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POP-Pincer Silyl Complexes of Group 9: Rhodium versus Iridium

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Supporting Information

ABSTRACT: 9,9-Dimethyl-4,5-bis(diisopropylphosphino)-xanthene (xant(P^iPr_2)$_2$) derivatives RhCl{xant(P^iPr_2)$_2$} (**1**) and IrHCl{xant(P^iPr_2)[^{i}PrPCH(Me)CH$_2$]} (**2**) react with diphenylsilane and triethylsilane to give the saturated d^6-compounds RhHCl(SiR_3){xant(P^iPr_2)$_2$} (SiR_3 = $SiHPh_2$ (**3**), $SiEt_3$ (**4**)) and IrHCl(SiR_3){xant(P^iPr_2)$_2$} (SiR_3 = $SiHPh_2$ (**5**), $SiEt_3$ (**6**)). Complexes **3** and **5** undergo a Cl/H position exchange process via the MH{xant(P^iPr_2)$_2$} (M = Rh (**8**), Ir (**E**)) intermediates. The rhodium complex **3** affords the square planar d^8-silyl derivative Rh($SiClPh_2$){xant(P^iPr_2)$_2$} (**7**), whereas the iridium derivative **5** gives IrH_2($SiClPh_2$){xant(P^iPr_2)$_2$} (**9**), which is stable. In agreement with the formation of **7**, the reactions of **8** with silanes are a general method to prepare square planar d^8-rhodium-silyl derivatives. Thus, the addition of triethylsilane and triphenylsilane to **8** initially leads to the dihydrides RhH_2(SiR_3){xant(P^iPr_2)$_2$} (SiR_3 = $SiEt_3$ (**10**), $SiPh_3$ (**11**)), which lose molecular hydrogen to afford Rh(SiR_3){xant(P^iPr_2)$_2$} (SiR_3 = $SiEt_3$ (**12**), $SiPh_3$ (**13**)). Treatment of **7** with $NaBAr^F{}_4$·2H_2O leads to the cationic five-coordinate d^6-species [RhH{Si(OH)Ph_2}{xant(P^iPr_2)$_2$}]$BAr^F{}_4$ (**14**) through a silylene intermediate. According to the participation of the latter in the formation of **14**, this cation is an efficient catalyst precursor for the monoalcoholysis of diphenylsilane with a wide range of alcohols, reaching turnover frequencies at 50% of conversion between 4000 and 76 500 h^{-1}. The X-ray structures of **3**, **6**, **7**, **9**, **12**, and **14** are also reported.

INTRODUCTION

Complexes containing diphosphine pincer ligands are attracting increased interest because their high stability and disposition of the donor atoms allow them to develop a marked ability to form less common coordination polyhedra and favor unusual metal oxidation states.[1] Thus, in the search for new transition-metal catalysts, more robust than those based on *trans*-M(P^iPr_3)$_2$ metal fragments, we synthesized the ligands 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene (xant-(P^iPr_2)$_2$) and 4,6-bis(diisopropylphosphino)dibenzofuran (dbf-(P^iPr_2)$_2$) three years ago.[2] These diphosphines were subsequently used to prepare POP-complexes of Os(II), Os(III), Os(IV), and Os(VI), some of which proved to be promising alternatives to ruthenium for the direct synthesis of imines from alcohols and amines, with liberation of molecular hydrogen,[3] and for the regioselective head-to-head (*Z*)-dimerization of terminal alkynes.[4] We have recently widened our work to rhodium and iridium. Thus, following the previously developed methodology to access the chemistry of the *trans*-Rh(P^iPr_3)$_2$ and *trans*-Ir(P^iPr_3)$_2$ metal fragments, we performed the reactions of the dimers [M(μ-Cl)(C_8H_{14})$_2$]$_2$ (M = Rh, Ir) with xant(P^iPr_2)$_2$ that afforded the square planar rhodium(I) derivative RhCl{xant(P^iPr_2)$_2$} (**1**)[5] and the iridium(III) complex IrHCl{xant(P^iPr_2)[^{i}PrPCH(Me)CH$_2$]} (**2**) in high yields (Scheme 1).[6] Now, we have investigated the reactivity of **1** and **2** toward silanes.

Reactions of transition-metal complexes with silanes are of great current interest due to the relevance of M-SiR_3 intermediates[7] in transition-metal catalyzed processes such as the hydrosilylation of unsaturated organic substrates,[8] the direct synthesis of chlorosilanes,[9] and Si−H/OH coupling.[10] Silyl complexes containing pincer diphosphine ligands are very rare, in particular for rhodium and iridium. The linker groups encountered consist of either metalated aryl or amide units in anionic POCOP or PNP ligands or neutral PP_2 triphosphines (Chart 1). Brookhart[11] has studied the mechanism of (POCOP)IrH_2-catalyzed reduction of a variety of tertiary

Scheme 1

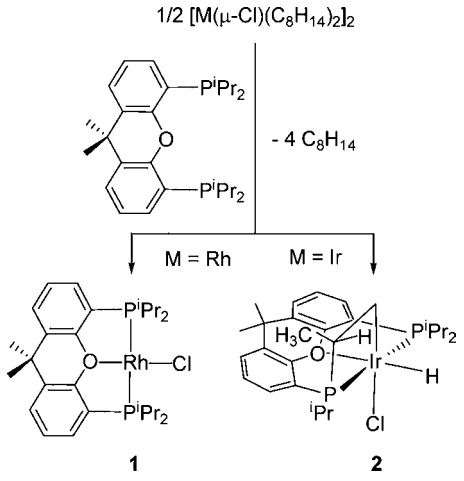

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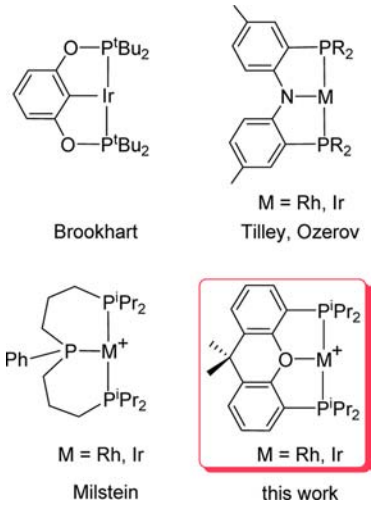
Chart 1

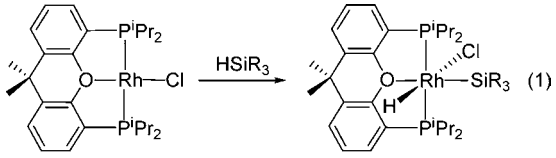


amides with H_2SiEt_2 (POCOP = 2,6-bis(di-*tert*-butylphophinito)phenyl) and established that the neutral silyl trihydride Ir(V) complex (POCOP)$IrH_3(SiHEt_2)$ is the catalytically active species, whereas the highly electrophilic η^1-silane derivative $[(POCOP)IrH(\eta^1\text{-}HSiEt_3)]^+$ catalyzes the hydrosilylation of ketones, aldehydes, esters, epoxides, allyl halides, and ethers. Tilley[12] has described synthetic pathways to a variety of (PNP)Ir−silyl and −silylene complexes (PNP = bis(*o*-diisopropylphosphinophenyl)amide) and explored the catalytic activation of the silylene species in the silane alcoholysis and aminolysis and for the hydrosilylation of ketones and alkenes. Ozerov[13] has provided insight into the relative thermodynamic affinity of the (PNP)Rh skeleton toward the oxidative addition of various halosilanes and how it compares with its affinity toward addition of other species. Milstein[14] has reported on the synthesis of rhodium and iridium complexes containing the triphosphine ligand $^iPr_2P(CH_2)_3P(Ph)(CH_2)_3P^iPr_2$ (PP_2) and described their reactivity toward $HSi(SEt)_3$.

This paper reports on the similarities and differences in the behavior of the metal fragments Rh{xant(P^iPr_2)$_2$} and Ir{xant(P^iPr_2)$_2$} toward silanes and on the catalytic activity of the five-coordinate d^6-complex [RhH{Si(OH)Ph$_2$}{xant(P^iPr_2)$_2$}]BAr^F_4 in the monoalcoholysis of diphenylsilane.

RESULTS AND DISCUSSION

Saturated d^6-Hydride-silyl Complexes. The square planar rhodium(I) complex RhCl{xant(P^iPr_2)$_2$} (**1**) oxidatively adds the Si−H bond of silanes. Thus, at room temperature, the treatment of toluene solutions of this compound with 1.1 equiv of diphenylsilane and triethylsilane leads to the saturated d^6-hydride-silyl derivatives $RhHCl(SiR_3)\{xant(P^iPr_2)_2\}$ (SiR_3 = $SiHPh_2$ (**3**), $SiEt_3$ (**4**)), which were isolated as white solids in 81% (**3**) and 56% (**4**) yield, according to eq 1.



Complex **3** was characterized by X-ray diffraction analysis. Figure 1 gives a view of its structure. As expected for a pincer

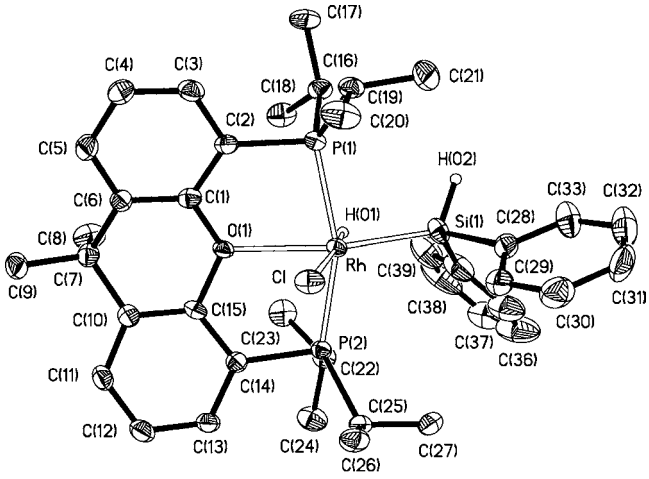


Figure 1. ORTEP diagram of complex **3** (50% probability ellipsoids). Hydrogen atoms (except hydride and Si−H) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−Cl = 2.4367(9), Rh−P(1) = 2.2885(9), Rh−P(2) = 2.3046(9), Rh−Si(1) = 2.2660(10), Rh−O(1) = 2.384(2); P(1)−Rh−P(2) = 160.27(3), P(1)−Rh−O(1) = 80.83(6), P(2)−Rh−O(1) = 79.58(6), Si(1)−Rh−O(1) = 158.32(6).

coordination of the diphosphine, the Rh(POP) skeleton is T-shaped with the rhodium atom situated in the common vertex and P(1)−Rh−P(2), P(1)−Rh−O(1), and P(2)−Rh−O(1) angles of 160.27(3)°, 80.83(6)°, and 79.58(6)°, respectively. So, the coordination geometry around the metal center can be rationalized as a distorted octahedron with the silyl group *trans*-disposed to the oxygen atom of the diphosphine (Si(1)−Rh−O(1) = 158.32(6)°) and the hydride *trans*-disposed to the chloride ligand. This ligand disposition is consistent with a concerted *cis*-addition of the Si−H bond along the O−Rh−Cl axis of **1** with the silyl group directed toward the chloride ligand.[15] The Rh−Si bond length of 2.2660(10) Å compares well with Rh(III)−Si single bond distances previously reported.[16]

The ^{1}H, ^{31}P{^{1}H}, and ^{29}Si{^{1}H} NMR spectra of **3** and **4**, in benzene-d_6, at room temperature are consistent with the structure shown in Figure 1. Thus, the ^{1}H NMR spectra show hydride resonances at −15.90 (**3**) and −16.29 (**4**) ppm which appear as double triplets with H−Rh and H−P coupling constants of about 24 and 15 Hz, respectively. In agreement with equivalent P^iPr_2 groups, the ^{31}P{^{1}H} NMR spectra contain at 42.9 (**3**) and 41.6 (**4**) ppm doublets with P−Rh coupling constants of 112 and 120 Hz, respectively. In the ^{29}Si{^{1}H} NMR spectra, the silyl groups display at 4.1 (**3**) and 40.3 (**4**) ppm double triplets with Si−Rh and Si−P coupling constants of 36 and 13 Hz (**3**) and 32 and 11 Hz (**4**).

Iridium is more reducing than rhodium and shows higher tendency to form coordinatively saturated compounds.[6,17] As a consequence, the iridium dimer $[Ir(\mu\text{-}Cl)(C_8H_{14})_2]_2$ reacts with xant(P^iPr_2)$_2$ to afford the saturated d^6 complex **2** (Scheme 1). However, the latter undergoes demetalation by reductive elimination to act as a synthon of the unsaturated d^8 species IrCl{xant(P^iPr_2)$_2$} (**A**),[6] the iridium(I) counterpart of **1**. Thus, at room temperature, the treatment of toluene solutions of **2** with 1.1 equiv of diphenylsilane and triethylsilane affords $IrHCl(SiR_3)\{xant(P^iPr_2)_2\}$ (SiR_3 = $SiHPh_2$ (**5**), $SiEt_3$ (**6**)), the

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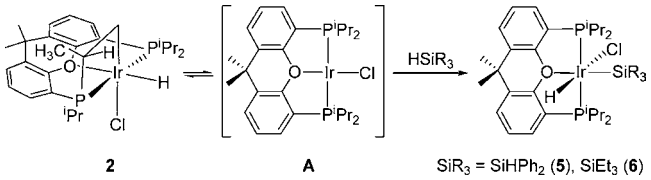
iridium counterparts of **3** and **4**, which were isolated as white solids in 41% (**5**) and 68% (**6**) yield, according to Scheme 2.

Scheme 2



Complex **6** was characterized by X-ray diffraction analysis. Figure 2 gives a view of its structure. Like for **3** the M(POP)

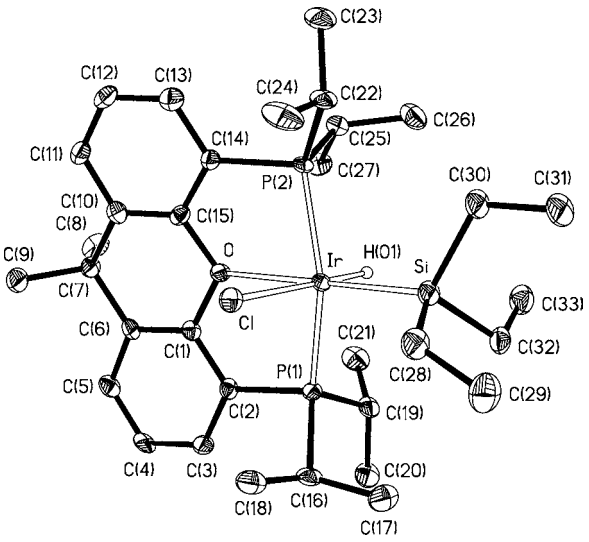


Figure 2. ORTEP diagram of complex **6** (50% probability ellipsoids). Hydrogen atoms (except hydride) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir−Cl = 2.4733(12), Ir−P(1) = 2.3012(12), Ir−P(2) = 2.2968(12), Ir−Si = 2.3402(14), Ir−O 2.374(3); P(1)−Ir−P(2) = 155.00(4), P(1)−Ir−O = 80.19(8), P(2)−Ir−O = 77.45(9), Si−Ir−O = 179.66(9).

skeleton is T-shaped with the iridium atom situated in the common vertex and P(1)−Ir−P(2), P(1)−Ir−O, and P(2)−Ir−O angles of 155.00(4)°, 80.19(8)°, and 77.45(9)°, respectively. Thus, the octahedral coordination polyhedron around the metal center is as that of the rhodium analogue, with the silyl group *trans* to the oxygen atom of the diphosphine (Si−Ir−O = 179.66(9)°), whereas the hydride lies *trans* to the chloride ligand. The Ir−Si bond length of 2.3402(14) Å agrees well with those reported for other Ir(III)-SiR_3 derivatives.[18]

The ^{1}H, ^{31}P{^{1}H}, and ^{29}Si{^{1}H} NMR spectra of **5** and **6**, in benzene-d_6, at room temperature are consistent with those of **3** and **4** and with the structure shown in Figure 2. The presence of a hydride ligand in these compounds is strongly supported by the ^{1}H NMR spectra, which contain at −19.91 (**5**) and −20.06 (**6**) ppm triplets with H−P coupling constants of 14.5 and 16.0 Hz, respectively. As expected for equivalent P^iPr_2 groups, the ^{31}P{^{1}H} NMR spectra show singlets at 29.9 (**5**) and 29.0 (**6**) ppm. The silyl groups display at −36.3 (**5**) and −7.6 (**6**) ppm triplets with Si−P coupling constants of 10 and 8 Hz, respectively, in the ^{29}Si{^{1}H} NMR spectra.

Cl/H Position Exchange. The diphenylsilyl complex **3** is unstable in solution. In toluene at 50 °C, it releases molecular hydrogen to give the rhodium(I) derivative Rh(SiClPh$_2$){xant-(P^{i}Pr$_2$)$_2$} (**7**), which contains a chlorodiphenylsilyl group resulting from an additional migration of the chloride ligand from the metal center to the silicon atom. Under these conditions, the reaction is quantitative after 5 days, as judged by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

Complex **7** was isolated as red crystals in 95% yield and characterized by X-ray diffraction analysis. Figure 3 shows a

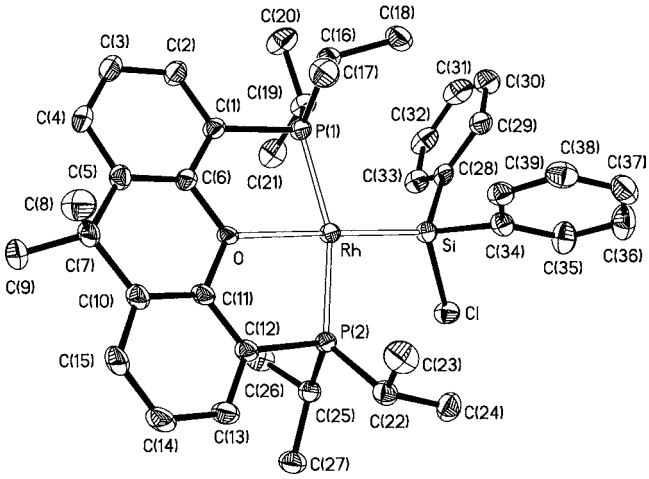


Figure 3. ORTEP diagram of complex **7** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−P(1) = 2.2664(8), Rh−P(2) = 2.2728(7), Rh−Si = 2.2581(8), Rh−O = 2.2609(18); P(1)−Rh−P(2) = 161.97(3), P(1)−Rh−O = 81.25(5), P(2)−Rh-O = 81.19(5), Si−Rh−O = 179.35(6).

view of its structure. The coordination geometry around the rhodium atom is almost square planar[19] with the diphosphine coordinated in the expected pincer fashion (P(1)−Rh−P(2) = 161.97(3)°, P(1)−Rh−O = 81.25(5)°, P(2)−Rh−O = 81.19(5)°) and the silyl group *trans* disposed to the oxygen atom of the diphosphine (Si−Rh−O = 179.35(6)°). The greatest deviation from the best plane through the rhodium, silicon, P(1), oxygen, and P(2) atoms is 0.0506(4) Å for Rh. The Rh−Si bond length of 2.2581(8) Å compares well with those reported for the few Rh(I)-silyl complexes characterized by X-ray diffraction analysis.[19,20] In agreement with the high symmetry of the molecule, the ^{1}H and ^{13}C{^{1}H} NMR spectra show two signals for the methyl groups of the phosphine isopropyl substituents (δ^1_H, 1.19 and 1.01; δ^{13}_C, 20.3 and 17.9) and a signal for the methyl substituents of the central heterocycle (δ^1_H, 1.24; δ^{13}_C, 31.0), whereas the ^{31}P{^{1}H} NMR spectrum contains at 49.4 ppm a doublet with a P−Rh coupling constant of 153.1 Hz. The silyl group displays at 49.2 ppm a double triplet with Si−Rh and Si−P coupling constants of 82 and 22 Hz, respectively, in the ^{29}Si{^{1}H} NMR spectrum.

The formation of **7** could be rationalized according to pathways *a* and *b* of Scheme 3. The reductive elimination of HSiClPh$_2$ from **3** should initially afford the previously described square planar rhodium(I) derivative RhH{xant(P^{i}Pr$_2$)$_2$} (**8**).[6] The oxidative addition of the H−Si bond of HSiClPh$_2$ along the O−Rh−H axis of **8** with the silyl group directed toward the oxygen atom of the diphosphine should lead to the *cis*-dihydride intermediate **B** (pathway *a*), while the same addition with the silyl group on the hydride ligand should afford the *trans*-dihydride intermediate **C** (pathway *b*). The reductive elimination of molecular hydrogen from **B** would be a fast

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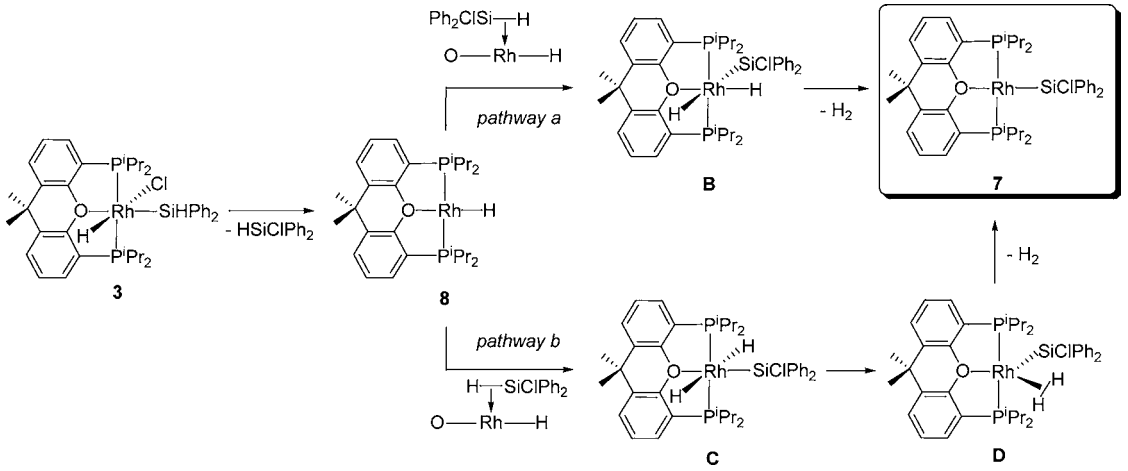
Scheme 3

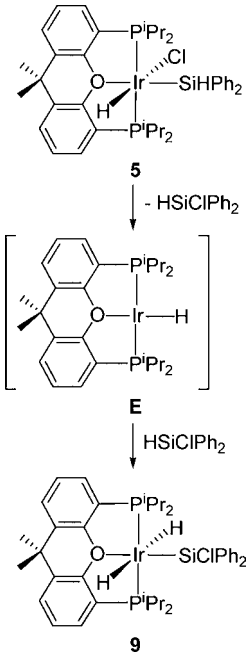


reaction given the *cis*-orientation of the hydride ligands and the marked preference of the Rh{xant(P^iPr_2)$_2$} skeleton for the unsaturated d^8 species. However, the *trans*-disposition of the hydride ligands in **C** prevents the three-centered transition state for their reductive elimination. So, the loss of molecular hydrogen requires the previous dissociation of the oxygen atom of the diphosphine, which should became bidentate.[21] The dissociation of the oxygen atom of the diphosphine should allow the formation of the dihydrogen intermediate or transition state **D**, which could easily give **7**.

Complex **5**, the iridium counterpart of **3**, is also unstable in solution. In toluene at 50 °C, it evolves into the *trans*-dihydride $IrH_2(SiClPh_2)${xant(P^iPr_2)$_2$} (**9**) that is the iridium counterpart of intermediate **C** (Scheme 3). The transformation is quantitative after 2 days, as judged by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The formation of **9** can be rationalized in a similar manner to that of **C** via a square planar iridium(I) monohydride intermediate IrH{xant(P^iPr_2)$_2$} (**E**), analogous to **8**, which should be generated by reductive elimination of $HSiClPh_2$. Thus, the subsequent oxidative addition of the H−Si bond of the formed silane along the O−Ir−H axis of **E** with the silyl group directed toward the hydride ligand could afford the *trans*-dihydride (Scheme 4). In favor of this proposal, we have observed that the addition of 2.0 equiv of diphenylsilane to a benzene-d_6 solution of **6** in an NMR tube at 50 °C affords **9**, via **5**, and $HSiEt_3$. In this context, it should be noted that complex **9** is more stable than **5** in spite of the destabilization produced by the strong *trans* influence of the hydride ligands mutually *trans* disposed.[22] This fact is consistent with density functional theory (DFT) calculations on the model complexes $Os(SiR_3)$-$Cl(CO)(PH_3)_2$ (R = F, Cl, OH, Me), which have revealed that a linear combination of Si-R σ^* orbitals is responsible for some π-acceptor capacity of the silyl group. This component increases its contribution to the bond as the electronegativity of the substituent at the silicon atom also increases.[23] The difference in behavior between rhodium and iridium in this Cl/H position exchange process agrees well with the higher preference of iridium for the saturated d^6 species.[6,17]

The *trans*-dihydride **9** was isolated as a white solid in 60% yield and characterized by X-ray diffraction analysis. An ORTEP drawing of the molecule is shown in Figure 4. The structure proves the Cl/H position exchange and the *trans* disposition of the hydride ligands (H(01)−Ir−H(02) = 173(3)°). The coordination polyhedron around the iridium

Scheme 4



atom can be rationalized as a distorted octahedron with the diphosphine *mer*-coordinated (P(1)−Ir−P(2) = 159.01(4)°, P(1)−Ir−O = 81.04(7)°, P(2)−Ir−O = 80.77(7)°) and the silyl group *trans* disposed to the oxygen atom of the diphosphine (Si−Ir−O = 167.72(7)°). The Ir−Si bond length of 2.2655(11) Å compares well with that of **6**.

The ^1H, $^{31}P\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra in benzene-d_6, at room temperature, are consistent with the structure shown in Figure 4. In agreement with the presence of *trans*-hydrides, the ^1H NMR spectrum shows at −4.90 ppm a triplet with a H−P coupling constant of 16.6 Hz. As expected for equivalent P^iPr_2 groups, the $^{31}P\{^1H\}$ NMR spectrum contains at 47.9 ppm a singlet. The silyl group displays at −4.8 ppm a triplet with a Si−P coupling constant of 20 Hz in the $^{29}Si\{^1H\}$ NMR spectrum.

Square-Planar Rhodium(I)-silyl Complexes. The formation of **7** according to Scheme 3 suggested that the monohydride **8** should be an efficient starting material to prepare square planar rhodium(I)-silyl derivatives in a general manner. The addition of 1.1 equiv of triethylsilane and

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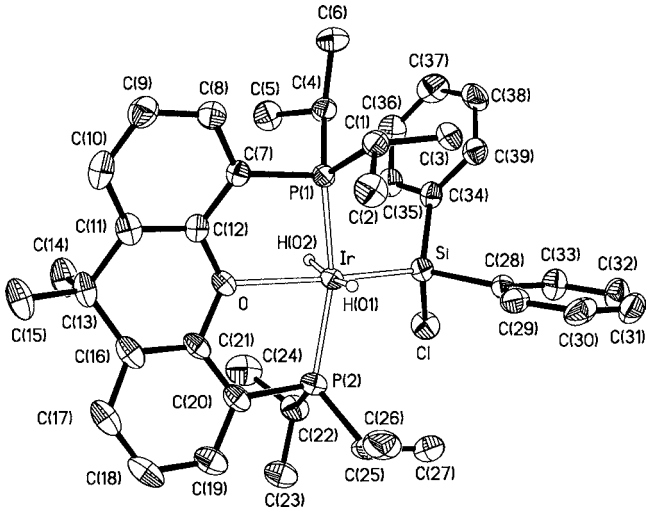


Figure 4. ORTEP diagram of complex **9** (50% probability ellipsoids). Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–P(1) = 2.2811(10), Ir–P(2) = 2.2704(10), Ir–Si = 2.2654(11); P(1)–Ir–P(2) = 159.01(4), P(1)–Ir–O = 81.04(7), P(2)–Ir–O = 80.77(7), Si–Ir–O = 167.72(7), H(01)–Ir–H(02) = 173(3).

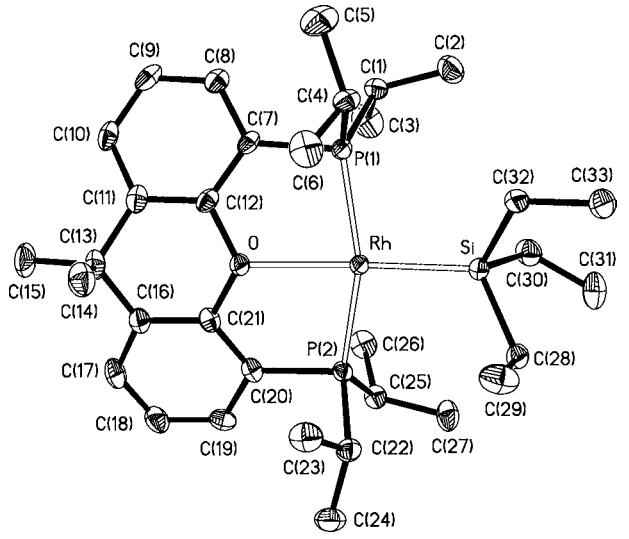
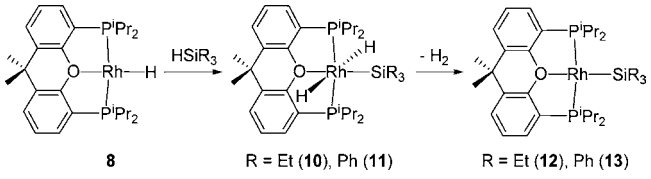


Figure 5. ORTEP diagram of complex **12** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh–P(1) = 2.2541(8), Rh–P(2) = 2.2573(8), Rh–Si = 2.3090(8), Rh–O = 2.3149(18); P(1)–Rh–P(2) = 158.51(3), P(1)–Rh-O = 81.39(5), P(2)–Rh–O = 81.57(5), Si–Rh–O = 170.0(5).

triphenylsilane to the toluene solutions of **8** leads to the *trans*-dihydride derivatives $RhH_2(SiR_3)\{xant(P^iPr_2)_2\}$ (SiR_3 = $SiEt_3$ (**10**), $SiPh_3$ (**11**)), which release molecular hydrogen to afford the rhodium(I) complexes $Rh(SiR_3)\{xant(P^iPr_2)_2\}$ (SiR_3 = $SiEt_3$ (**12**), $SiPh_3$ (**13**)). The reductive elimination of molecular hydrogen could take place in a similar manner to those shown in Scheme 3 or via a protonation–dehydrogenation mechanism, as reported by Brookhart for a related PNP-Ir system,[24] catalyzed by traces of H_2O. The trend of **10** and **11** to lose molecular hydrogen is in contrast with the behavior of **4** and $RhH_2Cl\{xant(P^iPr_2)_2\}$ and consistent with the inertness of the monohydride **8** toward molecular hydrogen.[6]

Scheme 5



The dihydride intermediates **10** and **11** were spectroscopically detected and fully characterized when the reactions were performed in a NMR tube at 258 K. Their ^1H NMR spectra show at −5.63 (**10**) and −5.02 (**11**) ppm double triplets, with H–Rh and H–P coupling constants of 17.6 and 18.0 (**10**) Hz and 19.3 and 16.1 (**11**) Hz, corresponding to the hydride ligands. The $^{31}P\{^1H\}$ NMR spectra contain at 61.6 (**10**) and 59.3 (**11**) ppm doublets with Rh–P coupling constants of 126 and 120 Hz, respectively. The silyl groups display at 33.0 (**10**) and 9.4 (**11**) ppm double triplets, with Si–Rh and Si–P coupling constants of 33 and 9 (**10**) Hz and 42 and 12 (**11**) Hz, in the $^{29}Si\{^1H\}$ NMR spectra.

The square planar complexes **12** and **13** were isolated as red solids in a 58% and 81% yield, respectively. The triethylsilyl derivative **12** was characterized by X-ray diffraction analysis. Figure 5 shows an ORTEP drawing of the molecule. Like for **7**, the coordination geometry around the rhodium atom is almost square planar with the diphosphine coordinated in a *mer*-fashion (P(1)–Rh–(2) = 158.51(3)°, P(1)–Rh–O = 81.39(5)°, P(2)–Rh–O = 81.57(5)°) and the silyl group *trans* disposed to the oxygen atom of the diphosphine (Si–Rh–O = 170.0(5)°). In this case, the greatest deviation from the best plane through the rhodium, silicon, P(1), oxygen, and P(2) atoms is 0.1198(4) Å for Rh. The Rh–Si bond length of 2.3090(8) Å compares well with that of **7**. In agreement with Figure 5, the $^{31}P\{^1H\}$ NMR spectra of **12** and **13** contain at 46.0 and 44.7 ppm doublets with P–Rh coupling constants of 171 and 159 Hz, respectively, whereas the $^{29}Si\{^1H\}$ NMR spectra show at 25.0 (**12**) and 14.4 (**13**) ppm double triplets with Si–Rh and Si–P coupling constants of 54 and 19 (**12**) Hz and 66 and 21 (**13**) Hz.

Catalytic Monoalcoholysis of Ph_2SiH_2. The square planar rhodium(I) complex **7** is the entry to an interesting rhodium(III)-silylol species. Treatment of its fluorobenzene solutions with 1.2 equiv of $NaBAr^F{}_4{\cdot}2H_2O$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl), at room temperature, for 1 h results in chloride abstraction from the silyl group and the formation of the five-coordinate hydride-silylol derivative $[RhH\{Si(OH)Ph_2\}\{xant(P^iPr_2)_2\}]BAr^F{}_4$ (**14**). Its formation can be rationalized according to Scheme 6. The chloride abstraction should initially afford the silylene intermediate **F**, which could subsequently undergo the heterolytic addition of an O–H bond of water to give the hydride-silylol derivative.

Complex **14** was isolated as a white solid in 76% yield and characterized by X-ray diffraction analysis. The structure proves its formation. Figure 6 shows a view of the cation of the salt. The geometry around the rhodium atom can be described as a distorted trigonal bipyramid with the P^iPr_2 groups of the pincer in apical positions (P(1)–Rh–P(2) = 157.16(3)°, P(1)–Rh–O(1) = 83.47(5)°, P(2)–Rh–O(1) = 84.13(5)°) and inequivalent angles within the Y-shaped equatorial plane (O(1)–Rh–Si = 138.62(5)°, O(1)–Rh–H(01) = 156.0(12)°, and Si–Rh–H(01) = 65.3(12)°). The Rh–Si bond length of 2.3000(8) Å is about 0.03 Å longer than that of the saturated rhodium(III) derivative **3**. In agreement with the

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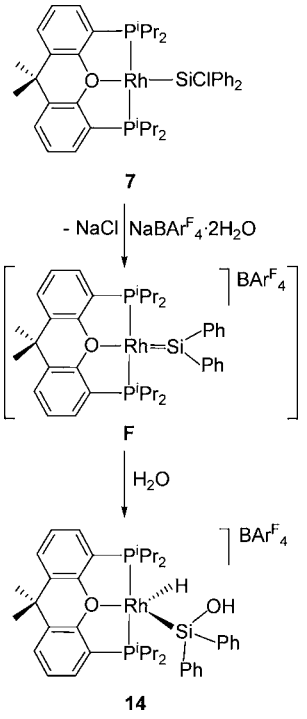
Scheme 6



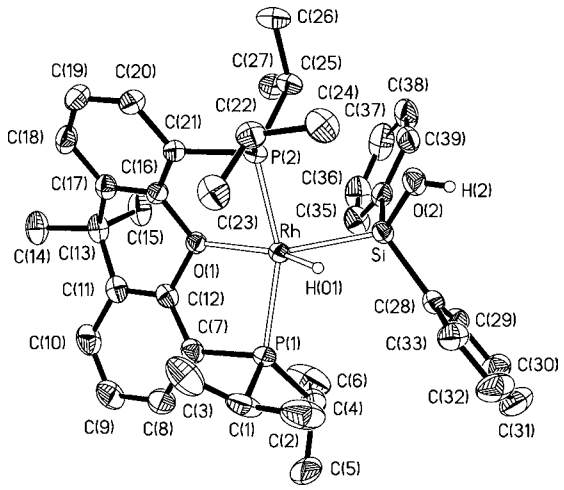


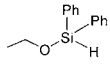
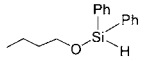
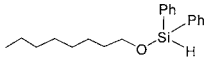
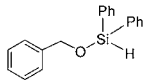
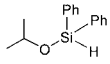
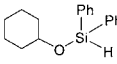
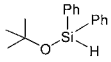
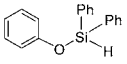
Figure 6. ORTEP diagram of the cation of complex **14** (50% probability ellipsoids). Hydrogen atoms (except hydride and O–H) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh–P(1) = 2.3165(7), Rh–P(2) = 2.2794(7), Rh–Si = 2.3000(8), Rh–O(1) = 2.1859(17); P(1)–Rh–P(2) = 157.16(3), P(1)–Rh–O(1) = 83.47(5), P(2)–Rh–O(1) = 84.13(5), O(1)–Rh–Si = 138.62(5), Si–Rh–H(01) = 65.3(12), O(1)–Rh–H(01) = 156.0(12).

presence of the hydride ligand, the ^{1}H NMR spectrum, in dichloromethane-d_2, at 233 K shows at −17.43 ppm a double triplet with H–Rh and H–P coupling constants of 39.4 and 12.5 Hz, respectively, whereas the OH- resonance appears at 3.25 ppm as a broad singlet. As expected for equivalent P^iPr_2 groups coordinated to a Rh(III) center, the $^{31}P\{^{1}H\}$ NMR spectrum at 233 K contains at 52.1 ppm a doublet with a P–Rh coupling constant of 119 Hz. The silylol group displays at 26.1 ppm a double triplet with Si–Rh and Si–P coupling constants of 32 and 7 Hz, respectively, in the $^{29}Si\{^{1}H\}$ NMR spectrum at 233 K.

Tilley has demonstrated that iridium-silylene complexes are active catalyst for the alcoholysis of silanes.[12c] This prompted us to investigate the alcoholysis of the diphenylsilane promoted by **14** (eq 2), since its formation seems to take place through the silylene intermediate **F**. The reactions were performed in toluene at 32 °C, using 0.17 mol % of catalyst and silane and alcohol concentrations of 0.3 M. Under these conditions, alkoxysilanes $HSi(OR)Ph_2$ were selectively formed in quantitative yield, after seconds or a few minutes, with spectacularly high turnover frequencies at 50% conversion ($TOF_{50\%}$), which range from 4000 to 76 500 h^{-1}, and isolated in high yields between 71% and 92% (Table 1).

$$H_2SiPh_2 + ROH \xrightarrow[\text{toluene, } 32^\circ C]{0.17 \text{ mol\% } \mathbf{14}} HSi(OR)Ph_2 + H_2 \qquad (2)$$

Table 1. Monoalcoholysis of H_2SiPh_2 Catalyzed by $[RhH\{Si(OH)Ph_2\}\{xant(P^iPr_2)_2\}]BAr^F_4$ (14)[a]

Run	Alcohol	Product	$TOF_{50\%}$ (h^{-1})	Isolated yield (%)
1	methanol		25300	89
2	ethanol		44000	87
3	1-butanol		53000	83
4	1-octanol		63600	71
5	benzyl alcohol		25000	71
6	2-propanol		76500	92
7	cyclohexylalcohol		62800	75
8	*t*-butanol		18000	81
9	phenol		4000	72

[a]0.17 mol % **14**, 0.3 M H_2SiPh_2, 0.3 M alcohol in toluene (5 mL) at 32 °C. Turnover frequencies [(mol product/mol Rh)/time] were calculated at 50% conversion.

Primary, secondary, and tertiary alcohols, as well as phenol were successfully used. For primary alcohols, the reaction rates increase as the length of the carbon chain increases, that is, in the sequence methanol (run 1) < ethanol (run 2) < 1-butanol (run 3) < 1-octanol (run 4). The secondary alcohols 2-propanol (run 6) and cyclohexanol (run 7) yield the corresponding alkoxysilanes with $TOF_{50\%}$ values similar or higher than 1-octanol. Although the reactions with the tertiary *t*-butanol (run 8) and with phenol (run 9) are also very efficient, these substrates afford the lowest $TOF_{50\%}$ values, 18 000 h^{-1} and 4000 h^{-1}, respectively.

The selective monoalcoholysis of the silane is notable and fully consistent with the participation of a silylene species as key

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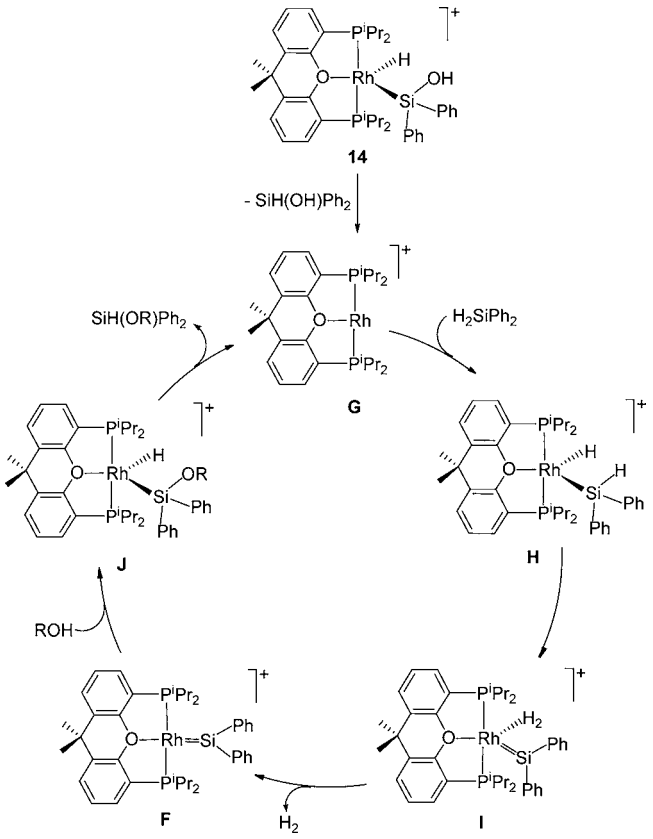
Scheme 7



intermediate of the process. The nucleophilic attack of the alcohol to an η^2-silane complex, M(η^2-H-SiR$_3$), has been considered an alternative manner of generating silylethers.[25] However, such possibility cannot justify the selectivity observed in this case. Furthermore, it should imply the heterolytic cleavage of the H−Si bond, which should require an electrophilic metal center, and this does not seem to be the case of Rh(I).[26] It should be also noted that in contrast to standard methods involving the treatment of silylchloride with an alcohol in the presence of a base that generates hydrochloride salts byproducts,[27] this process is environmentally benign and occurs with liberation of molecular hydrogen.

The catalysis can be rationalized according to Scheme 7. The reductive elimination of HSi(OH)Ph$_2$ from **14** could initially afford the rhodium(I) intermediate **G**, which should oxidatively add diphenylsilane to give **H**. Thus, the elimination of molecular hydrogen from the latter through **I** could lead to the silylene **F**, which should form **J** in a similar manner as **14**. Then, the reductive elimination of the alkoxysilane from **J** could generate **G** again.

CONCLUDING REMARKS

This study has revealed that the square planar d^8-complexes MCl{xant(P^{i}Pr$_2$)$_2$} (M = Rh, Ir) oxidatively add the Si−H bond of tertiary and secondary silanes, along the O−M−Cl axis with the silyl group directed toward the chloride ligand, to give d^6-chloro-hydride-silyl derivatives MHCl(SiR$_3$){xant(P^{i}Pr$_2$)$_2$} and MHCl(SiHR$_2$){xant(P^{i}Pr$_2$)$_2$}. Complexes containing secondary silyl groups undergo a Cl/H position exchange to afford dihydride-chlorosilyl compounds MH$_2$(SiClR$_2$){xant(P^{i}Pr$_2$)$_2$}, through Cl-SiHR$_2$ reductive elimination and subsequent H-SiClR$_2$ oxidative addition to MH{xant(P^{i}Pr$_2$)$_2$} intermediates. According to the higher oxidizing character of the 4d metals, the rhodium species lose molecular hydrogen and, as a consequence, the addition of the H−Si bond of silanes to the square planar monohydride complex RhH{xant(P^{i}Pr$_2$)$_2$} leads to square planar d^8-silyl compounds Rh(SiR$_3$){xant(P^{i}Pr$_2$)$_2$}, in a general manner, through the corresponding d^6 intermediates MH$_2$(SiR$_3$){xant(P^{i}Pr$_2$)$_2$}. Interestingly, the abstraction of chloride from Rh(SiClPh$_2$){xant(P^{i}Pr$_2$)$_2$} in the presence of water yields the five-coordinate d^6-species [RhH{Si(OH)Ph$_2$}{xant(P^{i}Pr$_2$)$_2$}]$^+$, as a result of the addition of an O−H bond of water to the Rh−Si double bond of a silylene intermediate. In agreement with the participation of the latter in the formation of this cationic compound, it is a very efficient catalyst precursor for the selective monoalcoholysis of diphenylsilane that reaches turnover frequencies (TOF) at 50% of conversion up to 76 500 h^{-1}.

In conclusion, the Rh{xant(P^{i}Pr$_2$)$_2$} metal fragment favors unsaturated d^8-square planar, Rh(SiR$_3$){xant(P^{i}Pr$_2$)$_2$}, and d^6-five coordinate, [RhH{Si(OH)Ph$_2$}{xant(P^{i}Pr$_2$)$_2$}]$^+$, silyl complexes whereas the Ir{xant(P^{i}Pr$_2$)$_2$} metal fragment stabilizes saturated d^6-silyl derivatives, IrHCl(SiR$_3$){xant(P^{i}Pr$_2$)$_2$} and IrH$_2$(SiR$_3$){xant(P^{i}Pr$_2$)$_2$}. The stabilization of saturated d^6-Rh{xant(P^{i}Pr$_2$)$_2$} species seems to need the presence of a coordinated π-donor ligand such as chloride.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except fluorobenzene that was dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. The alcohols used in the catalytic reactions were dried by standard procedures and distilled under argon prior to use. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz and Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}), external 85% H$_3$PO$_4$ (^{31}P{^{1}H}), or external SiMe$_4$ (^{29}Si{^{1}H}). Coupling constants J and N are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). Xant(P^{i}Pr$_2$)$_2$,[2] IrHCl{xant(P^{i}Pr$_2$)[^{i}PrPCH(Me)CH$_2$]} (**2**),[6] RhCl{xant(P^{i}Pr$_2$)$_2$} (**1**),[6] RhH{xant(P^{i}Pr$_2$)$_2$} (**8**),[6] and NaBAr$^F_4$·2H$_2$O[28] were prepared by published methods.

Reaction of RhCl{xant(P^{i}Pr$_2$)$_2$} (1) with H$_2$SiPh$_2$: Preparation of RhHCl(SiHPh$_2$){xant(P^{i}Pr$_2$)$_2$} (3). Diphenylsilane (109 μL, 0.57 mmol) was added to a solution of **1** (300 mg, 0.52 mmol) in toluene (3 mL). After the resulting solution was stirred for 10 min at room temperature, it was evaporated to dryness to afford a white residue. Addition of pentane afforded a white solid that was washed with pentane (2 × 3 mL) and dried in vacuo. Yield: 320.0 mg (81%). Anal. Calcd. for C$_{39}$H$_{52}$ClOP$_2$RhSi: C, 61.21; H, 6.85. Found: C, 60.75; H, 6.72. HRMS (electrospray, m/z): calcd. for C$_{39}$H$_{52}$OP$_2$RhSi [M − Cl]$^+$: 729.2312; found: 729.2352. IR (neat compound, cm^{-1}): ν(Rh−H) 2097 (w); ν(Si−H) 2054 (m); ν(C−O−C) 1093 (m). ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 293 K, δ): 8.35 (d, J_{H-H} = 7.4, 4H, C*H* SiHPh$_2$), 7.33 (t, J_{H-H} = 7.4, 4H, C*H* SiHPh$_2$), 7.21 (t, J_{H-H} = 7.4, 2H, C*H* SiHPh$_2$), 7.13 (d, J_{H-H} = 7.6, 2H, C*H*-arom), 7.07 (m, 2H, C*H*-arom), 6.88 (t, J_{H-H} = 7.6, 2H, C*H*-arom), 6.13 (t, J_{H-P} = 11.2, 1H, Si−H), 2.40 (m, 2H, PC*H*(CH$_3$)$_2$), 1.96 (m, 2H, PC*H*(CH$_3$)$_2$), 1.51 (dvt, J_{H-H} = 7.2, N = 14.4, 6H, PCH(C*H*$_3$)$_2$), 1.32 (s, 3H, CH$_3$), 1.24 (dvt, J_{H-H} = 7.9, N = 16.4, 6H, PCH(C*H*$_3$)$_2$), 1.20 (s, 3H, CH$_3$), 1.11 (dvt, J_{H-H} = 7.6, N = 15.8, 6H, PCH(C*H*$_3$)$_2$), 0.78 (dvt, J_{H-H} = 6.5, N =

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12.9, 6H, PCH(CH_3)$_2$), −15.90 (dt, J_{H-Rh} = 24.5, J_{H-P} = 14.2, 1H, Rh−H). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 293 K, δ): 154.1 (vt, N = 11.1, *C*-arom), 142.9 (t, J_{C-P} = 1.5, *C*-arom, SiHPh$_2$), 137.2 (s, *C*H-arom SiHPh$_2$), 132.2 (vt, N = 5.0, *C*-arom), 131.1 (s, *C*H-arom SiHPh$_2$), 128.3 (s, *C*H-arom), 128.0 (s, *C*H-arom), 127.4 (s, *C*H-arom SiHPh$_2$), 124.0 (vt, N = 5.2, *C*H-arom), 123.1 (vt, N = 26.5, *C*-arom), 34.6 (s, *C*(CH$_3$)$_2$), 34.0, 28.7 (both s, C(*C*H$_3$)$_2$), 27.1 (vt, N = 22.5, P*C*H(CH$_3$)$_2$), 26.6 (dvt, J_{C-Rh} = 2.3, N = 26.7, P*C*H(CH$_3$)$_2$), 22.5 (s, PCH(*C*H$_3$)$_2$), 19.6 (s, PCH(*C*H$_3$)$_2$), 19.3 (vt, N = 6.3, PCH(CH$_3$)$_2$), 17.0 (s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, 293 K, δ): 42.9 (d, J_{P-Rh} = 112). $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 293 K, δ): 4.1 (dt, J_{Si-Rh} = 36, J_{Si-P} = 13).

Reaction of RhCl{xant(P^{i}Pr$_2$)$_2$} (1) with HSiEt$_3$: Preparation of RhHCl(SiEt$_3$){xant(P^{i}Pr$_2$)$_2$} (4). Triethylsilane (42 μL, 0.25 mmol) was added to a solution of **1** (134 mg, 0.23 mmol) in toluene (3 mL). After the resulting solution was stirred for 1 h at room temperature, it was evaporated to dryness to afford a white residue. Addition of pentane afforded a white solid that was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 90.0 mg (56%). Anal. Calcd. for $C_{33}H_{56}ClOP_2RhSi$: C, 56.85; H, 8.10. Found: C, 56.80; H, 8.10. HRMS (electrospray, m/z): calcd. for $C_{33}H_{56}OP_2RhSi$ $[M - Cl]^+$: 661.2625; found: 661.2750. IR (cm^{-1}): ν(Rh−H) 2094 (w). ^1H NMR (400.13 MHz, C_6D_6, 293 K, δ): 7.20 (m, 2H, C*H*-arom), 7.11 (d, J_{H-H} = 7.6, 2H, C*H*-arom), 6.89 (t, J_{H-H} = 7.6, 2H, C*H*-arom), 2.86 (m, 2H, PC*H*(CH$_3$)$_2$), 2.20 (m, 2H, PC*H*(CH$_3$)$_2$), 1.57 (dvt, J_{H-H} = 7.4, N = 15.6, 6H, PCH(C*H*$_3$)$_2$), 1.45 (m, 6H PCH(C*H*$_3$)$_2$ + 6H Si(C*H*$_2$CH$_3$)$_3$), 1.37 (t, J_{H-H} = 6.8, 9H, Si(CH$_2$C*H*$_3$)$_3$), 1.31 (s, 3H, CH$_3$), 1.20 (dvt, J_{H-H} = 7.6, N = 16.8, 6H, PCH(C*H*$_3$)$_2$), 1.18 (s, 3H, CH$_3$), 0.85 (dvt, J_{H-H} = 6.6, N = 13.0, 6H, PCH(C*H*$_3$)$_2$), −16.29 (dt, J_{H-Rh} = 23.9, J_{H-P} = 15.7, 1H, Rh−H). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 293 K, δ): 154.4 (vt, N = 10.5, *C*-arom), 132.2 (vt, N = 4.2, *C*-arom), 130.4 (s, *C*H-arom), 127.2 (s, *C*H-arom), 123.8 (s, *C*H-arom), 123.6 (vt, N = 27.2, *C*-arom), 34.6 (s, *C*(CH$_3$)$_2$), 32.7 (s, C(*C*H$_3$)$_2$), 28.0 (dvt, J_{C-Rh} = 3.4, N = 26.0, PCH(*C*H$_3$)$_2$), 27.9 (s, C(*C*H$_3$)$_2$), 27.6 (vt, N = 19.6, PCH(*C*H$_3$)$_2$), 20.3 (vt, N = 4.4, PCH(*C*H$_3$)$_2$), 20.1, 20.0, 17.7 (all s, PCH(*C*H$_3$)$_2$), 14.6 (s, Si(*C*H$_2$CH$_3$)$_3$), 10.1 (s, Si(CH$_2$*C*H$_3$)$_3$). $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, 293 K, δ): 41.6 (d, J_{P-Rh} = 120). $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 293 K, δ): 40.3 (dt, J_{Si-Rh} = 32, J_{Si-P} = 11).

Reaction of 2 with H$_2$SiPh$_2$: Preparation of IrHCl(SiHPh$_2$){xant(P^{i}Pr$_2$)$_2$} (5). Diphenylsilane (37 μL, 0.20 mmol) was added to a solution of **2** (123 mg, 0.18 mmol) in toluene (1 mL). After the resulting solution was stirred for 2 h at room temperature, it was evaporated to dryness to afford a yellowish residue. Addition of pentane afforded a white solid that was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 65.0 mg (41%). Anal. Calcd. for $C_{39}H_{52}ClIrOP_2Si$: C, 54.82; H, 6.13. Found: C, 54.47; H, 5.98. HRMS (electrospray, m/z): calcd. for $C_{39}H_{51}ClOP_2IrSi$ $[M - H]^+$: 853.2490; found: 853.2422. IR (cm^{-1}): ν(Ir−H) 2223 (w); ν(Si−H) 2035 (w); ν(C−O−C) 1093 (m). ^1H NMR (300.08 MHz, C_6D_6, 293 K, δ): 8.32 (d, J_{H-H} = 7.4, 4H, C*H* SiHPh$_2$), 7.32 (t, J_{H-H} = 7.4, 4H, C*H* SiHPh$_2$), 7.19 (t, J_{H-H} = 7.4, 2H, C*H* SiHPh$_2$), 7.07 (m, 4H, C*H*-arom), 6.86 (t, J_{H-H} = 7.5, 2H, C*H*-arom), 6.02 (t, J_{H-P} = 8.1, 1H, Si−H), 2.59 (m, 2H, PC*H*(CH$_3$)$_2$), 2.07 (m, 2H, PC*H*(CH$_3$)$_2$), 1.43 (dvt, J_{H-H} = 7.0, N = 14.3, 6H, PCH(C*H*$_3$)$_2$), 1.32 (dvt, J_{H-H} = 7.9, N = 16.3, 6H, PCH(C*H*$_3$)$_2$), 1.27 (s, 3H, CH$_3$), 1.22 (s, 3H, CH$_3$), 1.09 (dvt, J_{H-H} = 7.7, N = 16.2, 6H, PCH(C*H*$_3$)$_2$), 0.80 (dvt, J_{H-H} = 6.7, N = 13.5, 6H, PCH(C*H*$_3$)$_2$), −19.91 (t, J_{H-P} = 14.5, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (75.46 MHz, C_6D_6, 293 K, δ): 154.5 (vt, N = 9.7, *C*-arom), 142.7 (s, *C*-arom, SiHPh$_2$), 137.2 (s, *C*H-arom SiHPh$_2$), 132.1 (vt, N = 4.8, *C*-arom), 131.4 (s, *C*H-arom SiHPh$_2$), 128.0 (s, *C*H-arom), 127.4 (s, *C*H-arom SiHPh$_2$), 125.1 (vt, N = 32.6, *C*-arom), 124.5 (vt, N = 5.3, *C*H-arom), 34.4 (s, *C*(CH$_3$)$_2$), 33.0, 30.8 (both s, C(*C*H$_3$)$_2$), 27.1 (vt, N = 22.5, PCH(CH$_3$)$_2$), 26.6 (vt, N = 26.7, PCH(CH$_3$)$_2$), 20.4, 19.5, 19.3, 17.6 (all s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 293 K, δ): 29.9 (s). $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 293 K, δ): −36.3 (t, J_{Si-P} = 10).

Reaction of 2 with HSiEt$_3$: Preparation of IrHCl(SiEt$_3$){xant(P^{i}Pr$_2$)$_2$} (6). Triethylsilane (27 μL, 0.16 mmol) was added to a solution of **2** (100 mg, 0.15 mmol) in toluene (3 mL). After the resulting solution was stirred for 1 h at room temperature, it was evaporated to dryness to afford a white residue. Addition of pentane afforded a white solid that was washed with pentane (3 × 2 mL) and dried in vacuo. Yield: 80 mg (68%). Anal. Calcd. for $C_{33}H_{56}ClIrOP_2Si$: C, 50.39; H, 7.18. Found: C, 50.13; H, 7.36. HRMS (electrospray, m/z): calcd. for $C_{33}H_{56}IrOP_2Si$ $[M - Cl]^+$ 751.3200; found: 751.3231. IR (cm^{-1}): ν(Ir−H) 2227 (w). ^1H NMR (300.13 MHz, C_6D_6, 293 K, δ): 7.20 (m, 2H, C*H*-arom), 7.07 (dd, J_{H-H} = 7.6, J_{H-H} = 1.5, 2H, C*H*-arom), 6.87 (t, J_{H-H} = 7.6, 2H, C*H*-arom), 3.09 (m, 2H, PC*H*(CH$_3$)$_2$), 2.28 (m, 2H, PC*H*(CH$_3$)$_2$), 1.59 (dvt, J_{H-H} = 7.3, N = 15.7, 6H, PCH(C*H*$_3$)$_2$), 1.46−138 (m, 21H, 6H PCH(C*H*$_3$)$_2$ + 15H Si(C*H*$_2$CH$_3$)$_3$), 1.25 (s, 3H, CH$_3$), 1.21 (s, 3H, CH$_3$), 1.19 (dvt, J_{H-H} = 7.4, N = 15.6, 6H, PCH(C*H*$_3$)$_2$), 0.84 (dvt, J_{H-H} = 6.9, N = 13.8, 6H, PCH(C*H*$_3$)$_2$), −20.06 (t, J_{H-P} = 16.0, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 293 K, δ): 154.9 (vt, N = 9.0, *C*-arom), 132.5 (vt, N = 4.8, *C*-arom), 130.6 (s, *C*H-arom), 127.5 (s, *C*H-arom), 125.6 (vt, N = 33.9, *C*-arom), 124.4 (vt, N = 4.5, *C*H-arom), 34.5 (s, *C*(CH$_3$)$_2$), 31.3, 29.9 (both s, C(*C*H$_3$)$_2$), 28.8 (vt, N = 32.3, PCH(CH$_3$)$_2$), 28.3 (vt, N = 22.9, PCH(CH$_3$)$_2$), 20.5, 19.8, 19.7, 18.4 (all s, PCH(*C*H$_3$)$_2$), 13.2 (s, Si(*C*H$_2$CH$_3$)$_3$), 10.4 (s, Si(CH$_2$*C*H$_3$)$_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 293 K, δ): 29.0 (s). $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 293 K, δ): −7.6 (t, J_{Si-P} = 8).

Preparation of Rh(SiClPh$_2$){xant(P^{i}Pr$_2$)$_2$} (7). A Schlenk flask provided with a Teflon closure was charged with a solution of **3** (300 mg, 0.39 mmol) in toluene (3 mL) under argon atmosphere. After being stirred for 5 days at 50 °C (the reaction was periodically checked by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy) the resulting red solution was evaporated to dryness. Pentane was added to afford an orange solid, which was washed with pentane (2 × 3 mL) and dried in vacuo. Yield: 284 mg (95%). Anal. Calcd. for $C_{39}H_{50}ClOP_2RhSi$: C, 61.38; H, 6.60. Found: C, 61.52; H, 6.55. HRMS (electrospray, m/z) calcd. for $C_{39}H_{51}ClOP_2RhSi$: $[M + H]^+$: 763.1922; found: 763.1936. IR (cm^{-1}): ν(C−O−C) 1091 (w). ^1H NMR (300.13 MHz, C_6H_6, 293 K, δ): 8.40 (d, J_{H-H} = 7.3, 4H, C*H* SiClPh$_2$), 7.33 (t, J_{H-H} = 7.3, 4H, C*H* SiClPh$_2$), 7.22 (t, J_{H-H} = 7.3, 2H, C*H* SiClPh$_2$), 7.16 (m, 2H, C*H*-arom), 7.08 (t, J_{H-H} = 7.5, 2H, C*H*-arom), 6.87 (t, J_{H-H} = 7.5, 2H, C*H*-arom), 2.27 (m, 4H, PC*H*(CH$_3$)$_2$), 1.24 (s, 6H, CH$_3$), 1.19 (dvt, J_{H-H} = 7.7, N = 15.4, 12H, PCH(C*H*$_3$)$_2$), 1.01 (dvt, J_{H-H} = 7.2, N = 13.4, 12H, PCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.46 MHz, C_6D_6, 293 K, δ): 155.7 (vt, N = 13.6, *C*-arom), 149.1 (dt, J_{C-Rh} = 4.3, J_{C-P} = 1.6, *C*-arom SiClPh$_2$), 137.2 (s, *C*H-arom SiClPh$_2$), 131.5 (vt, N = 5.4, *C*-arom), 131.4 (s, *C*H-arom), 127.4 (s, *C*H-arom), 127.3 (s, *C*H-arom SiClPh$_2$), 126.8 (s, *C*H-arom SiClPh$_2$), 124.5 (vt, N = 15.0, *C*-arom), 124.4 (vt, N = 4.0, *C*H-arom), 34.2 (s, *C*(CH$_3$)$_2$), 31.0 (s, C(*C*H$_3$)$_2$), 25.5 (dvt, J_{Rh-C} = 2.9, N = 21.2, PCH(CH$_3$)$_2$), 20.3 (vt, N = 8.1, PCH(CH$_3$)$_2$), 17.9 (s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 293 K, δ): 49.4 (d, J_{P-Rh} = 153.1). $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 293 K, δ): 49.2 (dt, J_{Si-Rh} = 82, J_{Si-P} = 22).

Isomerization of IrHCl(SiHPh$_2$){xant(P^{i}Pr$_2$)$_2$} (5) to IrH$_2$(SiClPh$_2$){xant(P^{i}Pr$_2$)$_2$} (9). **5** (100 mg, 0.11 mmol) was dissolved in toluene (3 mL) and heated at 50 °C for 48 h. After this time (the reaction was periodically checked by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy) the solution was evaporated to ca. 0.2 mL to afford a white residue. Addition of pentane afforded a white solid that was washed with pentane (1 × 1 mL) and dried in vacuo. Yield: 60 mg (60%). Anal. Calcd. for $C_{39}H_{52}ClIrOP_2Si$: C, 54.82; H, 6.13. Found: C, 54.85; H, 6.12. HRMS (electrospray, m/z): calcd. for $C_{39}H_{51}ClIrOP_2Si$ $[M - H]^+$: 853.2490; found: 853.2421. IR (cm^{-1}): ν(Ir−H) 2035 (w); ν(C−O−C) 1093 (m). ^1H NMR (300.08 MHz, C_6D_6, 293 K, δ): 8.37 (d, J_{H-H} = 7.0, 4H, C*H* SiClPh$_2$), 7.29 (t, J_{H-H} = 7.0, 4H, C*H* SiClPh$_2$), 7.18 (t, J_{H-H} = 7.0, 2H, C*H* SiClPh$_2$), 7.11 (m, 2H, C*H*-arom), 6.92 (dd, J_{H-H} = 7.4, J_{H-H} = 1.3, 2H, C*H*-arom), 6.86 (t, J_{H-H} = 7.4, 2H, C*H*-arom), 2.32 (m, 4H, PC*H*(CH$_3$)$_2$), 1.15 (dvt, J_{H-H} = 7.3, N = 15.8, 12H, PCH(C*H*$_3$)$_2$), 1.13 (s, 6H, CH$_3$), 1.08 (dvt, J_{H-H} = 6.8, N = 14.2, 12H, PCH(C*H*$_3$)$_2$), −4.90 (t, J_{H-P} = 16.6, 2H, Ir−H). $^{13}C\{^1H\}$ NMR (75.46 MHz, C_6D_6, 293 K, δ): 156.9 (vt, N = 10.4, *C*-arom), 145.1 (s, *C*-arom SiClPh$_2$), 137.3 (s, *C*H-arom SiClPh$_2$), 132.4 (vt, N = 5.1, *C*-arom), 130.1 (s, *C*H-arom SiClPh$_2$), 128.2 (s, *C*H-arom), 126.6 (s, *C*H-arom), 126.5 (s, *C*H-arom SiClPh$_2$), 124.7 (vt, N = 2.8, *C*H-arom), 124.5 (vt, N = 31.2, *C*-arom), 34.4 (s, *C*(CH$_3$)$_2$),

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29.4 (s, C(CH_3)$_2$), 24.6 (vt, N = 31.2, PCH(CH_3)$_2$), 18.9 (vt, N = 4.5, PCH(CH_3)$_2$), 17.7 (s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 293 K, δ): 47.9 (s). ^{29}Si{^{1}H} NMR (59.63 MHz, C_6D_6, 293 K, δ): −4.8 (t, J_{Si-P} = 20).

Reaction of 6 with 2.0 equiv of H_2SiPh_2. In an NMR tube **6** (23.5 mg, 0.03 mmol) was dissolved in benzene-d_6 (0.4 mL), and diphenylsilane (11.5 μL, 0.06 mmol) was added. The tube was then immersed in an oil bath at 50 °C, and the reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 26 h, the ^{1}H and ^{31}P{^{1}H} NMR spectra show signals corresponding to **6**, **5**, and **9** in a 50:26:24 molar ratio.

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (8) with $HSiEt_3$ at Low Temperature: Spectroscopic Detection of $RhH_2(SiEt_3)${xant-(P^{i}Pr$_2$)$_2$} (10). A screw-top NMR tube containing a solution of **8** (26.7 mg, 0.05 mmol) in toluene-d_8 and cooled at 195 K was treated with $HSiEt_3$ (7.8 μL, 0.05 mmol). Immediately the NMR tube was introduced in a NMR probe precooled at 258 K. The immediate and quantitative conversion to $RhH_2(SiEt_3)${xant(P^{i}Pr$_2$)$_2$} (**10**) was observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies (in solution at this temperature **12** was observed as a minor product with time). ^{1}H NMR (400.13 MHz, C_7D_8, 258 K, δ): 7.06 (m, 2H, C*H*-arom), 6.93 (dd, J_{H-H} = 7.5, J_{H-H} = 1.2, 2H, C*H*-arom), 6.85 (t, J_{H-H} = 7.5, 2H, C*H*-arom), 2.44 (m, 4H, PC*H*(CH_3)$_2$), 1.46 (t, J_{H-H} = 7.7, 9H, Si(CH_2CH_3)$_3$), 1.32 (dvt, J_{H-H} = 8.4, N = 15.9, 12H, PCH(CH_3)$_2$), 1.24 (m, 6H, Si(CH_2CH_3)$_3$), 1.16 (s, 6H, CH_3), 1.10 (dvt, J_{H-H} = 6.7, N = 13.5, 12H, PCH(CH_3)$_2$), −5.63 (dt, J_{H-Rh} = 17.6, J_{H-P} = 18.0, 2H, RhH_2). ^{13}C{^{1}H} NMR (100.62 MHz, C_7D_8, 258 K, δ): 156.8 (vt, N = 11.5, *C*-arom), 133.7 (vt, N = 4.7, *C*-arom), 129.0 (s, *C*H-arom), 125.0 (s, *C*H-arom), 123.5 (vt, N = 3.9, *C*H-arom), 122.7 (vt, N = 26.2, *C*-arom), 34.8 (s, *C*(CH_3)$_2$), 26.2 (br, C(CH_3)$_2$), 25.0 (s, *C*H(CH_3)$_2$), 19.4 (vt, N = 7.9, PCH(CH_3)$_2$), 18.2 (br, PCH(CH_3)$_2$), 16.8 (s, Si(CH_2CH_3)$_3$), 10.7 (s, Si(CH_2CH_3)$_3$). ^{31}P{^{1}H} NMR (161.98 MHz, C_7D_8, 258 K, δ): 61.6 (d, J_{P-Rh} = 126). ^{29}Si{^{1}H} NMR (79.49 MHz, C_7D_8, 258 K, δ): 33.0 (dt, J_{Si-Rh} = 33, J_{Si-P} = 9).

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (8) with $HSiPh_3$ at Low Temperature: Spectroscopic detection of $RhH_2(SiPh_3)${xant-(P^{i}Pr$_2$)$_2$} (11). A solution of $HSiPh_3$ (12.9 mg, 0.05 mmol) in 0.5 mL of toluene-d_8 was added to a screw-top NMR tube containing **8** (27 mg, 0.05 mmol) and cooled at 195 K. Immediately the NMR tube was introduced into a NMR probe precooled at 258 K. The immediate and quantitative conversion to $RhH_2(SiPh_3)${xant(P^{i}Pr$_2$)$_2$} (**11**) was observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies (in solution at this temperature **13** was observed as a minor product with time). ^{1}H NMR (400.13 MHz, C_7D_8, 258 K, δ): 7.53 (d, J_{H-H} = 5.8, 6H, C*H*-arom), 7.27 (t, J_{H-H} = 7.2, 6H, C*H*-arom), 7.22 (m,, 2H, C*H*-arom), 7.19 (d, J_{H-H} = 1.9, 3H, CH-arom), 6.95 (d, J_{H-H} = 7.5, 2H, C*H*-arom), 6.84 (t, J_{H-H} = 7.5, 2H, C*H*-arom), 2.08 (m, 4H, PC*H*(CH_3)$_2$), 1.24 (s, 6H, CH_3), 1.01 (dvt, J_{H-H} = 7.8, N = 15.4, 12H, PCH(CH_3)$_2$), 0.95 (dvt, J_{H-H} = 6.3, N = 14.1, 12H, PCH(CH_3)$_2$), −5.02 (dt, J_{H-Rh} = 19.3, J_{H-P} = 16.1, 2H, RhH_2). ^{13}C{^{1}H} NMR (100.62 MHz, C_7D_8, 258 K, δ): 157.1 (vt, N = 11.4, *C*-arom), 148.9 (s, *C*-arom), 138.4 (s, *C*H-arom), 136.1 (s, *C*H-arom), 133.8 (vt, N = 4.3, *C*-arom), 130.0 (s, *C*H-arom), 129.3 (s, *C*H-arom), 128.3 (s, *C*H-arom), 123.9 (vt, N = 6.6, *C*H-arom), 122.9 (vt, N = 26.0, *C*-arom), 35.0 (s, *C*(CH_3)$_2$), 29.8 (s, C(CH_3)$_2$), 25.1 (vt, N = 19.7, PCH(CH_3)$_2$), 20.5, 17.7 (both s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, C_7D_8, 258 K, δ): 59.3 (d, J_{P-Rh} = 120). ^{29}Si{^{1}H} NMR (79.49 MHz, C_7D_8, 258 K, δ): 9.4 (dt, J_{Si-Rh} = 42, J_{Si-P} = 12).

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (8) with $HSiEt_3$ at Room Temperature: Preparation of $Rh(SiEt_3)${xant(P^{i}Pr$_2$)$_2$} (12). Triethylsilane (33 μL, 0.20 mmol) was added to a solution of **8** (100.0 mg, 0.18 mmol) in toluene (3 mL). After the resulting solution was stirred for 5 min at room temperature, it was evaporated to dryness to afford a red residue. Addition of pentane afforded a red solid that was washed with pentane (2 × 0.5 mL) and dried in vacuo. Yield: 70.0 mg (58%). Anal. Calcd. for $C_{33}H_{55}OP_2RhSi$: C, 59.99; H, 8.39. Found: C, 59.90; H, 8.20. HRMS (electrospray, m/z): calcd. for $C_{33}H_{56}OP_2RhSi$ [M + H]$^+$: 661.2625; found: 661.2612. IR (cm^{-1}): ν(C−O−C) 1102 (m). ^{1}H NMR (400.13 MHz, C_6D_6, 293 K, δ): 7.33 (m, 2H, CH-arom), 7.12 (d, J_{H-H} = 7.5, 2H, CH-arom), 6.92 (t, J_{H-H} = 7.5, 2H, CH-arom), 2.52 (m, 2H, PC*H*(CH_3)$_2$), 1.56 (t, J_{H-H} = 7.5, 9H, Si(CH_2CH_3)$_3$), 1.39 (m, 12H PCH(CH_3)$_2$ + 6H Si(CH_2CH_3)$_3$), 1.27 (s, 6H, CH_3), 1.10 (dvt, J_{H-H} = 6.7, N = 13.2, 12H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 293 K, δ): 155.9 (vt, N = 13.6, C-arom), 131.8 (vt, N = 4.0, C-arom), 130.9 (s, CH-arom), 126.5 (s, CH-arom), 126.7 (vt, N = 12.5, C-arom), 123.9 (s, CH-arom), 34.4 (s, *C*(CH_3)$_2$), 30.4 (s, C(CH_3)$_2$), 26.6 (dvt, J_{C-Rh} = 3.3, N = 20.7, PCH(CH_3)$_2$), 20.6 (vt, N = 4.2, PCH(CH_3)$_2$), 18.5 (s, PCH(CH_3)$_2$), 13.7 (dt, J_{C-Rh} = 5.6, J_{C-P} = 3.2, Si(CH_2CH_3)$_3$), 11.1 (s, Si(CH_2CH_3)$_3$). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, 293 K, δ): 46.0 (d, J_{P-Rh} = 171.3). ^{29}Si{^{1}H} NMR (59.63 MHz, C_6D_6, 293 K, δ): 25.0 (dt, J_{Si-Rh} = 54, J_{Si-P} = 19).

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (8) with $HSiPh_3$ at Room Temperature: Preparation of $Rh(SiPh_3)${xant(P^{i}Pr$_2$)$_2$} (13). Triphenylsilane (54.0 mg, 0.20 mmol) was added to a solution of **8** (100.0 mg, 0.18 mmol) in toluene (3 mL). After the resulting solution was stirred for 1 h at room temperature, it was evaporated to dryness to afford a dark residue. Addition of pentane afforded a red solid that was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 120.0 mg (81%). Anal. Calcd. for $C_{45}H_{55}OP_2RhSi$: C, 67.15; H, 6.89. Found: C, 66.76; H, 6.62. HRMS (electrospray, m/z): calcd. for $C_{45}H_{56}OP_2RhSi$ [M + H]$^+$: 805.2625; found: 805.2616. IR (cm^{-1}): ν(C−O−C) 1103 (m). ^{1}H NMR (300.13 MHz, C_6H_6, 293 K, δ): 8.38 (d, J_{H-H} = 8.2, 6H, C*H* $SiPh_3$), 7.30 (t, J_{H-H} = 7.5, 6H, C*H* $SiPh_3$), 7.21 (d, J_{H-H} = 7.5, 3H, C*H* $SiPh_3$), 7.20 (m, 2H, C*H*-arom), 7.12 (d, J_{H-H} = 7.6, 2H, C*H*-arom), 6.88 (t, J_{H-H} = 7.6, 2H, C*H*-arom), 1.63 (m, 4H, PC*H*(CH_3)$_2$), 1.28 (s, 6H, CH_3), 1.06 (dvt, J_{H-H} = 7.2, N = 16.6, 12H, PCH(CH_3)$_2$), 0.99 (dvt, J_{H-H} = 7.0, N = 13.0, 12H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.46 MHz, C_6D_6, 293 K, δ): 155.9 (vt, N = 13.8, *C*-arom), 149.1 (dt, J_{C-Rh}= 2.7, J_{C-P} = 2.3, *C*-arom $SiPh_3$), 138.5 (s, C*H*-arom $SiPh_3$), 131.7 (vt, N = 5.1, *C*-arom), 131.2 (s, *C*H-arom), 126.8 (s, C*H*-arom $SiPh_3$), 126.7 (s, C*H*-arom), 126.6(s, *C*H-arom $SiPh_3$), 125.6 (dvt, J_{C-Rh} = 1.8, N = 14.5, *C*-arom), 124.1 (vt, N = 3.5, *C*H-arom), 34.4 (s, *C*(CH_3)$_2$), 30.5 (s, C(CH_3)$_2$), 25.5 (dvt, J_{C-Rh} = 3.0, N = 19.4, PCH(CH_3)$_2$), 20.5 (vt, N = 8.4, PCH(CH_3)$_2$), 17.9 (s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6, 293 K, δ): 44.7 (d, J_{P-Rh} = 159). ^{29}Si{^{1}H} NMR (59.63 MHz, C_6D_6, 293 K, δ): 14.4 (dt, J_{Si-Rh} = 66, J_{Si-P} = 21).

Reaction of $Rh(SiClPh_2)${xant(P^{i}Pr$_2$)$_2$} (7) with $NaBAr^F_4{\cdot}2H_2O$: Preparation of [RhH{Si(OH)Ph$_2$}{xant(P^{i}Pr$_2$)$_2$}]BAr^F_4 (14). Sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate ($NaBAr^F_4{\cdot}2H_2O$) (150 mg, 0.17 mmol) was added to a red solution of **7** (100 mg, 0.13 mmol) in fluorobenzene (3 mL). After being stirred for 1 h at room temperature, the resulting yellowish solution was evaporated to dryness, affording a yellowish residue. The addition of dichloromethane afforded a suspension that was filtered through Celite to remove the sodium salts. The solution thus obtained was evaporated to dryness. Addition of pentane afforded a white solid that was washed with pentane (3 × 1 mL) and dried in vacuo. Yield: 160.0 mg (76%). Anal. Calcd. for $C_{71}H_{64}BF_{24}O_2P_2RhSi$: C, 53.00; H, 4.00. Found: C, 53.40; H, 4.42. HRMS (electrospray, m/z): calcd. for $C_{39}H_{52}O_2P_2RhSi$ [M]$^+$: 745.2261; found: 745.2294. IR (cm^{-1}): ν(O−H) 3643 (w); ν(C−O−C) 1090 (m). ^{1}H NMR (300.13 MHz, CD_2Cl_2, 233 K, δ): 7.80−7.30 (m, 28H, C*H*-arom), 3.25 (s, 1H, O*H*), 2.49 (m, 4H, PC*H*(CH_3)$_2$), 1.91 (s, 3H, CH_3), 1.75 (m, 4H, PC*H*(CH_3)$_2$), 1.34 (m, 3H CH_3 + 6H PCH(CH_3)$_2$), 1.04 (m, 6H, PCH(CH_3)$_2$), 0.97 (m, 6H, PCH(CH_3)$_2$), 0.21 (m, 6H, PCH(CH_3)$_2$), −17.43 (dt, J_{H-Rh} = 39.4, J_{H-P} = 12.5, 1H, Rh−H). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 233 K, δ): 162.2 (q, J_{C-B} = 49.9, *C*-B Ar^F_4), 157.8 (vt, N = 12.7, *C*-arom), 140.2 (dt, J_{C-Rh} = 1.3, J_{P-C} = 2.7, C-arom Si(OH)Ph), 135.2 (s, CH-arom Ar^F_4), 134.3 (vt, N = 5.7, *C*-arom), 131.4 (s, *C*H-arom Si(OH)Ph), 130.9 (s, CH-arom Si(OH)Ph), 130.4 (s, *C*-arom Ar^F_4), 129.7 (s, *C*H-arom), 129.3 (qq, J_{C-F} = 31.4, J_{C-B} = 2.9, *C*-CF_3 Ar^F_4), 128.3 (s, C*H*-arom Si(OH)Ph$_2$), 127.8 (vt, N = 5.5, *C*H-arom), 125.0 (q J_{C-F} = 272, CF_3 Ar^F_4), 119.2 (vt, N = 25.6, *C*-arom), 117.9 (spt, J_{C-F} = 3.7, CH-arom Ar^F_4), 35.8 (s, *C*(CH_3)$_2$), 34.2 (s, C(CH_3)$_2$), 26.8 (vt, N = 27.4, PCH(CH_3)$_2$), 25.2 (s, C(CH_3)$_2$), 23.5 (vt, N = 18.8, PCH(CH_3)$_2$), 20.3, 20.0, 18.2, 17.0 (all s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 233 K, δ): 52.1 (d, J_{P-Rh} = 119).

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^{29}Si{^{1}H} NMR (59.63 MHz, CD_2Cl_2, 233 K): δ 26.1 (dt, J_{Si-Rh} = 32, J_{Si-P} = 7).

Reactions of Alcoholysis of Diphenylsilane Catalyzed by RhH{Si(OH)Ph$_2$}{xant(P^{i}Pr$_2$)$_2$}]BAr$^F_4$ (14). In a typical procedure, the alcohol (except PhOH, that was dissolved in 200 μL of toluene) (1.57 mmol) was added via syringe to a solution of the catalyst (2.6×10^{-3} mmol), H_2SiPh_2 (1.57 mmol) in toluene (5 mL) placed into a 25 mL flask attached to a gas buret and immersed in a 32 °C bath, and the mixture was vigorously shaken (500 rpm) during the run. The reaction was monitored by measuring the volume of the evolved hydrogen with time until hydrogen evolution stopped. A representation of gas evolution versus time is included as Supporting Information. The solution was then passed through a column (silica gel) to remove the catalyst. Removal of the solvent gave the silyl ether. The product was analyzed by ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectroscopy.

Spectroscopic Data of the Products of the Monoalcoholysis. *HSi(OMe)Ph$_2$*. ^{1}H NMR (300.13 MHz, $CDCl_3$, 293 K, δ): 7.58 (dd, J_{H-H} = 7.6, J_{H-H} = 1.9, 4H, C*H*-arom), 7.42−7.24 (m, 6H, C*H*-arom), 5.37 (s, 1H, Si-*H*), 3.54 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 293 K, δ): 134.8 (s, *C*H-arom), 133.8 (s, *C*-arom), 130.5 (s, *C*H-arom), 128.2 (s, *C*H-arom), 52.5 (s, O-*C*H$_3$). ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −14.5 (s).

HSi(OEt)Ph$_2$. ^{1}H NMR (300.13 MHz, $CDCl_3$, 293 K, δ): 7.62 (dd, J_{H-H} = 7.7, J_{H-H} = 1.8, 4H, C*H*-arom), 7.42−7.34 (m, 6H, C*H*-arom), 5.41 (s, 1H, Si-*H*), 3.84 (q, J_{H-H} = 7.0, 2H, CH_2), 1.24 (t, J_{H-H} = 7.0, 3H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 293 K, δ): 134.8 (s, *C*H-arom), 134.3 (s, *C*-arom), 130.4 (s, *C*H-arom), 128.1 (s, *C*H-arom), 60.7 (s, O-*C*H$_2$), 18.3 (s, *C*H$_3$). ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −17.6 (s).

HSi(O^{n}Bu)Ph$_2$. ^{1}H NMR (400.13 MHz, $CDCl_3$, 293 K, δ): 7.60 (dd, J_{H-H} = 7.8, J_{H-H} = 1.7, 4H, C*H*-arom), 7.39−7.32 (m, 6H, 2H, C*H*-arom), 5.40 (s, 1H, Si-*H*), 2.19 (t, J_{H-H} = 6.5, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.36 (m, 2H, CH_2), 0.86 (t, J_{H-H} = 7.4, 3H, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, 293 K): δ 134.8 (s, *C*H-arom), 134.3 (s, *C*-arom), 130.4 (s, *C*H-arom), 128.1 (s, *C*H-arom), 64.7 (s, O-*C*H$_2$), 34.7 (s, *C*H$_2$), 19.1 (s, *C*H$_2$), 13.9 (s, *C*H$_3$) . ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −17.4 (s).

HSi(O^{n}Octyl)Ph$_2$. ^{1}H NMR (400.13 MHz, $CDCl_3$, 293 K, δ): 7.61 (dd, J_{H-H} = 7.8, J_{H-H} = 1.6, 4H, C*H*-arom), 7.40−7.33 (m, 6H, C*H*-arom), 5.40 (s, 1H, Si-*H*), 3.75 (t, J_{H-H} = 6.4, 2H, CH_2), 1.58 (m, 2H, CH_2), 1.35−1.15 (m, 10H, CH_2), 0.86 (t, J_{H-H} = 6.7, 3H, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, 293 K, δ): 134.8 (s, *C*H-arom), 134.3 (s, *C*-arom),130.4 (s, *C*H-arom), 128.1 (s, *C*H-arom), 65.1 (s, O-*C*H$_2$), 32.5, 32.0, 29.4, 25.9, 22.8 (all s, CH_2), 14.3 (s, CH_3). ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −17.4 (s).

HSi(OCH$_2$Ph)Ph$_2$. ^{1}H NMR (400.13 MHz, $CDCl_3$, 293 K, δ): 7.62 (dd, J_{H-H} = 7.9, J_{H-H} = 1.5, 4H, C*H*-arom), 7.41−7.28 (m, 11H, C*H*-arom), 5.47 (s, 1H, Si-*H*), 4.83 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, 293 K, δ): 140.2 (s, *C*-arom), 134.8 (s, *C*H-arom), 133.8 (s, *C*-arom), 130.6, 128.4, 128.2, 127.4, 126.9 (all s, *C*H-arom), 66.7 (s, CH_2). ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −16.1 (s).

HSi(O^{i}Pr)Ph$_2$. ^{1}H NMR (300.13 MHz, $CDCl_3$, 293 K): δ 7.60 (dd, J_{H-H} = 7.6, J_{H-H} = 1.9, 4H, C*H*-arom), 7.43−7.29 (m, 6H, C*H*-arom), 5.44 (s, 1H, Si*H*), 4.15 (sept, J_{H-H} = 6.1, 1H, C*H*), 1.21(d, J_{H-H} = 6.1, 6H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 293 K): δ 135.0 (s, *C*-arom), 134.8 (s, CH-arom), 130.3 (s, CH-arom), 128.1 (s, CH-arom), 67.5 (s, O-CH), 25.4 (s, CH_3). ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −20.5 (s).

HSi(OCy)Ph$_2$. ^{1}H NMR (400.13 MHz, $CDCl_3$, 293 K, δ): 7.61 (dd, J_{H-H} = 7.8, J_{H-H} = 1.7, 4H, C*H*-arom), 7.39−7.31 (m, 6H, C*H*-arom), 5.38 (s, 1H, Si-*H*), 3.72 (m, 1H, C*H*), 1.57, 1.77−1.11 (m, 10H, CH_2). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, 293 K, δ): 135.0 (s, *C*-arom), 134.7 (s, *C*H-arom), 130.3 (s, *C*H-arom), 128.1 (s, *C*H-arom), 73.1 (s, O-CH), 35.4, 25.7, 24.2 (all s, CH_2) . ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −20.9 (s).

HSi(O^{t}Bu)Ph$_2$. ^{1}H NMR (400.13 MHz, $CDCl_3$, 293 K, δ): 7.60 (dd, J_{H-H} = 7.7, J_{H-H} = 1.8, 4H, C*H*-arom), 7.40−7.30 (m, 6H, C*H*-arom), 5.55 (s, 1H, Si-*H*), 1.31 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, 293 K, δ): 136.2 (s, *C*-arom), 134.6, 130.0, 128.0 (all s, CH-arom), 73.8 (s, O-*C*), 31.7 (s, *C*H$_3$). ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −29.5 (s).

HSi(OPh)Ph$_2$. ^{1}H NMR (400.13 MHz, $CDCl_3$, 293 K, δ): 7.65 (d, J_{H-H} = 6.4, 4H, C*H*-arom), 7.41−7.28 (m, 7H, C*H*-arom), 7.18−7.12 (m, 2H, C*H*-arom), 6.92 (m, 2H, C*H*-arom), 5.72 (s, 1H, Si-*H*). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, 293 K, δ): 155.5 (s, *C*-arom), 134.8 (s, *C*H-arom), 133.0 (s, *C*-arom), 130.8 (s, *C*-arom), 129.8 (s, *C*H-arom), 128.3 (s, *C*H-arom), 122.0 (s, *C*H-arom), 119.4 (s, *C*H-arom). ^{29}Si{^{1}H} NMR (59.63 MHz, $CDCl_3$, 293 K, δ): −19.8 (s).

Structural Analysis of Complexes 3, 6, 7, 9, 12, and 14. Crystals suitable for the X-ray diffraction were obtained by slow diffusion of pentane into solutions of **3** and **6** in toluene, of diethyl ether into solutions of **14** in dichloromethane, and by slow evaporation of benzene (**7**) or pentane (**9** and **12**). X-ray data were collected on a Bruker Smart APEX (**3**, **6**, **7**) and Bruker Apex II CCD (**9**, **12**, **14**) diffractometers equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 (**7**, **12**) or 40 (**3**, **6**, **9**, **14**) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (**7**, **14**), 20 s (**3**, **6**), 30 s (**9**), or 40 s (**12**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[29] The structures were solved by the Patterson (Rh atom of **3**, **7**, **12**, and **14**, and Ir atoms of **6** and **9**) or direct methods and conventional Fourier techniques and refined by full-matrix least-squares on F^2 with SHELXL97.[30] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. Hydride ligands were observed in the difference Fourier maps but refined with restrained bond length. One of the benzene crystallization molecules of **7** and two of the CF_3 groups of the BAr$^F_4$ anion of **14** were found to be disordered. These disordered atoms were refined isotropically with restrained geometry. For all structures, the highest electronic residuals were observed in the close proximity of the metal centers and make no chemical sense.

Crystal Data for **3**. $C_{39}H_{52}ClOP_2RhSi{\cdot}0.5C_7H_8$, M_W 811.26, colorless, prism (0.15 × 0.13 × 0.09), monoclinic, space group *C*2/*c*, *a*: 31.6766(18) Å, *b*: 11.6863(7) Å, *c*: 22.6325(13) Å, β = 107.2060(10)°, *V* = 8003.2(8) Å^3, *Z* = 8, D_{calc}: 1.347 g cm^{-3}, *F*(000): 3400, *T* = 100(2) K, μ 0.635 mm^{-1}. 39319 measured reflections (2θ: 4−57°, ω scans 0.3°), 9550 unique (R_{int} = 0.0454); minimum/maximum transmission factors 0.748/0.862. Final agreement factors were R^1 = 0.0471 (7392 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1203; data/restraints/parameters 9550/0/436; GOF = 1.056. Largest peak and hole 1.683 and −0.504 e/Å^3.

Crystal Data for **6**. $C_{33}H_{56}ClIrOP_2Si$, M_W 786.46, colorless, prism (0.18 × 0.07 × 0.06), monoclinic, space group *C*2/*c*, *a*: 38.867(3) Å, *b*: 9.4817(8) Å, *c*: 18.9847(16) Å, β = 90.5580(10)°, *V* = 6995.9(10) Å^3, *Z* = 8, D_{calc}: 1.493 g cm^{-3}, *F*(000): 3200, *T* = 100(2) K, μ 4.043 mm^{-1}. 31 121 measured reflections (2θ: 4−57°, ω scans 0.3°), 8313 unique (R_{int} = 0.0428); minimum/maximum transmission factors 0.582/0.862. Final agreement factors were R^1 = 0.0441 (7026 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1140; data/restraints/parameters 8313/1/368; GOF = 1.064. Largest peak and hole 4.199 and −2.541 e/Å^3.

Crystal Data for **7**. $C_{39}H_{50}ClOP_2RhSi{\cdot}2C_6H_6$, M_W 919.40, red, prism (0.22 × 0.13 × 0.09), triclinic, space group $P\bar{1}$, *a*: 10.2599(7) Å, *b*: 11.9553(8) Å, *c*: 20.3304(14) Å, α = 77.8960(10)°, β = 84.2760(10)°, γ = 71.9240(10)°, *V* = 2316.3(3) Å^3, *Z* = 2, D_{calc}: 1.318 g cm^{-3}, *F*(000): 964, *T* = 120(2) K, μ 0.557 mm^{-1}. 27059 measured reflections (2θ: 2−57°, ω scans 0.3°), 10623 unique (R_{int} = 0.0386); minimum/maximum transmission factors 0.642/0.862. Final agreement factors were R^1 = 0.0460 (8775 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0940; data/restraints/parameters 10623/0/488; GOF = 1.071. Largest peak and hole 0.747 and −0.793 e/Å^3.

Crystal Data for **9**. $C_{39}H_{52}ClIrOP_2Si{\cdot}1/4(C_5H_{12})$, M_W 872.52, colorless, irregular prism (0.16 × 0.14 × 0.10), monoclinic, space group *C*2/*c*, *a*: 23.228(3) Å, *b*: 23.110(3) Å, *c*: 17.543(2) Å, β = 122.110(2)°, *V* = 7976.6(16) Å^3, *Z* = 8, D_{calc}: 1.453 g cm^{-3}, F(000): 3540, *T* = 100(2) K, μ 3.554 mm^{-1}. 43 448 measured reflections (2θ:

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2−59°, ω scans 0.3°), 10458 unique (R_{int} = 0.0488); minimum/maximum transmission factors 0.487/0.704. Final agreement factors were R^1 = 0.0323 (7537 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0804; data/restraints/parameters 10458/5/435; GOF = 0.941. Largest peak and hole 2.390 and −1.020 e/Å^3.

Crystal Data for **12**. $C_{33}H_{55}OP_2RhSi$, M_W 660.71, dark red, prism (0.17 × 0.12 × 0.07), orthorhombic, space group $P2(1)2(1)2(1)$, a: 8.5450(9) Å, b: 18.3095(19) Å, c: 22.353(2) Å, V = 3497.3(6) Å^3, Z = 4, D_{calc}: 1.255 g cm^{-3}, F(000): 1400, T = 100(2) K, μ 0.637 mm^{-1}. 37 385 measured reflections (2θ: 3−59°, ω scans 0.3°), 9055 unique (R_{int} = 0.0629); minimum/maximum transmission factors 0.747/0.944. Final agreement factors were R^1 = 0.0337 (7333 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0665; Flack parameter 0.44(2); data/restraints/parameters 9055/0/357; GOF = 0.955. Largest peak and hole 1.056 and −0.457 e/Å^3.

Crystal Data for **14**. $C_{71}H_{64}BF_{24}O_2P_2RhSi{\cdot}OC_4H_{10}$, M_W 1683.09, colorless, prism (0.23 × 0.22 × 0.17), triclinic, space group $P\bar{1}$, a: 10.1457(10) Å, b: 19.559(2) Å, c: 19.979(2) Å, α = 87.073(2) °, β = 88.661(2) °, γ = 77.015(2) °, V = 3858.0(7) Å^3, Z = 2, D_{calc}: 1.449 g cm^{-3}, F(000): 1716, T = 100(2) K, μ 0.382 mm^{-1}. 42965 measured reflections (2θ: 3−59°, ω scans 0.3°), 19600 unique (R_{int} = 0.0360); minimum/maximum transmission factors 0.778/0.944. Final agreement factors were R^1 = 0.0498 (14559 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1389; data/restraints/parameters 19600/18/978; GOF = 1.062. Largest peak and hole 1.491 and −0.839 e/Å^3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **3**, **6**, **7**, **9**, **12**, and **14**. NMR spectra of complexes **10** and **11** and a plot of hydrogen evolution versus time for the monoalcoholysis of diphenylsilane catalyzed by complex **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (b) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (c) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (d) *The Chemistry of Pincer Compounds*; Morales-Morales, D.; Jensen, C. M., Eds.; Elsevier Science: Amsterdam: The Netherlands, 2007. (e) Benito-Garagorri, D.; Kirchner, K. *Acc. Chem. Res.* **2008**, *41*, 201. (f) Whited, M. T.; Grubbs, R. H. *Acc. Chem. Res.* **2009**, *42*, 1607. (g) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761. (h) Haibach, M. C.; Kundu, S.; Brookhart, M.; Goldman, A. S. *Acc. Chem. Res.* **2012**, *45*, 947.

(2) Asensio, G.; Cuenca, A. B.; Esteruelas, M. A.; Medio-Simón, M.; Oliván, M.; Valencia, M. *Inorg. Chem.* **2010**, *49*, 8665.

(3) Esteruelas, M. A.; Honczek, N.; Oliván, M.; Oñate, E.; Valencia, M. *Organometallics* **2011**, *30*, 2468.

(4) Alós, J.; Bolaño, T.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Valencia, M. *Inorg. Chem.* **2013**, *52*, 6199.

(5) Recent findings on Rh(POP) chemistry: (a) Goldman and co-workers have described the synthesis and reactivity of related rhodium complexes with xant(P^{t}Bu$_2$)$_2$ and 2,5-bis((di-*tert*-butylphosphino) methyl)furan. See: Haibach, M. C.; Wang, D. Y.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Sci.* **2013**, *4*, 3683. (b) Weller and co-workers have reported on the hydroacylation of alkynes catalyzed by Rh-DPEphos complexes. See: Pawley, R. J.; Huertos, M. A.; Lloyd-Jones, G. C.; Weller, A. S.; Willis, M. C. *Organometallics* **2012**, *31*, 5650. (c) Haynes and co-workers have isolated an acetyl-Rh-xantphos complex during the study of the mechanism of methanol carbonylation. See: Williams, G. L.; Parks, C. M.; Smith, C. R.; Adams, H.; Haynes, A.; Meijer, A. J. H. M.; Sunley, G. J.; Gaemers, S. *Organometallics* **2011**, *30*, 6166. (d) Julian and Hartwig have discovered a Rh-POP catalyst for the intramolecular hydroamination of aminoalkenes. See: Julian, L. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 13183.

(6) Esteruelas, M. A.; Oliván, M.; Vélez, A. *Inorg. Chem.* **2013**, *52*, 5339.

(7) Corey, J. Y. *Chem. Rev.* **2011**, *111*, 863.

(8) (a) Roy, A. K. *Adv. Organomet. Chem.* **2008**, *55*, 1. (b) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, 2781. (c) Troegel, D.; Stohrer, J. *Coord. Chem. Rev.* **2011**, *255*, 1440.

(9) See for example: (a) Esteruelas, M. A.; Herrero, J.; López, F. M.; Martín, M.; Oro, L. A. *Organometallics* **1999**, *18*, 1110. (b) Díaz, J.; Esteruelas, M. A.; Herrero, J.; Moralejo, L.; Oliván, M. *J. Catal.* **2000**, *195*, 187. (c) Esteruelas, M. A.; Herrero, J.; Oliván, M. *Organometallics* **2004**, *23*, 3891. (d) Yang, J.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 12656. (e) Yang, J.; Brookhart, M. *Adv. Synth. Catal.* **2009**, *351*, 175.

(10) See for example: (a) Goikhman, R.; Aizenberg, M.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 10894. (b) Field, L. D.; Messerle, B. A.; Rehr, M.; Soler, L. P.; Hambley, T. W. *Organometallics* **2003**, *22*, 2387. (c) Chandrasekhar, V.; Boomishankar, R.; Nagendran, S. *Chem. Rev.* **2004**, *104*, 5847. (d) Muraoka, T.; Abe, K.; Haga, Y.; Nakamura, T.; Ueno, K. *J. Am. Chem. Soc.* **2011**, *133*, 15365.

(11) (a) Yang, J.; White, P. S.; Schauer, C. K.; Brookhart, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4141. (b) Yang, J.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2008**, *130*, 17509. (c) Park, S.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 640.

(12) (a) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2008**, *130*, 9226. (b) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 11161. (c) Calimano, E.; Tilley, T. D. *Organometallics* **2010**, *29*, 1680. (d) Calimano, E.; Tilley, T. D. *Dalton Trans.* **2010**, *39*, 9250.

(13) Gatard, S.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2008**, *27*, 6257.

(14) Goikhman, R.; Aizenberg, M.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2002**, *21*, 5060.

(15) (a) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531. (b) Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 3486. (c) Esteruelas, M. A.; Oliván, M.; Oro, L. A. *Organometallics* **1996**, *15*, 814.

(16) See for example: (a) Osakada, K.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 2063. (b) Osakada, K.; Sarai, S.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 3973. (c) Turculet, L.; Feldman, J. D.; Tilley, T. D. *Organometallics* **2004**, *23*, 2488. (d) McBee, J. L.; Tilley, T. D. *Organometallics* **2009**, *28*, 5072. (e) Hoffmann, F.; Wagler, J.; Böhme, U.; Roewer, G. *J. Organomet. Chem.* **2012**, *705*, 59.

(17) Esteruelas, M. A.; Oro, L. A. *Coord. Chem. Rev.* **1999**, *193*−*195*, 557.

(18) See for example: (a) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A.; Apreda, M.-C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1989**, *8*, 1158. (b) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L. *Organometallics* **1996**, *15*, 823. (c) Vicent, C.; Viciano, M.; Mas-Marzá, E.; Sanaú, M.; Peris, E. *Organometallics* **2006**, *25*, 3713. (d) Sangtrirutnugul, P.; Tilley, T. D.

Organometallics **2007**, *26*, 5557. (e) Bleeke, J. R.; Thananatthanachon, T.; Rath, N. P. *Organometallics* **2008**, *27*, 2436.
(19) Square-planar rhodium(I)-silyl complexes are somewhat rare: (a) Thorn, D.; Harlow, R. L. *Inorg. Chem.* **1990**, *29*, 2017. (b) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359. (c) Hoffmann, P.; Meier, C.; Hiller, W.; Heckel, M.; Riede, J.; Schmidt, U. *J. Organomet. Chem.* **1995**, *490*, 51. (d) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472. (e) Aizenberg, M.; Ott, J.; Elsevier, C. J.; Milstein, D. *J. Organomet. Chem.* **1998**, *551*, 81.
(20) Hendriksen, D. E.; Oswald, A. A.; Ansell, G. B.; Leta, S.; Kastrup, R. V. *Organometallics* **1989**, *8*, 1153.
(21) See for example: (a) van der Veen, L. A.; Keever, P. H.; Schoemaker, G. C.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Lutz, M.; Spek, A. L. *Organometallics* **2000**, *19*, 872. (b) Fox, D. J.; Duckett, S. B.; Flaschenriem, C.; Brennessel, W. W.; Schneider, J.; Gunay, A.; Eisenberg, R. *Inorg. Chem.* **2006**, *45*, 7197. (c) Marimuthu, T.; Bala, M. D.; Friedrich, H. B. *J. Coord. Chem.* **2009**, *62*, 1407. (d) Jian, Y.; Peng, S.; Li, X.; Wen, X.; He, J.; Jiang, L.; Dang, Y. *Inorg. Chim. Acta* **2011**, *368*, 37. (e) Pontiggia, A. J.; Chaplin, A. B.; Weller, A. S. *J. Organomet. Chem.* **2011**, *696*, 2870.
(22) (a) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2007**, *129*, 8850.
(23) Hübler, K.; Hunt, P. A.; Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Schwerdtfeger, P.; Wright, L. J. *Organometallics* **1997**, *16*, 5076.
(24) Findlater, M.; Bernskoetter, W. H.; Brookhart, M. *J. Am. Chem. Soc.* **2010**, *132*, 4534.
(25) See for example: (a) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (b) Doyle, M. P.; High, K. G.; Bagheri, V.; Pieters, R. J.; Lewis, P. J.; Pearson, M. M. *J. Org. Chem.* **1990**, *55*, 6082. (c) Barber, D. E.; Lu, Z.; Richardson, T.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4709. (d) Chang, S.; Scharrer, E.; Brookhart, M. *J. Mol. Catal. A: Chem.* **1998**, *130*, 107.
(26) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927.
(27) (a) Kim, S.; Chang, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3669. (b) DSa, B. A.; McLeod, D.; Verkade, J. G. *J. Org. Chem.* **1997**, *62*, 5057.
(28) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.
(29) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. *SADABS: Area-detector absorption correction*; Bruker-AXS: Madison, WI, 1996.
(30) *SHELXTL*, Package v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.