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The Reaction of $[\text{Cp}^*\text{RhCl}_2]_2$, Aniline and a Terminal Alkyne - Formation of Cyclometallated Rhodium(III) Complexes

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Abstract: The reaction of $[\text{Cp}^\text{RhCl}_2]_2$ with an aniline ($\text{R}'\text{NH}_2$) and a terminal alkyne (RCCH) afforded the N-containing cyclometallated rhodium complexes $\text{Cp}^*\text{Rh}(\text{Cl})[\text{N}(\text{R}')=\text{C}(\text{CH}_2\text{R})\text{CH}=\text{CR}]$ via a hydroamination and a 1,2-insertion of an alkyne. A reaction pathway has been proposed on the basis of deuterium labelling experiments and computational studies.*

Introduction

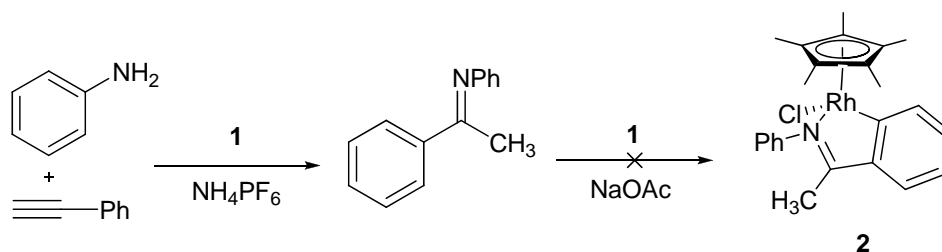
N-containing cyclometallated compounds have been the focus of much attention in the last few decades,¹ due to their interesting reactivity in C–C bond forming reactions.² More specifically, cyclometallated compounds which incorporate an internal imine functionality are proposed as intermediates in a number of organic transformations.³ Cyclometallated rhodium complexes which include a nitrogen donor atom are known to possess excellent photoreduction property,⁴ and reactivity towards C–H bond functionalization reactions,⁵ and have also been screened recently as catalysts for the transfer hydrogenation of ketones and imines.⁶ The syntheses of such complexes have included transmetallation,⁷ condensation of keto metallacyclic complexes with amines,⁸ and ortho C–H activation of the corresponding aromatic imine,⁹ or amine.¹⁰ In contrast, such N-containing cyclometallated complexes with Cp^*Rh ($\text{Cp}^* =$ pentamethylcyclopentadienyl) have, with possibly one exception,¹¹ involved acetate-assisted orthometallation of an imine, pyridine or related species.^{5a-b,12}

In an earlier study, we have found that $[\text{Cp}^*\text{RhCl}_2]_2$, **1** catalyses the hydroamination of terminal alkynes with anilines to afford ketimines.¹³ Since **1** can effectively cyclometallate

aromatic imines in the presence of acetate, we thought that the two separate steps may be combined to yield N-containing cyclometallated rhodium complexes in a single step. To the best of our knowledge, there is only one report of a similar strategy, which involves the single step synthesis of alkenyl ketone rhodium complexes using water and phenylacetylenes.¹⁴ We wish to report here our attempt at this.

Results and discussion

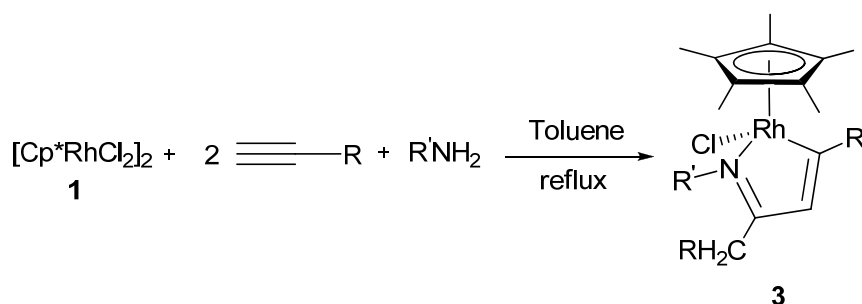
As mentioned above, we thought that a one-pot reaction of **1**, aniline and phenyl acetylene (PhCCH) may possibly lead to an N-containing cyclometallated rhodium complex via the formation and orthometallation of a ketimine (Scheme 1).



Scheme 1

We have found, however, that the reaction in the presence of additives (KPF₆ and CH₃COONa) failed to give **2**. Instead, cyclometallated rhodium complexes **3** were obtained, without any additive, in 60-70% isolated yields (Scheme 2). The overall reaction requires an alkyne hydroamination as well as a 1,2-insertion of an alkyne. Typically, ten equivalents of the alkyne is required; use of four equivalents gave incomplete reaction and the aniline adduct [Cp**Rh*Cl₂NH₂R'] (**4**).¹³ A change of the solvent (to THF or DCE) did not give any improvement in yield, and the reaction failed to proceed at ambient temperature. Both electron-donating and -withdrawing substituents on the alkyne and the aniline are tolerated, and the reaction proceeded smoothly with aliphatic amines as well. Attempts at extending the substrate scope to aliphatic alkynes (1-hexyne and 1-octyne) and internal alkynes

(diphenylacetylene and 1-phenyl-1-propyne) were unsuccessful; only the corresponding analogues of **4** were obtained.



	R	R'	Yield (%)
a	Ph	Ph	68
b	Ph	4-CH ₃ C ₆ H ₄	70
c	Ph	4-CH ₃ OC ₆ H ₄	72
d	Ph	4-ClC ₆ H ₄	60
e	Ph	4-BrC ₆ H ₄	67
f	Ph	CH ₂ Ph	62
g	Ph	C ₃ H ₁₁	55

	R	R'	Yield (%)
h	3-CH ₃ C ₆ H ₄	Ph	64
i	4-CH ₃ C ₆ H ₄	Ph	63
j	4-CH ₃ OC ₆ H ₄	Ph	69
k	4-ClC ₆ H ₄	Ph	71
l	4-BrC ₆ H ₄	Ph	63
m	3-CH ₃ C ₆ H ₄	4-CH ₃ OC ₆ H ₄	69
n	4-CH ₃ C ₆ H ₄	4-CH ₃ OC ₆ H ₄	64
o	4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	66

Scheme 2

The products **3** have all been characterised spectroscopically and analytically, and the structures of **3c**, **3k** and **3l** have been confirmed by single crystal X-ray diffraction studies; the quality of the structural determination for **3k** is significantly poorer than that of the other two. An ORTEP plot for **3c** is shown in Figure 1, and a common atomic numbering scheme with selected bond parameters for **3c**, **3k** and **3l** are collected in Table 1.

Similar cyclometallated rhodium complexes which have been structurally characterised include [Cp*RhCl{C₆H₄-2-C(H)=N(CH₂)₂OCH₃-κC,N}] (**5a**) and [Cp*RhCl{C₆H₄-2-C(H)=NPh-κC,N}] (**5b**).^{12f} The Rh-N bond lengths (~2.093 Å for **3** vs 2.089(2) and 2.115(3) Å for **5a** and **5b**, respectively) and the chelate bite angle (~78° vs 78.73(7)° and 78.33(12)° for **5a** and **5b**, respectively) are similar to these related Cp*Rh cyclometallated complexes. Although the Rh-C(3) bond lengths in **3** are not significantly shorter than those in **5a** and **5b** (2.027(2) Å and 2.032(3) Å, respectively), the C(1)-N and

C(2)-C(3) bond lengths appear to have significant double bond character. In fact, the C(2)-C(3) bond (~ 1.35 Å) are significantly shorter than the corresponding bond in **5a** and **5b** (1.407(3) and 1.399(5) Å, respectively) even though this is part of an aromatic ring in the latter compounds. Consistent with this are the C1-N-C(Ar') and C1-C2-C3 bond angles, which are indicative of sp^2 hybridisation at the N and C(2) atoms. Although an NBO analysis on **3a** and **5b** did not show any difference in the bond order (Wiberg bond index), the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the complexes **3** exhibited a doublet resonance at ~ 216 ppm for C(3), typical of a carbene carbon, in contrast to the ~ 184 ppm reported for **5**. Thus there is considerable carbene character in the Rh-C bond of **3**, and delocalisation of the π -electrons within the 5-membered metallacycle. Presumably, the difference between **3** and **5** lies in the fused aromatic ring system to the metallacycle in the latter, which tends to localise the π -electron density within the aromatic ring.

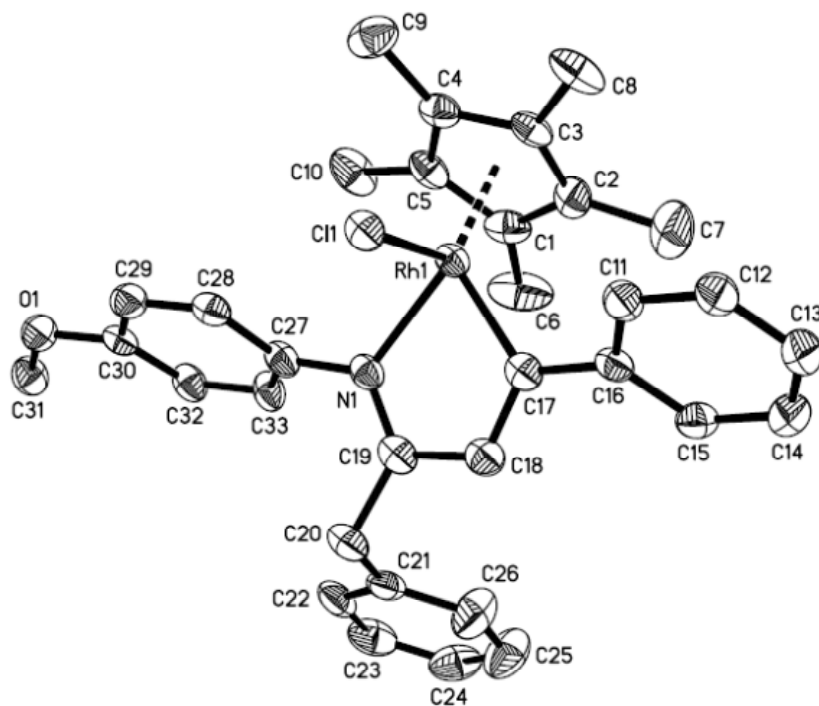
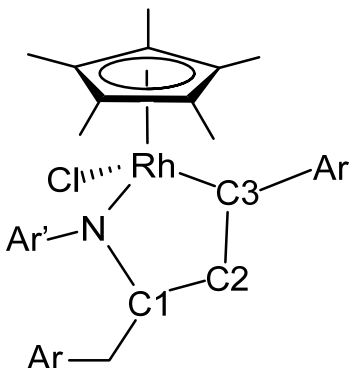


Figure 1. ORTEP plot of **3c**. All H atoms have been omitted, and only one orientation of the disordered benzyl group is shown. Thermal ellipsoids are plotted at the 50% probability level.

Table 1. Common atomic numbering scheme and selected bond lengths (Å) and angles (°) for **3c**, **3k** and **3l**.

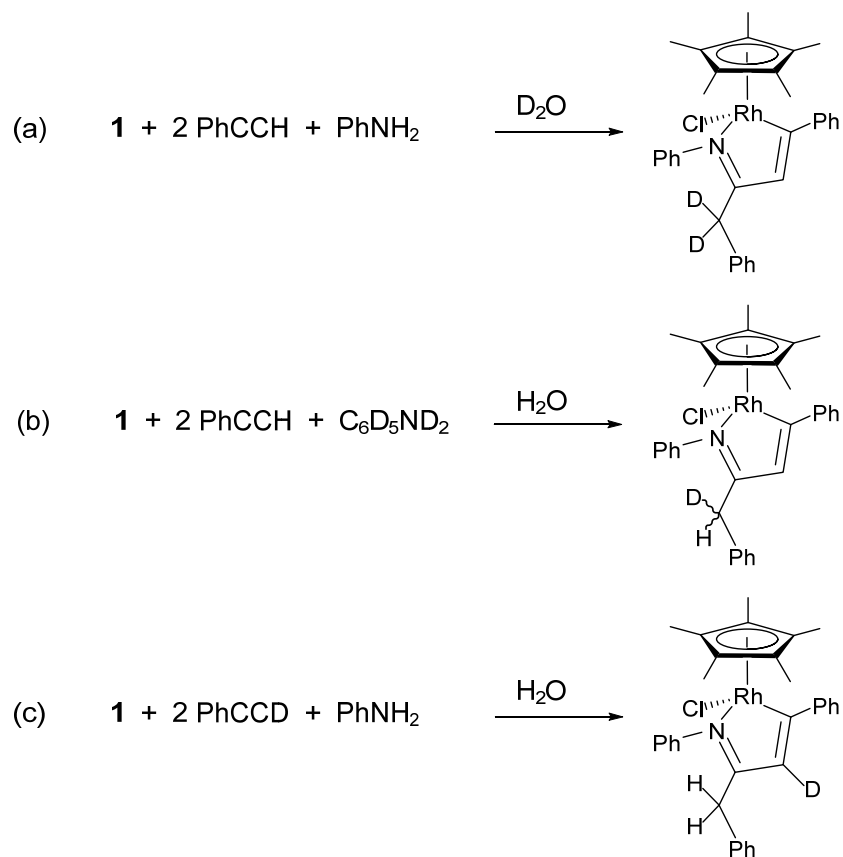


Bond parameter	3c	3k	3l
Rh-Cl	2.4036(10)	2.399(2)	2.3910(8)
Rh-N	2.093(4)	2.096(7)	2.093(3)
Rh-C3	2.012(4)	2.036(8)	2.021(3)
N-C1	1.303(5)	1.301(10)	1.301(4)
N-C(Ar')	1.430(5)	1.432(11)	1.434(3)
C1-C2	1.433(6)	1.452(12)	1.439(5)
C2-C3	1.357(6)	1.347(12)	1.354(5)
N-Rh-C3	78.14(15)	78.7(3)	78.48(12)
C1-N-C(Ar')	121.4(5)	122.6(7)	122.5(3)
C1-C2-C3	117.1(4)	117.0(7)	116.3(3)

Mechanistic considerations

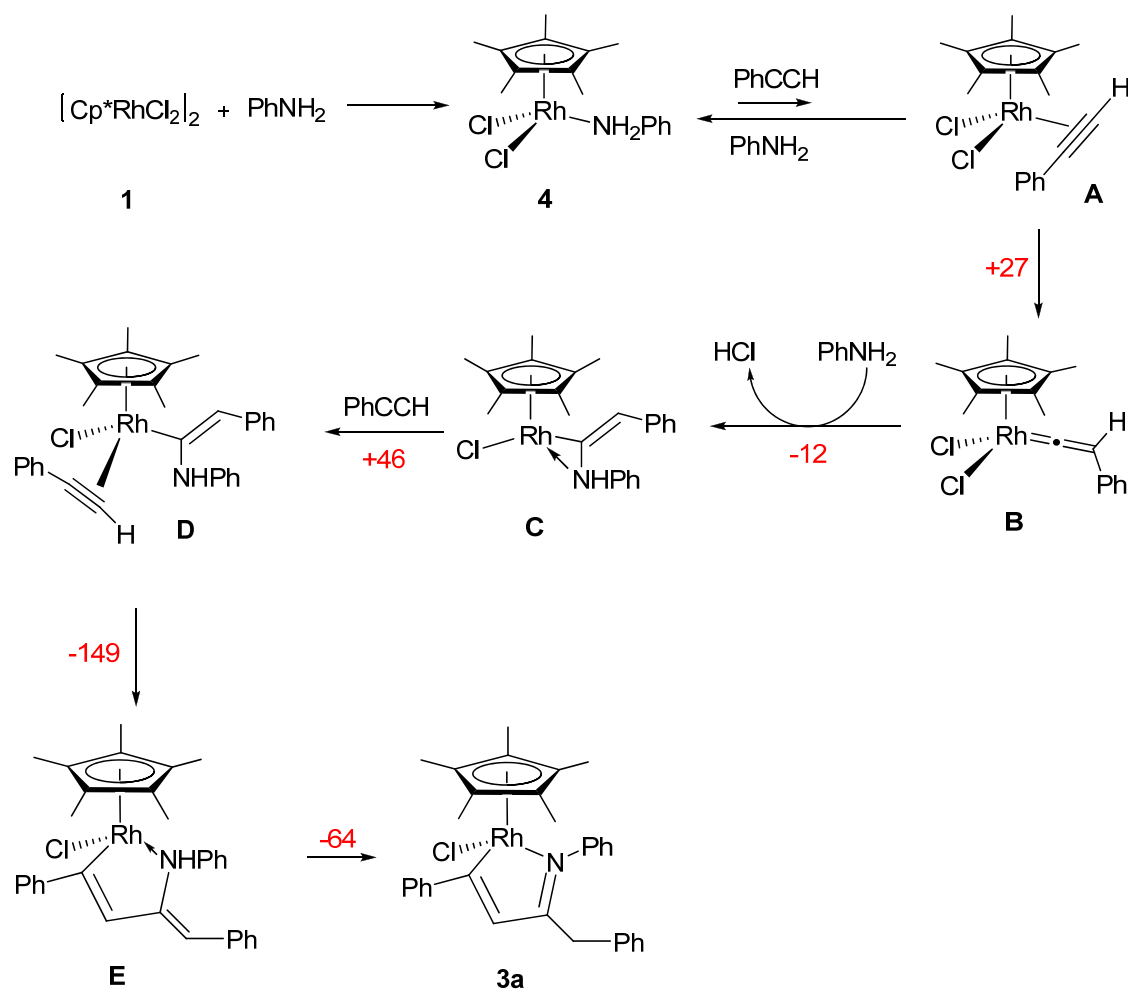
The reactions afforded **4** in the absence of a large excess of the alkynes, and **4** was also obtained in good yields from the reaction of aniline with **1**. With excess alkynes, **4** formed **3** in similar yields to the one-pot reaction. Isotopic labelling experiments employing (a) aniline and PhCCH in the presence of D₂O, (b) *d*₇-aniline and PhCCH, and (c) aniline and PhCCD, yielded **3a** with both, one and none, respectively, of the diastereotopic CH₂ protons being deuterated (Scheme 3). These results are consistent with the source for each of these protons being water and aniline. In case (c), the alkenic CH of the metallacycle was also

deuterated. A proposed reaction pathway that accounts for these observation is shown in Scheme 4; the energetics for the various steps (for aniline and phenylacetylene) have also been computed with density functional theory, and the computed energies (ΔG^\ominus , in kJ mol^{-1}) from **B** onwards are also given.



Scheme 3

Presumably, in the presence of an excess of the appropriate alkyne, the coordinated aniline in the initial reaction product **4** is replaced. The alkyne species **A** rapidly rearranges to the vinylidene complex **B** via an intermolecular 1,3-H shift. The enamine intermediate **C** is formed by nucleophilic attack of aniline at the vinylidene α -carbon atom and HCl elimination; this is consistent with our earlier proposed pathway for the alkyne hydroamination reaction.¹³ In the intermediate **C**, the N atom of the enamine is also bonded to the metal centre; this lies $\sim 2 \text{ kJ mol}^{-1}$ below the alternative in which the N atom is not bound.

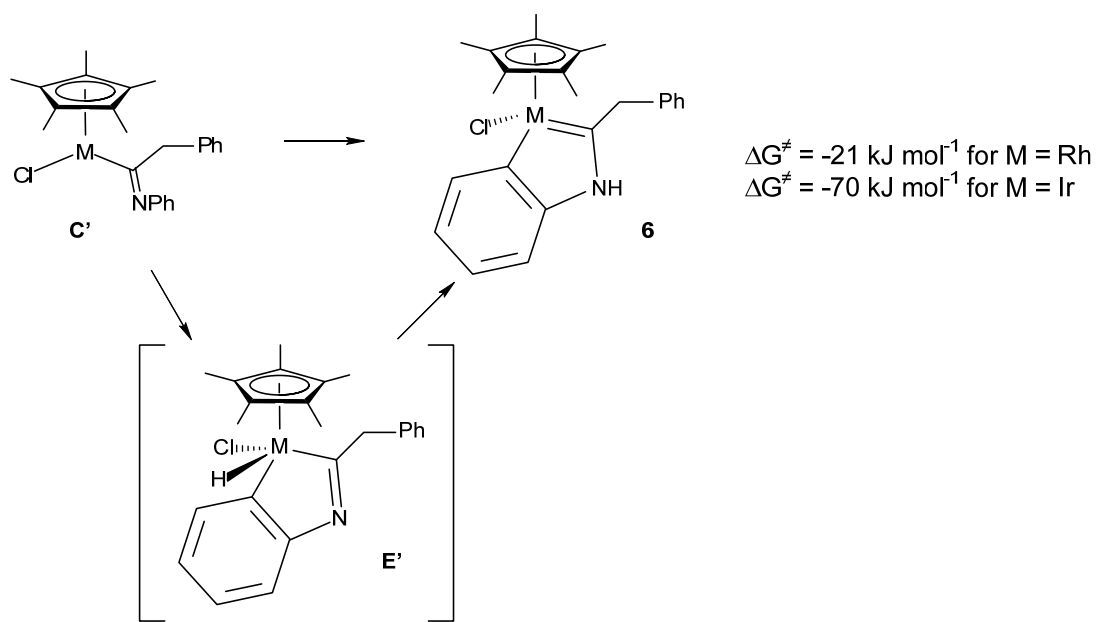


Scheme 4

The steps from **C** through to the final product **3a** involves a *I,2*-insertion of an alkyne, an enamine-imine tautomerisation and binding of the N atom to Rh forming the metallacycle. There are several alternatives for this sequence of events, including pathways involving a 4-membered metallacycle from **B**,¹⁵ but we have found that these structures which formally contain a Rh(V) centre could not be optimised (see also below). The sequence depicted starts with a *I,2*-insertion and metallacycle formation from **C** to **E**, with a ΔG^\ddagger of -103 kJ mol^{-1} ; the presumed intermediate with the alkyne coordinated (**D**) lies $+46 \text{ kJ mol}^{-1}$ above **C**. The binding of the alkyne in **D** shows asymmetry, as has been observed earlier for a closely-related system.¹³ The deuterium labelling experiment (c) above shows that the $\equiv\text{C-H}$ bond is not cleaved in the insertion step. The final step is an enamine to imine tautomerisation, which

has been shown to involve an intramolecular 1,3-H shift,¹⁶ and is consistent with the labelling experiment (b). The free energy for this step is quite exergonic, larger than what may be expected from the enamine-imine tautomerisation. It therefore suggests that a major contribution arises from delocalisation of the electron density within the metallacycle. Although no kinetic barriers were computed, the negative or small computed energies involved in the steps suggest that the proposed reaction pathway is reasonable.

One further aspect of this reaction which intrigued us is that although the alkyne insertion step is overall exergonic from **C** to **E**, it does not appear clear why **C** (or its tautomer **C'**) could not have undergone cyclometallation to an aminocarbene, as we have observed in a similar reaction with the iridium analogue of **1**, viz., [Cp*IrCl₂]₂, **1a**.¹⁷ Indeed, such a reaction from **C'** to **6** is computed to have a ΔG° of -21 and -70 kJ mol⁻¹ for rhodium and iridium, respectively, with the same model chemistry (Scheme 5). The difference in the reaction pathway taken is thus not clear from the energetics. We believe that the difference lies in the inability of **C** (or **C'**) to undergo oxidative addition when M = Rh. We assume that this step proceeds through **E'**, which would require the formation of an unfavourable Rh(V) species; our attempts at optimisation of a structure **E'** for M = Rh invariably failed. This may also be the reason why the reaction to **2** failed. In contrast, the computed ΔG° from **C'** to **E'**, and from **E'** to **6** for M = Ir are +56 and -126 kJ mol⁻¹, respectively.



Scheme 5

Concluding remarks

In this study we have reported that N-containing cyclometallated rhodium complexes **3** can be obtained efficiently in a one-pot reaction involving the dirhodium complex **1**, an aniline and a terminal alkyne. The reaction pathway has been studied experimentally via labelling experiments, as well as computationally, and we believe that the difference between **1** and its iridium analogue **1a** lies in the reduced tendency for rhodium to orthometallate via a Rh(V) species.

Experimental Section

General. All reactions and manipulations, except for TLC separations, were performed under argon by using standard Schlenk techniques. The starting material **1** was prepared according to the published method.¹⁸ All other chemicals were from commercial sources and used as supplied without further purification. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 on a JEOL ECA400 or ECA400SL spectrometer and were referenced to residual solvent resonances. FAB mass and high resolution mass spectra (HRMS) were recorded in ESI mode

on a Thermo Finnigan Mat95XP and Waters UPLC-Q-TOF mass spectrometers respectively. Elemental analyses were performed by the microanalytical laboratory in NTU.

Reaction of 1 with alkyne and aniline. In a typical reaction, to a solution of **1** (40 mg, 64 μmol) and phenylacetylene (130 μL , 20-fold excess) in 1,2-dichloroethane (4 mL) was added aniline (12 μL , 100 μmol). The reaction mixture was then stirred at reflux overnight. The solvent was then removed under reduced pressure and the residue obtained was dissolved in the minimum amount of dichloromethane for chromatographic separation on silica gel TLC plates. Elution with hexane/ethylacetate (4:1, v/v) yielded **3a** as a yellow solid.

Similar procedures were used with the other alkynes and anilines, and these are given in the Supporting Information.

Crystallographic studies. Diffraction quality crystals were grown either by slow diffusion of hexane into a dichloromethane solution (**3c** and **3l**) or by slow cooling from MeOH (**3k**), and then mounted onto quartz fibres. X-ray data were collected on a Bruker X8 APEX system, using Mo K α radiation, with the SMART suite of programs.¹⁹ Data were processed and corrected for Lorentz and polarisation 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. Hydrogen atoms were placed in calculated positions and refined with a riding model. The crystal of **3c** exhibited disorder of the benzyl group, which was modelled with two alternative sites, with occupancies summed to unity. A disordered methanol solvate was found in the crystal of **3k**. This was modelled with two alternative sites, with their occupancies summed to unity. Appropriate restraints on the bond and thermal parameters were placed on the disordered parts. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

Computational studies. The reaction energetics were studied using DFT theory utilising the Becke's three parameter hybrid function²³ and Lee-Yang-Parr's gradient-corrected correlation function²⁴ (B3LYP). The LanL2DZ (Los Alamos Effective Core Potential Double- ζ) basis set together with polarisation functions are employed for the Rh atom, and the 6-311+G(2d,p) basis set for all the other atoms. Spin-restricted calculations were used for geometry optimization, and harmonic frequencies were then calculated to characterize the stationary points as equilibrium structures with all real frequencies, and to evaluate zero-point energy (ZPE) corrections. Bond order analysis was carried out with the NBO program implemented within Gaussian 03W.²⁵ All calculations were performed using the Gaussian 03 suite of program.²⁶

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Supporting Information Available: Crystallographic data in CIF format, experimental details and characterisation for the complexes, and details of deuterium labelling experiments. Ordering information is given on any current masthead page.

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