Protonolysis of an α-hydroxyl ligand for the generation of a $PC_{carbene}P$ pincer complex and subsequent reactivity studies

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ABSTRACT: Rhodium α-hydroxylalkyl complex (**1**) reacts rapidly with Brookhart's acid, $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$, to generate a cationic $PC_{carbene}P$ complex (**2**). Complex **2** can also be accessed from salt metathesis of an α-hydroxyalkyl hydrochlorido rhodium(III) complex (**4**) with $Na[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$. The reactivity of compound **2** is explored through a series of reactions with various nucleophilic and electrophilic reagents.

Tridentate *meridional* ligands, better known as pincer ligands, have played an instrumental role in the development of transition metal catalysts capable of performing difficult bond transformations.[1] Within this ligand class, PCP type pincers have proven versatile, especially amongst base metal systems, given their ability to partake in metal-ligand cooperative bond activation.[2] In particular, recent reports of $PC_{carbene}P$ pincers have demonstrated these ligands' ability to activate challenging N-H, O-H and C-H bonds on base metals.[3]

Given the propensity of phosphines to react with generic alkylidene precursors (i.e. diazocarbenes), $PC_{carbene}P$ pincer systems[4] have previously only been accessible via two related methods; namely double C-H activation,[2b] and C-H activation/dehydrohalogenation[3,5] of methylene bridged bis-phosphino proligands (Figure 1).[6] With the exception of a report concerning nickel, these methods are restricted to noble metals (Pd, Rh, Ir, Ru, Os).[2b,5,7] Piers recently reported the extent of this methodology using rhodium systems.[7b] In such systems, prolonged heating in high boiling point solvents for several days is required to obtain mediocre yields. Piers's report also highlights restrictions on phosphino substituents to alkyl groups in order to generate a sufficiently electron rich metal centre to promote C-H activation. As such this method can neither be extended to metals that perform poorly at C-H activation (i.e. early or first row transition metals) nor to aryl phosphino pincer proligands, which are generally easier to synthesize, less prone to oxidation and commercially available.

The first cationic rhodium and iridium $PC_{carbene}P$ pincer complexes have also been recently reported by Piers.[8] Such complexes are generated upon the salt metathesis of rhodium or iridium $PC_{carbene}P$ chloride complexes synthesized via double C-H activation (a process taking several days at elevated temperatures). Cationic group 9 $PC_{carbene}P$ pincer complexes have the advantage of variable ligand exchange/attachment at the coordination site *trans* to the carbene ligand, thus direct access to such species is desirable.

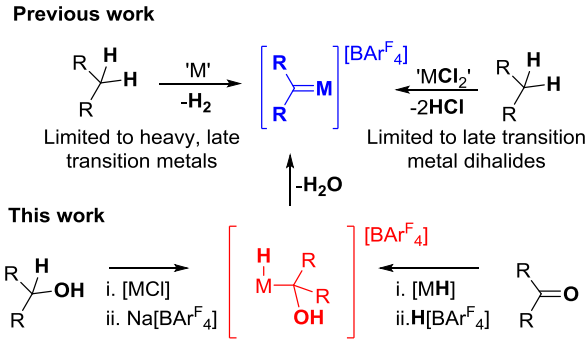
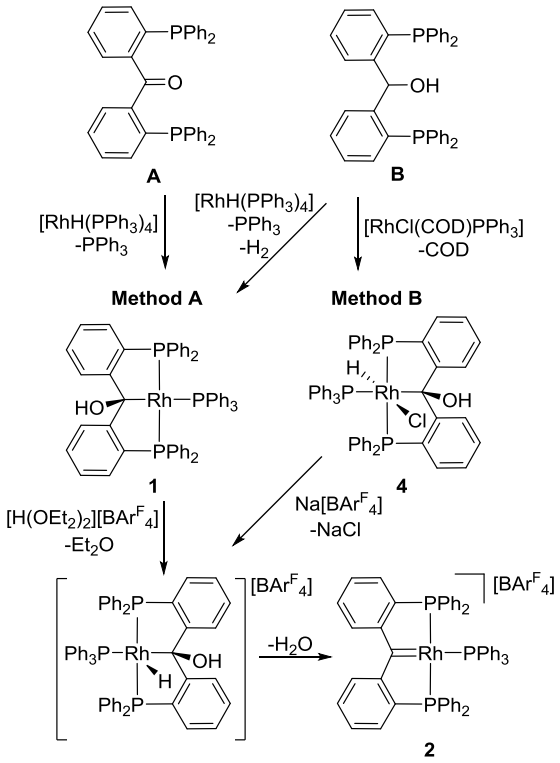


Figure 1. Access to metal alkylidene complexes via double C-H activation and dehydrochlorination (above) has been reported. Formation of metal carbene complexes through dehydration (below) is reported herein.



Scheme 1. Synthesis of the cationic $PC_{carbene}P$ rhodium complex **2** via hydride insertion and protonolysis (method **A**) or C-H activation and salt metathesis (method **B**).

As an alternative to accessing metal organyls via C-H activation, our group (and others) have used aldehyde or ketone insertion into metal hydrides as a means of accessing α-hydroxyalkyl metal complexes.[9] In contrast to noble metals, hydride transfer from acidic first row transition metal hydrides generally favours the formation of α-hydroxyalkyl complexes, as opposed to alkoxide complexes.[10] Upon realization that such complexes may be susceptible to dehydration, we herein report access to cationic $PC_{carbene}P$ pincer complexes via protonolysis of α-hydroxyalkyl complexes, representing a new synthetic methodology towards accessing metal alkylidene systems from alcohol and ketone based ligands.

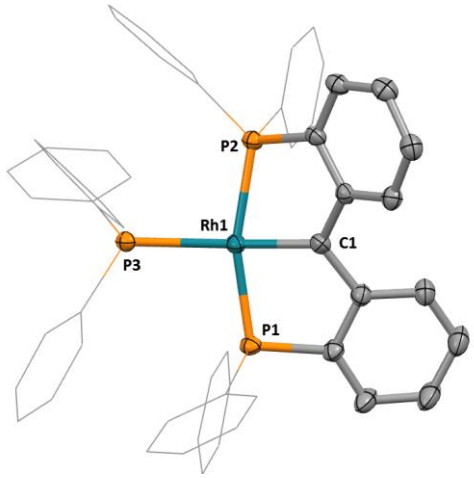


Figure 2. Molecular structure of **2**. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Rh1-P1, 2.305(1); Rh1-C1, 1.927(6); Rh1-P2, 2.272(1); Rh1-P3, 2.421(1); C1-Rh1-P3, 167.8(2); P1-Rh1-P2, 162.1(1).

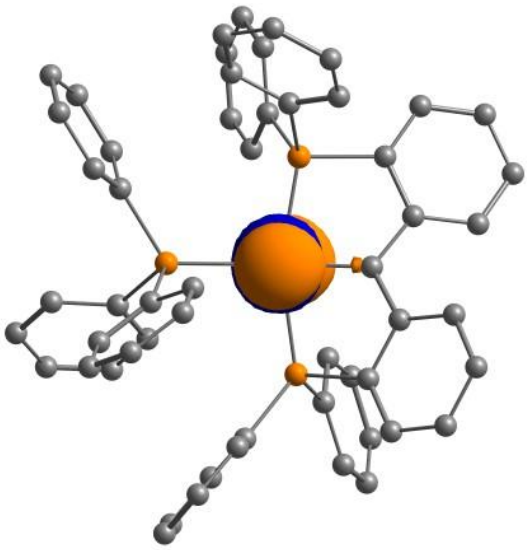


Figure 3. Calculated structure of **2** showing HOMO *iso*-surface (0.05 a.u. cutoff).

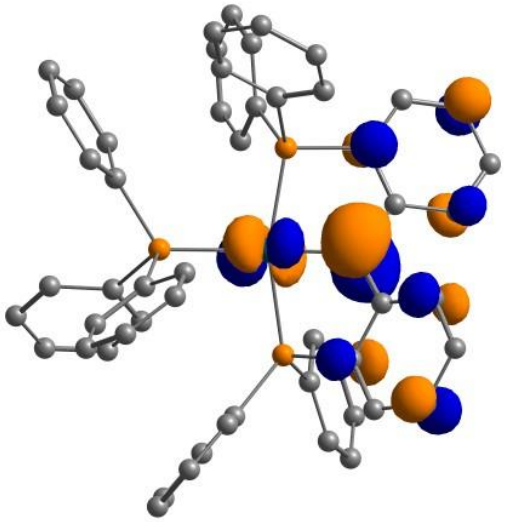
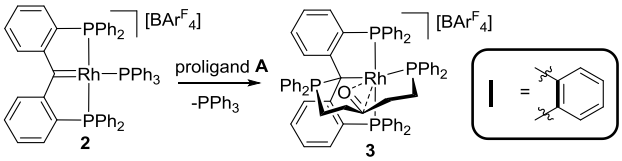


Figure 4. Calculated structure of **2** showing LUMO *iso*-surface (0.05 a.u. cutoff).



Scheme 2. Reaction of **2** with proligand **A**.

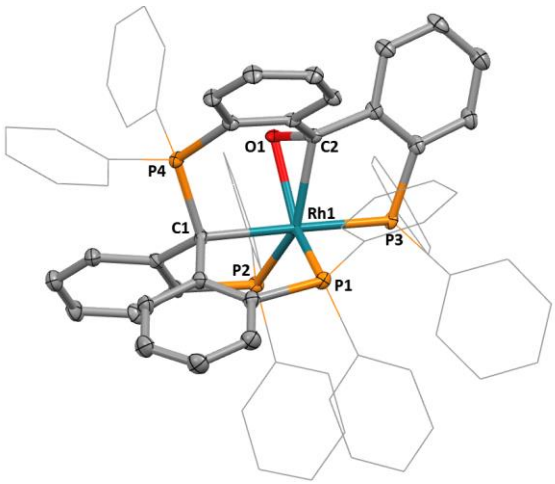
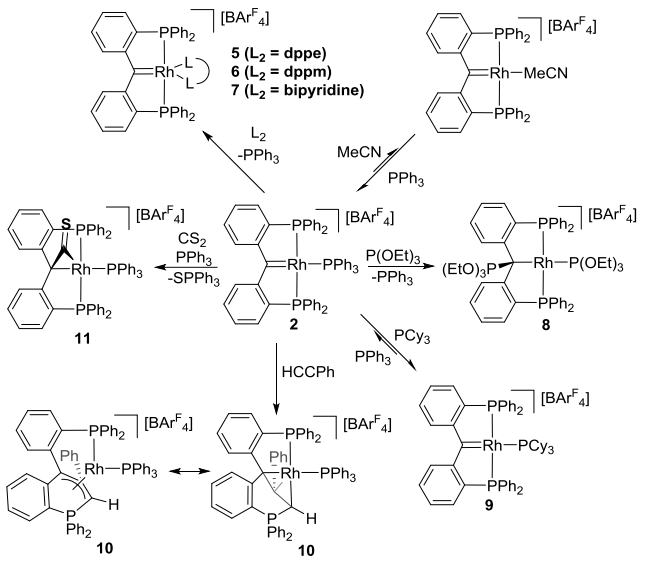


Figure 5. Molecular structure of **3**. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Rh1-P1, 2.268(2); Rh1-P2, 2.346(2); Rh1-P3, 2.318(2); Rh1-C1, 2.272(6); Rh1-O1, 2.133(4); Rh1-C2, 2.166(6); C2-O1, 1.324(7); C1-P4, 1.868(6); C1-Rh1-P3, 177.0(2); P1-Rh1-P2, 116.1(1); C1-Rh1-C2, 98.9(2); C1-Rh1-O1, 86.4(2).

Recently, we published the synthesis of the α-hydroxylalkyl rhodium(I) complex (**1**) from the combination of a commercially available ketone POP ligand (**A**) or alcohol POP ligand (**B**) with $[RhH(PPh_3)_4]$.[9] Treatment of **1** with a stoichiometric quantity of $[H(OEt_2)_2][BAr^F_4]$ {$[BAr^F_4]^-$ = $[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]^-$} at room temperature resulted in immediate conversion to the $PC_{carbene}P$ complex **2** and water (method A, Scheme 1). NMR spectroscopy provided convincing evidence for the formation of **2**, with $^1J_{RhP}$ decreasing from 190 (PCP) and 121 Hz (PPh_3) in **1** to 160 (PCP) and 92 Hz (PPh_3) in **2**, suggesting the presence of a stronger *trans* influence ligand than the alkyl group in **1**. A ^{13}C NMR spectrum of **2** revealed a low-field resonance at 271.0 ppm, with $^1J_{RhC}$ of 48 Hz, and a *trans* $^2J_{PC}$ of 87 Hz, suggesting alkylidene formation. The molecular structure of **2** (Figure 2) reveals a short Rh1-C1 bond distance {Rh1-C1, 1.945(11) Å} indicative of a rhodium-carbon double bond.[7b,8] Furthermore, **2** adopts a geometry much closer to square planar as compared to **1** with angles around rhodium of 162.30(10)° (P1-Rh1-P2) and 167.6(4)° (P3-Rh1-C1) {*cf.* P1-Rh1-P2, 132.45(13)°; P3-Rh1-C1, 166.4(4)° in **1**}.[9] The geometry of optimized computed structures is in good agreement with the crystallographically obtained molecular structure (Figures 3 and 4).

Compound **2** was isolated via trituration with *n*-hexane. The generation of pure samples of **2** was complicated by the production of by-product **3** (Figure 5). The yield of **2** was found to be highly dependent on the stoichiometry of reagents used to generate **1**. Although **2** was found to be stable in the presence of excess PPh_3, small amounts of unreacted **A** resulted in the generation of by-product **3**. By-product **3** was generated intentionally by the addition of an equivalent of ligand **A** to a solution of **2** in DCM (Scheme 2). Ligand **A** displaces PPh_3 in **2** and coordinates in a κ^2-P,(η^2-CO) fashion to the rhodium centre and a



Scheme 3. Reactions of **2** with various reagents.

κ^1-P fashion to the electrophilic alkylidene carbon, thus generating four distinct phosphorus environments in an on-metal generated pentadentate ligand. Due to phosphorus coordination, the molecular structure of **3** reveals that the Rh1-C1 distance has been elongated from 1.945(11) (in **2**) to 2.272(6) Å (Figure 4), which is indicative of the loss of the rhodium carbon double bond.

Compound **2** was also generated by the salt metathesis of compound **4** with Na[BAr^F_4] in a reaction that was quantitative as judged by ^{31}P NMR spectroscopy (method B, Scheme 1). As isolation of **4** is easier as compared to **1**, this method was preferred to avoid any generation of **3**. α-Hydroxyalkyl **4**, also reported by our group, has been shown to be relatively acidic, for example reaction with Li[$N(SiMe_3)_2$] results in loss of HCl from **4** to generate **1**.[9] Similarly, metathesis with Na[BAr^F_4] generates an intermediate cationic metal hydride with sufficiently high hydride Brønsted acidity (*cf.* **4**) to induce elimination of water. Generation of **2** from **4** suggests that protonation of the metal centre in **1** followed by hydride migration to the hydroxyl group may present a valid reaction pathway (Scheme 1). Indeed, DFT analysis of **1** showed the HOMO to be dominated by metal d_{z2} character, but with notable contribution from the hydroxyl motif.[9] In contrast, the HOMO of **2** was largely metal-centred (Figure 3).

Neutral rhodium and iridium, and cationic palladium $PC_{carbene}P$ pincer complexes have been reported to be electrophilic at the carbene centre.[11] Thus, cationic rhodium $PC_{carbene}P$ pincers would therefore be expected to be highly electrophilic at the metal-carbene position.[10] Indeed, DFT analysis of **2** reveals that its LUMO resides predominantly on the rhodium and carbene carbon atoms, and is dominated by the Rh=C π* interaction (Figure 4). To explore the implications of this dual-centre electrophilicity, the reactivity of **2** was investigated through the addition of a range of chemical reagents (Scheme 3).

The strong *trans* effect of the pincer central carbene donor enabled displacement of PPh_3 from **2** with various donors. In addition to the demonstration of this displacement by ligand **A** (above), monodentate ligands, $P(OEt)_3$ and PCy_3, and bidentate ligands, dppe, dppm and 2,2'-bipyridine, were found to displace

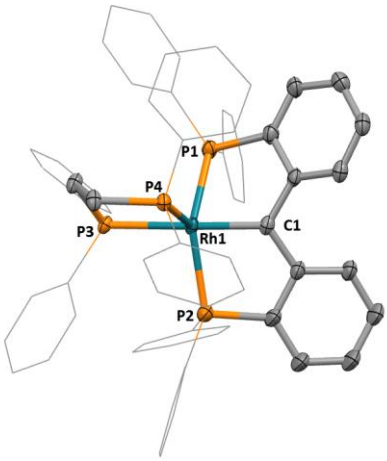


Figure 6. Molecular structure of **5**. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Rh1-P1, 2.319(2); Rh1-C1, 1.983(6); Rh1-P2, 2.362(2); Rh1-P3, 2.348(2); Rh1-P4, 2.328(2); C1-Rh1-P3, 168.5(2); P1-Rh1-P2, 141.2(1).

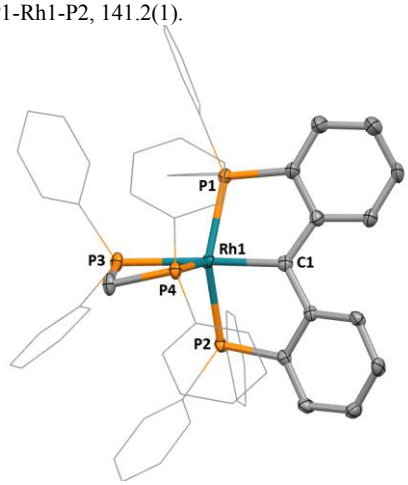


Figure 7. Molecular structure of **6**. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Rh1-P1, 2.323(1); Rh1-C1, 2.022(4); Rh1-P2, 2.315(1); Rh1-P3, 2.387(1); Rh1-P4, 2.329(1); C1-Rh1-P3, 177.0(1); P1-Rh1-P2, 143.6(1).

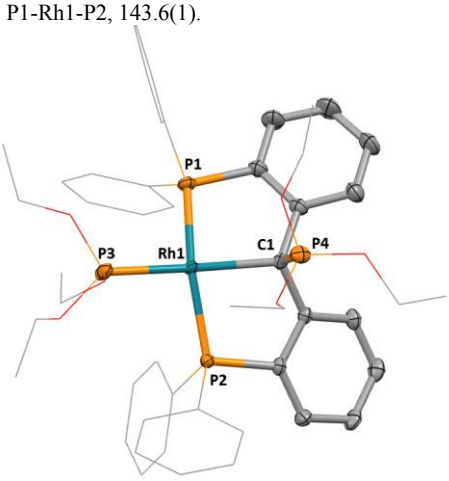


Figure 8. Molecular structure of **8**. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Rh1-P1, 2.228(1); Rh1-C1, 2.181(4); Rh1-P2, 2.260(1); Rh1-P3, 2.218(1); C1-P4, 1.752(4); C1-Rh1-P3, 170.2(1); P1-Rh1-P2, 153.5(1).

PPh_3. Indeed, the lability of PPh_3 in **2** is exemplified when **2** is dissolved in MeCN solvent. Upon dissolution in MeCN, **2** is

converted into [($PC_{carbene}P$)Rh(NCMe)][BAr^F_4] (Scheme 3). ^{31}P NMR spectroscopy revealed that the signal assigned to the $PC_{carbene}P$ ligand in **2** (multiplicity = dd) had shifted down field from δ_P 47.2 to 52.3, and that the signal no longer showed coupling to phosphorus, but was present as a doublet ($^1J_{RhP}$ = 141.5 Hz). Dynamic interchange between PPh_3 and MeCN ligands was also apparent by a broad signal at 66.5 ppm (Integration: 1 P). The addition of an equivalent of $B(C_6F_5)_3$ sequestered the free PPh_3, resulting in the disappearance of the signal at 66.5 ppm and the concomitant formation of Ph_3P-$B(C_6F_5)_3$.

Reaction of dppe, dppm and bipyridine led to complete displacement of PPh_3 and formation of ligand substitution products **5**, **6** and **7** respectively (Figures 6 and 7). Similarly, $P(OEt)_3$ displaced PPh_3, but excess $P(OEt)_3$ was found to attack the electrophilic alkylidene position, generating **8** (Figure 8).

Reaction of **2** with an equivalent of PCy_3 also led to substitution of PPh_3 and production of **9**. However, this reaction reached an equilibrium where **2** and **9** were in a 3:7 ratio ($\Delta G_{298\,K}$ ~ -1 kcal mol^{-1}). The addition of a large excess (> 10 equiv.) of PCy_3 drove the reaction towards compound **9** (> 90%), allowing trituration of the product with *n*-hexane.

The carbonic ^{13}C NMR signal for **2**, as well as for compounds **5**, **6**, **7** and **9** (where the integrity of the alkylidene motif was preserved), is much more upfield than previously reported Rh=C ^{13}C signals for neutral monodentate rhodium alkylidenes.[12] This can be attributed to a smaller paramagnetic contribution from the electron poor metals studied herein. However, $^1J_{RhC}$ values provided strong evidence for strong Rh-C interactions consistent with previously reported rhodium alkylidenes ($^1J_{RhC}$ > 30 Hz).

Piers and co-workers found that reaction of phenyl acetylene with [$PC_{carbene}P^{iPr}Ni(PPh_3)$] {$PC_{carbene}P^{iPr}$: = $C(C_6H_4\text{-}2\text{-}(P^iPr_2))_2$} resulted in formation of a $PCH_{sp3}P$ pincer nickel (II) phenyl acetylide complex.[2] In contrast, compound **2** reacted with phenyl acetylene to produce compound **10**. The formation of compound **10** is reminiscent of related Frustrated Lewis Pair chemistry in which the carbene centre and phosphine donor of the $PC_{carbene}P$ ligand assume the roles of Lewis acid and base respectively.[13] After the phenyl acetylene motif bridges the phosphine/carbene donor/acceptor, a phosphonium allyl coordination is assumed by the ligand (Scheme 3). The formation of such phosphonium allyl ligands within the metal coordination sphere is rare, but not unprecedented.[14] The allylic nature of the generated P-heterocycle is typified by the C-C allylic bond lengths between C1-C2 and C2-C3 of 1.420(8) and 1.454(8) Å respectively (Figure 9).

It was hoped that addition of CS_2 to **2** would result in a cationic thiocarbonyl complex analogous to cationic rhodium $PC_{carbene}P$ carbonyls reported by Piers.[8] The generation of thiocarbonyls from rhodium triphenylphosphine complexes is well documented.[15] However, formation of a terminal thiocarbonyl complex was not observed, and rather a rhodium-carbene bridging thiocarbonyl, or η^2-thioketene **11**, was generated in addition to $SPPh_3$. The limiting quantity of PPh_3 sourced from complex **2** needed for both the formulation of **11** and the desulfurization of CS_2 reduced the available yield of **11** and resulted in an intractable by-product. However, repeating the reaction with an additional equivalent of PPh_3 provided quantitative formation of **11** and $SPPh_3$ (as judged by ^{31}P NMR spectroscopy).

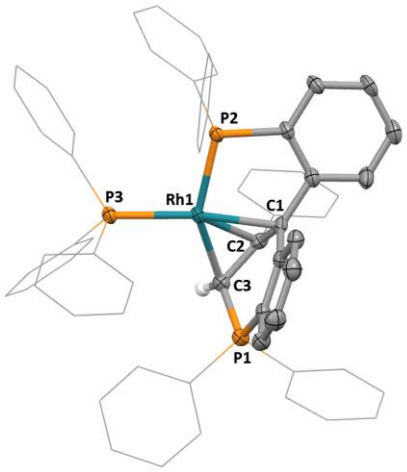


Figure 9. Molecular structure of **10**. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°):Rh1-C1, 2.153(5); Rh1-C2, 2.107(6); Rh1-C3, 2.215(6); Rh1-P2, 2.221(2); Rh1-P3, 2.304(2); P1-C3, 1.733(6); C1-C2, 1.420(8); C2-C3, 1.454(8); C1-Rh1-P3, 167.5(2); P2-Rh1-P3, 99.9(1).

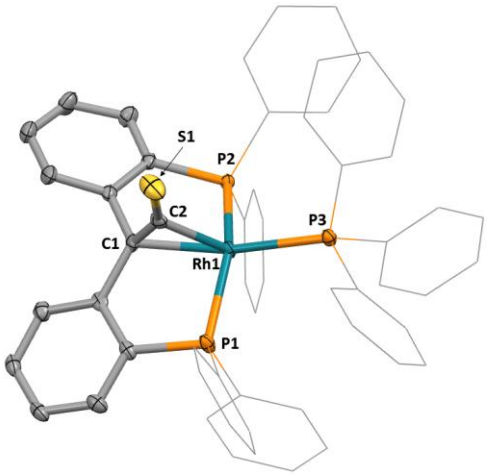


Figure 10. Molecular structure of **11**. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Rh1-P1, 2.282(1); Rh1-C1, 2.160(3); Rh1-P2, 2.332(1); Rh1-P3, 2.376(1); C1-Rh1-P3, 162.5(1); P1-Rh1-P2, 148.2(1).

The molecular structure of compound **11** reveals an elongation in Rh1-C1 {2.160(3) as compared to the parent carbene **2**: 1.945(11)} indicative of loss of carbon metal multiple bond character (Figure 10). A drastic shortening in the Rh1-P3 distance of the phosphine *trans* to C1 is also noted as compared to **2**, indicating that the thioketene is a weaker *trans* influence ligand than the carbene in **2**.

In summary, we have reported a novel method of accessing $PC_{carbene}P$ pincer complexes using commercially available, air-stable reagents. Our method dehydrates a precursor α-hydroxyalkyl complex through either direct treatment with acid (method A, Scheme 1), or *in situ* generation of a cationic acidic α-hydroxyalkyl hydrido complex through salt metathesis (method B, Scheme 1), producing the target $PC_{carbene}P$ complex rapidly at room temperature. It was found that the resulting rhodium $PC_{carbene}P$ complex **2** reacted with a range of nucleophilic reagents at the rhodium centre and electrophilic carbene positions.

Given the reported accessibility of first row transition metal α-hydroxyalkyl complexes, this strategy may enable synthetic

routes to base metal $PC_{carbene}P$ complexes. The use of commercially available reagents also allows the exploration of $PC_{carbene}P$ complexes as catalysts by chemists without synthetic organometallic expertise.

General information. All syntheses were carried out in N_2 atmosphere using a glovebox or with standard Schlenk techniques. All reactions were performed in glassware that was oven-dried for at least 12 h. Ligands **A**[16] and **B**[17], complexes $[RhH(PPh_3)_4]$,[18] **1** and **4**,[9] and $[H(OEt_2)_2][BAr^F_4]$,[19] $Na[BAr^F_4]$[20] and $[B(C_6F_5)_3]$[21] were prepared according to reported methods. Toluene, DCM, *n*-hexane, diethyl ether, and acetonitrile were dried over activated alumina using a LC Technology Solutions Inc. SP-1 solvent purification system and then deoxygenated prior to use. THF was distilled over sodium and benzophenone under a nitrogen atmosphere and stored over 4 Å molecular sieves prior to use. CD_2Cl_2 and C_6D_6 used was stirred over CaH_2 at room temperature under a nitrogen atmosphere overnight prior to distillation under reduced pressure and storage over 4 Å molecular sieves. NMR spectra were recorded on an AV500 spectrometer. All chemical shifts are quoted in parts per million (ppm) relative to $SiMe_4$ (^1H, ^{13}C) or H_3PO_4 (85%) (^{31}P). ^1H, ^{13}C and/or ^{31}P NMR spectrometry was employed to verify the purity of isolated compounds. HRMS (ESI-TOF) spectra were obtained using an Agilent Technologies 6230 TOF LC/MS. Single crystals were measured on a four circles goniometer Kappa geometry Bruker AXS D8 Venture equipped with a Photon 100 CMOS active pixel sensor detector.

Preparation of complex 2. *Method A.* A solution of complex **1** generated from $[RhH(PPh_3)_4]$ (11.5 mg, 0.01 mmol) and ligand **A** (5.5 mg, 0.01 mmol) in C_6D_6 (0.6 mL) according to our previously reported method was treated *in situ* with $[H(OEt_2)_2][BAr^F_4]$ (10.1 mg, 0.01 mmol) at room temperature. The solution immediately turned black, indicative of the formation of complex **2**. The solution was concentrated by evaporation and then *n*-hexane was added to give a biphasic mixture. The top layer was decanted to leave behind a black residue that was subsequently washed with *n*-hexane (3 x 3 mL). The residue was dried under vacuum to give a black foamy solid (15 mg, 85 %).

Method B. DCM (20 mL) was added to a mixture of complex **4** (500.0 mg, 0.52 mmol) and $Na[BAr^F_4]\cdot 2THF$ (538.9 mg, 0.52 mmol) at room temperature to give a black coloured solution. After stirring at room temperature for 2 h, the solution was filtered and then concentrated by evaporation. The solution was layered with *n*-hexane and then left to stand at room temperature. Subsequently, black crystals of complex **2** were isolated and then dried under vacuum (802 mg, 87 %). ^1H NMR (500 MHz, CD_2Cl_2, 298 K) = δ_H 6.77 – 6.88 (m, 6H, Ar-*H*), 6.93 – 7.02 (m, 6H, Ar-*H*), 7.19 – 7.47 (m, 27H, Ar-*H*), 7.57 (s (br), 4H, $[BAr^F_4]$ Ar-*H*), 7.74 (s (br), 8H, $[BAr^F_4]$ Ar-*H*), 7.79 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 8.09 – 8.17 (m, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) = δ_C 117.7 – 118.0 (m), 125.0 (q, $^1J_{CF}$ = 272.4 Hz), 128.8 (d, *J* = 9.7 Hz), 128.9 – 129.0 (m), 129.2 (t, *J* = 5.1 Hz), 129.3 – 129.5 (m), 129.6 – 129.8 (m), 130.7 (s), 131.4 (s), 132.6 (d, *J* = 36.7 Hz), 133.7 (s), 134.0 – 134.4 (m), 134.9 (s), 135.2 (s), 144.6 (vtdd, $^1J_{CP}$ = 20.1 (vt), $^2J_{CRh}$ = 6.8 (d), $^3J_{CP}$ = 3.1 (d) Hz), 162.2 (q, $^1J_{CB}$ = 49.9 Hz), 164.6 (t, $^1J_{CB}$ = 20.1 Hz), 271.5 (dd, $^2J_{CP}$ = 74.1 (d), $^1J_{CRh}$ = 41.5 (d) Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K) = δ_P 21.0 (dt, $^1J_{PRh}$ = 92.3 (d), $^2J_{PP}$ = 30.7 (t) Hz, 1P), 49.1 (dd, $^1J_{RhP}$ = 158.8 (d), $^2J_{PP}$ = 30.7 (t) Hz, 2P). HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{55}H_{43}P_3Rh$ 899.1627; Found 899.1627.

Preparation of complex 3. DCM (5 mL) was added to a mixture of complex **2** (100 mg, 0.057 mmol) and Ligand **A** (31.2 mg, 0.057 mmol) at room temperature and mixed. After standing at room temperature overnight, the reaction solution was evaporated to give an oily residue. *n*-Hexane (5 mL) was added to the residue, triturated and then removed by cannula. This washing process was repeated two further times. The residue was then dissolved in DCM (1 mL) and then layered with *n*-hexane (10 mL). Red crystals of the products were isolated and then dried under vacuum (80 mg, 69%). ^1H NMR (500 MHz, CD_2Cl_2, 298 K) = δ_H 5.87 (dd, *J* = 11.3, 7.7 Hz, 2H, Ar-*H*), 6.34 (t, *J* = 8.5 Hz, 1H, Ar-*H*), 6.46 – 6.69 (m, 5H, Ar-*H*), 6.72 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 6.76 – 7.01 (m, 16H, Ar-*H*), 7.02 – 7.57 (m, 30H, Ar-*H*), 7.59 (s (br), 4H, $[BAr^F_4]$ Ar-*H*), 7.78 (s (br), 8H, $[BAr^F_4]$ Ar-*H*), 7.97 (dd, *J* = 8.3, 3.8 Hz, 1H, Ar-*H*). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) = δ_C 108.3 – 108.6 (m), 114.5 (d, *J* = 88.3 Hz), 117.8 – 118.1 (m), 121.8 – 129.9 (m), 130.2 – 130.5 (m), 130.6 – 130.9 (m), 131.2 (s), 131.4 (s), 131.5 (d, *J* = 2.9 Hz), 132.0 (dd, *J* = 14.3, 6.6 Hz), 132.3 – 132.7 (m), 132.8 – 133.6 (m), 134.3 (dd, *J* = 27.9, 18.8 Hz), 135.3 (s), 135.8 (s), 135.9 (s), 136.1 (s), 136.6 (s), 136.8 (s), 137.0 – 137.3 (m), 137.5 (s), 137.6 – 137.9 (m), 138.1 – 138.5 (m), 142.0 – 142.6 (m), 144.4 – 145.0 (m), 151.4 – 151.6 (m), 152.1 – 152.8 (m), 153.4 (dd, *J* = 32.1, 3.7 Hz), 162.2 (q, $^1J_{CB}$ = 49.9 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K) = δ_P 31.4 (dddd, $^1J_{PRh}$ = 96.5 (d), $^2J_{PP}$ = 41.8 (d), $^3J_{PP}$ = 21.8 (d), $^4J_{PP}$ = 6.4 Hz (d), 1P), 33.1 (ddd, $^1J_{PRh}$ = 133.0 (d), $^2J_{PP}$ = 72.8 (d), $^3J_{PP}$ = 21.8 (d) Hz, 1P), 35.2 (s, 1P), 47.5 (ddd, $^1J_{PRh}$ = 180.3 (d), $^2J_{PP}$ = 72.8 (d), $^2J_{PP}$ = 41.8 Hz). HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{74}H_{56}OP_4Rh$ 1187.2331; Found 1187.2344.

Preparation of complex 5. DCM (1 mL) was added to a mixture of complex **2** (30 mg, 0.017 mmol) and dppe (6.5 mg, 0.017 mmol) at room temperature and mixed. After standing at room temperature overnight, the reaction solution was evaporated to give an oily residue. *n*-Hexane (5 mL) was added to the residue, triturated and then removed by cannula. This washing process was repeated two further times. The residue was then dissolved in DCM (1 mL) and then layered with *n*-hexane (10 mL). Dark brown crystals of the product were isolated and then dried under vacuum (18 mg, 56%). ^1H NMR (500 MHz, CD_2Cl_2, 298 K) = δ_H 1.47 – 3.12 (m, 4H, -C*H*$_2$-C*H*$_2$-), 5.45 – 8.00 (m, 59H, Ar-*H*), 8.22 – 8.44 (m, 1H, Ar-*H*). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) = δ_C 19.5 – 31.8 (m, -*C*H$_2$-*C*H$_2$-), 117.9 (s), 121.8 – 128.3 (m), 128.5 – 129.8 (m), 130.7 (s), 131.1 – 131.4 (m), 131.4 – 132.5 (m), 133.2 – 133.8 (m), 133.9 – 134.2 (m), 135.2 (s), 144.3 – 145.2 (m), 160.3 (t, *J* = 14.5 Hz), 162.2 (q, $^1J_{CB}$ = 49.9 Hz), 240.6 – 244.8 (m, Rh=*C*). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K) = δ_P 38.8 (s (b), 1P, dppe *P*), 46.4 (dt, $^1J_{PRh}$ = 136.5 (d), $^2J_{PP}$ = 28.6 (t) Hz, 2P, PCP pincer *P*'s), 80.6 (s (b), 1P, dppe *P*). HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{63}H_{52}P_4Rh$ 1035.2069; Found 1035.2057.

Preparation of complex 6. A solution of complex **2** (88.2 mg, 0.05 mmol) in DCM (2 mL) was treated dropwise with a solution of dppm (19.2 mg, 0.05 mmol) in DCM (2 mL) at room temperature. After stirring for 10 min at room temperature, the reaction solution was evaporated to give an oily residue. *n*-Hexane (8 mL) was added to the residue, triturated and then re-

moved by cannula. This washing process was repeated two further times. The residue was then dissolved in DCM (1 mL) and then layered with *n*-hexane (10 mL). Dark red crystals of the product were isolated and then dried under vacuum (56 mg, 59%). NMR data suggests that complex **6** is present as two isomers in equilibrium when dissolved in CD_2Cl_2 solvent. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) = δ_H 1.08 – 1.38 (m, 2H, C*H*$_2$), 3.96 (t, *J* = 10.4 Hz, 2H, C*H*$_2$), 5.84 – 8.16 (m, 118H, Ar-*H*), 8.16 – 8.39 (m, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) = δ_C 6.5 – 7.1 (m, *C*H$_2$), 39.9 (t, $^2J_{CP}$ = 23.5 Hz, *C*H$_2$), 117.9 (p, *J* = 4.0 Hz), 121.8 – 128.3 (m), 128.7 (d, *J* = 9.5 Hz), 128.8 – 129.1 (m), 129.1 – 129.3 (m), 129.3 – 129.5 (m), 129.5 (s), 129.6 – 129.8 (m), 130.1 (s), 130.6 – 131.8 (m), 132.4 – 132.7 (m), 132.7 – 132.9 (m), 133.0 – 133.1 (m), 133.1 – 134.2 (m), 134.3 – 134.6 (m), 134.9 (s), 135.0 (d, *J* = 8.9 Hz), 135.3 (s), 143.0 – 143.9 (m), 153.1 – 153.7 (m), 162.2 (q, $^1J_{CB}$ = 49.8 Hz), 237.0 (ddd, $^2J_{CP}$ = 89.0, $^1J_{CRh}$ = 31.3, $^2J_{CP}$ = 4.8 Hz, Rh=*C*). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K) = δ_P -10.6 – -9.7 (m, 1P), -7.6 (s (br), 1P), 5.6 – 8.8 (m, 1P), 43.3 (s (br), 1P), 47.3 – 50.5 (m, 2P), 51.3 (dt, $^1J_{PRh}$ = 139.6 (d), $^2J_{PP}$ = 30.6 (t) Hz, 2P). HRMS (ESI-TOF) m/z: [M - H]$^+$ Calcd for $C_{55}H_{43}OP_3Rh$ 915.1582; Found 915.1546.

Preparation of complex 7. A solution of complex **2** (88.2 mg, 0.05 mmol) in DCM (3 mL) was treated dropwise with a solution of 2,2'-bipyridine (7.8 mg, 0.05 mmol) in DCM (3 mL) at room temperature. After stirring for 2 min at room temperature, the reaction solution was evaporated to give an oily residue. *n*-Hexane (8 mL) was added to the residue, triturated and then removed by cannula. This washing process was repeated two further times. The residue was dried under vacuum to yield a dark yellow foamy solid (78 mg, 94 %). ^{1}H NMR (500 MHz, C_6D_6, 298 K) = δ_H 6.06 (t, *J* = 6.3 Hz, 1H, Ar-*H*), 6.54 – 7.50 (m, 31H, Ar-*H*), 7.51 – 7.82 (m, 6H, Ar-*H*), 7.87 – 8.16 (m, 2H, Ar-*H*), 8.42 (s, 8H, [BAr$^F_4$] Ar-*H*). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) = δ_C 117.8 – 118.4 (m), 121.1 (s), 122.0 – 128.4 (m), 128.9 (t, *J* = 4.8 Hz), 129.4 – 130.4 (m), 130.5 (s), 132.2 (t, *J* = 6.5 Hz), 133.0 (s), 133.5 – 133.6 (m), 133.7 – 134.0 (m), 134.8 (t, *J* = 4.9 Hz), 135.3 (s), 135.4 (s), 137.0 (s), 138.3 (s), 153.0 (s), 153.4 (s), 162.8 (q, *J* = 49.8 Hz), 167.8 (td, *J* = 23.7, 2.5 Hz), 197.9 (d, *J* = 47.9 Hz, Rh=*C*). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K) = δ_P 47.8 (d, $^1J_{PRh}$ = 151.3 Hz, 2P, PCP pincer *P*'s). HRMS (ESI-TOF) m/z: [M]$^+$ Calcd for $C_{47}H_{36}N_2P_2Rh$ 793.1403; Found 793.1403.

Preparation of complex 8. A solution of complex **2** (30 mg, 0.017 mmol) in DCM (10 mL) was treated with triethylphosphite (6 µL, 0.035 mmol) at room temperature and mixed. After standing at room temperature overnight, the reaction solution was evaporated to give an oily residue. *n*-Hexane (10 mL) was added to the residue, triturated and then removed by cannula. This washing process was repeated two further times. The residue was then dissolved in DCM (1 mL) and then layered with *n*-hexane (10 mL). Orange crystals of the product were isolated and then dried under vacuum (22 mg, 71%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) = δ_H 0.4 – 1.2 (m, 18H, C*H*$_3$), 3.2 – 3.9 (m, 12H, C*H*$_2$), 7.0 – 8.3 (m, 40H, Ar-*H*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) = δ_C 15.8 (s, P(OCH$_2$*C*H$_3$)), 15.8 (s, P(OCH$_2$*C*H$_3$)), 60.7 (s (br), P(O*C*H$_2$CH$_3$)), 68.0 (s (br), P(O*C*H$_2$CH$_3$)), 117.7 – 118.0 (m), 121.8 – 128.3 (m), 128.5 (s (br)), 128.8 – 129.7 (m), 130.6 (s), 130.7 (s (br)), 132.3 (s (br)), 133.0 (s (br)), 134.1 (s (br)), 135.2 (s), 136.3 (s), 137.8 (s (br)), 144.3 – 144.8 (m), 147.3 (s (br)), 162.2 (q, *J* = 49.9 Hz). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) = δ_P 38.4 (s (br), 1P, C-*P*(OEt)$_3$), 40.9 (d (br), $^1J_{PRh}$ = 122.3 Hz, 2P, PCP pincer P's), 119.4 (d (br), $^1J_{PRh}$ = 185.5 Hz, 1P, Rh-*P*(OEt)$_3$). HRMS (ESI-TOF) m/z: [M]$^+$ Calcd for $C_{49}H_{58}O_6P_4Rh$ 969.2233; Found 969.2225.

Preparation of complex 9. DCM (3 mL) was added to a mixture of complex **2** (30 mg, 0.017 mmol) and PCy_3 (4.8 mg, 0.017 mmol) at room temperature and mixed. After 2 min, the reaction solution was evaporated to give an oily residue. *n*-Hexane (10 mL) was added to the residue, triturated and then removed by cannula. This washing process was repeated two further times. The residue was dissolved in DCM and then analysed by ^{31}P NMR spectroscopy, which identified the ratio of **2** : **9** was 3 : 7. Additional PCy_3 (47.8 mg) was added and the previously described process of evaporation, trituration and washing with *n*-hexane was conducted. The residue was dried under vacuum to yield complex **9** as a dark green solid (25 mg, 84%). ^{1}H NMR (500 MHz, C_6D_6, 298 K) = δ_H 0.50 – 0.72 (m, 5H, cyclohexyl-*H*), 0.74 – 0.86 (m, 3H, cyclohexyl-*H*), 0.94 – 1.15 (m, 6H, cyclohexyl-*H*), 1.20 – 1.52 (m, 19H, cyclohexyl-*H*), 6.39 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 6.80 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.00 (dt, *J* = 7.6 (d), 3.8 (t) Hz, 3H, Ar-*H*), 7.04 – 7.21 (m, 12H, Ar-*H*), 7.48 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.65 (s, 4H, [BAr$^F_4$] Ar-*H*), 7.79 (s (br), 7H, Ar-*H*), 8.40 (s, 8H, [BAr$^F_4$] Ar-*H*). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) = δ_C 26.0 (s, cyclohexyl-*C*), 27.0 (d, $^2J_{CP}$ = 9.8 Hz, cyclohexyl-*C*), 30.4 (s, cyclohexyl-*C*), 35.9 (d, $^1J_{CP}$ = 14.3 Hz, cyclohexyl-*C*), 117.9 – 118.3 (m), 122.0 – 128.6 (m), 129.3 (t, *J* = 4.7 Hz), 129.5 – 130.4 (m), 131.7 (s), 132.2 (t, *J* = 21.0 Hz), 133.5 (d, *J* = 18.4 Hz), 133.7 (s), 134.8 (s (br)), 135.5 (s), 144.6 (td, *J* = 20.0 (t), 5.1 (d) Hz), 162.8 (q, *J* = 49.8 Hz), 164.6 (t, *J* = 19.9 Hz), 266.1 – 267.5 (m, Rh=*C*). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K) = δ_P 25.5 (dt, $^1J_{PRh}$ = 82.7 (d), $^2J_{PP}$ = 30.6 (t) Hz, 1P, *P*Cy$_3$), 45.7 (dd, $^1J_{PRh}$ = 165.6 (d), $^2J_{PP}$ = 30.6 (t) Hz, 2P, PCP pincer *P*'s). HRMS (ESI-TOF) m/z: [M]$^+$ Calcd for $C_{55}H_{61}P_3Rh$ 917.3036; Found 917.3082

Preparation of complex 10. A solution of complex **2** (40 mg, 0.023 mmol) in DCM (1 mL) was treated with phenylacetylene (8 µL, 0.068 mmol) at room temperature and mixed. After standing at room temperature overnight, the reaction solution was then layered with *n*-hexane (10 mL). Red crystals of the product were isolated and then dried under vacuum (40 mg, 95%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) = δ_H 3.36 – 3.60 (m, 1H, allyl C-*H*), 6.37 – 6.55 (m, 2H, Ar-*H*), 6.76 – 8.04 (m, 58H, Ar-*H*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) = δ_C 35.7 (dddd, $^1J_{CP}$ = 64.5 (d), $^2J_{CP}$ = 38.2 (d), $^1J_{CRh}$ = 12.4 (d), $^2J_{CP}$ = 5.1 (d) Hz, allyl *C*-H), 91.7 – 92.3 (m, allyl-C-*C*-C-H), 110.1 (d, *J* = 9.9 Hz), 111.2 (d, $^1J_{CP}$ = 96.7 Hz, Ar-*C*-P), 117.6 – 118.3 (m), 120.7 (d, *J* = 95.9 Hz), 121.8 – 128.3 (m), 128.4 – 129.9 (m), 129.9 – 130.3 (m), 130.5 (s), 130.9 (d, *J* = 41.8 Hz), 131.4 (d, *J* = 7.9 Hz), 132.0 (d, *J* = 10.3 Hz), 132.2 (s), 132.3 (s), 132.6 (d, *J* = 11.3 Hz), 133.8 – 134.6 (m), 134.7 (s), 135.2 (s), 141.1 (d, *J* = 5.9 Hz, allyl-C-*C*-C-H), 144.6 (s), 146.2 (d, *J* = 25.7 Hz), 150.3 (dd, *J* = 44.4, 6.0 Hz), 162.2 (q, *J* = 49.8 Hz). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K) = δ_P 6.5 (d, $^3J_{PP}$ = 13.2 Hz, 1P, allyl-*P*Ph$_2$), 36.2 (dd, $^1J_{PRh}$ = 185.3 (d), $^2J_{PP}$ = 29.6 (d) Hz, 1P, *P*Ph$_3$), 49.5 (ddd, $^1J_{PRh}$ = 189.3 (d), $^2J_{PP}$ = 29.6 (d), $^3J_{PP}$ = 13.2 (d) Hz, 1P, Rh-*P*Ph$_2$). HRMS (ESI-TOF) m/z: [M]$^+$ Calcd for $C_{63}H_{49}P_3Rh$ 1001.2097; Found 1001.2104.

Preparation of complex 11. A solution of complex **2** (100.0 mg, 0.057 mmol) and triphenylphosphine (14.9 mg, %) in DCM (20 mL) was treated with carbon disulfide (4 µL, 0.067 mmol)

at room temperature and mixed. After stirring at room temperature overnight, the reaction solution was concentrated under vacuum and then layered with *n*-hexane (15 mL). Red crystals of the product were isolated and then dried under vacuum (93 mg, 90%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) = δ_H 6.75 – 7.88 (m, 54H, Ar-*H*), 8.28 (d, *J* = 8.2 Hz, 1H, Ar-*H*). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) = δ_C 65.7 (ddt, $^{2}J_{CP}$ = 33.1 (d), $^{1}J_{CRh}$ = 8.9 (d), $^{2}J_{CP}$ = 4.6 Hz (t), Rh-*C*), 117.8 – 118.1 (m), 121.8 – 128.3 (m), 128.8 (d, *J* = 10.2 Hz), 128.8 – 128.9 (m), 129.0 – 130.0 (m), 129.6 (dt, *J* = 48.9 (d), 5.2 (t) Hz), 130.8 (s), 131.2 (s), 131.3 (d, *J* = 2.1 Hz), 132.2 (d, *J* = 6.7 Hz), 132.4 (s), 133.5 (dt, *J* = 24.6 (d), 6.0 (t) Hz), 134.5 (d, *J* = 12.8 Hz), 134.6 (s), 134.9 – 135.3 (m), 146.1 (td, *J* = 13.9 (t), 4.7 (d) Hz), 162.3 (q, *J* = 49.7 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K) = δ_P 24.9 (dt, $^{1}J_{PRh}$ = 141.4 (d), 31.8 (t) Hz, 1P, *P*Ph_3), 36.5 (dd, $^{1}J_{PRh}$ = 127.4 (d), 32.1 (d) Hz, 2P, PCP pincer *P*'s). HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{56}H_{43}P_3RhS$ 943.1348; Found 943.1353.

Reaction between complex 2 and B(C_6F_5)$_3$. A solution of complex **2** (17.6 mg, 0.01 mmol) was dissolved in CH_3CN and then analysed by ^{31}P NMR spectroscopy (spectra were recorded unlocked). B(C_6F_5)$_3$ (5.1 mg, 0.01 mmol) was then added and heated at 60 °C. The formation of Ph_3P-B(C_6F_5)$_3$ was observed by ^{11}B and ^{31}P NMR spectroscopy over a period of 7 days to monitor the reaction progress. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K) = δ_P 52.7 (d, 2 P, $^{1}J_{RhP}$ = 130.3 Hz).

ASSOCIATED CONTENT

The Supporting Information, including experimental and computation details, is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

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