture of **4i**, **4i'**, **4-Me**, **4-F**.

Table 2.6. Computational study on the regioselectivity.

Experiment	ΔG° (kJmol ⁻¹)	Equilibrium constant (K) 298K
<p style="text-align: center;">4i' 4i</p>	-0.5	1.2
<p style="text-align: center;">4j' 4j</p>	-0.8	1.7

2.8 Conclusion

It was found that the reductive elimination of Cp*Ir(CO)(C≡CPh)₂ (**3a-H**) to Cp*Ir(CO)(PhC≡CC≡CPh) (**4a-H**) was dependent on the solvent; it only occurred at an appreciable rate in the protic solvent methanol. The experimental kinetic barrier pointed to a large negative entropy of activation, and suggested that the reductive elimination was mediated by the attack of methoxide ions (Scheme 2.8); the proposed reaction mechanism was supported by a computational study.

Scheme 2.8

Experimental and computational data also showed that substitution at the phenyl ring of **3a-H** had little effect on the reductive elimination, but substitution of the ancillary ligand CO with other two-electron donors effectively shut it down; the latter is consistent with the proposed mechanism for the reductive elimination in MeOH. Nevertheless, the more electron-deficient alkyne moiety of the diyne ligand in **4a-H** was preferentially bound to the iridium metal centre.

It was also found that the reaction of $[\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2]$ (**1a**) with PhCClLi (**2-H**) to form **3a-H** and **4a-H** was more complex than it was originally assumed. The reaction appeared to proceed via the monoalkynyl $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})\text{Cl}$ (**A**), which could then undergo attack by a second phenylacetylide to afford either the kinetic product **3a-H**, or an ionic complex $[\text{Cp}^*\text{Ir}(\text{COCl})(\text{C}\equiv\text{CPh})_2]^- \text{Li}^+$ (**B**), the equivalent of **INT1** above, and eventually to the thermodynamic product **4a-H**.

Extension of this work to reductive elimination involving the formation of $\text{C}(\text{sp})\text{-C}(\text{sp}^2)$ and $\text{C}(\text{sp})\text{-C}(\text{sp}^3)$ bonds in $\text{Cp}^*\text{Ir}(\text{CO})(\text{alkynyl})(\text{alkenyl})$ and $\text{Cp}^*\text{Ir}(\text{CO})(\text{alkynyl})(\text{alkyl})$, respectively, will be interesting.

2.9 Experimental

2.9.1 Computational studies

The computational studies were carried out using density function theory (DFT) utilizing Becke's three-parameter hybrid function,¹² and Lee-Yang-Parr's gradient-corrected correlation function (B3LYP).¹³ The basis set used was the LANL2DZ (Los Alamos Effective Core Potential Double- ζ) augmented with an f polarization function¹⁴ for the iridium atom, and 6-311+G(2d,p) for the light atoms. For calculations involving solvated species, the polarized continuum model (PCM) using methanol as the solvent was employed to approximate a solvent field. Spin-restricted calculations were used for geometry optimization, harmonic frequencies and to evaluate zero-point energy corrections. Equilibrium structures were characterized as stationary points as with all real frequencies, and transition states were characterised by one negative frequency and checked against IRC calculations as connecting between the expected equilibrium structures. Tabulated enthalpies and free energies refer to a standard state of $T=298$ K unless otherwise noted. Natural Bond Orbital (NBO) analysis was carried out with the NBO program implemented within Gaussian.^{15, 16} All calculations were performed using the Gaussian 09 suite of program.¹⁷

2.9.2 General Procedures

All reactions and manipulations were performed under argon using standard Schlenk techniques. All other reagents were from commercial sources and used without further purification. The error for temperature measurements are ± 1 K. ^1H NMR and ^{13}C NMR spectra were recorded on a BBFO1 400 MHz NMR spectrometer; chemical shifts reported are with respect to the residual ^1H resonance in CDCl_3 . Mass spectra (nominal and high-resolution) were obtained in ESI mode on a TOF mass spectrometer with MeOH as solvent. Elemental analyses were performed by the microanalytical laboratory in NUS. The

complexes $[\text{Cp}^*\text{IrCl}_2]_2$,¹⁸ and **1x**,¹⁹ were synthesized according to the literature methods.

2.9.3 Kinetic measurements

The kinetic measurements were obtained by dissolving a sample of **3** (0.005 mmol), the halide salt (for the halide acceleration measurements only) and the internal standard (1,3,5-trimethoxybenzene, 1 mg) in CD_3OD (0.4 mL) in a Carius NMR tube. The sample was heated in an oil bath at the pre-determined temperature, and the NMR spectrum recorded at room temperature (23 °C) at regular time intervals. The spectra were recorded using 90° pulses, with 16 scans each, and a 22s pulse delay.

2.9.4 Reaction of **1a** with **2-H**

Lithium phenylacetylide (**2-H**) was freshly prepared from the reaction of $^n\text{BuLi}$ (1.6 M in hexane, 1 mL) with phenylacetylene (0.11 mL) in THF (5 mL) at -78°C . To a solution of **1a** (72 mg, 0.17 mmol) in THF (2.0 mL) maintained at -78°C was added the lithium phenylacetylide (2.0 mL). The solution was stirred for 30 min, and then unreacted lithium phenylacetylide was destroyed by quenching with “wet” THF. The solution was concentrated under reduced pressure, and the crude was then purified by TLC plates using ethyl acetate: hexane (1:3, v/v) as eluent to give **3a-H**. If the solution was stirred for 12 h at room temperature, only **4a-H** was obtained.

Compound **3a-H**: Yield = 31 mg (33%). Yellow solid. $\text{Cp}^*\text{Ir}(\text{CO})(\text{CCPh})_2$ ^1H NMR (CDCl_3): δ 7.4-7.1 (m, 10H, aromatic), 2.14 (s, 15H, Cp^*). ^{13}C $\{^1\text{H}\}$ NMR (400 MHz, CDCl_3): δ 164.1 (CO), 132.1 (Ph-CH), 131.2 ($\text{C}\equiv\text{C}$ or Ph-C), 131.1 ($\text{C}\equiv\text{C}$ or Ph-C), 128.33 (Ph-CH), 128.28 (Ph-CH), 127.9 ($\text{C}\equiv\text{C}$ or Ph-C), 127.6 (Ph-CH), 127.5 ($\text{C}\equiv\text{C}$ or Ph-C), 125.5 (Ph-CH), 100.9 (Ph-CH), 98.8 ($\text{C}\equiv\text{C}$), 97.5 ($\text{Cp}^*\text{-C}$), 63.8 ($\text{C}\equiv\text{C}$), 9.4 ($\text{Cp}^*\text{-CH}_3$). IR (Hex): 2139w, 2045s cm^{-1} . ESI-MS⁺: m/z : 558 $[\text{M}]^+$. HRMS-ESI m/z : calculated for **3a-H** $\text{C}_{27}\text{H}_{25}\text{OIr}$: 560.1691, found: 560.1704.

Compound **4a-H**: Yield = 33 mg (35%). Yellow solid. ^1H NMR (CDCl_3): δ 7.7-

7.3 (m, 10H, aromatic), 2.06 (s, 15H, Cp*). ^{13}C $\{^1\text{H}\}$ NMR (400 MHz, CDCl_3): δ 173.4 (CO), 131.3 (Ph-CH), 131.1 (Ph-CH), 128.3 (Ph-CH), 128.2 (Ph-C), 128.0 (Ph-C), 127.6 (Ph-CH), 127.5 (Ph-CH), 124.8 ($\text{C}\equiv\text{C}$ or Ph-C), 98.7 ($\text{C}\equiv\text{C}$ or Ph-C), 97.5 (Ph-CH), 94.7 ($\text{C}\equiv\text{C}$ or Ph-C), 79.4 (Cp*-C), 62.0 ($\text{C}\equiv\text{C}$), 10.0 (Cp*-CH₃). IR (Hex): 2165w, 1970s cm^{-1} . ESI-MS⁺: m/z: 558 [M]⁺. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{OIr}$: C, 58.15; H, 4.52. Found: C, 58.21; H, 4.27. HRMS-ESI m/z: calculated for **4a-H** $\text{C}_{27}\text{H}_{25}\text{OIr}$: 558.1535, found: 558.1549.

2.9.5 Reaction of **1b-1g** with **2-H**

In a typical reaction, lithium phenylacetylide was freshly prepared from the reaction of $^n\text{BuLi}$ (1.6 M in hexane, 0.08 mL) with phenylacetylene (0.014 mL, 0.13 mmol) in THF (1.0 mL) at -78°C . To a solution of **1b** (0.050 mmol) in THF (1.0 mL) at 23°C was added the lithium phenylacetylide solution (1.0 mL, 2.5 eq). The resulting mixture was refluxed for 12 h, and then unreacted lithium phenylacetylide was destroyed by quenching with “wet” THF. The solution was filtered through a short column of neutral alumina to remove the lithium salts, and then the solvent was removed under reduced pressure. X-ray diffraction quality crystals of **3b-H** were grown from an ethyl acetate/hexane solution at 4°C . A similar procedure was employed for **1c-1g**. The amounts of reagents used and the yields of products are listed in Table 2.7.

Table 2.7. Amount of **1x** used, and the yield of products **3x** obtained, in the reactions with **2-H**. For all reactions, **2-H** was prepared from PhC≡CH (14 μ L, 0.125 mmol) and nBuLi (0.08 mL).

x	Amount of 1x	Yield of 3x-H (mg, mmol, %)
b	26mg, 0.05mmol	25, 0.038, 75
c	35mg, 0.05mmol	29, 0.035, 70
d	24mg, 0.05mmol	27, 0.044, 89
e	33mg, 0.05mmol	36, 0.045, 90
f	32mg, 0.05mmol	33, 0.043, 85
g	27mg, 0.05mmol	27, 0.041, 82

Table 2.8. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR, IR and MS data for **3x-H**.

Product	^1H NMR	$^{31}\text{P}\{^1\text{H}\}$ NMR	IR (DCM), cm^{-1}	HRMS Found (Calcd)
3b-H	(CDCl ₃): δ 7.27-7.02 (m, 10 H, aromatic), 3.86 (d, $^3J_{\text{HP}}=11.6$ Hz, 9 H, P(OMe) ₃), 1.99 (d, $^3J_{\text{HP}}=3.2$ Hz, 15 H, Cp*)	(CDCl ₃): 79.7	2118, 2109s	654.1878 (654.1875)
3c-H	(CDCl ₃): δ 7.50-7.05 (m, 25 H, aromatic), 1.76 (d, $^3J_{\text{HP}}=4.8$ Hz, 15 H, Cp*)	(CDCl ₃): 60.0	2114s	840.2338 (840.2345)
3d-H	(CDCl ₃): δ 7.50-7.00 (m, 10 H, aromatic), 1.99 (d, $^3J_{\text{HP}}=2.0$ Hz, 15 H, Cp*), 1.74 (d, $^3J_{\text{HP}}=11.2$ Hz, 9 H, PMe ₃)	(CDCl ₃): -34.3	2102s	606.2072 (606.2028)
3e-H	(CDCl ₃): δ 7.35-6.87 (m, 25 H, aromatic), 1.66 (d, $^3J_{\text{HP}}=2.0$ Hz, 15 H, Cp*)	(CDCl ₃): 2.3	2107s	792.2325 (792.2497)
3f-H	(CDCl ₃): δ 7.77-6.78 (m, aromatic), 5.42 (d, $^2J_{\text{HH}}=15.2$ Hz, 1 H, CH ₂), 5.34 (d, $^2J_{\text{HH}}=15.2$ Hz, 1 H, CH ₂), 4.89 (d, $^2J_{\text{HH}}=14.8$ Hz, 1 H, CH ₂), 4.69 (d, $^2J_{\text{HH}}=15.2$ Hz, 1 H, CH ₂), 1.63 (s, 15 H, Cp*)		2108s, 2097s	778.2928 (778.2899)
3g-H	(C ₆ D ₆): δ 7.65-6.69 (m, 14 H, aromatic), 3.87 (s, 6 H, CH ₃), 1.71 (s, 15 H, Cp*)		2118s, 2100s	676.2420 (676.2430)

2.9.6 Reaction of **1a** with **2-Me** and **2-F**

Compounds **2-Me** and **2-F** were freshly prepared from the reaction of ⁿBuLi (1.6 M in hexane, 0.03 mL, 0.05 mmol) with 4-methylphenylacetylene (0.007 mL, 0.05 mmol), and 4-fluorophenylacetylene (0.006 mL, 0.05 mmol), respectively, in THF (2 mL) at –78 °C. To a solution of **1a** (21 mg, 0.05 mmol) in THF (2.0 mL), maintained at –78 °C, was added **2-F** followed by **2-Me**. The solution was stirred for 30 min, and then allowed to warm up to room temperature. The solution was concentrated under reduced pressure, and the crude was then purified on silica gel TLC plates using ethyl acetate:hexane (1:3, v/v) as eluent to give one band which comprised a mixture of **4i**, **4i'**, **4-Me** and **4-F**. Yield = 13 mg (44%; R_f = 0.70). Yellow solid.

2.9.7 Reaction of **1a** with **2-X**

In a typical reaction, lithium arylacetylide was freshly prepared from the reaction of ⁿBuLi (1.6 M in hexane, 0.18 mL) with arylacetylene (0.30 mmol) in THF (1.0 mL) at –78 °C. To a solution of **1a** (42 mg, 0.10 mmol) in THF (1.0 mL) maintained at –78 °C was added the lithium arylacetylide solution (1.0 mL, 3.0 eq). The solution was stirred for 30 min, and then unreacted lithium phenylacetylide was destroyed by quenching with “wet” THF. The solution was concentrated under reduced pressure, and the crude was then purified by column chromatography on alumina using ethyl acetate: hexane (1:3, v/v) as eluent to give **3-X** and **4-X**. If the solution was stirred for 12h at room temperature, only **4-X** was obtained.

Table 2.9. Amount of **2-X** used, and the yield of products **4-X** obtained, in the reactions with **1a** (42 mg, 0.10 mmol). For all reactions, 0.18 mL of ⁿBuLi was used to prepare **2-X** from the corresponding alkyne.

X	Amount of 2-X	Yield of 4-X (mg, mmol, %)
Me	38 μL, 0.30 mmol	42, 0.071, 71
OMe	39 μL, 0.30 mmol	43, 0.069, 69
Cl	42 mg, 0.30 mmol	26, 0.041, 41
F	35 μL, 0.30 mmol	43, 0.072, 72

Table 2.10. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, HRMS and IR data for **3-X** and **4-X**.

Product	^1H NMR	$^{13}\text{C}\{^1\text{H}\}$ NMR	HRMS Found (Calcd)	IR (DCM), cm^{-1}
4-Me	(CDCl_3): δ 7.60-7.15 (m, 8 H, aromatic), 2.87 (s, 3 H, Me), 2.37 (s, 3 H, Me), 2.07 (s, 15 H, Cp*)	(CDCl_3): δ 173.5 (CO), 137.6 (C=C or Ph-C), 137.4 (C=C or Ph-C), 131.2 (Ph-CH), 131.0 (C=C or Ph-C), 129.1 (Ph-CH), 129.0 (Ph-CH), 125.2 (C=C or Ph-C), 121.8 (C=C or Ph-C), 98.4 (C=C or Ph-C), 97.4 (Ph-CH), 93.8 (C=C or Ph-C), 78.8 (Cp*-C), 60.7 (C=C), 21.5 (CH_3), 21.4 (CH_3), 10.0 (Cp*- CH_3)	588.2022 (588.2004)	2160w, 1950s
4-OMe	(CDCl_3): δ 7.62-6.86 (m, 8 H, aromatic), 3.84 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 2.06 (s, 15 H, Cp*)	(CDCl_3): δ 173.6 (CO), 159.2 (C=C or Ph-C), 159.1 (C=C or Ph-C), 132.6 (C=C or Ph-C), 132.5 (Ph-CH), 120.8 (C=C or Ph-C), 117.2 (C=C or Ph-C), 114.0 (Ph-CH), 113.8 (Ph-CH), 97.6 (C=C or Ph-C), 97.4 (Ph-CH), 92.8 (C=C or Ph-C), 78.1 (Cp*-C), 59.1 (C=C), 55.31 (OMe), 55.28 (OMe), 10.0 (Cp*- CH_3)	624.2242 (624.2216)	2159w, 1948s
4-Cl	(CDCl_3): δ 7.59-7.29 (m, 8 H, aromatic), 2.05 (s, 15 H, Cp*)	(CDCl_3): δ 173.1 (CO), 133.6 (C=C or Ph-C), 133.3 (C=C or Ph-C), 132.2 (Ph-CH), 128.7 (Ph-CH), 128.6 (Ph-CH), 126.5 (C=C or Ph-C), 123.2 (C=C or Ph-C), 98.3 (C=C or Ph-C), 97.6 (Ph-CH), 94.5 (C=C or Ph-C), 80.3 (Cp*-C), 63.0 (C=C), 10.0 (Cp*- CH_3)	628.0835 (628.0912)	2160w, 1955s
4-F	(CDCl_3): δ 7.65-7.01 (m, 8 H, aromatic), 2.06 (s, 15 H, Cp*)	(CDCl_3): δ 173.2 (CO), 163.4 (d, C=C or Ph-C), 160.9 (C=C or Ph-C), 132.9 (d, Ph-CH), 132.8 (Ph-CH), 124.2 (Ph-C), 120.9 (Ph-C), 115.6 (Ph-CH), 115.4 (Ph-CH), 97.6 (Ph-CH), 97.5 (Ph-C), 93.7 (C=C or Ph-C), 78.9 (Cp*-C), 61.1 (C=C), 10.0 (Cp*- CH_3)	596.1514 (596.1503)	2161w, 1953s
3-OMe	(CDCl_3): δ 7.31 (d, $^2J_{\text{HH}}=8.8$ Hz, 4 H, aromatic), 6.75 (d, $^2J_{\text{HH}}=8.8$ Hz, 4 H, aromatic), 3.77 (s, 6 H, OMe), 2.13 (s, 15 H, Cp*)	(CDCl_3): δ 164.2 (CO), 133.2 (Ph-CH), 120.5 (C=C or Ph-C), 113.2 (Ph-CH), 110.8 (C=C or Ph-C), 97.9 (Cp*-C), 60.7 (C=C), 55.2 (OMe), 9.4 (Cp*- CH_3)	620.1881 (620.1903)	2129w, 2036s
3-Me	(CDCl_3): δ 7.27 (d, $^2J_{\text{HH}}=8.8$ Hz, 4 H, aromatic), 7.01 (d, $^2J_{\text{HH}}=8.0$ Hz, 4 H, aromatic), 2.31 (s, 6 H, Me), 2.13 (s, 15 H, Cp*)	(CDCl_3): δ 164.1 (CO), 135.1 (C=C or Ph-C), 131.2 (Ph-CH), 128.4 (Ph-CH), 124.9 (C=C or Ph-C), 100.9 (C=C or Ph-C), 98.6 (Cp*-C), 62.2 (C=C), 21.4 (Me), 9.4 (Cp*- CH_3)	588.2011 (588.2004)	2127w, 2037s
3-Cl	(CDCl_3): δ 7.28 (d, $^2J_{\text{HH}}=8.4$ Hz, 4 H, aromatic), 7.16 (d, $^2J_{\text{HH}}=8.4$ Hz, 4 H, aromatic), 2.13 (s, 15 H, Cp*)	(CDCl_3): δ 163.7 (CO), 133.3 (Ph-CH), 131.2 (C=C or Ph-C), 127.9 (Ph-CH), 126.3 (C=C or Ph-C), 101.0 (C=C or Ph-C), 97.9 (Cp*-C), 65.3 (C=C), 9.4 (Cp*- CH_3)	628.0911 (628.0912)	2128w, 2040s
3-F	(CDCl_3): δ 7.34-6.87 (m, 8 H, aromatic), 2.14 (s, 15 H, Cp*)	(CDCl_3): δ 162.2 (CO), 133.6 (C=C or Ph-C), 133.5 (C=C or Ph-C), 114.7 (Ph-CH), 114.5 (Ph-CH), 114.1 (C=C or Ph-C), 100.9 (Cp*-C), 62.9 (C=C), 9.4 (Cp*- CH_3)	596.1494 (596.1503)	2129w, 2038s

2.9.8 X-ray Crystallographic Studies

Red single crystals of **3e-H** and **4a-H** suitable for diffraction analysis were grown by slow evaporation from hexane/dichloromethane solutions at 4 °C. The crystals selected were mounted on quartz fibers. X-ray data for **3e-H** were collected at 123(2) K, and for **4a-H** were collected at 223(2) K on a Bruker X8 APEX system, using Mo K α radiation, with the SMART suite of programs.²⁰ The data were processed and corrected for Lorentz and polarization effects with SAINT,²¹ and for absorption effects with SADABS.²² Structural solution and refinement were carried out with the SHELXTL suite of programs.²³ The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The organic hydrogen atoms were placed in calculated positions and refined with a riding model. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

2.9.9 Details of Kinetic Analyses

The conversion of **3a-H** to **4a-H** was followed by monitoring the intensity (I) in of the Cp* resonance of **3a-H** and OMe resonance of the internal standard (1,3,5-trimethoxy benzenze) in the ¹H NMR spectrum.

If the conversion of **3a-H** to **4a-H** follows mass balance and first order kinetics, then

$d[\mathbf{3a-H}]/dt = -k[\mathbf{3a-H}]$ where $[\mathbf{3a-H}]$ is the concentration of **3a-H** at time t, or,
 $\ln(I_{\mathbf{3a-H}}/I_{\text{standard}}) = -kt$.

A plot of $\ln(I_{\mathbf{3a-H}}/I_{\text{standard}})$ vs t will give a straight line with slope $-k$.

Mass balance for the reaction was checked by plotting (I/I_{standard}) vs t for **3a-H**, **4a-H** and their sum, and only data points for the extent of reaction in which

$(I_{\mathbf{3a-H}}/I_{\text{standard}})/[(I_{\mathbf{3a-H}}/I_{\text{standard}}) + (I_{\mathbf{4a-H}}/I_{\text{standard}})] > 90\%$

were employed in the Eyring and Arrhenius plots.

Using the Arrhenius equation in the form: $\ln(k) = (-E_a/R) \cdot (1/T) + A$; a plot of $\ln(k)$ versus $1/T$ gives a straight line with slope $-E_a/R$. $E_a = 56 \pm 8 \text{ kJ mol}^{-1}$.

Using the Eyring equation in the form: $\ln(k/T) = (-\Delta H^\ddagger/R)(1/T) + \ln(k_b/h) + \Delta S^\ddagger/R$;

where k_b is Boltzmann's constant, and h is Planck's constant,

a plot of $\ln(k/T)$ versus $1/T$ gives a straight line with slope $-\Delta H^\ddagger/R$ and intercept $\{\ln(k_b/h) + \Delta S^\ddagger/R\}$ (Appendix Figure 2.7). $\Delta H^\ddagger = +53(8) \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -171(24) \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta G^\ddagger = +104(7) \text{ kJ mol}^{-1}$.

Table 2.11. Crystal and refinement data for **3e-H** and **4a-H**.

Identification code	3e-H	4a-H
Empirical formula	C ₄₄ H ₄₀ IrP	C ₂₇ H ₂₅ IrO
Formula weight	791.93	557.67
Temperature, K	123(2) K	223(2)
Crystal system	Triclinic	Monoclinic
Space group	P $\bar{1}$	P2 ₁ /c
a, Å	9.2032(7)	18.4357(8)
b, Å	12.3501(10)	16.7744(7)
c, Å	17.2016(13)	7.2934(3)
α , deg	110.750(4)	90
β , deg	91.313(4)	94.3090(10)
γ , deg	109.088(4)	90
Volume, Å ³	1706.4(2)	6982.4(7)
Z	2	4
Density (calculated), Mg/m ³	1.541	1.647
Absorption coefficient, mm ⁻¹	3.990	5.951
F(000)	792	1088
Crystal size, mm ³	0.14 x 0.06 x 0.04	0.26 x 0.20 x 0.06
Reflections collected	10878	34349
Independent reflections	10878	4591
Max. and min. transmission	0.8567 and 0.6050	0.7166 and 0.3068
Data / restraints / parameters	10878 / 0 / 420	4591 / 0 / 362
Goodness-of-fit on F ²	0.974	1.164
Final R indices [I > 2 σ (I)]	R1 = 0.0313	R1 = 0.0335
R indices (all data)	R1 = 0.0412	R1 = 0.0369
Largest diff. peak and hole (e.Å ⁻³)	2.077 and -1.905	2.672 and -0.641

2.10 References

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Chapter 3: Reactivity of the diyne species $\text{Cp}^*\text{Ir}^{\text{I}}(\text{CO})(\eta^2\text{-ArC}\equiv\text{CC}\equiv\text{CAr})$

The chemistry of transition metal complexes containing η^2 -bound alkyne ligands have been well-documented as they are important intermediates in many transition metal catalysed reactions involving alkynes, such as in the formation of metallacycles.¹ In contrast, reports on the chemistry of transition metal complexes containing diyne ligands are scarce; one is a simple ligand displacement reaction (Scheme 3.1),² and another involved a CO-insertion reaction with a metal carbonyl to give a bimetallic complex (Scheme 3.2).³

TTP = meso-5,10,15,20-tetraphenylporphyrinato

Scheme 3.1

Scheme 3.2

Although there has been, to the best of our knowledge, no reports on the reaction of metal-diyne complexes with alkynes, the corresponding chemistry of metal-alkyne complexes is of course very important and well-known. For example, reactions with alkynes to afford metallacyclopentadienes (Scheme 3.3) are relevant to the Pauson-Khand reaction,⁴ and there are also examples leading to C-C coupling to form phenylvinyl complexes (Scheme 3.4).⁵

Scheme 3.3

Scheme 3.4

We had initially thought that the diyne complexes $\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-ArC}\equiv\text{CC}\equiv\text{CAr})$ **4a-X** may exhibit similar reactivity as alkyne complexes, i.e., ligand substitution with two-electron donor ligands like phosphines, and coupling reactions with alkynes but found that there are some unique aspects. Our investigations into their reactivity are reported in this chapter.

3.1 Intramolecular cycloaddition with two-electron donor ligands

3.1.1 Reaction of **4a-H** with **5**

The reaction of $\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-PhC}\equiv\text{C-C}\equiv\text{CPh})$ **4a-H** with PPh_3 **5c** in refluxing toluene gave one major product, **6c-H**, in 63% yield (Scheme 3.5). Complex **6c-H** has been characterised spectroscopically and analytically, and its structure has also been confirmed by a single crystal X-ray diffraction study; an ORTEP plot showing its molecular structure, together with selected bond parameters, is given in Figure 3.1.

Scheme 3.5

The bond parameters of **6c-H** are consistent with its formulation as an iridacyclobutenone: The C=O bond length (1.224(4) Å) is elongated compared to the C≡O bond (1.159(5) Å) in **4a-H**, and the ketonic character is also corroborated by the $\nu_{\text{C=O}}$ at $\sim 1660\text{ cm}^{-1}$; the two C-C bond lengths of the iridacycle, C(11)-C(12) = 1.488(4) Å and C(12)-C(13) = 1.373(4) Å, correspond to a single C-C and a double C=C bond, respectively. The Ir-C bond lengths of the iridacycle (Ir(1)-C(11) = 2.054(3) Å and Ir(1)-C(13) = 2.058(3) Å) are, however, rather shorter than an Ir-C single bond (~ 2.16),⁶ but longer than those in N-iridacycles (~ 2.0 Å) which are known to exhibit Ir=C double bond behavior.⁷ The IrCCC iridacycle is essentially planar; the mean deviation from the best plane is $\ll 0.01$ Å.

Figure 3.1. ORTEP plot of **6c-H** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1-C11=2.054(3); Ir1-C13=2.058(3); Ir1-P1=2.2510(8); C11-C12=1.488(4); C12-C13=1.373(4); C13-C14=1.414(4); C14-C15=1.206(4); C15-C16=1.433(4); C12-C22=1.464(4); C11-O1=1.224(4); C13-Ir1-C11=63.47(12); C12-C11-Ir1=97.3(2); C11-C12-C13=98.1(3); Ir1-C13-C12=101.1(2); Ir1-C13-C14=130.2(2); C13-C12-C22=132.9(3); O1-C11-Ir1=132.8(2).

The reaction could be extended to other two-electron donor ligands, such as, CO, *t*-BuNC, and other phosphanes, to give the corresponding iridacyclobutenones **6x-H**; substitution on the phenyl rings of the diyne, both electron-withdrawing and –donating groups, are also tolerated. With an increase

in electron-donating ability of the ancillary ligand, the C=O vibration of the ketone group in the iridacycle shifted to lower frequency (Scheme 3.6).

In the reaction with CO, a minor product **7a-H** was also isolated in 7% yield. The ^1H NMR spectrum of **7a-H** showed a singlet at 1.91 ppm for the Cp* ligand, compared to 2.03 ppm in **6a-H**, and multiplets for the ten aromatic protons. The IR spectrum showed a strong CO stretch at 1995 cm^{-1} and a weak C=O stretch at 1698 cm^{-1} , compared to the 1994 and 1683 cm^{-1} , respectively, in **6a-H**. Its MS spectrum showed the same molecular ion peak as **6a-H**. Although diffraction-quality crystal of **7a-H** was not obtained, it may be tentatively identified as an isomer of **6a-H** on the basis of its spectroscopic characteristics; the proposed structure is depicted in Scheme 3.6. A similar isomer, i.e., **7b-H**, was also identified spectroscopically for the reaction with *t*-BuNC, but only trace amounts of the corresponding isomers were detected (from TLC separation) for the others.

Diyne complex	Ligand (L)	Iridacycle 6x-Y	Yield (%)	C=O vibration (cm ⁻¹)
4a-H	CO	6a-H	62	1683
4a-H	t-BuNC	6b-H	69	1666
4a-H	PPh ₃	6c-H	63	1643
4a-H	PMePh ₂	6d-H	99	1641
4a-H	PBu ₃	6e-H	42	1639
4a-H	PMe ₃	6f-H	35	1638
4a-H	P(OPh) ₃	6g-H	82	1664
4a-H	P(OMe) ₃	6h-H	47	1654
4a-OMe	PPh ₃	6c-OMe	37	1639
4a-Me	PPh ₃	6c-Me	32	1641
4a-Cl	PPh ₃	6c-Cl	28	1642
4a-F	PPh ₃	6c-F	63	1642

Scheme 3.6

3.1.2 Kinetic studies

In order to examine the mechanism of the intramolecular cycloaddition, the reaction of **4a-H** with two equivalents of **5c** in refluxing C₆D₆ was monitored by ¹H NMR spectroscopy; it showed that **4a-H** converted cleanly to **6c-H** (Figure 3.2).

Figure 3.2. ^1H NMR spectral overlay for the cycloaddition of **4a-H** to **6c-H** at 353 K from 0 to 38 h.

The stereoelectronic effects of the incoming ligand on the rate of conversion was also examined by similar kinetic measurements with different ligands **5b-h**. The conversion followed first-order kinetics (it followed first-order respect to phosphane, and zero-order respect to **4a-H**, in Figure A3.1); a plot of $\ln [\mathbf{4a-H}]$ versus reaction time t was linear, with slope = $-k$, the rate constant (Figure 3.3 and Table 3.1). The results suggest that the reaction rate is correlated to the cone angle of the incoming ligand – the larger the cone angle, the slower the rate, for example, PMePh_2 and PPh_3 have similar electronic parameters χ but the reaction rate is faster for the less bulky PMePh_2 . Conversely, there is no apparent trend in the rate in relation to the electronic property - P(OPh)_3 , PBU_3 and PMePh_2 have similar cone angles and their χ values are in the order: $\text{P(OPh)}_3 >$

$\text{PMePh}_2 > \text{PBu}_3$, but the rates follow the order: $\text{PBu}_3 \sim \text{P(OPh)}_3 > \text{PMePh}_2$. It may therefore be concluded that steric effects of the incoming ligand is dominant.

Figure 3.3. Plot of $\ln[4\mathbf{a}\text{-H}]$ vs time for reaction between $4\mathbf{a}\text{-H}$ and $5\mathbf{x}$ at 353 K as measured by ^1H NMR spectroscopy.

Table 3.1. Observed rates for the reaction $4\mathbf{a}\text{-H} + 5\mathbf{x} \rightarrow 6\mathbf{x}\text{-H}$, and the stereoelectronic parameters for $5\mathbf{b}$, $5\mathbf{c}$, $5\mathbf{d}$, $5\mathbf{e}$, $5\mathbf{g}$ and $5\mathbf{h}$.⁸

Ligand	χ value	Cone angles (θ)	Rate constant (10^{-5})
t-BuNC (5b)	—	—	6.9
PPh_3 (5c)	13	145	0.8
PMePh_2 (5d)	11	136	1.7
PBu_3 (5e)	4	132	2.1
P(OPh)_3 (5g)	29	128	2.0
P(OMe)_3 (5h)	23	107	2.4

More detailed kinetic studies were carried out on the reactions of **4a-H** with 1 atm of CO, and with two equivalents of PPh₃, at a number of different temperatures; the rate plots for the latter reaction are shown in Figure 3.4. Mass balance for the reactions were checked by plotting the scaled concentrations vs time for **4a-H**, the product **6x**, and their sums; only data points in which $([\mathbf{4a-H}] + [\mathbf{6x}])/[\mathbf{4a-H}]_0 > 90\%$ were employed in the Eyring plots (Figures A3.4 and A3.5 for **5a** and **5c**, respectively), from which the kinetic parameters were calculated (Table 3.2). The large negative activation entropy ($\Delta S^\ddagger$) for both reactions imply that the rate-limiting step is associative.

Figure 3.4. Plot of $\ln[\mathbf{4a-H}]$ vs time for reaction between **4a-H** and **5c** at various temperatures as measured by ¹H NMR spectroscopy. $[\mathbf{5c}] = 0.02 \text{ mmol}/0.4 \text{ ml} = 50 \text{ mol}/\text{m}^3$.

Table 3.2. Kinetic parameters for the reaction of **4a-H** to **6a-H** and **6c-H**.

Ligand	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
5a	66(8)	-163(23)	115(7)
5c	70(8)	-175(21)	122(6)

3.1.3 Computational studies

It is proposed that the reaction proceeds via a CO insertion to form a metallacyclobutenone **INT**, followed by association of the incoming ligand (Scheme 3.7). Given the kinetic studies above, the second step should be rate-limiting.

Scheme 3.7

The free energy changes for the proposed reaction pathway have been computed with density functional theory using both the B3LYP and M06 density functionals, and with the LANL2DZ (Los Alamos Effective Core Potential Double- ζ) basis set augmented with an f polarization function for the iridium atom,⁹ and 6-311+G(2d,p) for the light atoms. The computational study was carried out for a number of ligands **L** (CO, PH₃, PMe₃, PPh₃ and CH₃NC). The transition states (**TS1** and **TS2**), and the intermediate **INT**, have all been located; the free energy profile for **L** = CO computed using the B3LYP density functional is depicted in Figure 3.5.

Figure 3.5. Computed free energy changes using B3LYP in the proposed pathway for the reaction of **4a-H** with CO. Figures given are the free energies (kJ mol⁻¹) with respect to **4a-H**.

The first transition state, **TS1**, between **4a-H** and **INT**, is shown in Figure 3.6. NBO analyses show that the charge on the Ir centre increased from -0.17 in **4a-H** to $+0.11$ in **INT**, consistent with the change from a formal Ir(I) towards an Ir(III) centre.

Figure 3.6. Computationally optimised geometry of **TS1** with selected bond lengths.

The regioselectivity of the reaction should depend only on the relative stability of the intermediate **INT** and its isomer **INT'**; the former leads to **6** and the latter to **7**. These intermediates differ in the relative positions of the phenyl and alkynyl substituents on the iridacycle (Figure 3.7). Unlike **6c-H**, the iridacycle in **INT** (and **INT'**) is clearly puckered; the dihedral angle for the $\text{C}(=\text{O})\text{IrC}=\text{C}$ plane is 26.5° , and may avoid anti-aromaticity.¹⁰ The intermediate **INT** was computed to lie 13 kJ mol^{-1} below **INT'**, indicating that **INT** and hence the formation of **6** are strongly favoured. This is corroborated by the ^1H NMR spectrum for the reaction mixture of **4a-H** with **5b**, which shows that **6b-H** and **7b-H** are formed in a $\sim 10:1$ ratio.

Figure 3.7. Computationally optimised geometry of the intermediate **INT** (left) and **INT'** (right), with selected bond lengths.

The computed energetics, using both density functionals, are given in Table 3.3; $\Delta G_1^\ddagger$ is the kinetic barrier from **4a-H** to **INT**, $\Delta G_2^\ddagger$ is the kinetic barrier from **INT** + **L** to the product (**6x-H**), and $\Delta G^\ddagger$ is the overall kinetic barrier with respect to **4a-H**. The computed kinetic barriers were $\Delta G_1^\ddagger = 110 \text{ kJ mol}^{-1}$ and $\Delta G_2^\ddagger = 59 \text{ kJ mol}^{-1}$ for the first and second steps, respectively, for **L** = **CO**; the corresponding values computed using the M06 density functionals were similar, at 104 and 65 kJ mol^{-1} , respectively. These corresponded to an overall $\Delta G^\ddagger$ of 127 or 135 kJ mol^{-1} , for the B3LYP and M06 density functionals, respectively, and are reasonably close to the experimental value of $115 \pm 7 \text{ kJ mol}^{-1}$, although given that the kinetic studies were with an excess of **CO**, this may approximate more closely to the first step being rate-limiting, i.e., $\Delta G_1^\ddagger$ being the kinetic barrier. Similarly, the computed $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for the overall reaction are $+84 \text{ kJ mol}^{-1}$ and $-148 \text{ J mol}^{-1} \text{ K}^{-1}$ (B3LYP), comparing well to the experimental values of $+66(8) \text{ kJ mol}^{-1}$ and $-163(23) \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

Kinetic studies with the phosphanes and isonitrile were carried out with a lower stoichiometry (2 equivalents) and hence the rate-limiting step for these

should be the second, ligand association step. Consistent with this is the higher activation barrier ($\Delta G^\ddagger = 122 \pm 6 \text{ kJ mol}^{-1}$) measured for $L = \text{PPh}_3$, compared to the values of +132 and +179 kJ mol^{-1} computed with the M06 and B3LYP density functionals, respectively (Table 3.3). This second step is expected to be affected by steric hindrance from the Cp^* and metallacycle, and this is apparent in the intrinsic reaction coordinate (IRC) analysis for **TS2**; in going from **INT** to **6x-H**, there is a decrease in the cone angle of the incoming ligand, and the dihedral angle for the Ir-C(=O)-C-Ph plane changes from 140° to 176° . The Ir...P distance in **TS2** is quite different for $L = \text{PH}_3$ and PPh_3 (3.31 and 3.76 Å, respectively), which suggests that the kinetic barrier is influenced by the steric bulk of the ligand. Furthermore, the kinetic measurements show that for $L = \text{CO}$ or $t\text{-BuNC}$, which are linear and hence less bulky ligands compared to the phosphanes, the barriers are much lower.

Table 3.3. Computed kinetic and thermodynamic parameters for the reaction **4a-H** + **L** $\rightarrow$ **6x-H** using the B3LYP and M06 density functionals. $\Delta G_2^\ddagger$ is the kinetic barrier from **INT** + **L** to the product (**6x-H**), and $\Delta G^\ddagger$ is the overall kinetic barrier with respect to **4a-H**.

L	$\Delta G_2^\ddagger$ (kJ mol^{-1})		$\Delta G^\ddagger$ (kJ mol^{-1})		ΔG° (kJ mol^{-1})	
	M06	B3LYP	M06	B3LYP	M06	B3LYP
CO	65	59	135	127	-39	-28
PH ₃	56	79	126	147	+35	+60
PMe ₃	49	81	119	149	-33	+12
CH ₃ NC	68	76	139	145	-18	-10
PPh ₃	61	111	132	179	-6	-10

In this computational study, we have chosen to carry out the computations with both the B3LYP and M06 density functionals as it has been suggested that

the latter is better for organometallic systems.¹¹ Furthermore, we have observed that although the reaction did proceed with PMe₃, the computed ΔG° for the reaction using the B3LYP density functional contradicted this, unlike that computed with the M06 density functional. On the other hand, the trend in the kinetic barriers computed using the M06 density functional did not appear to agree well with our experimental measurements which showed that the rate was faster with isonitrile than with the phosphanes.

3.1.4 Reaction of **6c-H** with RLi (R=Me, *n*-Bu)

An NBO analysis of **6c-H** showed that the charge on the carbon atom of the alkyne adjacent to the phenyl ring was very close to 0, compared to the other carbon atoms which were negatively charged. This suggested that nucleophilic attack may occur there. It has been reported that rhenacyclobutenones reacted with alcohols and amines,¹² hence, the reaction of [Cp*Ir(PPh₃){C(C≡CC₆H₅)=C(C₆H₅)C=O}] **6c-H** with amines and alcohols was explored but these failed to proceed. Complex **6c-H** did, however, react with 20 equivalents of ⁿBuLi or MeLi to afford **8a** or **8b**, respectively (Scheme 3.8).

Scheme 3.8

Both complexes have been characterized by ¹H and ³¹P{¹H} NMR, MS and HRMS, and in the case of **8b**, also by a single crystal X-ray crystallographic

study. The ORTEP plot for **8b** is shown in Figure 3.8, with selected bond parameters. The bond parameters are consistent with the formulation as **8b**: The C=O bond length (1.238(8) Å) is compatible with the C=O (1.224(4) Å) in **6c-H**, and the two C-C bond lengths of C(11)-C(12) and C(12)-C(19) (1.493(10) and 1.348(9), respectively) for the iridacycle correspond to a single and double bond, respectively. The Ir-C bond lengths of the iridacycle (Ir(1)-C(11) and Ir(1)-C(20) at 2.058(7) and 2.063(7) Å, respectively) are, however, rather shorter than an Ir-C single bond (~2.16),⁶ but longer than those in N-iridacycles (~2.0 Å) which exhibited Ir=C double bond behavior.⁷

This reaction clearly required a C-H activation and an oxidation; the overall stoichiometry for the reaction being:

The low yield of the reaction did not make it worthwhile to investigate the reaction pathway further.

Figure 3.8. ORTEP plot of **8b** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1-C11=2.058(7); Ir1-C20=2.063(7); Ir1-P1=2.2639(19); C11-O1=1.238(8); C11-C12=1.493(10); C12-C19=1.348(9); C19-C20=1.464(10); C20-C21=1.349(9); C21-C23=1.493(10); C19-C28=1.468(10); C12-C13=1.475(10); C20-Ir1-C11=78.8(3); C12-C11-Ir1=115.9(5); C11-C12-C19=112.4(6); Ir1-C20-C19=113.9(5); C23-C21-C20=108.6(6); C21-C20-C19=109.1(6); C20-C19-C28=107.5(6).

3.2 Reaction of $\text{Cp}^*\text{Ir}^{\text{I}}(\text{CO})(\text{ArC}\equiv\text{CC}\equiv\text{CAr})$ with alkyne

Metal-alkyne complexes can react with alkynes to form metallacyclopentadienes; with asymmetrical alkynes, the regioselectivity is determined mainly by steric factors.¹³ The reaction of **4a-H** with terminal alkynes, such as, phenylacetylene gave only one product, as deduced from the ^1H NMR spectrum of the reaction mixture (Scheme 3.9).

Scheme 3.9

The products **9a-X** were not very stable in solution and were only characterized spectroscopically. The ^1H NMR and MS spectra of **4a-H**, for example, were consistent with the incorporation of one molecule of phenylacetylene. A reaction of **4a-H** with PhCCD afforded **9a-H** in which the resonance at 5.07 ppm, which corresponded to the proton on the iridapentadiene was absent, suggesting that the proton of phenylacetylene was retained. This is essentially an alkyne coupling reaction, which is well-known.

Although the above reaction did not proceed with internal alkynes, **4a-H** reacted with the internal alkyne 3-hexyne under UV irradiation to afford a red solution, from which **10** was isolated and characterised crystallographically after TLC separation (Scheme 3.10). The IR spectrum of the crystals was the same as that of the product isolated initially from the TLC plates, suggesting that **10** was relatively stable. Attempts to extend the reaction to other alkynes, such as, 2-butyne or diphenylacetylene, were unsuccessful.

Scheme 3.10

Figure 3.9. ORTEP plot of **10** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1-C11=1.911(2); Ir1-C12=2.194(2); Ir1-C13=2.136(2); C38-O2=1.227(3); C11-C12=1.418(3); C12-C13=1.462(3); C32-C35=1.352(3); C25-O1=1.212(3); C11-C12-C13=110.11(18); C12-C22-C32=110.57(16); C13-C12-C22=121.98(18); C12-C13-C38=115.03(18); C11-Ir1-C13=71.14(9).

The ORTEP plot showing the molecular structure of **10** is shown in Figure 3.9, together with selected bond parameters. The bond parameters are consistent with the formulation, in particular, the C(11)-C(12) and C(12)-C(13) bond lengths (1.418(3) and 1.462(3), respectively) are between those for a C-C single bond (~ 1.54 Å) and C=C double bond (~ 1.33 Å), and is consistent with this being an allyl ligand. A computational study show that the HOMO comprises an interaction between the π orbital of the allyl group and the metal centre (Figure 3.10).

Figure 3.10. HOMO of **10**.

The crystal structure shows that **10** could not have been derived from a simple coupling of **4a-H** with 3-hexyne, and also that another oxygen atom source was involved in this reaction; either water or molecular oxygen. The reaction proceeded with the exclusion of oxygen, and deliberate introduction of oxygen did not increase the yield. These observations suggest that molecular oxygen is not the source of the ketonic oxygens in **10**. Under a CO atmosphere,

the reaction afforded **6a-H** (identified by its IR and ^1H NMR spectroscopic characteristics) instead, suggesting that the source of the ketone functionalities in **10** is not CO. Presumably, therefore, the source of the oxygen atoms is water. It is clear that the formation pathway for **10** is complex which, together with the low yield involved, precluded further mechanistic studies or speculation on the formation pathway.

3.3 Acid Hydrolysis of $\text{Cp}^*\text{Ir}^{\text{I}}(\text{CO})(\text{PhC}\equiv\text{CC}\equiv\text{CPh})$

Complex **4a-H** reacted with aq. triflic acid to afford the complex **11** in 35% yield (Scheme 3.11). It has been characterized by ^1H NMR spectroscopy, mass spectrometry, and also by single crystal X-ray crystallography; an ORTEP plot showing the molecular structure, together with selected bond parameters, are shown in Figure 3.11.

Scheme 3.11

Figure 3.11. ORTEP plot of **11** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1-C12=2.146(13); Ir1-C21=2.019(13); C1-O1=1.169(15); Ir1-C1=1.925(15); C12-C19=1.470(17); C19-C20=1.488(18); C20-C21=1.318(18); C19-O2=1.232(15); Ir1-C21-C20=113.3(10); C21-C20-C19=119.1(12); C20-C19-C12=112.6(11); C19-C12-Ir1=105.3(9).

This reaction is not catalysed by a weak acid such as CH_3COOH . A reaction using H_2^{18}O in the presence of triflic acid showed that the oxygen atom on the iridacycle originated from water; the mass spectrum showed a molecular ion peak corresponding to $[\text{Cp}^*\text{Ir}(\text{CO})\{\text{C}(\text{C}_6\text{H}_5)=\text{CHC}(=\text{O}^{18})\text{CHC}_6\text{H}_5\}]$, and the IR spectrum showed a shift in the $\text{C}=\text{O}$ vibration from 1639 cm^{-1} to 1598 cm^{-1} ; the position of this band on isotopic substitution was calculated (based on reduced mass) to be $\sim 1600\text{ cm}^{-1}$.

On the basis of the above, the proposed reaction pathway is as depicted in Scheme 3.12. Initial attack of **4a-H** by water at the Ir-bound alkyne moiety

gives the vinyl alcohol intermediate **C**, which can then rearrange to an acyl complex **D**. This can then cyclise intramolecularly to give final product **11**.

Scheme 3.12

3.4 Conclusion

In this chapter, the reactivity of the diyne species [Cp*Ir(CO)(η²-ArC≡CC≡CAr)] **4a-X** has been found to revolve around the metal-bound alkyne moiety (Scheme 3.13). This is exemplified by:

- CO insertion to form 4-membered iridacycles **6x-Y**,
- [2+2] cycloaddition with terminal alkynes to give iridacyclopentadienes **9a-X**, and
- Acid-catalysed alkyne hydrolysis to yield the iridacyclopentenone **11**.

This behaviour resembles to that of simpler metal-bound alkynes in that binding of the alkyne to the metal centre activates it.

Scheme 3.13

Detailed experimental and computation studies on the first reaction suggest that the reaction involved two main steps: insertion of CO into the metal-bound alkyne to form a 4-membered metallacyclic intermediate, followed by ligand association (Scheme 3.14). The second step is rate-limiting, except in the presence of excess ligand, and is susceptible to steric effects of the incoming ligand.

Scheme 3.14

3.5 Experimental

3.5.1 Computational studies

The computational studies were carried out using density function theory (DFT) utilizing either Becke's three-parameter hybrid function,¹⁴ and Lee-Yang-Parr's gradient-corrected correlation function (B3LYP),¹⁵ or the hybrid functional of Truhlar and Zhao (M06).¹⁶ If not mentioned, the studies are understood to be using B3LYP. The basis set used was the LANL2DZ (Los Alamos Effective Core Potential Double- ζ) augmented with an f polarization function for the iridium atom,¹⁷ and 6-311+G(2d,p) for the light atoms. Spin-restricted calculations were used for geometry optimization, harmonic frequencies and to evaluate zero-point energy corrections. Equilibrium structures were characterized as stationary points with all real frequencies, and transition states were characterised by one negative frequency and checked against IRC calculations as connecting between the expected equilibrium structures. Tabulated enthalpies and free energies refer to a standard state of $T=298$ K unless otherwise noted. All calculations were performed using the Gaussian 09 suite of program.¹⁸

3.5.2 General Procedures

All reactions and manipulations were performed under argon using standard Schlenk techniques. All other reagents were from commercial sources and used without further purification. The error for temperature measurements are ± 1 K. ^1H NMR and ^{13}C NMR spectra were recorded on a BBFO1 400 or AV 500 MHz NMR spectrometer; chemical shifts reported are with respect to the residual ^1H resonance of the solvent. High-resolution mass spectra were obtained in ESI mode on a Waters UPLC-Q-TOF mass spectrometer with MeOH as solvent. Elemental analyses were performed by the microanalytical laboratory at the National University of Singapore. The complexes $\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-ArC}\equiv\text{CC}\equiv\text{CAr})$ were prepared according to the method depicted in Chapter 2.

3.5.3 Reaction of 4a-H with 5

3.5.3.1 Reaction of 4a-H with CO 5a

Complex **4a-H** (28 mg, 0.050 mmol) was placed with toluene (5 mL) into a quartz Carius tube. After three freeze-pump-thaw cycles, CO gas (ca. 15 psi) was introduced at ambient temperature. The mixture was refluxed for 48 h. The solvent was removed under reduced pressure and the crude was then purified on TLC plates using DCM: hexane (1:1, v/v) as eluent to give **6a-H** and **7a-H**.

Compound **6a-H**: Yield = 18 mg, 31 μmol (62%). Red solid. ^1H NMR (CDCl_3): δ 8.06-7.20 (m, 10 H, Ph), 2.03 (s, 15H, Cp*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 175.1 (C=O), 166.8 (CO), 164.4 (C $\equiv$ C or Ph-C), 136.6 (C $\equiv$ C or Ph-C), 131.4 (Ph-CH), 128.9 (C $\equiv$ C or Ph-C), 128.6 (Ph-CH), 128.1 (Ph-CH), 127.2 (C $\equiv$ C or Ph-C), 126.1 (Ph-CH), 123.9 (C $\equiv$ C or Ph-C), 112.9 (C $\equiv$ C or Ph-C), 110.4 (C $\equiv$ C or Ph-C), 99.0 (Ph-CH), 90.9 (Cp*-C), 9.1 (Cp*-CH₃). IR (DCM): $\nu_{\text{C}\equiv\text{C}}$ 2158 (w), ν_{CO} 1994 (vs), $\nu_{\text{C=O}}$ 1683 (s) cm^{-1} . ESI-MS⁺: m/z 587 [M+H]⁺. Anal. Calcd for C₂₈H₂₅IrO₂: C, 57.42; H, 4.30. Found: C, 57.71; H, 4.35. HRMS-ESI: m/z 588.1647; calculated for C₂₈H₂₅IrO₂ [M+H]⁺ 588.1640.

Compound **7a-H**: Yield = 2 mg, 3 μmol (7%). Red solid. ^1H NMR (CDCl_3): δ 7.91-7.28 (m, 10 H, Ph), 1.91 (s, 15H, Cp*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 174.2 (C=O), 155.4 (CO), 139.2 (C $\equiv$ C or Ph-C), 131.7 (Ph-CH), 131.0 (C $\equiv$ C or Ph-C), 130.9 (C $\equiv$ C or Ph-C), 130.2 (Ph-CH), 129.7 (C $\equiv$ C or Ph-C), 128.3 (Ph-CH), 128.2 (Ph-CH), 128.0 (C $\equiv$ C or Ph-C), 126.8 (C $\equiv$ C or Ph-C), 123.5 (C $\equiv$ C or Ph-C), 99.1 (Ph-CH), 89.5 (Cp*-C), 9.3 (Cp*-CH₃). IR (DCM): ν_{CO} 1995 (vs), $\nu_{\text{C=O}}$ 1698 (s) cm^{-1} . ESI-MS⁺: m/z 587 [M+H]⁺.

3.5.3.2 Reaction of 4a-H with *t*-BuNC 5b

A similar procedure as above using **4a-H** (9 mg, 16 μmol) and *t*-BuNC (4 μL , 0.032 μmol) afforded **6b-H** and **7b-H**. Compound **6b-H**: Yield = 7 mg, 11 μmol (69%). Red solid. ^1H NMR (CDCl_3): δ 8.06-7.12 (m, 10H, Ph), 1.98 (s, 15H, Cp*), 1.41(s, 9H, *t*-BuNC). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 173.0 (C=O), 166.1 (C $\equiv$ C or Ph-

C), 137.6 (C≡C or Ph-C), 131.1 (Ph-CH), 128.5 (Ph-CH), 128.1 (Ph-CH), 127.9 (Ph-CH), 126.1 (C≡C or Ph-C), 125.8 (Ph-CH), 124.9 (C≡C or Ph-C), 117.4 (C≡C or Ph-C), 108.6 (C≡C or Ph-C), 95.2 (Ph-CH), 92.3 (Cp*-C), 57.1 (C-tBu), 31.5 (CH₃-tBu), 29.6 (NC), 9.2 (Cp*-CH₃). IR (DCM): $\nu_{\text{N}\equiv\text{C}}$ 2124 (w), $\nu_{\text{C}=\text{O}}$ 1666 (s) cm^{-1} . ESI-MS⁺: m/z 642 [M+H]⁺. Anal. Calcd for C₃₂H₃₄IrNO: C, 59.98; H, 5.35. Found: C, 59.62; H, 5.20. HRMS-ESI: m/z 643.2421; calculated for C₃₂H₃₄IrNO [M+H]⁺ 643.2426. Compound **7b-H**: Yield = 1 mg, 1 μmol (6%). Red solid. ¹H NMR (CDCl₃): δ 7.90-7.34 (m, 10H, Ph), 1.86 (s, 15H, Cp*), 1.40 (s, 9H, t-BuNC). ¹³C{¹H} NMR (CDCl₃): δ 170.3 (C=O), 159.7 (C≡C or Ph-C), 142.8 (C≡C or Ph-C), 140.9 (C≡C or Ph-C), 131.5 (Ph-CH), 129.6 (Ph-CH), 128.5 (Ph-CH), 128.0 (Ph-CH), 127.9 (Ph-CH), 127.2 (C≡C or Ph-C), 124.4 (C≡C or Ph-C), 95.3 (Ph-CH), 88.1 (Ph-C), 86.1 (Cp*-C), 57.0 (C-tBu), 31.5 (CH₃-tBu), 29.3 (NC), 9.3 (Cp*-CH₃). IR (DCM): $\nu_{\text{C}\equiv\text{C}}$ 2126 (w), $\nu_{\text{C}=\text{O}}$ 1650 (s) cm^{-1} . ESI-MS⁺: m/z 642 [M+H]⁺.

3.5.3.3 Reaction of **4a-H** with PPh₃ **5c**

To the solution of **4a-H** (28 mg, 0.05 mmol) in toluene (2.0 mL) was added PPh₃ (26 mg, 0.10 mmol). The solution was refluxed for 36 h, the solvent removed under reduced pressure, and the residue purified on TLC plates using ethyl acetate:hexane (1:3, v/v) as eluent to give **6c-H**.

Compound **6c-H**: Yield = 26 mg, 32 μmol (63%). Red solid. ¹H NMR (CDCl₃): δ 7.48-6.94 (m, 25 H, Ph), 1.61 (d, J_{HP} = 5.2 Hz, 15H, Cp*). ¹³C{¹H} NMR (CDCl₃): δ 176.9 (C=O), 165.6 (C≡C or Ph-C), 138.1 (C≡C or Ph-C), 134.4 (Ph-CH), 134.2 (Ph-CH), 132.4 (C≡C or Ph-C), 132.2 (C≡C or Ph-C), 132.1 (C≡C or Ph-C), 131.9 (C≡C or Ph-C), 130.9 (Ph-CH), 129.44 (Ph-CH), 129.42 (Ph-CH), 128.6 (Ph-CH), 128.4 (C≡C or Ph-C), 127.9 (C≡C or Ph-C), 127.7 (Ph-CH), 127.6 (Ph-CH), 127.0 (Ph-CH), 125.4 (C≡C or Ph-C), 125.2 (Ph-CH), 120.5 (C≡C or Ph-C), 120.4 (C≡C or Ph-C), 109.3 (C≡C or Ph-C), 95.09 (Ph-CH), 95.06 (Ph-CH), 93.1 (Cp*-C), 8.8 (Cp*-CH₃). ³¹P NMR (CDCl₃): δ 16.5 (PPh₃). IR (DCM): $\nu_{\text{C}=\text{O}}$ 1643 (w), $\nu_{\text{C}=\text{C}}$ 1597 (s) cm^{-1} . ESI-MS⁺: m/z 821 [M+H]⁺. Anal. Calcd for

C₄₅H₄₀IrOP: C, 65.91; H, 4.92. Found: C, 66.03; H, 5.05. HRMS-ESI: m/z found 822.2603; calculated for C₄₅H₄₀IrOP [M+H]⁺ 822.2596.

3.5.3.4 Kinetic measurements

Compound **4a-H** (0.01 mmol), internal standard *1,3,5*-trimethoxy benzene (1mg), and **5** (0.02 mmol) were dissolved in C₆D₆ (0.4 mL) and placed in a Carius NMR tube. The samples were heated in an oil bath at the pre-determined temperature, and the NMR spectrum recorded at room temperature (23 °C) at regular time intervals.

3.5.3.5 Reaction of 4a-X with PPh₃

In a typical reaction, to the solution of **4a-X** in toluene (2.0 mL) was added PPh₃ (2eq). The solution was refluxed for 36 h. The solvent was removed under reduced pressure, the crude was then purified on TLC plates using ethyl acetate: hexane (1:3, v/v) as eluent to give **6x-Y**.

Table 3.4. Amount of **4a-X** used, and the yield of products **6x-Y** obtained.

X	Amount of 4a-X	Amount of PPh₃	Yield of 6x-Y (mg, mmol, %)
Me	42 mg, 0.072 mmol	38 mg, 0.144 mmol	19, 0.021, 32
OMe	43 mg, 0.070 mmol	37 mg, 0.14 mmol	23, 0.026, 37
Cl	26 mg, 0.040 mmol	21 mg, 0.080 mmol	10, 0.011, 28
F	35 mg, 0.059 mmol	31 mg, 0.118 mmol	31, 0.036, 63

3.5.3.6 Reaction of 4a-H with 5

In a typical reaction, to the solution of **4a-H** (28 mg, 0.050 mmol) in toluene (2.0 mL) was added **5** (2eq). The solution was refluxed for 36 h. The solvent was removed under reduced pressure, the crude was then purified on TLC plates using ethyl acetate:hexane (1:3, v/v) as eluent to give **6x-H**.

Table 3.5. Amount of **5** used, and the yield of products **6x-H** obtained.

L	9	Amount of 9	Yield of 10 (mg, mmol, %)
PMePh ₂	9d	19 μ L, 0.10 mmol	47, 0.060, 99
PBu ₃	9e	25 μ L, 0.10 mmol	16, 0.021, 42
P(OPh) ₃	9g	26 μ L, 0.10 mmol	28, 0.041, 82
P(OMe) ₃	9h	12 μ L, 0.10 mmol	16, 0.023, 47

3.5.3.7 ¹H NMR analysis for the conversion of **4a-H** to **6x-H**

Compound **4a-H** (6 mg, 0.01 mmol), internal standard 1,3,5-trimethoxy benzene (1mg) and **5** (0.02 mmol) were dissolved in C₆D₆ (0.4 mL) in a Carius NMR tube. The samples were heated in an oil bath at the pre-determined temperature, and the NMR spectrum recorded at room temperature (23 °C) at regular time intervals.

5	5b	5c	5d	5e	5g	5h
Amount	3 μ L	5 mg	4 μ L	5 μ L	5 μ L	3 μ L

Table 3.6. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR, HRMS and IR data for **6x-Y**.

Complex	^1H NMR (CDCl ₃): δ	$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl ₃), δ	$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl ₃), δ	HRMS Found (Calcd)	IR (DCM), cm ⁻¹
6c-Me	7.54-6.86 (m, 23 H, Ph), 2.40 (s, 3H, Me), 2.22 (s, 3H, Me), 1.60 (d, $J_{\text{HP}} = 1.6$ Hz, 15H, Cp*).	176.7 (C=O), 171.1 (C $\equiv$ C or Ph-C), 165.3 (C $\equiv$ C or Ph-C), 138.0 (C $\equiv$ C or Ph-C), 135.5 (C $\equiv$ C or Ph-C), 134.8 (C $\equiv$ C or Ph-C), 134.3 (Ph-CH), 134.2 (Ph-CH), 132.5 (C $\equiv$ C or Ph-C), 132.0 (C $\equiv$ C or Ph-C), 130.8 (Ph-CH), 129.3 (Ph-CH), 127.6 (Ph-CH), 127.5 (Ph-CH), 125.1 (Ph-C), 122.3 (C $\equiv$ C or Ph-C), 119.0 (C $\equiv$ C or Ph-C), 118.9 (C $\equiv$ C or Ph-C), 109.0 (C $\equiv$ C or Ph-C), 95.0 (Ph-CH), 94.9 (Ph-CH), 92.6 (Cp*-C), 60.4 (C $\equiv$ C), 21.6 (Me), 21.3 (Me), 8.7 (Cp*-CH ₃).	16.4	848.2724 (848.2759)	VC=O 1641w VC=C 1587s
6c-OMe	7.56-6.60 (m, 23 H, Ph), 3.87 (s, 3H, OMe), 3.73 (s, 3H, OMe), 1.61 (d, $J_{\text{HP}} = 1.6$ Hz, 15H, Cp*).	176.6 (d, C=O), 171.1 (C $\equiv$ C or Ph-C), 164.3 (C $\equiv$ C or Ph-C), 159.4 (C $\equiv$ C or Ph-C), 157.2 (C $\equiv$ C or Ph-C), 134.3 (Ph-CH), 134.2 (Ph-CH), 132.6 (C $\equiv$ C or Ph-C), 132.5 (Ph-CH), 132.2 (C $\equiv$ C or Ph-C), 132.1 (C $\equiv$ C or Ph-C), 129.4 (Ph-CH), 129.3 (Ph-CH), 127.6 (Ph-CH), 127.5 (Ph-CH), 126.5 (Ph-CH), 117.5 (C $\equiv$ C or Ph-C), 117.0 (d, C $\equiv$ C or Ph-C), 116.8 (C $\equiv$ C or Ph-C), 114.3 (Ph-CH), 112.3 (Ph-CH), 108.6 (C $\equiv$ C or Ph-C), 95.0 (Ph-CH), 94.9 (Ph-CH), 92.2 (Cp*-C), 60.4 (C $\equiv$ C), 55.4 (OMe), 55.1 (OMe), 8.7 (Cp*-CH ₃).	16.5	882.2794 (882.2814)	VC=O 1639w VC=C 1604s
6c-Cl	7.53-7.00 (m, 23 H, Ph), 1.59 (d, $J_{\text{HP}} = 1.6$ Hz, 15H, Cp*).	176.9 (d, C=O), 171.1 (C $\equiv$ C or Ph-C), 164.7 (C $\equiv$ C or Ph-C), 136.3 (C $\equiv$ C or Ph-C), 134.3 (Ph-CH), 134.2 (Ph-CH), 134.1 (C $\equiv$ C or Ph-C), 132.2 (C $\equiv$ C or Ph-C), 131.9 (Ph-CH), 131.7 (C $\equiv$ C or Ph-C), 130.6 (C $\equiv$ C or Ph-C), 129.6 (Ph-CH), 129.5 (Ph-CH), 129.0 (Ph-CH), 127.7 (Ph-CH), 127.6 (Ph-CH), 127.2 (Ph-CH), 126.4 (Ph-CH), 123.5 (C $\equiv$ C or Ph-C), 121.0 (C $\equiv$ C or Ph-C), 120.9 (C $\equiv$ C or Ph-C), 108.5 (C $\equiv$ C or Ph-C), 95.2 (Ph-CH), 95.1 (Ph-CH), 93.7 (Cp*-C), 60.4 (C $\equiv$ C), 8.7 (Cp*-CH ₃).	16.5	890.1852 (890.1823)	VC=O 1642w VC=C 1596s
6c-F	7.56-6.72 (m, 23 H, Ph), 1.62 (s, 1H, Cp*).	176.8 (d, C=O), 171.1 (C $\equiv$ C or Ph-C), 164.5 (C $\equiv$ C or Ph-C), 163.5 (C $\equiv$ C or Ph-C), 161.9 (C $\equiv$ C or Ph-C), 161.1 (C $\equiv$ C or Ph-C), 159.4 (C $\equiv$ C or Ph-C), 134.6 (C $\equiv$ C or Ph-C), 134.3 (d, Ph-CH), 132.6 (d, Ph-CH), 132.4 (C $\equiv$ C or Ph-C), 131.8 (C $\equiv$ C or Ph-C), 129.5 (d, Ph-CH), 127.6 (d, Ph-CH), 126.8 (d, C $\equiv$ C or Ph-C), 121.2 (d, C $\equiv$ C or Ph-C), 116.0 (d, Ph-CH), 113.7 (d, Ph-CH), 107.8 (C $\equiv$ C or Ph-C), 95.1 (d, Ph-CH), 92.5 (Cp*-C), 60.4 (C $\equiv$ C), 8.7 (Cp*-CH ₃).	16.6*	858.2373 (858.2424)	VC=O 1642w VC=C 1599s

* ^{19}F NMR (CDCl₃): δ -110, -116 ppm.

Table 3.6. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR, HRMS and IR data for **6x-Y**(continued).

Complex	^1H NMR (CDCl ₃): δ	$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl ₃), δ	$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl ₃), δ	HRMS Found (Calcd)	IR (DCM), cm ⁻¹
6d-H	7.90-7.06 (m, 20 H, Ph), 1.94 (d, J_{HP} = 9.2 Hz, 3H, Me), 1.64 (d, J_{HP} = 1.6 Hz, 15H, Cp*).	170.6 (C=O), 165.9 (C $\equiv$ C or Ph-C), 137.8 (C $\equiv$ C or Ph-C), 137.7 (C $\equiv$ C or Ph-C), 134.7 (C $\equiv$ C or Ph-C), 134.6 (C $\equiv$ C or Ph-C), 134.2 (C $\equiv$ C or Ph-C), 134.1 (C $\equiv$ C or Ph-C), 132.81 (C $\equiv$ C or Ph-C), 132.75 (C $\equiv$ C or Ph-C), 132.7 (C $\equiv$ C or Ph-C), 132.6 (C $\equiv$ C or Ph-C), 131.0 (Ph-CH), 129.8 (C $\equiv$ C or Ph-C), 129.73 (C $\equiv$ C or Ph-C), 129.70 (C $\equiv$ C or Ph-C), 128.68 (Ph-CH), 128.6 (Ph-CH), 128.1 (Ph-CH), 128.0 (C $\equiv$ C or Ph-C), 127.9 (C $\equiv$ C or Ph-C), 127.8 (C $\equiv$ C or Ph-C), 127.7 (Ph-CH), 125.8 (C $\equiv$ C or Ph-C), 125.5 (Ph-CH), 125.1 (C $\equiv$ C or Ph-C), 120.8 (C $\equiv$ C or Ph-C), 109.4 (C $\equiv$ C or Ph-C), 94.7 (Ph-CH), 94.6 (Ph-CH), 93.0 (Cp*-C), 15.6 (Me), 8.7 (Cp*-CH ₃).	-0.5	758.2296 (758.2290)	VC=O 1641s VC=C 1596w
6e-H	7.97-7.09 (m, 10 H, Ph), 1.89 (d, J_{HP} = 1.2 Hz, 15H, Cp*), 1.73-1.28 (m, 18 H, CH ₂), 0.84 (t, $^2J_{\text{HH}}$ = 7.2 Hz, 9 H, CH ₃).	166.4 (C=O), 137.8 (C $\equiv$ C or Ph-C), 130.9 (Ph-CH), 128.5 (Ph-CH), 127.9 (Ph-CH), 127.8 (C $\equiv$ C or Ph-C), 125.6 (Ph-CH), 125.5 (C $\equiv$ C or Ph-C), 125.2 (C $\equiv$ C or Ph-C), 120.1 (C $\equiv$ C or Ph-C), 108.3 (C $\equiv$ C or Ph-C), 94.0 (C $\equiv$ C or Ph-C), 93.9 (C $\equiv$ C or Ph-C), 93.4 (Cp*-C), 25.7 (CH ₂), 25.5 (CH ₂), 25.4 (CH ₂), 24.3 (CH ₂), 24.2 (CH ₂), 13.8 (CH ₃), 9.3 (Cp*-CH ₃).	-9.8	760.3415 (760.3385)	VC=O 1639s VC=C 1597w
6f-H	8.08-7.04 (m, 25 H, Ph), 1.53 (d, J_{HP} = 2.8 Hz, 15H, Cp*).	171.2 (C=O), 167.1 (C $\equiv$ C or Ph-C), 151.8 (C $\equiv$ C or Ph-C), 151.7 (C $\equiv$ C or Ph-C), 137.7 (C $\equiv$ C or Ph-C), 131.2 (Ph-C), 129.4 (Ph-CH), 128.6 (Ph-CH), 128.3 (C $\equiv$ C or Ph-C), 127.9 (Ph-CH), 126.4 (C $\equiv$ C or Ph-C), 126.0 (Ph-CH), 124.7 (C $\equiv$ C or Ph-C), 124.1 (Ph-CH), 121.1 (Ph-CH), 121.0 (Ph-CH), 108.5 (C $\equiv$ C or Ph-C), 96.8 (Ph-CH), 96.7 (Ph-CH), 92.5 (C $\equiv$ C or Ph-C), 92.4 (C $\equiv$ C or Ph-C), 8.7 (d, Cp*-CH ₃).	76.0	868.2307 (868.2294)	VC=O 1638s VC=C 1597w
6g-H	8.08-7.04 (m, 25 H, Ph), 1.53 (d, J_{HP} = 2.8 Hz, 15H, Cp*).	171.2 (C=O), 167.1 (C $\equiv$ C or Ph-C), 151.8 (C $\equiv$ C or Ph-C), 151.7 (C $\equiv$ C or Ph-C), 137.7 (C $\equiv$ C or Ph-C), 131.2 (Ph-C), 129.4 (Ph-CH), 128.6 (Ph-CH), 128.3 (C $\equiv$ C or Ph-C), 127.9 (Ph-CH), 126.4 (C $\equiv$ C or Ph-C), 126.0 (Ph-CH), 124.7 (C $\equiv$ C or Ph-C), 124.1 (Ph-CH), 121.1 (Ph-CH), 121.0 (Ph-CH), 108.5 (C $\equiv$ C or Ph-C), 96.8 (Ph-CH), 96.7 (Ph-CH), 92.5 (C $\equiv$ C or Ph-C), 92.4 (C $\equiv$ C or Ph-C), 8.7 (d, Cp*-CH ₃).	76.0	868.2307 (868.2294)	VC=O 1664s VC=C 1597w
6h-H	8.00-7.12 (m, 10H, Ph), 3.58 (d, J_{HP} = 12.4 Hz, 9H, P(OMe) ₃), 1.94 (d, J_{HP} = 2.4 Hz, 15H, Cp*).	166.4 (C=O), 137.6 (C $\equiv$ C or Ph-C), 130.9 (Ph-CH), 128.6 (Ph-CH), 128.1 (C $\equiv$ C or Ph-C), 127.9 (Ph-CH), 126.1 (C $\equiv$ C or Ph-C), 125.8 (Ph-CH), 124.7 (C $\equiv$ C or Ph-C), 115.9 (C $\equiv$ C or Ph-C), 108.3 (C $\equiv$ C or Ph-C), 95.6 (C $\equiv$ C or Ph-C), 95.5 (C $\equiv$ C or Ph-C), 92.6 (Cp*-C), 51.6 (OMe), 9.0 (Cp*-CH ₃).	101	682.1821 (682.1824)	VC=O 1654s VC=C 1597w

3.5.3.8 Reaction of 6c-H with MeLi or ⁿBuLi

To a solution of **6c-H** (8 mg, 0.010 mmol) in THF (2.0 mL) was added MeLi (0.01 mL, 0.030 mmol) or ⁿBuLi (0.018 mL, 0.030 mmol). The solution was stirred for 12 h at room temperature, and then unreacted MeLi or ⁿBuLi was destroyed by quenching with “wet” THF. The solution was concentrated under reduced pressure, and the residue separated on TLC plates using ethyl acetate:hexane (1:3, v/v) as eluent to give **8b** or **8a** as a red solid.

Compound **8b**. Yield = 1 mg, 12%. ¹H NMR (CDCl₃): δ 7.20-6.98 (m, 24H, Ph), 1.67 (s, 3H, CH₃), 1.64 (d, 15H, ²J_{HP}=1.2 Hz, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 3.98 (PPh₃). ESI-MS⁺: m/z 835 [M+H]⁺. HRMS-ESI m/z calculated for **8b**, C₄₆H₄₂IrOP [M+H]⁺ 836.2759, found 836.2720.

Compound **8a**. Yield = 1 mg, 12%. ¹H NMR (CDCl₃): δ 7.20-6.54 (m, 24H, Ph), 1.64 (d, 15H, ²J_{HP}=1.6 Hz, Cp*), 1.28-1.24 (m, 6H, CH₂), 0.76 (t, 3H, ²J_{HH}=7.2 Hz, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 169.2 (C=O), 152.1 (C≡C or Ph-C), 150.2 (C≡C or Ph-C), 142.8 (C≡C or Ph-C), 135.9 (C≡C or Ph-C), 134.6 (C≡C or Ph-C), 129.8 (Ph-C), 128.5 (C≡C or Ph-C), 127.5 (C≡C or Ph-C), 127.2 (Ph-C), 126.6 (C≡C or Ph-C), 122.0 (C≡C or Ph-C), 121.2 (C≡C or Ph-C), 115.7 (C≡C or Ph-C), 96.2 (Ph-C), 31.1(CH₂), 28.8 (CH₂), 24.0 (CH₂), 14.0 (CH₃), 9.2 (Cp*-CH₃). ³¹P{¹H} NMR (CDCl₃): δ 3.79 (PPh₃). ESI-MS⁺: m/z 877 [M+H]⁺. HRMS-ESI m/z calculated for **8a**, C₄₉H₄₈IrOP [M+H]⁺ 878.3229, found 878.3214.

3.5.4 Reaction of 4a-H with alkynes

3.5.4.1 Reaction of 4a-H with phenylacetylene

To the solution of **4a-H** (21 mg, 0.038 mmol) in toluene (10.0 mL) was added phenylacetylene (8 μL, 0.075 mmol, 2 eq.). The solution was refluxed for 36 h. The solvent was removed under reduced pressure and the crude product was recrystallized from an ether /dcm solution to give **9a-H**.

Repeating this reaction with PhCCD (98% deuteration) in place of phenylacetylene led to 90% deuteration for CH signals of **9a-H**.

Compound **9a-H**: Yield =60%. Brown solid. ¹H NMR: δ 8.16-7.29 (m, 15 H, Ph),

5.08 (s, 1H, CH) 1.64 (s, 15H, Cp*). IR (DCM): $\nu_{\text{C}\equiv\text{C}}$ 2122 (w), ν_{CO} 1992 (s) cm^{-1} . MS ESI⁺ (m/z): 661[M+H⁺].

3.5.4.2 Reaction of 4a-H with 3-hexyne

Complex **4a-H** (13 mg, 0.023 mmol) and 3-hexyne (0.026 mL, 0.23 mmol) was placed with cyclohexane (5 mL) into a quartz Carius tube. The mixture was irradiated with a 450W UV lamp at room temperature, until the IR spectrum of the solution showed no starting material remaining (ca. 10 h). The solution was concentrated under reduced pressure. The solvent was removed under reduced pressure, the crude was then purified on TLC plates using ethyl acetate:hexane (1:5, v/v) as eluent to give **10**.

Compound **10**: Yield = 1 mg (6%). Red solid. ¹H NMR: δ 7.77-7.28 (m, 10 H, Ph), 2.54-0.78 (m, 10 H, CH₂, CH), 1.77 (s, 15H, Cp*), 1.28-1.24 (m, 6 H, CH₃), 0.96 (t, ³J_{HH} = 7.6 Hz, 3H, CH₃), 0.45 (t, ³J_{HH} = 7.4 Hz, 3H, CH₃). IR (DCM): $\nu_{\text{C}=\text{O}}$ 1678 (w), $\nu_{\text{C}=\text{O}}$ 1630 (s) cm^{-1} . MS ESI⁺ (m/z): 725 [M]⁺.

3.5.5 Reaction of 4a-H with water in the presence of triflic acid

To a solution of **4a-H** (28 mg, 0.050 mmol) in DCM (2.0 mL) was added CF₃COOH (38 μL , 0.5 mmol). The solution was stirred for 12 h at room temperature, the solvent was removed under reduced pressure, and the crude was then purified on TLC plates using ethyl acetate:hexane (1:3, v/v) as eluent to give **11** as a yellow solid.

Repeating this reaction in the presence of H₂¹⁸O led to the formation of [Cp*Ir(CO){C(C₆H₅)=CHC(=O¹⁸)CHC₆H₅}].

Compound **11**: Yield = 10 mg, 35%. ¹H NMR (CDCl₃): δ 7.35-6.99 (m, 10H, Ph), 4.03 (s, 1H, CH), 1.65 (s, 15H, Cp*). IR (DCM): ν_{CO} 1994 (s), $\nu_{\text{C}=\text{O}}$ 1639 (w) cm^{-1} . ESI-MS⁺: m/z 577 [M+H]⁺.

3.5.6 X-ray Crystallographic Studies

Red single crystals of **6c-H**, **8b**, **10** and **11** suitable for diffraction analysis were grown by slow evaporation from hexane/dichloromethane solutions at 4 °C. The crystals selected were mounted on quartz fibers. X-ray data for **6c-H**, **8b**, **10** and **11** were collected at 103(2) K on a Bruker X8 APEX system, using Mo K α radiation, with the SMART suite of programs.¹⁹ The data were processed and corrected for Lorentz and polarization effects with SAINT,²⁰ and for absorption effects with SADABS.²¹ Structural solution and refinement were carried out with the SHELXTL suite of programs.²² The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The organic hydrogen atoms were placed in calculated positions and refined with a riding model. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

Table 3.7. Crystal and refinement data for **6c-H**, **8b**, **10** and **11**.

Compound	6c-H	8b	10	11
Empirical formula	C ₄₅ H ₄₀ IrOP	C ₄₆ H ₄₂ IrOP	C ₃₈ H ₄₅ IrO ₂	C ₂₇ H ₂₇ IrO ₂
Formula weight	819.94	833.96	725.94	575.68
Temperature, K	103(2)	103(2)	103(2)	103(2)
Crystal system	Monoclinic	triclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P $\bar{1}$	P2 ₁ /n	P2 ₁ /c
a, Å	12.1553(3)	9.5302(6)	11.1647(3)	8.170(2)
b, Å	18.3522(5)	11.0434(10)	25.1488(8)	11.544(2)
c, Å	16.8631(4)	17.5217(18)	11.3806(3)	23.649(5)
α , deg	90	96.686(6)	90	90
β , deg	105.5840(10)	95.945(5)	107.3160(10)	97.426(7)
γ , deg	90	105.429(4)	90	90
Volume, Å ³	3623.47(16)	1748.0(3)	3050.61(15)	2211.7(9)
Z	4	2	4	4
Density (calculated), Mg/m ³	1.503	1.584	1.581	1.729
Absorption coefficient, mm ⁻¹	3.763	3.901	4.410	6.057
F(000)	1640	836	1464	1128
Crystal size, mm ³	0.24 x 0.20 x 0.16	0.02 x 0.06 x 0.28	0.18 x 0.26 x 0.28	0.06 x 0.08 x 0.12
Reflections collected	45903	36175	43115	24403
Independent reflections	11607 [R(int) = 0.0638]	7170 [R(int) = 0.1253]	9759 [R(int) = 0.0370]	3924 [R(int) = 0.1205]
Max. and min. transmission	0.5843 and 0.4654	0.9260 and 0.4080	0.5041 and 0.3715	0.7100 and 0.4400
Data / restraints / parameters	11607 / 0 / 438	7178 / 0 / 448	9759 / 0 / 379	3927 / 324 / 276
Goodness-of-fit on F ²	1.023	1.067	1.088	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0713	R1 = 0.0494, wR2 = 0.1004	R1 = 0.0252, wR2 = 0.0476	R1 = 0.0607, wR2 = 0.1410
R indices (all data)	R1 = 0.0518, wR2 = 0.0779	R1 = 0.0761, wR2 = 0.1136	R1 = 0.0321, wR2 = 0.0495	R1 = 0.1009, wR2 = 0.1705
Largest diff. peak and hole (e.Å ⁻³)	1.390 and -0.932	2.071 and -1.487	1.423 and -1.983	3.670 and -2.767

3.5.7 Details of kinetic analyses

The system can be considered to comprise the following:

with free energy profile:

Since the experimental kinetic information was obtained by measuring the rate of disappearance of **4a-H**,

$$\frac{d[4\mathbf{a-H}]}{dt} = -k_{obs}[4\mathbf{a-H}] = -k_1[4\mathbf{a-H}] + k_{-1}[\text{INT}]$$

(1)

or, $\ln [4\mathbf{a-H}] = -k_{obs}.t + \text{constant}$

Applying the steady-state approximation to **INT** (since it is not observed spectroscopically),

$$\frac{d[\mathbf{INT}]}{dt} = k_1[\mathbf{4a-H}] - k_{-1}[\mathbf{INT}] - k_2[\mathbf{INT}][\mathbf{L}] = 0$$

$$\Rightarrow [\mathbf{INT}] = \left(\frac{k_1}{k_{-1} + k_2[\mathbf{L}]} \right) [\mathbf{4a-H}]$$

Inserting this into equation (1) and simplifying gives

$$k_{obs} = \frac{k_1 k_2 [\mathbf{L}]}{k_{-1} + k_2 [\mathbf{L}]}$$

(2)

Since the computational studies show that **TS2** is always rate-limiting, $k_2[\mathbf{L}] \ll k_{-1}$.

Equation (2) then simplifies to

$$k_{obs} \sim (k_1 k_2 / k_{-1}) [\mathbf{L}]$$

(3)

Since the conversion of **4a-H** to **6x-H** was followed by monitoring the intensity (I) of the Cp* resonance of **4a-H** and OMe resonance of the internal standard (1,3,5-trimethoxy benzene) in the ¹H NMR spectrum,

$$\ln(I_{\mathbf{4a-H}}/I_{\text{standard}}) = -k_{obs}.t = -(k_1 k_2 / k_{-1}) [\mathbf{L}].t$$

The Eyring equation is: $\ln(k_{obs}/T) = (-\Delta H^\ddagger/R) \cdot (1/T) + \ln(k_B/h) + \Delta S^\ddagger/R$,

where k_B is Boltzmann's constant, and h is Planck's constant.

A plot of $\ln[k_{obs}/T]$ vs $1/T$ will then correspond to:

$$\ln\left(\frac{k_{obs}}{T}\right) = -\left(\frac{\Sigma\Delta H^\ddagger}{R}\right)\left(\frac{1}{T}\right) + \left(\frac{\Sigma\Delta S^\ddagger}{R}\right) + \ln\left(\frac{k_B}{h}\right) + \ln[L] \quad (4)$$

where $\Sigma\Delta H^\ddagger = \Delta H_1^\ddagger + \Delta H_2^\ddagger - \Delta H_{-1}^\ddagger$ and $\Sigma\Delta S^\ddagger = \Delta S_1^\ddagger + \Delta S_2^\ddagger - \Delta S_{-1}^\ddagger$

Note that this will be an approximation as $[L]$ is not a constant.

For all kinetic measurements, $[4a-H]_0 = 0.01 \text{ mmol}/0.4 \text{ ml} = 25 \text{ mol/m}^3$, and

$[L]_0 = 0.02 \text{ mmol}/0.4 \text{ ml} = 50 \text{ mol/m}^3$ for $L \neq \text{CO}$.

Mass balance for the reaction was checked by plotting (I/I_{standard}) vs t for **4a-H**,

6x-H and their sum, and only data points for the extent of reaction in which

$$(I_{4a-H}/I_{\text{standard}})/[(I_{4a-H}/I_{\text{standard}}) + (I_{6x-H}/I_{\text{standard}})] > 90\%$$

were employed in the Eyring plots.

For $L = \text{CO}$, the gas is in excess and hence the reaction approximates to first-order, and $k_2[L] \gg k_{-1}$.

Equation (2) then simplifies to

$$k_{obs} \sim k_I \text{ and } \ln(I_{4a-H}/I_{\text{standard}}) = -k_{obs} \cdot t$$

A plot of $\ln(I_{4a-H}/I_{\text{standard}})$ vs t will give a straight line with slope $-k_{obs} = -k_I$, and

a plot of $\ln(k_{obs}/T)$ versus $1/T$ gives a straight line with slope $-\Sigma\Delta H^\ddagger/R$ and intercept $\{\ln(k_B/h) + \Sigma\Delta S^\ddagger\}$.

3.6 References

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Chapter 4: The reactivity of $\text{Cp}^*\text{Ir}^{\text{III}}(\text{L})(\text{C}\equiv\text{CAr})_2$

In the course of the studies described above on the reductive elimination of the bis(alkynyl) iridium complexes $\text{Cp}^*\text{Ir}(\text{L})(\text{C}\equiv\text{CAr})_2$ **3x** to the diyne complexes $\text{Cp}^*\text{Ir}(\text{L})(\text{ArC}\equiv\text{CC}\equiv\text{CAr})$ **4x**, a number of side reactions were uncovered. These are related to the reactivity of metal bis(alkynyl) complexes which, as has been described in Chapter 1, remains poorly understood. The reactions which were uncovered are the following:

1. Hydration reaction – a product from such a reaction was first observed in an attempt at the synthesis of the bis(alkynyl) complex $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{C}^t\text{Bu})_2$.
2. Oxidation reaction - this was first observed in an attempt at the synthesis of the bis(alkynyl) complex $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}\equiv\text{CPh})_2$.
3. Arbuzov-type reaction – this was first observed as a side-product while studying the reductive elimination of $\text{Cp}^*\text{Ir}[\text{P}(\text{OMe})_3](\text{C}\equiv\text{CPh})_2$.

4.1 Hydration reaction

During the attempt to synthesise the bis(alkynyl) complex $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{C}-^t\text{Bu})_2$ **3a-^tBu** from the reaction of **1a** with two equivalents of $^t\text{BuCCLi}$, the acyl complex $[\text{Cp}^*\text{Ir}(\text{CO})(\text{C}(=\text{O})\text{CH}_2-^t\text{Bu})(\text{C}\equiv\text{C}-^t\text{Bu})]$ **12a-^tBu** was obtained instead (Scheme 4.1).

Scheme 4.1

Complex **12a-^tBu** has been characterized spectroscopically and analytically. The CH_2 protons are diastereotopic and appeared as doublets at 2.98

and 2.65 ppm in the ^1H NMR spectrum; the IR spectrum showed a weak $\text{C}\equiv\text{C}$ stretch at 2128 cm^{-1} , a strong $\text{C}\equiv\text{O}$ stretch at 2001 cm^{-1} , and a weak $\text{C}=\text{O}$ stretch at 1603 cm^{-1} .

It is likely that **12a-tBu** resulted from a hydration reaction, probably during the column purification on basic alumina, of the expected product $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{C}^t\text{Bu})_2$ **3a-tBu**. Indeed, the phenyl analogue **3a-H** reacted with water in the presence of basic alumina to afford the corresponding product **12a** in 58% yield (Scheme 4.2). An attempt at reacting **3a-H** with aq K_2CO_3 or NaOH , however, gave a complicated mixture but no **12a**, and the reaction did not proceed with silica nor in the absence of basic alumina.

Scheme 4.2

Complex **12a** has also been characterized spectroscopically and analytically, as well as by a single-crystal X-ray crystallographic study; the ORTEP plot and selected bond parameters are given in Figure 4.1.

Figure 4.1. ORTEP plot of **12a** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir2-C211=1.864(4); C211-O211=1.145(5); Ir2-C220=2.062(4); C220-O220=1.222(5); C220-C221=1.523(5); Ir2-C212=1.999(4); C212-C213=1.212(5); C213-C214=1.439(5); Ir2-C220-C221=119.7(3); C220-C221-C222=116.0(3); Ir2-C212-C213=174.0(3); C212-C213-C214=177.1(4); C220-Ir2-C211=93.20(16); C220-Ir2-C212=81.40(15).

A deuterium labelling experiment with D₂O in the reaction of **3a-H** showed that the protons of the CH₂ group originated from water. It is therefore proposed that the reaction proceeded via initial attack of hydroxide at an alkynyl ligand to form **E**, followed by hydrolysis to **F** and then an enol-keto rearrangement to **12a** (Scheme 4.3).

Scheme 4.3

Similar hydration reactions that have been reported include that of the bis(alkynyl) ruthenium complex $\text{TpRu}(\text{C}\equiv\text{CPh})_2(\text{NO})$ to afford a number of different products depending on the reaction conditions (Scheme 4.4).¹

Scheme 4.4

A closer example is the iridium-catalysed hydration of phenylacetylene in water through alkynyl, acyl and ketonyl intermediates; anti-Markovnikov and Markovnikov addition products could be obtained at pH 1 and pH 4, respectively (Scheme 4.5).²

Scheme 4.5

Unlike the reaction in Scheme 4.5, however, the effect of pH on the reaction of **3a-H** proceeded quite differently under acidic conditions; with aqueous HCl, the metallacycle $[\text{Cp}^*\text{Ir}(\text{CO})\{\text{C}_6\text{H}_4\text{-}I,2\text{-CH=CC(=O)C(=O)C}_6\text{H}_5\}]$ **13a-H** was obtained (Scheme 4.6). This metallacycle is formed via an oxidation reaction discussed below.

Scheme 4.6

4.2 Oxidation reaction

During an attempt at the synthesis of the bis(alkynyl) complex $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}\equiv\text{CPh})_2$ **3d-H** from the reaction of **1d** and **2a**, the complex $[\text{Cp}^*\text{Ir}(\text{PMe}_3)\{\text{C}_6\text{H}_4\text{-}I,2\text{-CH=CC(=O)C(=O)C}_6\text{H}_5\}]$ **13d-H** was isolated as a minor side-product. It is likely that **13d-H** resulted from the reaction of **3d-H** with either O_2 or water. Indeed, the reaction of **3d-H** with O_2 (1 atm) afforded **13d-H** in 47% yield, and was found to be mediated by acid; in the presence of 1 equivalent of CH_3COOH , the reaction was complete in 4 h (at 110°C), as opposed to more than 48 h in the absence of acid (Scheme 4.7). Complex **13d-H** is not very stable on silica as although the ^1H NMR spectrum of the reaction showed quantitative conversion, the isolated yield was only 47%.

Scheme 4.7

The reaction could be extended to bis(alkynyl) iridium complexes with other ancillary ligands, and both electron-withdrawing and -donating substituents on the phenyl ring of the alkynyls can also be tolerated (Scheme 4.8).

3x-Y	Y	L	13x-Y	Yield of 13x-Y
3b-H	H	P(OMe) ₃	13b-H	40
3c-H	H	P(OPh) ₃	13c-H	42
3e-H	H	PPh ₃	13e-H	14
3d-OMe	OMe	PMe ₃	13-OMe	23
3d-Me	Me	PMe ₃	13d-Me	52
3d-Cl	Cl	PMe ₃	13d-Cl	43
3d-F	F	PMe ₃	13d-F	30

Scheme 4.8

The complexes **13x-Y** have been completely characterized spectroscopically and analytically and the single crystal X-ray crystallographic study of **13e-H** has also been carried out; the ORTEP plot depicting its molecular structure, together with selected bond parameters, is given in Figure 4.2. The C6-C7 and C7-C8 bond lengths (1.440(6) and 1.358(6) Å, respectively) correspond to a C-C single (1.48 Å) and a C=C double bond (1.32 Å), respectively.³ The two C-O bond lengths (C9-O1 = 1.226(5) Å; C10-O2 = 1.227(5) Å) are typical of C(sp²)=O bonds (1.21 Å).³ The Ir-C bond lengths of the iridacycle (Ir1-C1 = 2.061(4) Å and Ir1-C8 = 2.046(4) Å) are in between that for an Ir-C single bond (~2.16),⁴ and those in N-iridacycles (~2.0 Å) which are known to exhibit Ir=C double bond behavior.⁵

Figure 4.2. ORTEP plot of **13e-H** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1-C8=2.046(4); Ir1-C1=2.061(4); Ir1-P1=2.2583(12); C6-C7=1.440(6); C7-C8=1.358(6); C9-O1=1.226(5); C10-O2=1.227(5); C8-Ir1-C1=78.32(16); C1-Ir1-P1=92.07(11); C7-C8-Ir1=116.1(3); C9-C8-Ir1=126.4(3); O1-C9-C8=127.1(4); O2-C10-C9=117.4(4); O2-C10-C11=122.2(4); C6-C1-Ir1=114.2(3); C1-C6-C7=113.3(4).

A similar oxidation of alkynyl ligands has previously been observed for a ruthenium system.⁶ In that case, an alkyne insertion into the Ru-alkynyl bond was followed by coordination of O₂, which then added across the alkyne functional group to form a 1,2-diketone moiety (Scheme 4.9).

Scheme 4.9

In the case of **13d-H**, oxidation of **3d-H** in the presence of D_2O led to the incorporation of deuterium on the iridacycle (Appendix C, spectra for **13d-H-D**), showing that the proton on the iridacycle originated from water. The ^1H NMR spectrum of a reaction carried out in the absence of oxygen (under an argon atmosphere) showed no change even after heating for 3 days, confirming that O_2 is necessary. The MS and IR spectra of a reaction carried out in the presence of H_2^{18}O did not show any incorporation of ^{18}O , thus indicating that water was not the source for the ketonic O atoms.

A reaction pathway that accounts for these observations is depicted in Scheme 4.10. Initial protonation at an alkynyl ligand in **3d-H** leads to a vinylidene intermediate **G**. A *1,2*-migration of the second alkynyl to form an intermediate

H is followed by oxidation of the C≡C triple bond (presumably via an O₂ species **I**) to form **J**. Ortho C-H activation of the phenyl ring to form **K** can then be followed by deprotonation to give **13d-H**.

Scheme 4.10

4.3 Arbuzov type reaction

During the kinetic study on the reductive elimination of [Cp*Ir[P(OMe)₃](C≡CPh)₂] **3b-H** in the presence of excess P(OMe)₃, it was found that the kinetics deviated from the first-order kinetics expected. The NMR spectrum showed the formation of other products, the major product of which

was identified as $[\text{Cp}^*\text{Ir}[\text{P}(\text{OMe})_3]\{\text{C}(\text{Ar})=\text{C}[\text{P}(=\text{O})(\text{OMe})_2]\text{C}=\text{CHAr}\}]$, **14b-H**. It was also found that **14b-H** was the result of a reaction between **3b-H** and $\text{P}(\text{OMe})_3$, the latter presumably from some decomposition of **3b-H**, and that the yield could be increased from 20% to 55% with the addition of CH_3COOH (Scheme 4.11).

Scheme 4.11

The reaction also worked with iridium bis(alkynyl) complexes with other ancillary ligands, and with both electron-withdrawing and –donating substituents on the phenyl rings of the alkynyl ligands (Scheme 4.12). The reaction also worked with $\text{P}(\text{OEt})_3$ in place of $\text{P}(\text{OMe})_3$ as reagent.

3x-Y	Y	L	R	14x-Y	Yield (%)
3b-OMe	OMe	P(OMe) ₃	Me	14b-OMe	34
3b-F	F	P(OMe) ₃	Me	14b-F	31
3d-H	H	PMe ₃	Me	14d-H	11
3e-H	H	PPh ₃	Me	14e-H	14
3b-H	H	P(OMe) ₃	Et	14f-H	57

Scheme 4.12

The products **14x-Y** have been characterised spectroscopically and analytically, and the structure of **14b-H** has also been confirmed by a single-crystal X-ray crystallographic study. The ORTEP plot for **14b-H**, together with selected bond parameters, are given in Figure 4.3.

Figure 4.3. ORTEP plot of **14b-H** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1-C20=2.062(3); Ir1-C18=2.093(3); C18-C19=1.477(4); C19-C20=1.360(4); C19-P2=1.776(3); P2-O6=1.472(2); P2-O4=1.588(2); C17-C18=1.345(4); Ir1-P1=2.1909(7); C18-Ir1-C20=64.12(11); Ir1-C20-C19=99.40(19); C20-C19-C18=102.0(2); C19-C18-Ir1=94.24(17); Ir1-C18-C17=140.5(2); C20-C19-P2=132.6(2).

A deuterium labelling experiment which involved carrying out the reaction of **3b-H** with P(OMe)₃ in CD₃OD (99.8% deuteration) afforded **14b-H** in which the proton on the exocyclic C=C was replaced by deuterium (90%). An experiment with HO=P(OMe)₂ instead of P(OMe)₃ did not give any **14b-H**, thus precluding the possibility of HO=P(OMe)₂, which could have been formed from P(OMe)₃,⁷ as the source of the O=P(OMe)₂ moiety. With P(OPh)₃, the reaction proceeded differently, although we have not attempted to identify the species

formed. All these observations are consistent with the Arbuzov reaction,⁸ and presumably an analogous pathway was followed (Scheme 4.13). As in the oxidation reaction above, therefore, initial protonation and *1,2*-alkynyl migration leads to the intermediate **H'**. Nucleophilic attack of the P(OMe)_3 at the triple bond is followed on by an Arbuzov-type reaction in the intermediate **L** to **14b-H**.

Scheme 4.13

It was also found that **14b-H** isomerized in the presence of 37% aq HCl to the ring extension product **15** (Scheme 4.14); this isomerisation did not occur with acetic acid. Presumably, a strong acid is required for this isomerisation.

Scheme 4.14

The complex **15** has been characterized spectroscopically and analytically, and also by a single-crystal X-ray crystallographic study. The ORTEP plot, with selected bond parameters, for **15** are given in Figure 4.4.

Figure 4.4. ORTEP plot of **15** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1-C14=2.073(4); Ir1-C11=2.059(4); C11-C12=1.368(5); C12-C13=1.453(5); C13-C14=1.351(5); C12-P2=1.766(4); P2-O4=1.475(3); C14-C23=1.484(5); Ir1-P1=2.2001(10); C11-Ir1-C14=78.45(15); Ir1-C14-C13=115.4(3); C14-C13-C12=115.6(4); C13-C12-C11=114.9(3); C12-C11-Ir1=115.6(3); C12-C11-C15=121.1(3).

A plausible pathway for this isomerisation involves initial protonation at the alkene group to give **M**, followed by a rearrangement to form **N** and deprotonation to afford **15** (Scheme 4.15).⁹

Scheme 4.15

4.4 Conclusion

In this chapter, three apparently disparate reactions involving the bis(alkynyl) species $[\text{Cp}^*\text{Ir}(\text{L})(\text{C}\equiv\text{CAr})_2]$ **3** were described – base hydrolysis to the acyl species $[\text{Cp}^*\text{Ir}(\text{CO})(\text{C}(=\text{O})\text{CH}_2\text{Ar})(\text{C}\equiv\text{CAr})]$ **12**, acid-mediated oxidation to a metallacycle $[\text{Cp}^*\text{Ir}(\text{L})\{\text{C}_6\text{H}_4\text{-}1,2\text{-CH=CC(=O)C(=O)Ar}\}]$ **13**, and an Arbuzov-type reaction to a metallacyclobutene $[\text{Cp}^*\text{Ir}(\text{L})\{\text{C}(\text{Ar})=\text{C}[\text{P}(=\text{O})(\text{OMe})_2]\text{C}=\text{CHAr}\}]$ **14**. In arriving at the reaction pathways for these three reactions, it is apparent that they are actually related (Scheme 4.16).

Scheme 4.16

The initiation of reaction is protonation of an alkynyl to form an alkenylidene; although the proposed reaction pathway above for the hydration reaction involved initial hydroxide attack, it may also be viewed as involving some form of protonation/activation to rearrange to a vinylidene. The α -carbon of the vinylidene is expected to carry a δ^+ charge, and hence susceptible to either nucleophilic attack or an alkynyl migration (the latter may be viewed as attack of an alkynide). With a weak base, attack by hydroxide leads ultimately to the acyl species **11**; there seems to be a fine balance to the basicity requirement as too strong a base leads to a complicated mixture, presumably from further attack by hydroxide ions. In the absence of a base, alkynyl migration can occur, and the resulting enynyl species can undergo attack by oxygen to form the oxidation product, or by a phosphite to undergo an Arbuzov-type reaction.

4.5 Experimental

4.5.1 General Procedures

All reactions and manipulations were performed under argon using standard Schlenk techniques. All other reagents were from commercial sources and used without further purification. ^1H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on a BBFO1 400 MHz or AV 500 MHz NMR spectrometer; chemical shifts reported are with respect to the residual ^1H resonance in CDCl_3 . Solution IR spectra were obtained on a Bruker ALPHA FTIR spectrometer as CH_2Cl_2 solution at a resolution of 2 cm^{-1} using a solution IR cell with NaCl windows and a pathlength of 0.1 mm. Mass spectra (nominal and high-resolution) were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer with MeOH as solvent. Elemental analyses were performed by the microanalytical laboratory in NUS.

4.5.2 Reaction of **3a-H** with basic alumina

To the solution of **3a-H** (20 mg, 36 μmol) in THF (8 mL) was added basic alumina (0.40 g, 4 mmol). The solution was refluxed for 12 h. The solution was filtered to remove the basic alumina, the filtrate was concentrated under reduced pressure, and the crude was then purified on TLC plates using ethyl acetate:hexane (1:3, v/v) as eluent to give **12a**.

Compound **12a**: Yield = 12 mg, 21 μmol (58%). Yellow solid. ^1H NMR (CDCl_3): δ 7.37-7.13 (m, 10H, Ph), 4.58 (d, $^2J_{\text{HH}} = 16\text{ Hz}$, 1H, CH), 3.97 (d, $^2J_{\text{HH}} = 16\text{ Hz}$, 1H, CH), 1.98 (s, 15H, Cp*). IR (DCM): $\nu_{\text{C}=\text{C}}$ 2128 (w), $\nu_{\text{C}=\text{O}}$ 2012 (s), $\nu_{\text{C}=\text{O}}$ 1603 (w) cm^{-1} . MS ESI $^+$ (m/z): 578 $[\text{M}+\text{H}]^+$.

Repeating this reaction in the presence of D_2O (99.9% deuteration) (2 μL , 80 μmol) led to 100% deuteration for CH_2 signals of **12a**.

4.5.3 Reaction of **1a** with ^tBuCClLi

Lithium *t*-butylacetylide was freshly prepared from the reaction of ⁿBuLi (1.6 M in hexane, 0.050 mL, 0.080 mmol) with *t*-Butylacetylene (0.010 mL, 0.080 mmol) in THF (1.0 mL) at -78 °C. To a solution of **1a** (18 mg, 0.040 mmol) in THF (1.0 mL) maintained at -78 °C was added lithium *t*-butylacetylide. The solution was warmed up to room temperature and continued to be stirred for 2 h at room temperature, and then unreacted lithium *t*-butylacetylide was destroyed by quenching with “wet” THF. The solution was concentrated under reduced pressure, and the crude was then purified on TLC plates using ethyl acetate: hexane (1:10, v/v) as eluent to give **12a-^tBu**.

Compound **12a-^tBu**: Yield = 3 mg, 14%. Yellow solid. ¹H NMR (CDCl₃): δ 2.98 (d, 1H, ²J_{HH}=12.6 Hz, CH₂), 2.65 (d, 1H, CH₂), 1.92 (s, 15H, Cp*), 1.21 (s, 9 H, CH₃), 0.97 (s, 9 H, CH₃). IR (DCM): ν_{C≡C} 2128 (w), ν_{CO} 2001 (s), ν_{C=O} 1603 (w) cm⁻¹. MS ESI⁺ (m/z): 538 [M+H]⁺.

4.5.4 Reaction of **3x-Y** with O₂ in the presence of CH₃COOH

Typical reaction of 3x-Y with O₂

Complex **3d-H** (61 mg, 0.1 mmol) with CH₃COOH (6 μL, 0.1 mmol) was placed with toluene (10 mL) into a Carius tube. The solution was subjected to three freeze-pump-thaw cycles, O₂ (1 atm) introduced, and the reaction then heated at 80 °C for 4 h. The solution was concentrated under reduced pressure, and the crude product purified on alumina column using dcm:hexane (1:3, v/v) as eluent to give **13d-H** (30 mg, 0.047 mmol) as a yellow solid.

Repeating this reaction with D₂O (99.9% deuteration) led to 40% deuteration for CH signal of **13d-H**. And repeating this reaction with Cp*Ir(PMe₃)(C≡CC₆D₅) in place of **3d-H** led to 95% deuteration for all the aromatic signals of **13d-H** but CH signal of **13d-H** still retain.

The same procedure was used for the other derivatives. The amount of reagents used and yield of products obtained are in Table 4.1, and characterisation data for

the products in Table 4.2.

Table 4.1. Amount of reagents **3x-Y** used and the yield of product **13x-Y** obtained.

3x-Y	Amount of 3x-Y used(mg, mmol)	Yield of 13x-Y (mg, mmol, %)
3d-OMe	66, 0.10	13d-OMe 10 mg, 0.014, 14
3d-Me	63, 0.10	13d-Me 15 mg, 0.023, 23
3d-Cl	68, 0.10	13d-Cl 37 mg, 0.043, 43
3d-F	64, 0.10	13d-F 29 mg, 0.052, 52
3e-H	79, 0.10	13e-H 25 mg, 0.030, 30
3b-H	65, 0.10	13b-H 27 mg, 0.040, 40
3c-H	84, 0.10	13c-H 37 mg, 0.042, 42

Table 4.2. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR, and HRMS data for **13x-Y**.

Product	^1H NMR	$^{13}\text{C}\{^1\text{H}\}$ NMR	$^{31}\text{P}\{^1\text{H}\}$ NMR	IR	HRMS Found (Calcd)
13d-H	(C_6D_6): δ 8.04-6.95 (m, 9 H, aromatic), 1.70 (d, $^3J_{\text{HP}}=1.6$ Hz, 15 H, Cp^*), 0.89 (d, $^3J_{\text{HP}}=10$ Hz, 9 H, PMe_3).	(C_6D_6): δ 153.8 (CO), 153.7 (CO), 149.8 (Ph-CH), 134.9 (Ph-C), 131.0 (Ph-CH), 128.3 (Ph-C), 126.6 (Ph-C), 126.4 (Ph-CH), 123.6 (Ph-CH), 122.8 (Ph-CH), 122.2 (Ph-CH), 114.2 (Ph-C), 94.5 (Ph-C), 93.33 (Ph-C), 93.31 (Ph-C), 13.8 (PMe_3), 13.4 (PMe_3), 8.9 ($\text{Cp}^*\text{-CH}_3$).	-39.3	1607, 1595	640.2073 (640.2082)
13d-OMe	(CDCl_3): δ 7.47-6.45 (m, 9 H, aromatic), 3.82 (s, 3 H, Ph-OMe), 3.80 (s, 3 H, Ph-OMe), 1.85 (d, $^3J_{\text{HP}}=0.8$ Hz, 15 H, Cp^*), 1.15 (d, $^3J_{\text{HP}}=10$ Hz, 9 H, PMe_3).	(CDCl_3): δ 158.3 (CO), 155.7 (CO), 153.0 (Ph-C), 147.7 (CH), 132.2 (Ph-CH), 121.9 (Ph-CH), 118.5 (Ph-C), 113.9 (Ph-C), 113.7 (Ph-CH), 113.5 (Ph-C), 105.4 (Ph-CH), 96.7 (Ph-C), 93.58 (Ph-C), 93.55 (Ph-C), 93.1 ($\text{Cp}^*\text{-C}$), 55.3 (OMe), 55.1 (OMe), 14.1(d, $^2J_{\text{CP}}=40$ Hz, PMe_3), 9.2 ($\text{Cp}^*\text{-CH}_3$).	-38.3	1604, 1578	698.2123 (698.2137)
13d-Me	(CDCl_3): δ 7.51-6.68 (m, 9 H, aromatic), 2.35 (s, 3 H, Ph-Me), 2.30 (s, 3 H, Ph-Me), 1.84 (d, $^3J_{\text{HP}}=1.6$ Hz, 15 H, Cp^*), 1.14 (d, $^3J_{\text{HP}}=10$ Hz, 9 H, PMe_3).	(CDCl_3): δ 148.6 (CO), 136.3 (CO), 136.02 (Ph-C), 136.0 (CH), 133.1 (Ph-C), 132.0 (Ph-C), 130.8 (Ph-CH), 130.5 (Ph-C), 129.0 (Ph-CH), 127.6 (Ph-C), 123.0 (Ph-C), 122.0 (Ph-C), 121.6 (Ph-C), 93.46 (Ph-C), 93.48 ($\text{Cp}^*\text{-C}$), 21.4 (Me), 21.3 (Me), 14.1(d, $^2J_{\text{CP}}=40$ Hz, PMe_3), 9.2 ($\text{Cp}^*\text{-CH}_3$).	-38.5	1608, 1585	666.2093 (666.2239)
13d-Cl	(CDCl_3): δ 7.53-6.84 (m, 9 H, aromatic), 1.83 (d, $^3J_{\text{HP}}=1.6$ Hz, 15 H, Cp^*), 1.16 (d, $^3J_{\text{HP}}=10.4$ Hz, 9 H, PMe_3).	(CDCl_3): δ 157.6 (CO), 155.7 (CO), 148.4 (CH), 134.0 (Ph-C), 132.4 (Ph-C), 132.1 (Ph-CH), 129.5 (Ph-C), 128.9 (Ph-C), 128.6 (Ph-CH), 128.1 (Ph-C), 124.3 (Ph-C), 122.7 (Ph-C), 121.4 (Ph-C), 93.8 (Ph-C), 93.7 ($\text{Cp}^*\text{-C}$), 14.1(d, $^2J_{\text{CP}}=40$ Hz, PMe_3), 9.1 ($\text{Cp}^*\text{-CH}_3$).	-39.0	1610, 1594	706.1176 (706.1146)
13d-F	(C_6D_6): δ 7.93-6.73 (m, 9 H, aromatic), 1.63 (d, $^3J_{\text{HP}}=1.6$ Hz, 15 H, Cp^*).	(CDCl_3): δ 155.2 (CO), 155.0 (CO), 148.0 (CH), 132.5 (Ph-CH), 132.4 (Ph-CH), 122.3 (Ph-C), 122.2 (Ph-C), 122.0 (Ph-C), 121.2 (Ph-C), 121.0 (Ph-C), 115.5 (Ph-CH), 115.3 (Ph-CH), 107.6 (Ph-C), 107.4 (Ph-C), 93.71 (Ph-C), 93.68 ($\text{Cp}^*\text{-C}$), 14.1(d, $^2J_{\text{CP}}=40$ Hz, PMe_3), 9.1 ($\text{Cp}^*\text{-CH}_3$).	-40.0	1600, 1585	674.1747 (674.1737)
13e-H	(C_6D_6): δ 7.80-6.71 (m, 25 H, aromatic), 1.57 (d, $^3J_{\text{HP}}=1.6$ Hz, 15 H, Cp^*).	(C_6D_6): δ 200.2 (CO), 197.8 (CO), 164.3 (Ph-CH), 158.1 (Ph-C), 136.2 (Ph-CH), 135.5 (Ph-C), 134.6 (Ph-CH), 134.5 (Ph-CH), 132.6 (Ph-CH), 131.6 (Ph-CH), 129.8 (Ph-CH), 128.3 (Ph-CH), 128.0 (Ph-CH), 127.0 (Ph-CH), 125.7 (Ph-CH), 124.2 (Ph-CH), 122.3 (Ph-CH), 95.3 (Ph-C), 95.2 ($\text{Cp}^*\text{-C}$), 8.8 ($\text{Cp}^*\text{-CH}_3$).	7.8	1614, 1597	824.2407 (824.2395)
13b-H	(C_6D_6): δ 7.98-6.95 (m, 10 H, aromatic), 3.21 (d, $^3J_{\text{HP}}=11.6$ Hz, 9 H, P(OMe)_3), 1.75 (d, $^3J_{\text{HP}}=2.8$ Hz, 15 H, Cp^*).	(C_6D_6): δ 160.0 (Ph-C), 151.1 (Ph-C), 149.6 (CO), 149.4 (CO), 136.8 (Ph-CH), 136.7 (Ph-CH), 130.9 (Ph-CH), 128.3 (Ph-CH), 126.5 (Ph-CH), 123.3 (Ph-CH), 122.8 (Ph-CH), 122.5 (Ph-CH), 95.3 (Ph-C), 95.2 (Ph-C), 94.3 ($\text{Cp}^*\text{-C}$), 51.8 (d, $^2J_{\text{CP}}=6$ Hz P(OMe)_3), 8.9 ($\text{Cp}^*\text{-CH}_3$).	83.4	1610, 1597	686.1752 (686.1773)
13c-H	(C_6D_6): δ 7.79-6.73 (m, 25 H, aromatic), 1.65 (d, $^3J_{\text{HP}}=2.8$ Hz, 15 H, Cp^*).	(C_6D_6): δ 159.9 (Ph-C), 152.4 (Ph-CH), 152.2 (Ph-CH), 152.1 (Ph-CH), 148.9 (CO), 148.7 (CO), 136.9 (Ph-C), 131.2 (Ph-CH), 129.1 (Ph-CH), 128.3 (Ph-CH), 126.6 (Ph-CH), 126.4 (Ph-C), 124.6 (Ph-C), 124.4 (Ph-C), 123.7 (Ph-CH), 123.4 (Ph-C), 123.1 (Ph-C), 120.9 (Ph-CH), 99.3 (Ph-C), 96.4 (Ph-C), 96.3 (Ph-C), 94.5 ($\text{Cp}^*\text{-C}$), 8.6 ($\text{Cp}^*\text{-CH}_3$).	59.4	1610, 1594	872.2260 (872.2243)

(Anal. Calcd for **13d-H** $\text{C}_{29}\text{H}_{34}\text{IrO}_2\text{P}$: C, 54.61; H, 5.37. Found: C, 54.37; H, 5.32).

4.5.5 Reaction of 3x-Y with P(OR)₃ in the presence of CH₃COOH

Typical reaction of 3x-Y with P(OR)₃ in the presence of CH₃COOH

To the solution of **3b-H** (16 mg, 0.024 mmol) in CH₃OH (10 mL) was added P(OMe)₃ (6 µL, 0.02 mmol) and CH₃COOH (3 µL, 0.02 mmol). The solution was heated at 70 °C overnight. The solution was concentrated under reduced pressure, and the crude was then purified by TLC plates on silica using ethyl acetate: hexane (2:1, v/v) as eluent to give **14b-H**.

Repeating this reaction with CD₃OD (99.8% deuteration) in place of CH₃OH without CH₃COOH led to the loss of CH signals by deuterium (90%) of **14b-H**. The same procedure was used for the other derivatives. The amount of reagents used and yield of products obtained are in Table 4.3, and characterisation data for the products in Table 4.4.

Table 4.3. Amount of reagents **3x-Y** used and the yield of product **14x-Y** obtained.

3x-Y	Amount of 3x-Y used(mg, mmol)	P(OR)₃	Amount of P(OR)₃ used(µL, mmol)	Amount of AcOH used(µL, mmol)	Yield of 14x-Y (mg, mmol, %)
3d-H	52, 0.08	P(OMe) ₃	19, 0.16	10, 0.16	14d-H 8, 0.011, 13
3b-H	16, 0.024	P(OMe) ₃	6, 0.048	3, 0.048	14b-H 10, 0.013, 55
3b-OMe	18, 0.025	P(OMe) ₃	6, 0.05	3, 0.05	14b-OMe 15, 0.023, 23
3b-F	28, 0.04	P(OMe) ₃	10, 0.08	5, 0.08	14b-F 10, 0.013, 31
3e-H	32, 0.04	P(OMe) ₃	10, 0.08	5, 0.08	14e-H 5, 0.006, 14
3b-H	65, 0.10	P(OEt) ₃	34, 0.20	11, 0.20	14f-H 45, 0.056, 57

Table 4.4. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR, and HRMS data for **14x-Y**.

Product	^1H NMR	$^{13}\text{C}\{^1\text{H}\}$ NMR	$^{31}\text{P}\{^1\text{H}\}$ NMR	HRMS Found (Calcd)
14d-H	(CDCl ₃): δ 7.82-7.10 (m, 11 H, aromatic), 3.57 (d, $^3J_{\text{HP}}=11.2$ Hz, 3 H, O=P(OMe) ₂), 3.49 (d, $^3J_{\text{HP}}=11.2$ Hz, 3 H, O=P(OMe) ₂), 2.06 (d, $^3J_{\text{HP}}=10.8$ Hz, 9 H, P(Me) ₃), 1.58 (d, $^3J_{\text{HP}}=1.6$ Hz, 15 H, Cp*).	(CDCl ₃): δ 175.3 (Ph-C or C=C), 141.1 (Ph-C or C=C), 127.6 (Ph-CH), 127.5 (Ph-CH), 127.1 (Ph-CH), 126.5 (Ph-CH), 125.8 (Ph-CH), 124.4 (Ph-CH), 115.9 (Ph-CH or =CH), 94.1 (Ph-C), 94.0 (Cp*-C), 51.2 (O=P(OMe)), 51.3 (O=P(OMe)), 20.9 (P(Me) ₃), 18.1 (P(Me) ₃), 17.7 (P(Me) ₃), 9.3 (Cp*-CH ₃).	16.3 (d), -43.8 (d)	716.2189 (716.2160)
14b-H	(CDCl ₃): δ 7.86-7.10 (m, 11 H, aromatic), 3.70 (d, $^3J_{\text{HP}}=10.8$ Hz, 9 H, P(OMe) ₃), 3.52 (d, $^3J_{\text{HP}}=11.6$ Hz, 3 H, O=P(OMe) ₂), 3.45 (d, $^3J_{\text{HP}}=10.8$ Hz, 3 H, O=P(OMe) ₂), 1.52 (d, $^3J_{\text{HP}}=2.4$ Hz, 15 H, Cp*).	(CDCl ₃): δ 142.0 (Ph-C), 127.7 (Ph-CH), 127.3 (Ph-CH), 127.0 (Ph-CH), 126.9 (Ph-C), 126.7 (Ph-CH), 126.2 (Ph-CH), 124.2 (Ph-CH), 117.5 (Ph-CH or =CH), 95.4 (Ph-C), 95.3 (Cp*-C), 53.3 (O=P(OMe)), 53.2 (O=P(OMe)), 51.4 (P(OMe) ₃), 51.1 (P(OMe) ₃), 51.0 (P(OMe) ₃), 8.9 (Cp*-CH ₃).	84.1, 15.5 (d)	764.2006 (764.2008)
14e-H	(CDCl ₃): δ 7.33-6.72 (m, 16 H, aromatic), 3.10 (d, $^3J_{\text{HP}}=11.2$ Hz, 3 H, O=P(OMe) ₂), 2.91 (d, $^3J_{\text{HP}}=11.2$ Hz, 3 H, O=P(OMe) ₂), 1.42 (d, $^3J_{\text{HP}}=1.6$ Hz, 15H, Cp*).	(CDCl ₃): δ 141.4 (Ph-C), 134.4 (Ph-CH), 134.3 (Ph-CH), 129.8 (Ph-CH), 129.5 (Ph-CH), 128.4 (Ph-CH), 128.2 (Ph-CH), 127.8 (Ph-CH), 127.7 (Ph-CH), 127.6 (Ph-CH), 127.5 (Ph-CH), 127.4 (Ph-CH), 126.8 (Ph-CH), 126.7 (Ph-CH), 126.6 (Ph-CH), 126.4 (Ph-CH), 125.9 (Ph-CH), 125.8 (Ph-CH), 124.2 (Ph-CH), 123.9 (Ph-CH), 118.2 (Ph-CH or =CH), 95.5 (Ph-C), 95.4 (Cp*-C), 51.3 (O=P(OMe)), 50.6 (O=P(OMe)), 9.0 (Cp*-CH ₃).	15.9 (d), 8.3 (d)	902.2651 (902.2630)
14f-H	(CDCl ₃): δ 7.85-7.11 (m, 11 H, aromatic), 4.13-3.89 (m, 4 H, O=P(OEt) ₂), 3.69 (d, $^3J_{\text{HP}}=11.2$ Hz, 9 H, P(OMe) ₃), 1.51 (d, $^3J_{\text{HP}}=1.6$ Hz, 15H, Cp*), 1.12 (t, $^2J_{\text{HH}}=6.8$ Hz, 3 H, CH ₃), 1.03 (t, $^2J_{\text{HH}}=6.8$ Hz, 3 H, CH ₃).	(CDCl ₃): δ 174.1 (Ph-C), 142.7 (Ph-C), 142.0 (Ph-C), 127.7 (Ph-CH), 127.4 (Ph-CH), 126.9 (Ph-CH), 126.6 (Ph-CH), 126.1 (Ph-CH), 124.2 (Ph-CH), 117.5 (Ph-CH or =CH), 95.4 (Ph-C), 95.3 (Cp*-C), 60.8 (d, CH ₂), 60.3 (d, CH ₂), 53.3 (P(OMe) ₃), 53.2 (P(OMe) ₃), 16.1 (q, O=P(OEt) ₂), 8.9 (Cp*-CH ₃).	84.3 (d), 12.4 (d)	792.2297 (792.2321)
14b-OMe	(CDCl ₃): δ 7.80-6.77 (m, 9 H, aromatic), 3.82 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 3.69 (d, $^3J_{\text{HP}}=11.2$ Hz, 9H, P(OMe) ₃), 3.54 (d, $^3J_{\text{HP}}=11.2$ Hz, 3 H, O=P(OMe) ₂), 3.48 (d, $^3J_{\text{HP}}=11.6$ Hz, 3 H, O=P(OMe) ₂), 1.52 (d, $^3J_{\text{HP}}=2.4$ Hz, 15 H, Cp*).	(CDCl ₃): δ 158.3 (Ph-C), 156.8 (Ph-C), 135.1 (Ph-C), 135.0 (Ph-C), 129.2 (Ph-CH), 127.6 (Ph-CH), 116.2 (Ph-CH), 113.2 (Ph-CH), 112.3 (Ph-CH or =CH), 95.4 (Ph-C), 95.3 (Cp*-C), 55.2 (OCH ₃), 55.1 (OCH ₃), 53.3 (O=P(OMe) ₂), 53.2 (O=P(OMe) ₂), 51.4 (P(OMe) ₃), 51.2 (P(OMe) ₃), 51.1 (P(OMe) ₃), 9.0 (Cp*-CH ₃).	83.6 (d), 15.7 (d)	824.2253 (824.2219)
14b-F	(CDCl ₃): δ 7.83-6.88 (m, 9 H, aromatic), 3.70 (d, $^3J_{\text{HP}}=10.8$ Hz, 9 H, P(OMe) ₃), 3.55 (d, $^3J_{\text{HP}}=11.2$ Hz, 3 H, O=P(OMe) ₂), 3.48 (d, $^3J_{\text{HP}}=11.2$ Hz, 3 H, O=P(OMe) ₂), 1.51 (d, $^3J_{\text{HP}}=2.8$ Hz, 15H, Cp*).	(CDCl ₃): δ 175.1 (Ph-C), 129.2 (Ph-CH), 129.1 (Ph-CH), 127.8 (Ph-C), 127.7 (Ph-CH), 116.3 (Ph-CH), 114.6 (Ph-CH), 114.3 (Ph-CH), 114.0 (Ph-CH), 113.8 (Ph-CH or =CH), 95.4 (Ph-C), 95.3 (Cp*-C), 53.5 (O=P(OMe) ₂), 53.4 (O=P(OMe) ₂), 51.6 (P(OMe) ₃), 51.5 (P(OMe) ₃), 51.2 (P(OMe) ₃), 51.1 (P(OMe) ₃), 8.9 (Cp*-CH ₃).	83.0 (d), 15.1 (d)	686.1752 (686.1773)

^{19}F NMR for **14b-F**: -116.2 ppm, -118.9 ppm. Anal. Calcd for **14e-H** C₄₆H₄₇IrO₃P₂: C, 61.25; H, 5.25. Found: C, 61.29; H, 5.12. Anal. Calcd for **13f-H** C₃₃H₄₅IrO₆P₂: C, 50.05; H, 5.73. Found: C, 50.54; H, 5.38.

4.5.6 Reaction of **14b-H** in the presence of HCl

To a solution of **14b-H** (20 mg, 0.026 mmol) in CH₃OH (10 mL) was added 37% HCl (10 μ L, 0.01 mmol). The solution was stirred at room temperature for 4h, concentrated under reduced pressure, and the crude was then purified on silica TLC plates using ethyl acetate: hexane (10:1, v/v) as eluent to give **15**.

Compound **15**: Yield = 12 mg, 60%. Yellow solid. ¹H NMR (CDCl₃): δ 7.50-7.05 (m, 11H, Ph), 3.70 (d, 9H, ³J_{HP}=11.2 Hz, P(OMe)₃), 3.47 (d, 3H, ³J_{HP}=10.8 Hz, O=P(OMe)), 3.27 (d, 3H, ³J_{HP}=11.2 Hz, O=P(OMe)), 1.31 (d, 15H, ³J_{HP}=2.4 Hz, Cp*). ³¹P NMR (CDCl₃): δ 75.58(d), 21.39(d). MS ESI⁺ (m/z): 765 [M+H]⁺. Anal. Calcd for C₃₁H₄₁IrO₆P₂: C, 48.75; H, 5.41. Found: C, 48.98; H, 5.39. HRMS-ESI m/z calculated for **15**, C₃₁H₄₁IrO₆P₂ [M]⁺ 764.2008, found 764.2038.

Repeating this reaction with [Cp*Ir[P(OMe)₃]]{C(Ar)=C[P(=O)(OMe)₂]C=CDAr} in place of **14b-H** did not lead to any retention of deuterium.

4.5.7 X-ray Crystallographic Studies

Yellow single crystals of **13e-H**, **14b-H**, **12a**, and **15** suitable for diffraction analysis were grown by slow evaporation from hexane/dichloromethane solutions at 4 °C. The crystals selected were mounted on quartz fibers. X-ray data for **13e-H**, **14b-H**, **12a**, and **15** were collected at 103(2) K on a Bruker X8 APEX system, using Mo K α radiation, with the SMART suite of programs.¹⁰ The data were processed and corrected for Lorentz and polarization effects with SAINT,¹¹ and for absorption effects with SADABS.¹² Structural solution and refinement were carried out with the SHELXTL suite of programs.¹³ The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The organic hydrogen atoms were placed in calculated positions and refined with a riding model. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

Table 4.5. Crystal and refinement data for **13e-H**, **14b-H**, **12a**, and **15**.

Identification code	13e-H	14b-H	12a	15
Empirical formula	C ₄₄ H ₄₀ IrO ₂ P	C ₃₁ H ₄₁ IrO ₆ P ₂	C ₂₇ H ₂₇ IrO ₂	C ₃₁ H ₄₃ IrO ₇ P ₂
Formula weight	823.93	763.78	575.69	781.79
Temperature, K	103(2)	103(2)	103(2)	103(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a, Å	10.601(5)	11.7801(3)	15.8034(6)	17.0338(11)
b, Å	36.988(14)	15.2312(4)	15.3994(5)	14.9400(10)
c, Å	9.732(5)	17.4667(5)	19.6537(7)	12.7672(8)
α, deg	90	90	90	90
β, deg	114.944(16)	101.7775(13)	106.854(2)	100.5248(16)
γ, deg	90	90	90	90
Volume, Å ³	3460(3)	3067.99(14)	4577.5(3)	3194.4(4)
Z	4	4	8	4
Density (calculated), Mg/m ³	1.582	1.654	1.671	1.626
Absorption coefficient, mm ⁻¹	3.943	4.498	5.853	4.324
F(000)	1648	1528	2256	1568
Crystal size, mm ³	0.18 x 0.08 x 0.06	0.28 x 0.32 x 0.38	0.30 x 0.30 x 0.22	0.14 x 0.28 x 0.34
Reflections collected	58325	9864	108230	10252
Independent reflections	11019 [R(int) = 0.0738]	99.4%	9317 [R(int) = 0.0697]	6514 [R(int) = 0.1015]
Max. and min. transmission	0.7978 and 0.5371	0.3660 and 0.2800	0.3592 and 0.2726	0.5830 and 0.3320
Data / restraints / parameters	11019 / 0 / 438	9864 / 0 / 371	9317 / 0 / 551	6514 / 0 / 380
Goodness-of-fit on F ²	1.061	1.039	1.032	1.026
Final R indices [I>2σ(I)]	R1 = 0.0427, wR2 = 0.0842	R1 = 0.0281, wR2 = 0.0658	R1 = 0.0240, wR2 = 0.0515	R1 = 0.0281, wR2 = 0.0660
R indices (all data)	R1 = 0.0660, wR2 = 0.0916	R1 = 0.0388, wR2 = 0.0700	R1 = 0.0322, wR2 = 0.0547	R1 = 0.0352, wR2 = 0.0698
Largest diff. peak and hole (e.Å ⁻³)	1.518 and -2.009	1.448 and -2.435	2.251 and -0.816	1.137 and -1.091

4.6 References

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Chapter 5: Conclusion

As set out in Chapter 1, the initial aim of this project was to study the reductive elimination of $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})_2$ (**3a-H**) to $\text{Cp}^*\text{Ir}(\text{CO})(\text{PhC}\equiv\text{CC}\equiv\text{CPh})$ (**4a-H**), and the chemistry of the two species. In the course of those investigations, it was found that the formation of **3a-H** from the reaction of $[\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2]$ (**1a**) with PhCCLi (**2-H**) was more complex than it was originally assumed. The reaction appeared to proceed via the monoalkynyl $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}\equiv\text{CPh})\text{Cl}$ (**A**), which could then undergo attack by a second phenylacetylide to afford either the kinetic product **3a-H**, or an ionic complex $[\text{Cp}^*\text{Ir}(\text{COCl})(\text{C}\equiv\text{CPh})_2]^- \text{Li}^+$ (**B**), the latter eventually leading to the thermodynamic product **4a-H** (Scheme 5.1). This reaction pathway was studied computationally.

Scheme 5.1

The reductive elimination of **3a-H** to **4a-H** was found to be dependent on the solvent; it only occurred at an appreciable rate in a protic solvent such as methanol. The mechanism of the reductive elimination was investigated

experimentally and computationally, and the evidence suggested that the reductive elimination was mediated by the attack of methoxide ions at the CO ligand. Substitution at the phenyl ring of **3a-H** had little effect on the reductive elimination, while substitution of the ancillary CO with other two-electron donors effectively shut down the reductive elimination. The proposed reaction pathway is reminiscent of that above, i.e., the reductive elimination is accelerated by the formation of an anionic intermediate, **INT1** (Scheme 5.2). Presumably, the formation of such an intermediate brought the formal oxidation state of the metal centre closer to that of the product and constituted the driving force for the reductive elimination. Extension of this work to reductive elimination involving the formation of Csp-Csp² and Csp-Cp³ bonds awaits further investigation. It could be concluded that the reductive elimination was curiously accelerated by anions. We believe that this involved attack of the methoxide anion at the CO ligand and thereby effectively lowering the kinetic barrier. In many transition-metal catalysed reactions, the extraction of anions to form a catalytically-active species is an integral part of the catalytic cycle. What we have found here, therefore, suggest that these anions may not always behave as innocent spectators.

Scheme 5.2

The reactivity of the bis(alkynyl) complexes **3** were found to exhibit a common thread, which was initial protonation of an alkynyl ligand to form an alkenylidene. Nucleophilic attack at, or alkynyl migration to (which may be viewed as attack of an alkynide), the α -carbon of the vinylidene then occurred (Scheme 5.3).

Scheme 5.3

The reactivity of the diyne species **4**, on the other hand, revolved around the metal-bound alkyne moiety (Scheme 5.4). This behaviour resembled that of simpler metal-bound alkynes in that binding of the alkyne to the metal centre activated it, except that the close proximity of a second alkyne moiety resulted in reactions involving the latter as well.

Scheme 5.4