ORGANOMETALLICS

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Protonolysis of an α-Hydroxyl Ligand for the Generation of a $PC_{carbene}P$ Pincer Complex and Subsequent Reactivity Studies

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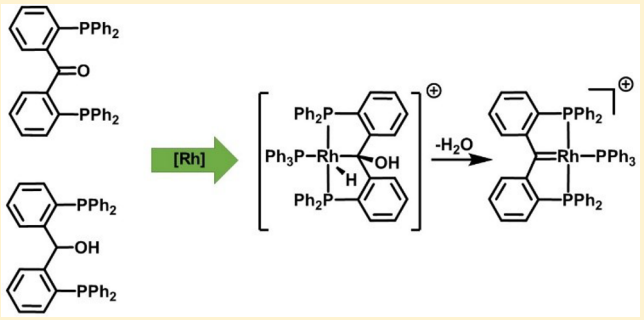
Supporting Information

ABSTRACT: A 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 among 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' report also highlights restrictions on phosphino substituents to alkyl groups in order to generate a sufficiently electron rich metal center to promote C−H activation. As such, this method can be extended neither 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

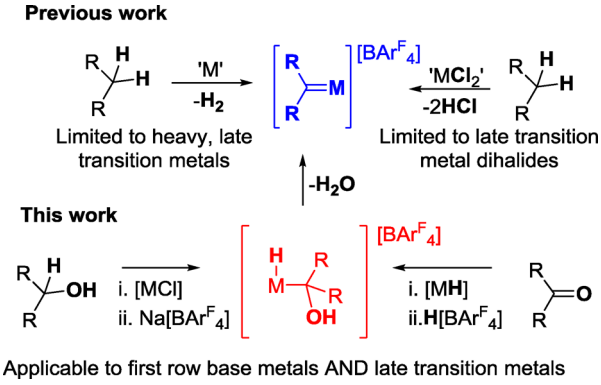


Figure 1. (top) Reported access to metal alkylidene complexes via double C−H activation and dehydrochlorination. (bottom) Formation of metal carbene complexes through dehydration reported herein.

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.

As an alternative to accessing metal organyls via C−H activation, our group (and others) has 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 favors the formation of α-hydroxyalkyl complexes, as opposed to alkoxide complexes.[10] Upon the 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

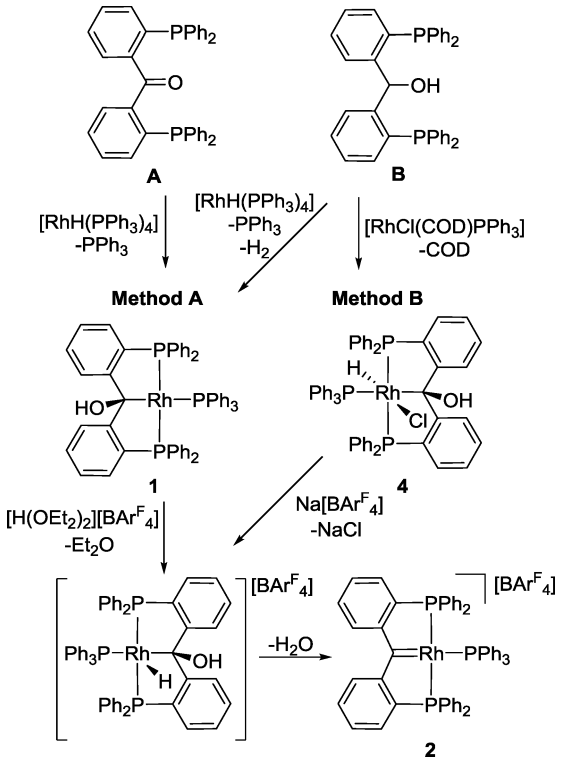
Received: June 16, 2017
Published: August 10, 2017

DOI: 10.1021/acs.organomet.7b00461
Organometallics 2017, 36, 3117−3124

synthetic methodology toward accessing metal alkylidene systems from alcohol- and ketone-based ligands.

Recently, we reported 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

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)



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 ligand having a stronger trans influence in comparison to the alkyl group in **1**. A ^{13}C NMR spectrum of **2** revealed a low-field resonance at 271.0 ppm, with a $^1J_{RhC}$ value of 48 Hz and a trans $^2J_{PC}$ value 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 in comparison 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 byproduct **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

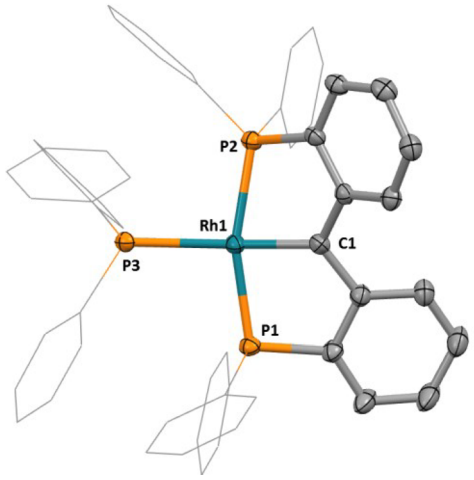


Figure 2. Molecular structure of **2**. Hydrogen atoms and anion are omitted, and thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): Rh1−P1, 2.305(1); Rh1−C1, 1.927(6); Rh1−P2, 2.272(1); Rh1−P3, 2.421(1); C1−Rh1−P3, 167.8(2); P1−Rh1−P2, 162.1(1).

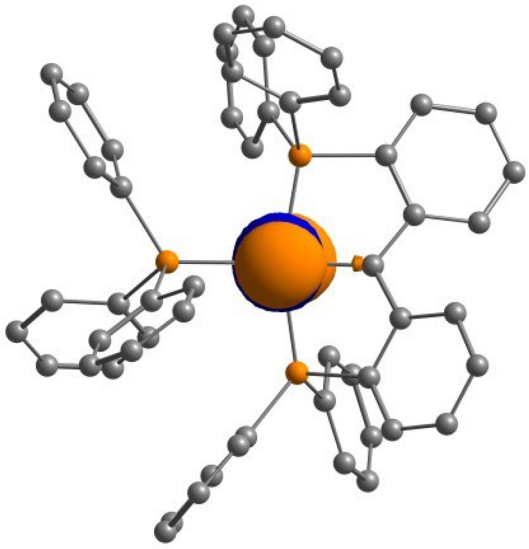


Figure 3. Calculated structure of **2** showing the HOMO isosurface (0.05 au cutoff).

presence of excess PPh_3, small amounts of unreacted **A** resulted in the generation of byproduct **3**. Byproduct **3** was generated intentionally by the addition of 1 equiv 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 center and a 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) Å (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 in comparison to **1**, this method was preferred to avoid any generation of **3**. α-Hydroxyalkyl **4**, also reported by our group, has been shown to

DOI: 10.1021/acs.organomet.7b00461
Organometallics 2017, 36, 3117−3124

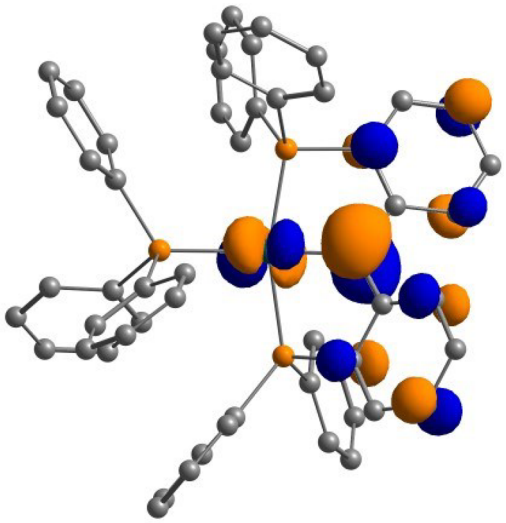


Figure 4. Calculated structure of **2** showing the LUMO isosurface (0.05 au cutoff).

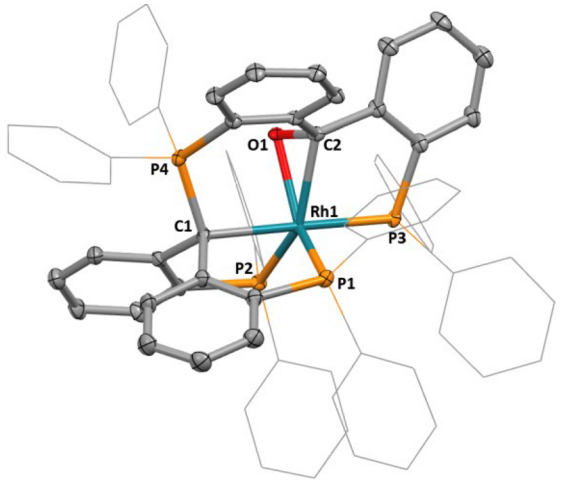
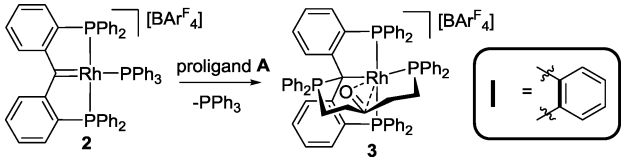


Figure 5. Molecular structure of **3**. Hydrogen atoms and anion are omitted, and thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): Rh1–P1, 2.268(2); Rh1–P2, 2.346(2); Rh1–P3, 2.318(2); Rh1–C1, 2.272(6); Rh1–O1, 2.133(4); Rh1–C2, 2.166(6); C2–O1, 1.324(7); 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).

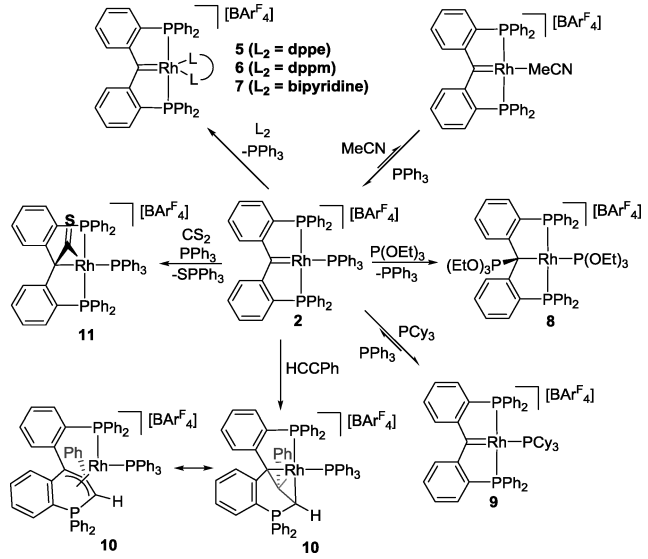
Scheme 2. Reaction of 2 with Proligand A



be relatively acidic; for example, the 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 center 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_{z^2} character, but with notable contribution from the hydroxyl motif.[9] In contrast, the HOMO of **2** was largely metal centered (Figure 3).

Neutral rhodium and iridium and cationic palladium PC$_{carbene}$P pincer complexes have been reported to be electrophilic at the carbene center.[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-center electrophilicity, the reactivity of **2** was investigated through the addition of a range of chemical reagents (Scheme 3).

Scheme 3. Reactions of 2 with Various Reagents



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), the monodentate ligands P(OEt)$_3$ and PCy$_3$ and bidentate ligands dppe, dppm, and 2,2′-bipyridine were found to displace 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 downfield 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 1 equiv of B(C$_6$F$_5$)$_3$ sequestered the free PPh$_3$, resulting in the disappearance of the signal at 66.5 ppm and the concomitant formation of Ph$_3$P–B(C$_6$F$_5$)$_3$.

Reaction of dppe, dppm, and bipyridine led to complete displacement of PPh$_3$ and formation of ligand substitution products **5**–**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 1 equiv of PCy$_3$ also led to substitution of PPh$_3$ and production of **9**. However, this reaction reached an

DOI: 10.1021/acs.organomet.7b00461
Organometallics 2017, 36, 3117–3124

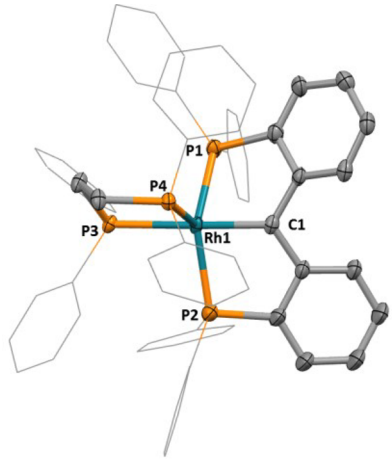


Figure 6. Molecular structure of **5**. Hydrogen atoms and anion are omitted, and thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): Rh1−P1, 2.319(2); Rh1−C1, 1.983(6); Rh1−P2, 2.362(2); Rh1−P3, 2.348(2); Rh1−P4, 2.328(2); C1−Rh1−P3, 168.5(2); P1−Rh1−P2, 141.2(1).

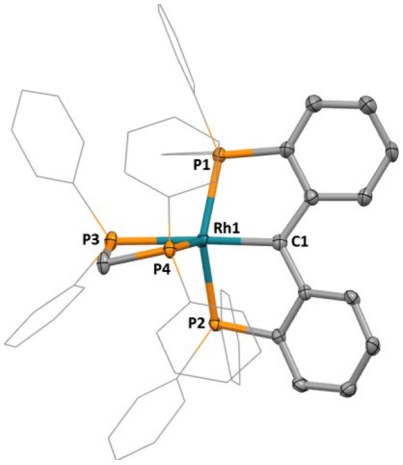


Figure 7. Molecular structure of **6**. Hydrogen atoms and anion are omitted, and thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): Rh1−P1, 2.323(1); Rh1−C1, 2.022(4); Rh1−P2, 2.315(1); Rh1−P3, 2.387(1); Rh1−P4, 2.329(1); C1−Rh1−P3, 177.0(1); P1−Rh1−P2, 143.6(1).

equilibrium where **2** and **9** were in a 3:7 ratio ($\Delta G_{298\,K} \approx -1$ kcal mol^{-1}). The addition of a large excess (>10 equiv) of PCy_3 drove the reaction toward 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**−**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 the reaction of phenylacetylene with [$PC_{carbene}P^{iPr}Ni(PPh_3)$] ($PC_{carbene}P^{iPr}$: = C-($C_6H_4$-2-($P^iPr_2$))$_2$) resulted in the formation of a $PCH_{sp^3}P$ pincer nickel(II) phenylacetylide complex.[2] In contrast, compound **2** reacted with phenylacetylene to produce compound **10**. The formation of compound **10** is reminiscent

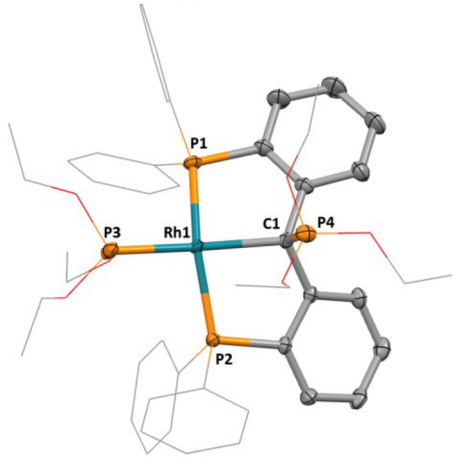


Figure 8. Molecular structure of **8**. Hydrogen atoms and anion are omitted, and thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): Rh1−P1, 2.228(1); Rh1−C1, 2.181(4); Rh1−P2, 2.260(1); Rh1−P3, 2.218(1); C1−P4, 1.752(4); C1−Rh1−P3, 170.2(1); P1−Rh1−P2, 153.5(1).

of related frustrated Lewis pair chemistry in which the carbene center and phosphine donor of the $PC_{carbene}P$ ligand assume the roles of Lewis acid and base, respectively.[13] After the phenylacetylene 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

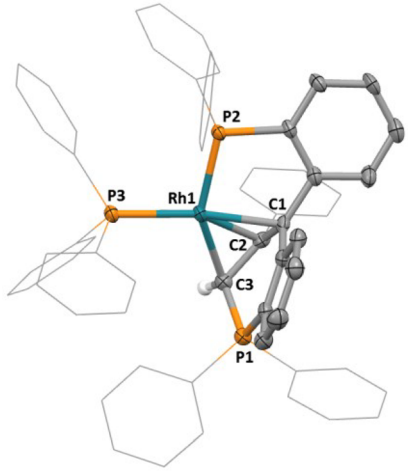


Figure 9. Molecular structure of **10**. Hydrogen atoms and anion are omitted, and thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): Rh1−C1, 2.153(5); Rh1−C2, 2.107(6); Rh1−C3, 2.215(6); Rh1−P2, 2.221(2); Rh1−P3, 2.304(2); P1−C3, 1.733(6); C1−C2, 1.420(8);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

DOI: 10.1021/acs.organomet.7b00461
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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 byproduct. However, repeating the reaction with an additional 1 equiv of PPh_3 provided quantitative formation of **11** and $SPPh_3$ (as judged by ^{31}P NMR spectroscopy).

The molecular structure of compound **11** reveals an elongation in Rh1−C1 (2.160(3) Å in comparison to the parent carbene **2** at 1.945(11) Å) indicative of loss of carbon−metal multiple-bond character (Figure 10). A drastic shortening

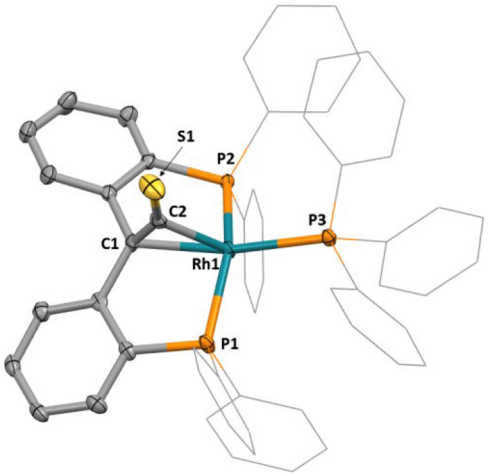

Figure 10. Molecular structure of **11**. Hydrogen atoms and anion are omitted, and thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): Rh1−P1, 2.282(1); Rh1−C1, 2.160(3); Rh1−P2, 2.332(1); Rh1−P3, 2.376(1); C1−Rh1−P3, 162.5(1); P1−Rh1−P2, 148.2(1).

in the Rh1−P3 distance of the phosphine trans to C1 is also noted in comparison 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 center 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.

EXPERIMENTAL SECTION

General Information. All syntheses were carried out under an 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 instrument. Single crystals were measured on a four-circle 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 × 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 solution. After it was stirred 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 it stood 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 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

DOI: 10.1021/acs.organomet.7b00461
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(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 it stood 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%). ^{1}H 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{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ_C 19.5−31.8 (m, −CH$_2$−CH$_2$−), 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{^{1}H} 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 it was stirred 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 removed by cannula. This washing process was repeated two further times. The residue was then dissolved in DCM (1 mL) and layered with *n*-hexane (10 mL). Dark red crystals of the product were isolated and then dried under vacuum (56 mg, 59%). NMR data suggest that complex **6** is present as two isomers in equilibrium on dissolution 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, CH$_2$), 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 it was stirred 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 triethyl phosphite (6 μL, 0.035 mmol) at room temperature and mixed. After it stood 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 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 analyzed by ^{31}P NMR spectroscopy, which identified that the ratio of **2** to **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 it stood 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.

DOI: 10.1021/acs.organomet.7b00461
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Preparation of Complex 11. A solution of complex **2** (100.0 mg, 0.057 mmol) and triphenylphosphine (14.9 mg, 0.057 mmol) in DCM (20 mL) was treated with carbon disulfide (4 μL, 0.067 mmol) at room temperature and mixed. After it was stirred 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). A solution of complex **2** (17.6 mg, 0.01 mmol) was dissolved in CH_3CN and then analyzed by ^{31}P NMR spectroscopy (spectra were recorded unlocked). B(C_6F_5)$_3$ (5.1 mg, 0.01 mmol) was then added, and the mixture was 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

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00461.

Experimental, crystallographic, and computational details (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 1546502, 1546504−1546508, and 1564183 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.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National University of Singapore and the Singapore Ministry of Education for financial support (WBS R-143-000-586-112 and R-143-000-666-114). T.K. wishes to thank Prof. Stuart A. Macgregor for providing access to high-performance computing facilities.

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