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Tetraphenylcyclopentadienyl rhodium complexes in stoichiometric and catalytic CH functionalization

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ABSTRACT

The use of $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ for stoichiometric and catalytic CH functionalization has been evaluated. For the substrates studied, CH activation, alkyne insertion and CN reductive elimination are all possible at room temperature, similar to corresponding reactions with $[RhCl_2(\eta\text{-}C_5Me_5)]_2$. The tetraphenylcyclopentadienyl ligand shows promise for controlling regioselectivity in catalytic CH functionalization.

1. Introduction

In recent years there has been a surge of interest in carboxylate assisted CH activation reactions particularly with Pd, Rh, and Ru catalysts [1–9]. The vast majority of Rh catalysts involve a pentamethylcyclopentadienyl (Cp*) ligand. However in the last few years there have been a number of examples with other substituents to tune the steric and electronic properties of the metal e.g. Fig. 1.

The ligands (**A**-**I**) in Fig. 1 include ones with bulky alkyl-substituents (**C**, **D**) [10–14] and ones with electron withdrawing ester (**A**) [15–17] or trifluoromethyl (**B**) [18,19] groups. Other examples contain fused rings (**E**, **H**) [20,21], and a heptamethylindenyl (**F**) has also been used [22]. The use of bulky chiral ligands has also been reported (**I**) [23]. Changing the substituents can have a beneficial effect on the catalysis in terms of both yield and selectivity [10,16,24] and some examples are shown in Fig. 2. Rovis et al. have recently used experimental and computational data to correlate reactivity and selectivity for substituted cyclopentadienyl Rh complexes in catalytic CH activation reactions [14]. However, in contrast to alkyl and ester groups there has been almost no work on aryl substituted cyclopentadienyl complexes (**G**). Notably, Miura reported that addition of tri- or tetra-phenyl substituted cyclopentadiene to reactions of phenyl pyrazole and diaryl alkynes catalyzed by $[RhCl_2(\eta\text{-}Cp^*)]_2$ led to improved yields of tetraarylnaphthalene products [1]. However, there was no information on the exact role of these dienes in the reactions. Here we report some stoichiometric and catalytic studies using $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ and make comparisons with $[RhCl_2(\eta\text{-}Cp^*)]_2$.

2. Results and discussion

The dimer $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ was synthesized in good yield by reaction of $C_5Ph_4H_2$ with $RhCl_3$ in an analogous method to the preparation of $[RhCl_2(\eta\text{-}Cp^*)]_2$ [25]. The ease of carboxylate assisted CH activation with $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ was tested by reaction with 1-phenylpyrazole and 2-phenylpyridine in the presence of NaOAc. These gave good yields of the cyclometallated products **1** and **2** respectively (Scheme 1).

The complexes show the expected signals in the ^1H NMR spectra. The presence of the four aryl groups means there is a lot of signal overlap in the aromatic region however the pyrazole signals in **1** are easily visible at δ 7.94, 7.70 and 6.42, and the proton next to the nitrogen of the pyridine in **2** is at δ 8.74. The single cyclopentadienyl proton is observed at δ 5.79 and 5.84, in **1** and **2** respectively.

Complex **2** was further characterised by X-ray crystallography and the structure is shown in Fig. 3. The Rh—N and Rh—C bond distances to the cyclometallated ligand [2.063(2) and 2.019(2) Å respectively] are slightly shorter than those [2.099(3) and 2.035(3) Å respectively] found in the related Cp* complex [26]. The C_5Ph_4H ligand is coordinated in a noticeable η^3-η^2 fashion. The bond lengths range from 2.139(2) Å [Rh—C(1)] to 2.316(2) Å [Rh—C(3)] with the shortest bond being to the CH carbon possibly for steric reasons, and the longest being Rh—C(3) and Rh—C(4) since these are *trans* to the cyclometalated carbon. In the corresponding Cp* complex the Rh—C(Cp*) bond lengths vary over a shorter range, from 2.159(3) to 2.262(3) Å.

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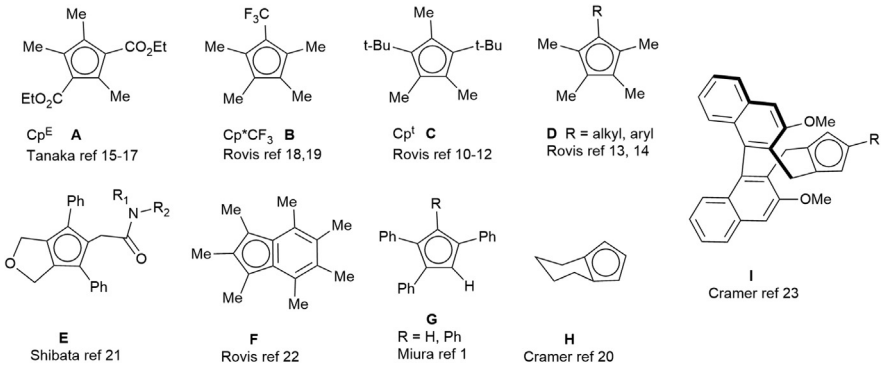


Fig. 1. Examples of substituted Cp ligands used in Rh(III) catalyzed CH activation.

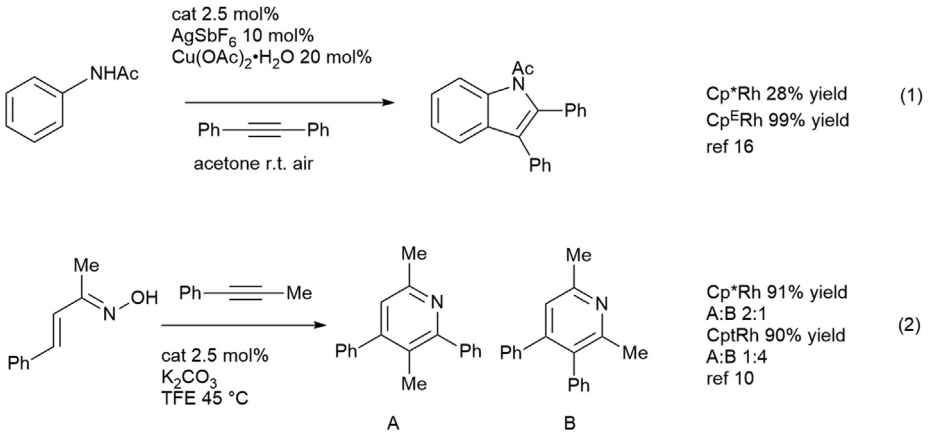
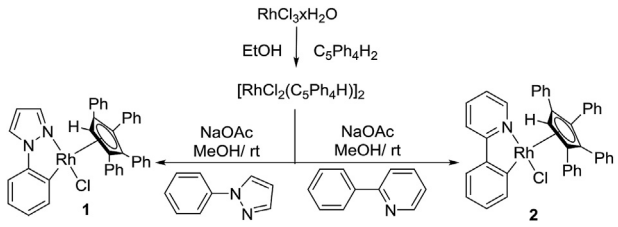


Fig. 2. Examples of the effect of Cp ligands in Rh(III) catalyzed CH activation.



Scheme 1. Synthesis of cyclometallated complexes.

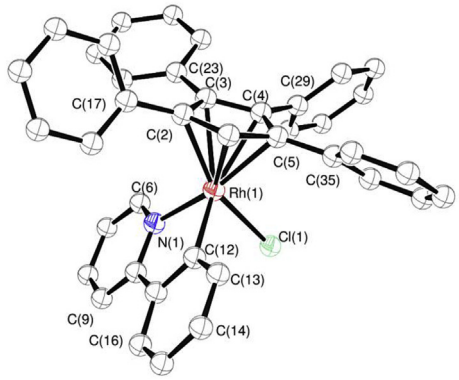


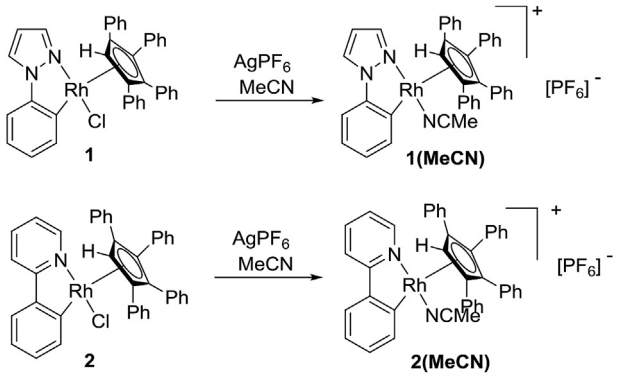
Fig. 3. Molecular structure of **2** hydrogen atoms are omitted for clarity; ellipsoids are set at 50%, with selected bond lengths (Å), Rh(1)—C(1) 2.139(2), Rh(1)—C(2) 2.172(2), Rh(1)—C(3) 2.316(2), Rh(1)—C(4) 2.291(2), Rh(1)—C(5) 2.173(2), Rh(1)—C(12) 2.019(2), Rh(1)—N(1) 2.063(2).

Next we investigated the reactivity of these complexes with respect to alkyne insertion. We have previously reported that such reactions are much faster if the chloride is replaced by MeCN [27]. Hence complexes **1** and **2** were converted to **1(MeCN)** and **2(MeCN)** respectively by reaction with $AgPF_6$ in MeCN (Scheme 2).

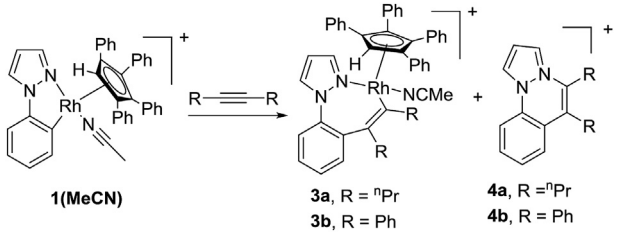
Complexes **1(MeCN)** and **2(MeCN)** were characterised in solution by NMR spectroscopy and mass spectrometry. The cyclopentadienyl proton being observed at δ 6.13 and 6.32 in **1(MeCN)** and **2(MeCN)** respectively. These signals are downfield by 0.3 and 0.5 ppm respectively from the neutral precursors as expected from forming a cationic complex. The coordinated MeCN molecules could also be observed in both cases.

Complexes **1(MeCN)** and **2(MeCN)** were then reacted with alkynes (Schemes 3 and 4 respectively). In each case two products are possible, the 7-membered ring products (**3** and **5**) formed by alkyne insertion and the heterocyclic cations (**4** and **6**) which are formed subsequently by reductive elimination. We have shown previously that the stability of the 7-membered ring complexes with a Cp^* ring is solvent dependent, loss of the monodentate ligand facilitating reductive elimination to form cationic heterocycles [28].

In the case of the reaction of **1(MeCN)** with 4-octyne in CD_2Cl_2 (Scheme 3) the initially formed product is almost exclusively **3a**, there is no starting material left as soon as the spectrum is run (within 15 min) so the initial alkyne insertion is relatively fast. The cyclopentadienyl proton experiences a significant shift upfield moving from δ 6.13 in **1(MeCN)** to δ 3.62 in **3a**. A similar, though smaller, upfield shift for the Me groups of the Cp^* group in the corresponding 7-membered ring complex has been reported previously and was attributed to a ring current from the C_6H_4 of the



Scheme 2. Formation of cationic (MeCN) complexes.



Scheme 3. Reaction of **1(MeCN)** with alkynes.

originally cyclometallated ligand [27,29]. This interaction is confirmed in the X-ray structure of **5b** (see below). Complex **3a** decomposes slowly in solution via C—N reductive elimination to form **4a**; after 24 h 32% of **4a** is formed. This is somewhat slower than in the case of the Cp* complex which gives 100% **4a** after 24 h. Note, in no cases were we able to isolate any Rh-containing products which might arise from the reductive elimination of the heterocyclic products **4**.

A similar result was found in the reaction of **1(MeCN)** with diphenylacetylene. In this case, in the ^{1}H NMR spectrum the cyclopentadienyl proton is observed at δ 4.21 consistent with formation of **3b**. This was more stable in solution than **3a**, after 24 h only a small amount (approximately 3%) of a second compound believed to be **4b** [30] was observed in the ^{1}H NMR spectrum. After 4 days the amount of **4b** had risen to 10%. For the corresponding reaction with the Cp* complex no reductive elimination was observed.

The same reactions were performed with phenylpyridine complex **2(MeCN)** (Scheme 4). The ^{1}H NMR spectrum of the reaction of

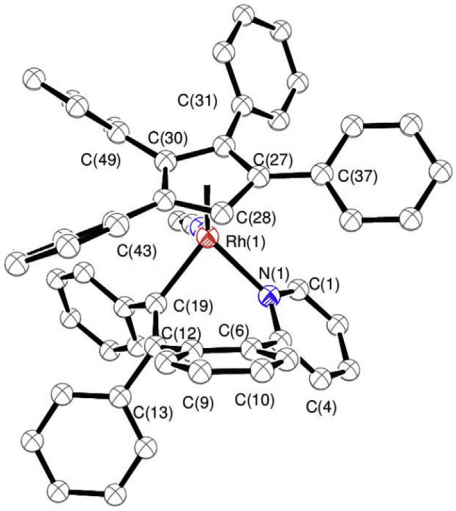
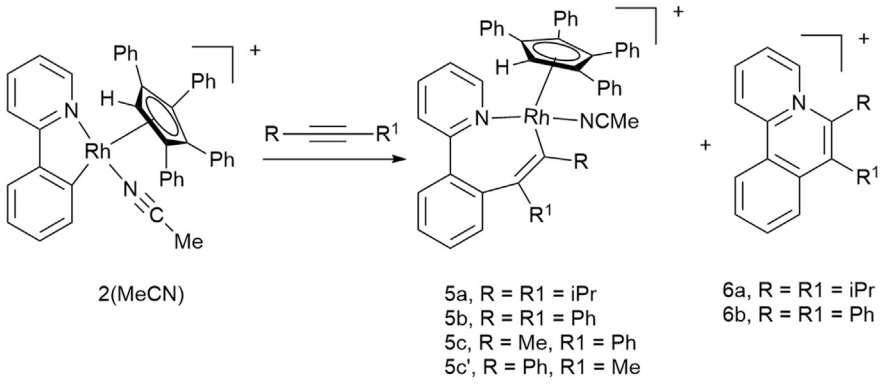


Fig. 4. Molecular structure of the cation of **5b** hydrogen atoms are omitted for clarity; ellipsoids are set at 50% with selected bond lengths (Å). Rh(1)-C(19) 2.076(3), Rh(1)-N(1) 2.123(3), Rh(1)-C(26) 2.268(3), Rh(1)-C(27) 2.284(3), Rh(1)-C(28) 2.157(3), Rh(1)-C(29) 2.213(3), Rh(1)-C(30) 2.187(3).

2(MeCN) with 4-octyne after 30 min showed a mixture of **5a** and **6a** (1:1) with no **2(MeCN)** remaining. The cyclopentadienyl proton of **5a** was observed at δ 3.40. After only 3.5 h the mixture had converted to **6a** (more than 90%). Under similar conditions the corresponding Cp* complex is more stable and has only converted to 30% of **6**a after 15 days. For the reaction of **2(MeCN)** with diphenylacetylene the initial ^{1}H NMR spectrum after 45 min showed mostly **5b** (90%) and a small amount of **6b** (10%). After 3 days more **5b** had converted to **6b** leaving a **5b**:**6b** ratio of 1:2.

Complex **5b** was sufficiently stable that it could be crystallised and the structure was determined by X-ray crystallography (Fig. 4). The Rh—N and Rh—C bond distances to the cyclometallated ligand [2.123(3) and 2.076(3) Å respectively] are slightly longer than those [2.063(2) and 2.019(2) Å respectively] in **2** described above. This may be due to the distortions enforced by the 7-membered ring. As can be seen the cyclopentadienyl ring lies above the originally cyclometallated phenyl which gives rise to a ring current causing the upfield shift of the cyclopentadienyl proton (δ 3.91). The C_5Ph_4H ligand is again coordinated in an η^3-η^2 fashion. The three shorter bond lengths range from 2.157(3) Å [Rh—C(28)] to 2.213(3) Å [Rh—C(29)] with the shortest bond again being to the CH carbon, the longer bonds Rh—C(26) and Rh—C(27) [2.268(3) and 2.284(3) Å respectively] being *trans* to the cyclometalated carbon.



Scheme 4. Reaction of **2(MeCN)** with alkynes.

The reaction of **2(MeCN)** with 1-phenylpropyne was also examined to investigate the regioselectivity of alkyne insertion. The reaction was carried out in d3-acetonitrile to try and hinder reductive elimination. The ^{1}H NMR spectrum showed the presence of two species in an approximately 5:1 ratio. Detailed nOe experiments showed an nOe between the Me of the alkyne and the single proton of the cyclopentadienyl ligand in the major isomer. Therefore the major isomer is assigned as **5c** with the Me next to Rh. This is the opposite regioselectivity normally seen for alkyne insertion with Cp*Rh complexes [10,31–33].

We have recently reported the catalytic synthesis of heterocyclic cations **4a** and **6a** from 4-octyne and 1-phenylpyrazole or 2-phenylpyridine respectively using $[RhCl_2(\eta\text{-}Cp^*)]_2$ as a catalyst in polar solvents [28]. Hence, we tested $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ as a catalyst for the same transformations. Reaction of phenylpyrazole and 4-octyne gave product **4a** in only 19% yield this contrasts with a yield of 88% using $[RhCl_2(\eta\text{-}Cp^*)]_2$ as catalyst. This may reflect the increased barrier to CN reductive elimination in **3a** mentioned above.

To test the effect of the sterically bulky C_5Ph_4H ligand on regioselectivity we examined the pyridine synthesis reported by Rovis (reaction 2 Fig. 2) [10]. Rovis found that product **A** arising from alkyne insertion with the Ph substituted end next to the metal was favoured with a Cp*Rh catalyst. This is the most common selectivity in alkyne insertion reactions with this catalyst. However, use of the more sterically bulky Cp^{t}Rh catalyst gave the opposite regioselectivity [10]. Hence, we repeated this reaction with $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ as a catalyst and were pleased to find a high yield (>90% conversion and 75% isolated yield) and good regioselectivity, A:B = 1:3.2. This is very similar to Rovis's result with Cp^{t}Rh catalyst i.e. insertion is favoured with the methyl group next to the metal rather than Ph as with $[RhCl_2(\eta\text{-}Cp^*)]_2$ as catalyst.

In Miura's original publication [1] tri or tetraarylcyclopentadiene was added to the reaction with $[RhCl_2(\eta\text{-}Cp^*)]_2$ as catalyst. We have investigated whether exchange of Cp ligands is possible. Thus reaction of $[RhCl_2(\eta\text{-}Cp^*)]_2$ with tetraphenylcyclopentadiene was attempted in DMF. After heating at 80 °C for 1 h the ^{1}H NMR spectrum showed evidence for a singlet at δ 6.4 consistent with formation of $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ the conversion increased to 25% after 6 h. Hence, it is clear that exchange of Cp ligands can occur under the conditions of catalysis. Indeed reaction of 1-phenylpyrazole with diphenylacetylene with $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ as catalyst gave conversion to the tetraphenylnaphthyl pyrazole as found previously by Miura [1].

3. Conclusions

$[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ is easily synthesized by reaction of $RhCl_3$ with $C_5Ph_4H_2$. In addition it can be formed by Cp exchange from $[RhCl_2(\eta\text{-}Cp^*)]_2$ under catalytic conditions. As for $[RhCl_2(\eta\text{-}Cp^*)]_2$, $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ undergoes acetate assisted CH activation and subsequent reactions with alkynes under mild conditions. In stoichiometric reactions with phenylpyrazole and phenyl pyridine some steps were faster with $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ compared to $[RhCl_2(\eta\text{-}Cp^*)]_2$, whilst others were slower suggesting that electronic and steric factors may balance out. In the catalytic formation of cationic heterocycles the overall catalytic efficiency with $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ was significantly reduced from Cp*. However, in the synthesis of pyridines the sterically crowded nature of the four aryl substituents gave comparable activity to Cp* but with opposite regioselectivity. Hence it is difficult to generalize about the relative reactivity of $[RhCl_2(\eta\text{-}Cp^*)]_2$, and $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$. The structural parameters suggest that for cyclometallated complexes the C_5Ph_4H ligand coordinates in a less symmetrical fashion (more η^3-η^2 rather than η^5) compared to Cp* and therefore may be more successful in reactions where ring-slippage is involved in the mechanism.

4. Experimental

4.1. General considerations

Unless stated otherwise all reactions were carried out under a nitrogen atmosphere, work up was carried out in air. Electrospray (ESI) mass spectra were recorded using a micromass Quattra LC mass spectrometer with acetonitrile as the solvent. NMR spectra were recorded on a Bruker DRX400 spectrometer operating at 400 (^{1}H) and 100 MHz (^{13}C) or a Bruker DRX500 spectrometer at 500 (^{1}H) and 125 MHz (^{13}C) at 298 K; chemical shifts (ppm) are referred to the residual protic solvent peaks and coupling constants are expressed in Hertz (Hz). Assignments of ^{1}H NMR and ^{13}C NMR signals were made where possible, using NOESY, HSQC, HMBC and DEPT experiments. All starting materials were obtained from Sigma Aldrich, or Alfa Aesar, and used without further purification.

4.1.1. Preparation of $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$

To a 100 mL 3 necked round bottom flask equipped with a stirrer bar and reflux condenser rhodium trichloride (300 mg, 1.4 mmol) and tetraphenylcyclopentadiene (518 mg, 1.4 mmol) 2-methyl-2-butanol (30 mL) and HCl (2 M, 1 mL) were added and the subsequent suspension was heated at reflux for 16 h. After cooling to room temperature, the red suspension was filtered and the solid was washed with diethyl ether (3 × 10 mL). The solid was redissolved in dichloromethane (20 mL) and the product was precipitated by the addition of hexane. The product was isolated by filtration as a dark red solid; yield: 454 mg (59%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.55–7.54 (m, 4H, $C_{Ar}H$), 7.47–7.42 (m, 6H, $C_{Ar}H$), 7.34–7.31 (m, 2H, $C_{Ar}H$), 7.28–7.25 (m, 4H, $C_{Ar}H$), 7.20–7.16 (m, 4H, $C_{Ar}H$), 6.38 (brs, 1H, C_5Ph_4H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 132.4 ($C_{Ar}H$), 131.8 ($C_{Ar}H$), 130.7 ($C_{Ar}H$), 129.7 ($C_{Ar}H$), 128.7 (C_{Ar}), 128.6 (C_{Ar}), 121.5 ($C_{Ar}H$), 101.0 (d, J_{CRh} = 6.0 Hz, C_{Ar}), 97.1 (d, J_{CRh} = 7.0 Hz, C_{Ar}), 79.8 (d, J_{CRh} = 7.0 Hz, C_{Ar}).

4.1.2. Preparation of **1**

A Schlenk tube was charged with $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ (100 mg, 0.09 mmol) and anhydrous sodium acetate (17.2 mg, 0.2 mmol), to which dry methanol (5 mL) was added, followed by 1-phenylpyrazole (26.4 μL, 0.2 mmol). The red suspension was stirred at room temperature for 6 h. During this time an orange solid precipitated out of the solution. The product was isolated by filtration and was washed with diethyl ether (10 mL) affording the product as an orange solid; yield 96 mg (82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 2.6 Hz, 1H, $H^{1/3}$), 7.70 (d, J = 2.1 Hz, 1H, $H^{1/3}$), 7.51–7.47 (m, 4H, $C_{Ar}H$), 7.31–7.10 (m, 14H, $C_{Ar}H$), 7.05–7.02 (m, 2H, $C_{Ar}H$), 6.99–6.96 (m, 2H, $C_{Ar}H$), 6.81 (td, J = 7.6, 1.0 Hz, 1H, $H^{6/7}$), 6.42 (t, J = 2.5 Hz, 1H, H^2), 5.79 (brs, 1H, C_5Ph_4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.6 (d, J_{CRh} = 30.7 Hz, C^9), 141.3 ($C^{1/3}$), 140.6 (C_{Ar}), 138.9 (C_{Ar}), 131.8 (C_{Ar}), 131.6 (C_{Ar}), 131.5 (C^4), 131.0 (d, J_{CRh} = 8.4 Hz, C_5Ph_4H), 130.4 (C_{Ar}), 129.5 (C_{Ar}), 128.3 (C_{Ar}), 128.3 (C_{Ar}), 128.2 (C_{Ar}), 128.0 (C_{Ar}), 128.0 (C_{Ar}), 126.4 ($C^{6/7}$), 126.7 ($C^{1/3}$), 123.9 (C_{Ar}), 111.8 (CAr), 111.7 (d, J_{CRh} = 3.2 Hz, C_5Ph_4H), 108.3 (C^2), 108.2 (d, J_{CRh} = 3.4 Hz, C_5Ph_4H), 97.1 (d, J_{CRh} = 5.8 Hz, C_5Ph_4H), 85.1 (d, J_{CRh} = 7.6 Hz, C_5Ph_4H). HRMS for $C_{38}H_{28}N_2Rh$ $[M-Cl]^+$: Calculated 615.1308: Actual 615.1296.

4.1.3. Preparation of **2**

A Schlenk tube was charged with $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$ (60 mg, 0.054 mmol) and anhydrous sodium acetate (13.2 mg, 0.12 mmol), to which dry methanol (5 mL) was added, followed by 2-phenylpyridine (21.6 μL, 0.15 mmol). The red suspension was

stirred at room temperature for 3 h. During this time an orange solid precipitated out of the solution. The product was isolated by filtration and was washed with diethyl ether (10 mL) affording the product as an orange solid; yield 52 mg (73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (d, $J = 5.5$ Hz, 1H, H^1), 7.75 (brd, $J = 8.0$ Hz, 1H, H^{10}), 7.68 (td, $J = 7.7$, 1.4 Hz, 1H, H^2), 7.64 (dd, $J = 7.7$, 1.1 Hz, 1H, H^8), 7.50–7.45 (m, 4H, $C_{Ar}H$), 7.37 (dd, $J = 7.7$, 0.7 Hz, 1H, H^1), 7.30–7.18 (m, 7H, $C_{Ar}H$), 7.14–7.07 (m, 3H, $C_{Ar}H$), 7.03–6.91 (m, 7H, $C_{Ar}H$), 6.88–6.86 (m, 2H, $C_{Ar}H$), 5.84 (d, $J = 0.6$ Hz, 1H, C_5Ph_4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 168.8 (d, $J_{CRh} = 31.1$ Hz, C^{11}), 164.0 (C_{Ar}), 151.8 (C^4), 142.6 (C_{Ar}), 137.5 (C^1), 136.5 (C^2), 131.3 (C_{Ar}), 130.8 (C_{Ar}), 130.7 ($C_{Ar}H$), 130.4 ($C_{Ar}H$), 130.2 (C_{Ar}), 129.4 (C_{Ar}), 129.2 ($C_{Ar}H$), 120.9 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 127.1 ($C_{Ar}H$), 127.0 ($C_{Ar}H$), 127.0 ($C_{Ar}H$), 126.9 ($C_{Ar}H$), 126.9 ($C_{Ar}H$), 126.8 ($C_{Ar}H$), 126.7 ($C_{Ar}H$), 126.7 ($C_{Ar}H$), 123.5 (C^8), 122.3 ($C_{Ar}H$), 120.9 ($C_{Ar}H$), 118.3 (C^{10}), 112.5 (d, $J_{CRh} = 3.0$ Hz, C_5Ph_4H), 108.6 (d, $J_{CRh} = 3.0$ Hz, C_5Ph_4H), 94.1 (d, $J_{CRh} = 7.0$ Hz, C_5Ph_4H), 88.5 (d, $J_{CRh} = 7.0$ Hz, C_5Ph_4H). HRMS for $C_{40}H_{29}NRh$ [M − Cl] $^+$: Calculated 626.1355: Actual 626.1354.

4.1.4. Preparation of **1(MeCN)**

A 50 mL round bottom flask was charged with **1** (50 mg, 0.077 mmol) to which acetonitrile (5 mL) was added. To the orange solution $AgPF_6$ (19.5 mg, 0.077 mmol) was added, this was followed by an immediate colour change to yellow. The suspension was allowed to stir at room temperature for 4 h. After which the solution was filtered through celite and reduced to dryness. The residue was redissolved in DCM (10 mL) and filtered through celite. The product was isolated as a yellow solid by removal of solvent; yield 57 mg (92%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.22 (d, $J = 2.7$ Hz, 1H, H^3), 7.82 (d, $J = 2.2$ Hz, 1H, H^1), 7.45–7.26 (m, 14H, $C_{Ar}H$), 7.22–7.18 (m, 3H, $C_{Ar}H$), 7.13–7.06 (m, 4H, $C_{Ar}H$), 6.98–6.92 (m, 3H, $C_{Ar}H$), 6.64 (t, $J = 2.5$ Hz, 1H, H^2), 6.13 (s, 1H, C_5Ph_4H), 2.05 (s, 3H, MeCN). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 148.0 (d, $J_{CRh} = 28.9$ Hz, C^9), 142.8 (C^1), 141.9 (C_{Ar}), 138.9 ($C_{Ar}H$), 131.8 ($C_{Ar}H$), 131.7 ($C_{Ar}H$), 130.3 ($C_{Ar}H$), 130.1 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 129.4 ($C_{Ar}H$), 129.2 ($C_{Ar}H$), 129.0 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 128.2 (C3), 127.5 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 124.6 (C_{Ar}), 113.4 ($C_{Ar}H$), 110.8 (C_{Ar}), 109.9 (C^2), 102.1 (d, $J_{CRh} = 7.3$ Hz, C_5Ph_4H), 99.2 (d, $J_{CRh} = 8.3$ Hz, C_5Ph_4H), 85.9 (d, $J_{CRh} = 7.8$ Hz, C_5Ph_4H), 4.0 (MeCN). HRMS for $C_{38}H_{28}N_2Rh$ [M-MeCN] $^+$: Calculated 615.1308: Actual 615.1317.

4.1.5. Preparation of **2(MeCN)**

A 50 mL round bottom flask was charged with **2** (34 mg, 0.05 mmol) to which acetonitrile (5 mL) was added. To the orange solution $AgPF_6$ (13 mg, 0.05 mmol) was added, this was followed by an immediate colour change to yellow. The suspension was allowed to stir at room temperature for 4 h. After which the solution was filtered through celite and reduced to dryness. The residue was redissolved in DCM (10 mL) anf filtered through celite. The product was isolated as an orange solid by removal of solvent; yield 36 mg (89%). ^{1}H NMR (500 MHz, MeCN-d_3): δ 8.70 (d, $J = 5.6$ Hz, 1H, H^4), 8.01 (d, $J = 7.1$ Hz, 1H, $C_{Ar}H$), 7.98 (td, $J = 7.7$, 1.34 Hz, 1H, H^9), 7.84 (dd, $J = 7.7$, 1.3 Hz, 1H, H^{10}), 7.42–7.39 (m, 4H, $C_{Ar}H$), 7.34–7.17 (m, 13H, $C_{Ar}H$), 7.08–7.00 (m, 5H, $C_{Ar}H$), 6.95–6.91 (m, 2H, $C_{Ar}H$), 6.32 (d, $J = 1.0$ Hz, 1H, C_5Ph_4H), 1.96 (s, 3H, MeCN). $^{13}C\{^1H\}$ NMR (125 MHz, MeCN-d_3): δ 164.8 (d, $J_{CRh} = 28.2$ Hz, C^{11}), 164.5 (C_{Ar}), 153.0 (C^4), 144.5 (C_{Ar}), 139.6 (C^9), 137.8 ($C_{Ar}H$), 131.1 ($C_{Ar}H$), 131.0 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 129.8 (C_{Ar}), 129.3 ($C_{Ar}H$), 128.8 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.6 ($C_{Ar}H$), 128.6 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 128.0 ($C_{Ar}H$), 125.1 (C^{10}), 124.8 ($C_{Ar}H$), 123.4 ($C_{Ar}H$), 120.1 ($C_{Ar}H$), 112.3 (d, $J_{CRh} = 3.9$ Hz, C_5Ph_4H), 110.4 (d, $J_{CRh} = 3.6$ Hz, C_5Ph_4H), 98.1 (d, $J_{CRh} = 7.0$ Hz, C_5Ph_4H), 96.6 (d, $J_{CRh} = 7.5$ Hz, C_5Ph_4H), 89.2 (d, $J_{CRh} = 7.5$ Hz,C_5Ph_4H). HRMS for $C_{40}H_{29}NRh$ [M-MeCN] $^+$: Calculated 626.1355: Actual 626.1345.

4.1.6. General method for the reaction of ***1(MeCN)*** or ***2(MeCN)*** with alkynes

Complex **1(MeCN)** or **2(MeCN)** was added to a Schlenk tube followed by acetonitrile (2 mL) and the alkyne (1 equivalent) and the solution was allowed to stir at room temperature. The solvent was removed affording the alkyne inserted complex. In non-coordinating solvents the complexes decompose over time hence the complexes were just characterised in solution.

4.1.7. Reaction of ***1(MeCN)*** with 4-octyne

This was done with **1(MeCN)** (30 mg, 0.037 mmol) and 4-octyne (5.5 μl, 0.037 mmol), and the reaction was stirred for 8 h to give **3a**. ^{1}H NMR (400 MHz, MeCN-d_3): δ 8.19 (dd, $J = 2.5$, 0.7 Hz, 1H, H^1), 8.01 (brd, $J = 2.7$ Hz, 1H, H^3). 7.44–7.20 (m, 13H, $C_{Ar}H$), 7.16–7.03 (m, 8H, $C_{Ar}H$), 6.89–6.84 (m, 1H, H^5), 6.72–6.69 (m, 2H, $C_{Ar}H$), 6.23–6.19 (m, 1H, H^8), 3.62 (s, 1H, C_5Ph_4H), 2.89–2.77 (m, 1H, H^{12}), 2.45–2.36 (m, 2H, $H^{12,15}$), 2.15 (s, 3H, MeCN), 2.04–1.98 (m, 1H, H^{15}), 1.17–1.07 (m, 2H, H^{16}), 1.00–0.91 (m, 1H, H^{13}), 0.87 (t, $J = 7.0$ Hz, $H^{14/17}$), 0.73–0.60 (m, 1H, H^{13}), 0.49 (t, $J = 7.0$ Hz, $H^{14/17}$). $^{13}C\{^1H\}$ NMR (125 MHz, MeCN-d_3): δ 162.6 (d, $J_{CRh} = 26.1$ Hz, C^{11}), 144.4 (C^1), 141.5 (C_{Ar}), 138.2 (C_{Ar}), 136.5 (C_{Ar}), 136.4 (C^3), 132.3 (C_{Ar}), 132.2 ($C_{Ar}H$), 131.8 ($C_{Ar}H$), 131.0 (C^8), 131.0 (C_{Ar}), 130.8 (C_{Ar}), 130.6 (C_{Ar}), 130.1 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 129.7 ($C_{Ar}H$), 129.5 ($C_{Ar}H$), 129.4 ($C_{Ar}H$), 129.2 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 127.8 ($C_{Ar}H$), 127.1 (C^5), 115.6 (d, $J_{CRh} = 3.0$ Hz, C_5Ph_4H), 114.8 (d, $J_{CRh} = 2.0$ Hz, C_5Ph_4H), 114.1 (d, $J_{CRh} = 9.0$ Hz, C_5Ph_4H), 110.6 (C^2), 93.8 (d, $J_{CRh} = 6.0$ Hz, C_5Ph_4H), 72.2 (d, $J_{CRh} = 9.0$ Hz, C_5Ph_4H), 45.2 (C^{12}), 37.1 (C^{15}), 23.5 ($C^{13/16}$), 23.1 ($C^{13/16}$), 14.5 ($C^{14/17}$), 13.8 ($C^{14/17}$). HRMS for $C_{46}H_{42}N_2Rh$ [M-MeCN]$^+$: Calculated 725.2403: Actual 725.2414.

4.1.8. Reaction of ***1(MeCN)*** with diphenylacetylene

This was done with **1(MeCN)** (0.054 mmol) and diphenylacetylene (0.054 mmol), and the reaction was stirred for 1 h to give **3b**. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.02 (d, $J = 2.0$ Hz, 1H, H^1), 7.90 (d, $J = 2.33$ Hz, 1 H, H^3), 7.56–7.54 (m, 1H, $C_{Ar}H$), 8.51–7.49 (m, 3 H, $C_{Ar}H$), 7.44–7.41 (m, 2 H, $C_{Ar}H$), 7.39–7.37 (m, 3 H, $C_{Ar}H$), 7.29–7.27 (m, 1 H, $C_{Ar}H$), 7.24–7.20 (m, 4 H, $C_{Ar}H$), 7.15–7.05 (m, 8 H, $C_{Ar}H$), 7.01–6.94 (m, 5 H, $C_{Ar}H$), 6.86 (brt, 1 H, $C_{Ar}H$), 6.79 (t, $J = 2.61$ Hz, 1 H, H^2), 6.76–6.73 (m, 2 H, $C_{Ar}H$), 6.67–6.65 (m, 2 H, $C_{Ar}H$), 6.11 (d, $J = 7.38$ Hz, 1 H, H^5), 6.01 (brd, $J = 6.44$ Hz, 1 H, $C_{Ar}H$), 4.21 (s, 1 H, $CpPh_4H$), 1.70 (s, 3 H, MeCN). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 164.1 (d, $J_{CRh} = 26.3$ Hz, C^{11}), 144.5 (C^1), 144.4 (C_{Ar}), 142.2 (C_{Ar}), 139.4 (C_{Ar}), 136.5 (C_{Ar}), 135.9 (C^3), 132.5 ($C_{Ar}H$), 132.1 ($C_{Ar}H$), 131.7 ($C_{Ar}H$), 131.2 ($C_{Ar}H$), 130.9 ($C_{Ar}H$), 130.7 ($C_{Ar}H$), 130.4 ($C_{Ar}H$), 130.2 ($C_{Ar}H$), 130.2 (C_{Ar}), 130.1 ($C_{Ar}H$), 130.0 (C_{Ar}), 129.9 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 129.3 (C_{Ar}), 129.2 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.4 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 128.0 ($C_{Ar}H$), 127.8 ($C_{Ar}H$), 126.5 ($C_{Ar}H$), 125.9 ($C_{Ar}H$), 123.7 (C_{Ar}), 118.1 (MeCN), 111.2 (C^2), 108.5 (C_{Ar}), 105.2 (d, $J_{CRh} = 8.1$ Hz, C_5Ph_4H), 102.5 (d, $J_{CRh} = 5.8$ Hz, C_5Ph_4H), 89.8 (C_{Ar}), 70.3 (d, $J_{CRh} = 8.7$ Hz, C_5Ph_4H), 3.1 (MeCN). HRMS for $C_{52}H_{38}N_2Rh$ [M-MeCN]$^+$: Calculated 793.2090: Actual 793.2101.

4.1.9. Reaction of ***2(MeCN)*** with 4-octyne

This was carried out in an NMR tube in MeCN-d_3 using **2(MeCN)** (27 mg, 0.033 mmol) and 4-octyne (4.9 μl, 0.033 mmol). The reaction was monitored and showed full conversion to **5a** after 6 h ^{1}H NMR (500 MHz, MeCN-d_3): δ 9.14 (d, $J = 5.9$ Hz, 1H, H^4), 7.96 (td, $J = 7.7$, 1.4 Hz, 1H, $C_{Ar}H$), 7.50–7.12 (m, 18H, $C_{Ar}H$), 7.07–7.01 (m, 4H, $C_{Ar}H$), 6.77–6.72 (m, 2H, $C_{Ar}H$), 6.12–6.10 (m, 1H, H^9), 3.40 (s, 1H, C_5Ph_4H), 2.91–2.85 (m, 1H, H^{13}), 2.54–2.42 (m, 2H, $H^{13,16}$), 2.11–2.05 (m, 1H, H^{16}), 1.12–1.04 (m, 2H, $H^{14,17}$), 0.98–0.92 (m, 1H, $H^{14/17}$), 0.88 (t, $J = 7.3$ Hz, 3H, $H^{15/18}$), 0.66–0.59 (m, 1H, $H^{14/17}$), 0.46 (t, $J = 7.3$ Hz, 3H, $H^{15/18}$). $^{13}C\{^1H\}$ NMR (125 MHz, MeCN-d_3): δ 165.1 (C_{Ar}), 156.0 (d, $J_{CRh} = 26.0$ Hz, C^{12}), 152.9 (C^4), 143.7 (C_{Ar}), 140.5

($C_{Ar}H$), 140.4 (C_{Ar}), 137.9 (C_{Ar}), 132.4 ($C_{Ar}H$), 132.2 ($C_{Ar}H$), 131.7 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 129.4 ($C_{Ar}H$), 129.3 ($C_{Ar}H$), 129.3 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 128.3 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 126.7 ($C_{Ar}H$), 125.3 ($C_{Ar}H$), 115.9 (d, $J_{CRh} = 3.0$ Hz, C_5Ph_4H), 114.3 (d, $J_{CRh} = 8.3$ Hz, C_5Ph_4H), 113.8 (d, $J_{CRh} = 2.0$ Hz, C_5Ph_4H), 94.4 (d, $J_{CRh} = 6.1$ Hz, C_5Ph_4H), 72.8 (d, $J_{CRh} = 9.0$ Hz, C_5Ph_4H), 44.9 (C^{13}), 37.0 (C^{16}), 23.9 ($C^{14/17}$), 23.1 ($C^{14/17}$), 14.5 ($C^{15/18}$), 13.9 ($C^{15/18}$). HRMS for $C_{48}H_{43}NRh$ $[M\text{-}MeCN]^+$: Calculated 736.2451: Actual 736.2458.

4.1.10. Reaction of **2(MeCN)** with diphenylacetylene

This was carried out in an NMR tube in MeCN-d_3, using **2(MeCN)** (17 mg, 0.021 mmol) and diphenylacetylene (4 mg, 0.021 mmol). The reaction was monitored and showed full conversion to **5b** in 22 h ^{1}H NMR (500 MHz, MeCN-d_3): δ 8.99 (d, $J = 5.8$ Hz, 1H, H^1), 8.05 (td, $J = 7.7.1.3$ Hz, 1H, H^3), 7.64 (dd, $J = 7.9$, 1.0 Hz, 1H, H^4), 7.55–7.53 (m, 2H, $C_{Ar}H$), 7.50–7.53 (m, 2H, $C_{Ar}H$), 7.44–7.38 (m, 3H, $C_{Ar}H$), 7.32–7.27 (m, 2H, $C_{Ar}H$), 7.23–7.18 (m, 5H, $C_{Ar}H$), 7.16–7.12 (m, 2H, $C_{Ar}H$), 7.08–7.06 (m, 2H, $C_{Ar}H$), 7.03 (t, $J = 7.9$ Hz, 1H, $C_{Ar}H$), 6.97–6.89 (m, 5H, $C_{Ar}H$), 6.31 (d, $J = 7.6$ Hz, 1H, H^7), 5.88 (d, $J = 7.4$ Hz, 1H, $C_{Ar}H$),3.91 (s, 1H, $CpPh_4H$), 2.30 (brs, 3H, MeCN). ^{13}C $\{^1H\}$ NMR (125 MHz, MeCN-d_3): δ 164.7 (C_{Ar}), 162.6 (d, $J_{CRh} = 27.2$ Hz, C^{13}), 153.3 (C^1), 151.6 (C_{Ar}), 145.4 (C_{Ar}), 144.7 (C_{Ar}), 141.0 (C^3), 139.1 (C_{Ar}), 132.5 ($C_{Ar}H$), 132.4 ($C_{Ar}H$), 131.9 ($C_{Ar}H$), 131.8 ($C_{Ar}H$), 131.6 ($C_{Ar}H$), 131.2 ($C_{Ar}H$), 131.1 (C_{Ar}), 130.9 (C_{Ar}), 130.6 ($C_{Ar}H$), 130.5 ($C_{Ar}H$), 130.4 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 129.7 ($C_{Ar}H$), 129.7 ($C_{Ar}H$), 129.5 ($C_{Ar}H$), 129.5 ($C_{Ar}H$), 129.4 ($C_{Ar}H$), 129.4 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.4 ($C_{Ar}H$), 128.3 ($C_{Ar}H$), 127.5 ($C_{Ar}H$), 126.6 ($C_{Ar}H$), 126.2 ($C_{Ar}H$), 125.8 ($C_{Ar}H$), 124.0 (C_{Ar}), 117.6 (d, $J_{CRh} = 4.0$ Hz, C_5Ph_4H), 109.4 (d, $J_{CRh} = 3.2$ Hz, C_5Ph_4H), 108.1 (d, $J_{CRh} = 7.9$ Hz, C_5Ph_4H), 101.0 (d, $J_{CRh} = 5.3$ Hz, C_5Ph_4H), 90.1 (C_{Ar}), 71.7 (d, $J_{CRh} = 8.8$ Hz, C_5Ph_4H), 1.8 (MeCN). HRMS for $C_{54}H_{39}NRh$ $[M\text{-}MeCN]^+$: Calculated 804.2138: Actual 804.2176.

4.1.11. Reaction of **2(MeCN)** with 1-phenyl-1-propyne

This was carried out in an NMR tube in MeCN-d_3, using **2(MeCN)** (43 mg, 0.053 mmol) and 1-phenyl-1-propyne (6.6 μl, 0.053 mmol). The reaction was monitored and showed full conversion to a mixture of **5c** and **5c'** after 6 h. The ^{1}H NMR spectrum of the mixture is very complicated so was not fully analysed. ^{1}H NMR (500 MHz CD_3CN): δ 9.18 (d, $J = 6.0$ Hz, 1H, H^1, minor), 8.98 (d, $J = 5.8$ Hz, 1H, H^1, major), 7.99 (td, $J = 7.8$, 1.6 Hz, 1H, ArH, minor), 7.96 (td, $J = 7.7$, 1.5 Hz, 1H, ArH, major), 7.56–7.09 (m, 23H, ArH, minor and major), 7.04 (t, $J = 7.9$ Hz, 2H, ArH, minor), 6.99 (t, $J = 8.0$ Hz, 2H, ArH, major), 6.91 (dd, $J = 8.3$, 1.1 Hz, 2H, ArH, major), 6.84 (dd, $J = 8.3$, 1.1 Hz, 2H, ArH, minor), 6.61 (m, 3H, major and minor), 6.3 (d, $J = 6.4$ Hz, 1H, ArH, major), 6.09 (dd, $J = 7.6$, 1.2 Hz, 1H, ArH, minor), 6.07 (dd, $J = 7.8$, 1.2 Hz, 1H, ArH, major), 3.76 (s, 1H, C_5Ph_4H, major), 3.63 (s, 1H, C_5Ph_4H, minor), 2.21 (s, 3H, *Me*, minor), 2.01 (s, 1.3H, *Me*CN, major and minor) 1.92 (s, 3H, *Me*, major). ^{13}C $\{^1H\}$ NMR (125 MHz, MeCN-d_3): δ 163.5 (C_{Ar}), 163.4 (C_{Ar}), 155.5 (d, $J_{CRh} = 26.0$ Hz, C^{13}), 152.0 ($C_{Ar}H$), 151.7 ($C_{Ar}H$), 150.2 (C_{Ar}), 144.1 (C_{Ar}), 143.8 (C_{Ar}), 142.7 (C_{Ar}), 139.4 ($C_{Ar}H$), 139.3 ($C_{Ar}H$), 137.5 (C_{Ar}), 136.7 (C_{Ar}), 132.3 (C_{Ar}), 132.1 ($C_{Ar}H$), 131.5 ($C_{Ar}H$),131.1 ($C_{Ar}H$), 130.8 ($C_{Ar}H$), 130.4 ($C_{Ar}H$), 130.2 (C_{Ar}), 130.0 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 129.6 (C_{Ar}), 129.6 (C_{Ar}), 129.3 ($C_{Ar}H$), 129.2 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 129.0 ($C_{Ar}H$), 128.8 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.6 (CAr), 128.5 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 128.0 ($C_{Ar}H$), 127.7 ($C_{Ar}H$), 127.7 ($C_{Ar}H$), 127.6 ($C_{Ar}H$), 127.5 ($C_{Ar}H$), 127.4 ($C_{Ar}H$), 127.3 ($C_{Ar}H$), 127.2 ($C_{Ar}H$), 125.9 ($C_{Ar}H$), 125.6 ($C_{Ar}H$), 125.5 ($C_{Ar}H$), 125.2 ($C_{Ar}H$), 125.1 ($C_{Ar}H$), 124.3 ($C_{Ar}H$), 124.2 ($C_{Ar}H$), 116.7 (MeCN), 116.6 (MeCN), 106.9 (d, $J_{CRh} = 2.7$ Hz, C_5Ph_4H), 107.8 (d, $J_{CRh} = 8.2$ Hz, C_5Ph_4H), 100.6 (d, $J_{CRh} = 5.2$ Hz, C_5Ph_4H), 70.0 (d, $J_{CRh} = 9.3$ Hz, C_5Ph_4H), 69.9 (d, $J_{CRh} = 8.9$ Hz, C_5Ph_4H), 27.8 (CH_3), 23.0 (CH_3), 2.80 (MeCN). HRMS for $C_{49}H_{37}NRh$ $[M\text{-}MeCN]^+$: Calculated 742.1981: Actual 742.1973.

4.1.12. Reaction of $[RhCl_2(\eta\text{-}Cp^*)]_2$ with $C_5Ph_4H_2$

A Schlenk tube was charged with $[RhCl_2(\eta\text{-}Cp^*)]_2$ (25 mg, 0.04 mmol) and $C_5Ph_4H_2$ (120 mg, 0.32 mmol), to which DMF (3 mL) was added. The mixture was heated at 80 °C for 6 h and was monitored by ^{1}H NMR spectroscopy. Observation of a broad singlet at δ 6.4 was taken as indication of the formation of $[RhCl_2(\eta\text{-}C_5Ph_4H)]_2$

4.1.13. Catalytic synthesis of pyridines

An oven dried Schlenk flask was charged with $[RhCl_2(C_5Ph_4H)]_2$ (13.5 mg, 0.0125 mmol, 2.5 mol%), K_2CO_3 (138.2 mg, 1.00 mmol), TFE (3 mL), oxime (80.6 mg, 0.50 mmol), 1-phenyl-1-propyne (69.0 μl, 64.0 mg, 0.551 mmol). The reaction was heated to 60 °C for 20 h. After this time the ^{1}H NMR spectrum was run and showed an A:B ratio of 1: 3.2, and a conversion of >95%. The reaction mixture was filtered through Celite, and rotary evaporated. The residue was purified via silica gel column chromatography on Biotage Isolera using 9:1 petroleum ether: EtOAc to obtain the product as a mixture of isomers (1: 3.0) as a yellow oil (97.1 mg, 75%). The ^{1}H NMR spectrum is in agreement with Rovis et al.

4.2. X-ray structure determinations

Data for **2** and **5b** were collected on a Bruker Apex 2000 CCD diffractometer using graphite monochromated Mo-Kα radiation, $\lambda = 0.7107$ Å. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections were applied. The structures were solved by direct methods and with structure refinement on F^2 employed SHELXTL version 6.10 [34]. Hydrogen atoms were included in calculated positions (C-H = 0.95–1.00 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5Ueq (C) for methyl hydrogen atoms and 1.2Ueq (C) for all other H atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters without positional restraints. Figures were drawn using the program ORTEP [35].

Supporting information

CCDC 1824696–1824697 (**2**, **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_ request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. NMR spectra for all compounds are available in the supplementary information.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.09.005.

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