New Tridentate Phosphine Rhodium and Iridium Complexes, Including a Stable Rhodium(I) Silyl. Si−S Activation and a Strong Effect of X in $(PP_2)M-X$ (X = H, Cl, Me) on Si−H Activation

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Rhodium and iridium complexes of the general formula $(PP_2)MX$ bearing the new triphosphine ligand $^{i}Pr_2P(CH_2)_3P(Ph)(CH_2)_3P^{i}Pr_2$ (PP_2) have been synthesized. Reactivity of the PP_2MX complexes toward $HSi(SEt)_3$ was studied. Whereas $(PP_2)RhCl$ and $(PP_2)IrCl$ do not react with $HSi(SEt)_3$, $(PP_2)RhH$ gives rise to the Rh(III) adduct $[(PP_2)Rh(H)_2Si(SEt)_3]$, and $(PP_2)RhMe$ (**3**) activates both the Si−H and the Si−S bonds of $HSi(SEt)_3$, affording the Rh(I) complexes $(PP_2)RhSi(SEt)_3$ (**5**) and $(PP_2)RhSEt$ (**6**). Only a few stable Rh(I) silyl complexes are known, and Si−S bond activation by transition-metal complexes has been rarely observed. The X-ray crystal structure of **5** exhibits a considerable distortion from square-planar geometry, the average angle between the trans-disposed ligands being 152.5°. In contrast to **3**, $(PP_2)IrMe$ (**8**) forms a stable Ir(III) adduct with $HSi(SEt)_3$, *fac*-$[(PP_2)Ir(Me)(H)(Si(SEt)_3)]$ (**9**). No Si−S activation was observed with **8**. Thus, the reactivity of $(PP_2)MX$ complexes toward $HSi(SEt)_3$ strongly depends on the nature of M and X.

Introduction

Transition-metal−thiosilyl compounds, $M-Si(SR)_3$, are a relatively new group of silyl complexes.[1,2] The Si−S bond is relatively weak[3] and is suitable for various transformations. Various thiosilyl complexes have attracted considerable attention in the past decade as precursors for metallasilylenes (compounds having a metal−silicon double bond) and other interesting transition-metal silyl derivatives.[1] They have also been utilized in mechanistic investigations.[2]

In continuation of our work on electron-rich late-metal silyl complexes,[2,4] we report here on the synthesis of Rh and Ir complexes containing the new chelating triphosphine ligand $^{i}Pr_2P(CH_2)_3P(Ph)(CH_2)_3P^{i}Pr_2$ (PP_2) and describe their transformations and reactivity toward tris(ethylthio)silane, $HSi(SEt)_3$.[5]

Results and Discussion

The ligand PP_2 was prepared using a procedure analogous to that reported for the synthesis of $Cy_2P(CH_2)_3P(Ph)(CH_2)_3PCy_2$.[6] Reaction of PP_2 with the rhodium dimer $[(COE)_2RhCl]_2$ (COE = cyclooctene, C_8H_{14}) at room temperature in THF afforded the complex $(PP_2)RhCl$ (**1**), which was used as a precursor for the synthesis of other Rh(I) complexes. Upon treatment of **1** with ^{t}BuLi, the hydrido complex $(PP_2)RhH$ (**2**) was readily formed. Apparently, the reaction proceeded through β-hydrogen elimination from the unobserved intermediate $(PP_2)Rh^{t}Bu$. Isobutene formation was detected by ^{1}H NMR.

Another Rh(I) complex, $(PP_2)RhMe$ (**3**), was readily prepared by treating complex **1** with MeLi.

The reactivity of complexes **1**−**3** toward the thiosilane $HSi(SEt)_3$ was examined.

Unexpectedly, the 16e$^-$ Rh(I) chloride **1** did not change upon addition of $HSi(SEt)_3$ at room temperature, as determined by NMR. In contrast, the Rh(I) hydride **2** reacted with $HSi(SEt)_3$ at room temperature to yield the stable Rh(III) dihydride complex *mer,cis*-$PP_2Rh(H)_2Si(SEt)_3$ (**4**), which was unambiguously characterized by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits a doublet of triplets and a doublet of doublets, indicating one unique phosphine and two equal phosphines. Two hydride signals are observed in ^{1}H NMR, a doublet of doublets of doublets of triplets at

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(1) For example: (a) Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 5607 and references therein. (b) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635. (c) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, 115, 7884.

(2) Aizenberg, M.; Goikhman, R.; Milstein, D. *Organometallics* **1996**, *15*, 1075.

(3) The BDE of the Si−S bond was estimated as 79 kcal/mol; see: Baldwin, J. C.; Lappert, M. F.; Pedley, J. B.; Treverton, J. A. *J. Chem. Soc. A* **1967**, 1980.

(4) (a) Aizenberg, M.; Ott, J.; Elsevier, C. J.; Milstein, D. *J. Organomet. Chem.* **1998**, 551, 81. (b) Goikhman, R.; Aizenberg, M.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 10894. (c) Aizenberg, M.; Milstein, D. *Organometallics* **1996**, *15*, 3317. (d) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456. (e) Goikhman, R.; Aizenberg, M.; Kraatz, H. B.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 5865. (f) Aizenberg, M.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 317. (g) Aizenberg, M.; Milstein, D. *Science* **1994**, 265, 359. (h) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1826.

(5) (a) Lambert, J. B.; Shulz, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 2201. (b) Wolinsky, L.; Tieckelmann, H.; Post, H. W. *J. Org. Chem.* **1951**, *16*, 395.

(6) Uriarte, R.; Mazanec, T. J.; Tan, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79.

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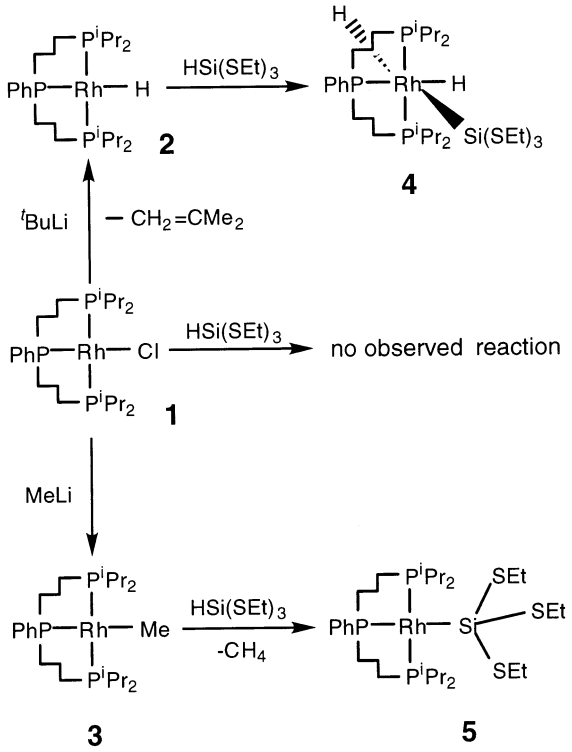
Scheme 1



−9.05 ppm for the hydride trans to the unique phosphorus atom ($^2J_{H-Ptrans}$ = 123 Hz) and a multiplet centered at −9.25 ppm for the hydride located cis to all phosphorus atoms.

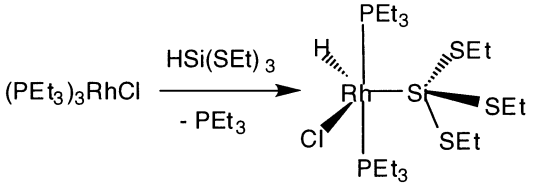
The methyl rhodium complex **3** slowly reacted with $HSi(SEt)_3$ in pentane solution at −20 °C to give the *Rh(I)* silyl complex $(PP_2)Rh(Si(SEt)_3)$ (**5**) as the main product. Only a few Rh(I) silyl complexes are known.[4a,g,7] The reaction apparently proceeded via the Rh(III) intermediate $[(PP_2)Rh(Me)(H)(Si(SEt)_3)]$ (unobserved), which spontaneously eliminated methane (which was detected by ^1H NMR). Complex **4** was formed in a small amount as a byproduct of this reaction. It was presumably formed in two steps: (a) C−Si reductive elimination from the intermediate, giving complex **2** and $MeSi(SEt)_3$ (an observed singlet at 0.63 ppm in ^1H NMR probably belongs to this compound), and (b) $HSi(SEt)_3$ oxidative addition to complex **2** to give the observed complex **4**. The product ratio **5**:**4** was about 8:1, indicating that C−H reductive elimination significantly prevailed over that of C−Si. This result is in accordance with our previous finding that C−Si and C−H reductive elimination can be competitive, with the latter being the more favorable process.[4f]

Scheme 1 briefly summarizes the synthesis and transformations of the $(PP_2)Rh$ complexes.

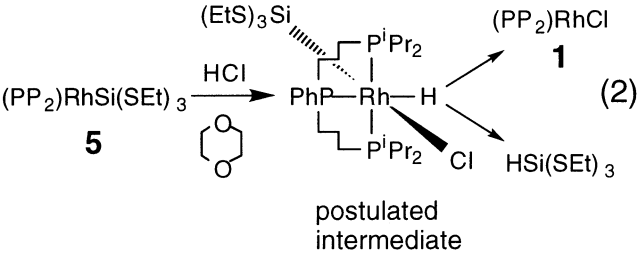
Thus, complexes of the type PP_2RhX react very differently with $HSi(SEt)_3$, depending on X. In the case of X = Cl no reaction is observed, with X = H a stable Rh(III) adduct is formed, and when X = Me, Si−H oxidative addition followed by C−H reductive elimination takes place, forming a Rh(I) silyl complex.

The fact that rhodium dihydrido silyl complexes are thermodynamically stable, unlike the unobserved rhodium methyl hydrido silyls, was reported.[4a]

The result that $(PP_2)RhCl$ (**1**) does not add the silane, whereas the analogous methyl and hydride complexes readily undergo Si−H activation, is unexpected. Comparing complex **1** to a similar square-planar complex bearing three alkylphosphine ligands and a chloride, namely $(Et_3P)_3RhCl$, we observed that the latter complex readily reacted with $HSi(SEt)_3$ at room temperature, giving the Rh(III) adduct $(Et_3P)_2Rh(Cl)(H)(Si(SEt)_3)$ in quantitative yield and liberating 1 equiv of Et_3P (eq 1).[8]



To check whether the reason for the lack of observed reactivity between the chloride complex **1** and the silane is kinetic or thermodynamic, we tried to generate the expected oxidative addition product $(PP_2)Rh(Cl)(H)(Si(SEt)_3)$ by another route. Interestingly, treatment of $(PP_2)Rh(Si(SEt)_3)$ (**5**) with an HCl solution in dioxane resulted in formation of the chloride complex **1** and free thiosilane as the only products (eq 2), suggesting that



the PP_2 chloride adduct with the thiosilane is unstable, unlike the Et_3P-containing adduct. This may be due to steric factors in the triphosphine complex, resulting in phosphine dissociation in the case of the Et_3P complex, whereas the chelate effect disfavors chelate opening in the case of the PP_2 complex. Generation of free Et_3P in eq 1 as compared with elimination of the thiosilane rather than one phosphine "arm" in eq 2 demonstrates the high binding energy of the chelate.

Complex **5** slowly decomposes at room temperature. It was crystallized from pentane at −30 °C as deep red prisms. The crystal structure of **5** (Figure 1, Table 1) exhibits a considerable distortion from square planarity, the angles between the trans-disposed ligands being substantially smaller than 180°. A similar distortion was observed in a series of Rh(I) compounds having a

(7) (a) Mitchell, G. P.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 2912. (b) Hofmann, P.; Meier, C.; Hiller, W.; Heckel, M.; Riede, J.; Schmidt, M. U. *J. Organomet. Chem.* **1995**, 490, 51. (c) Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1990**, *29*, 2017. (d) Hendriksen, D. E.; Oswald, A. A.; Ansell, G. B.; Leta, S.; Kastrup, R. V. *Organometallics* **1989**, 8, 1153. (e) Joslin, F. L.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 504

(8) A similar pathway was observed in the reaction of silanes with $(Ph_3P)_3RhCl$ and $(^iPr_3P)_2RhCl$, leading to five-coordinated adducts: (a) Nagashima, H.; Tatebe, K.; Ishibashi, T.; Nakaoka, A.; Sakakibara, J.; Itoh, K. *Organometallics* **1995**, *14*, 2868. (b) Osakada, K.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 2063. Although in the latter paper the structures of the adducts are postulated as distorted square pyramids, the reported Si−Rh−Cl angles of 111.1 and 126.4° allows us to conclude that the structures are intermediate between square pyramidal and TBP, probably closer to a TBP configuration.

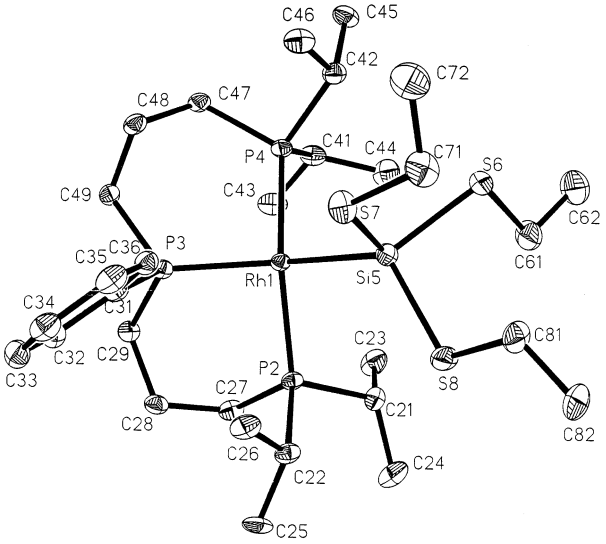


Figure 1. Perspective view (ORTEP) of **5**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in a Molecule of 5

Rh(1)−P(2)	2.3107(10)	Rh(1)−P(3)	2.2842(14)
Rh(1)−P(4)	2.3221(9)	Rh(1)−Si(5)	2.3747(14)
P(3)−Rh(1)−P(2)	91.05(4)	P(3)−Rh(1)−P(4)	91.86(4)
P(2)−Rh(1)−P(4)	153.06(3)	P(3)−Rh(1)−Si(5)	151.78(4)
P(2)−Rh(1)−Si(5)	93.57(4)	P(4)−Rh(1)−Si(5)	96.40(4)

Table 2. Crystallographic Parameters for the Structure of 5

empirical formula	$C_{30}H_{61}P_3RhS_3Si$
formula mass	741.88
color and habit	red prism
cryst size, mm	0.5 × 0.5 × 0.4
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	10.818(2)
b, Å	10.942(2)
c, Å	17.750(4)
α, deg	84.71(3)
β, deg	72.57(3)
γ, deg	63.71(3)
V, Å^3	1795.2(6)
Z	2
d(calcd), g/cm^3	1.372
μ, mm^{-1}	0.837
diffractometer	Rigaku AFC5R
radiation (*λ*, Å)	Mo Kα (0.710 73)
monochromator	graphite
temp, K	120(2)
mode	*ω*
scan speed, deg/min	16
scan width, deg	1.8
collcn range, deg	$1.2 \le \theta \le 27.5$
hkl range	$-14 \le h \le 13$, $-14 \le k \le 7$, $-23 \le l \le 22$
no. of rflns	
collected	8755
indep	8187
R1	0.0572
wR2	0.1458

similar triphosphine ligand, $PhP(CH_2CH_2CH_2PPh)_2$-(PP_2*).[9] It was shown that the tetrahedral distortion from planar geometry of PP_2*RhX complexes depends on the bulk of the X ligand: for X = Cl, Py, PEt_3, the average angles between the trans-disposed ligands are 175, 164, and 156°, respectively. In complex **5** the average value is 152.5°, which is comparable with the value observed for $[PP_2$*$RhPEt_3]^+$.[9] The Rh−Si bond distance of 2.375 Å in **5** is comparable to that observed in the case of other Rh(I) silyls.[4a,g,7]

Table 3. $^{31}P\{^1H\}$ NMR Data (C_6D_6; δ in ppm, J in Hz) for Complexes 1−6

	PP_2RhX					
	X = Cl (**1**)	X = H (**2**)	X = Me (**3**)	X = $(H)_2Si(SEt)_3$ (Rh^{III}, **4**)	X = $Si(SEt)_3$ (**5**)	X = SEt (**6**)
$\delta(PP_2)$, dt	21.5	9.2	2.4	8.3	−6.3	10.1
$^1J_{P-Rh}$	173	125	118	85	120	148
$\delta(PP_2)$, dd	15.7	44.2	23.2	33.6	23.1	17.4
$^1J_{P-Rh}$	125	145	145	94	131	132
$^2J_{P-P}$	49	41	46	36	50	48

Reaction of **3** with $HSi(SEt)_3$ at room temperature proceeded less selectively than at −20 °C, resulting in both Si−H and Si−S activation (Scheme 2). Si−H oxidative addition prevailed, the product ratio **5**:**6** being about 4:1. Complex **6**, observed in the reaction mixture, was synthesized independently from **3** and HSEt. Formation of $MeSiH(SEt)_2$ was clearly observed by ^1H NMR (δ 5.31 ppm (q, $^3J_{H-H}$ = 3.3 Hz, H−Si); δ 0.41 ppm (d, $^3J_{H-H}$ = 3.3 Hz, CH_3−Si)).

We are aware of only one example of Si−S oxidative addition to a metal center, namely $PhS-SiCl_3$ addition to Pt(0) complexes.[10]

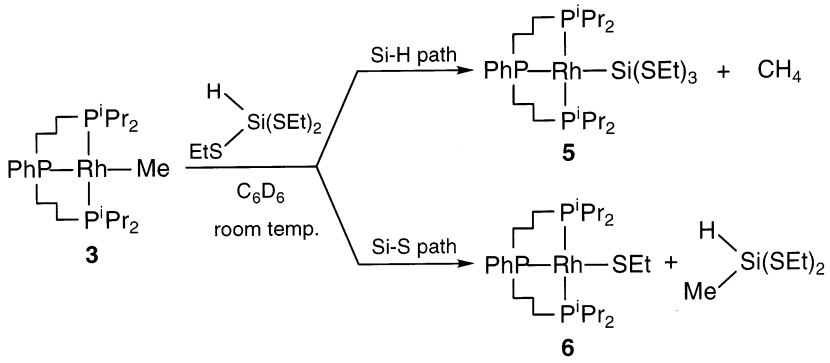
The $^{31}P\{^1H\}$ NMR data of the rhodium complexes is presented in Table 3. All the complexes except for **4** exhibit $^1J_{P-Rh}$ coupling in the range of 118−173 Hz, which is typical for Rh(I) compounds, whereas ^{31}P NMR of the Rh(III) complex **4** exhibits smaller $^1J_{P-Rh}$ (85 and 94 Hz) and $^2J_{P-P}$ (36 Hz) coupling constants. Complex **1** exhibits the signal of the unique P atom downfield relative to the signal of the terminal P atoms, a result of the lower chloride trans influence.

The reactivity of the rhodium(I) complexes was compared with that of the corresponding iridium(I) analogues. Similarly to the chloride Rh(I) complex **2**, the analogous unsaturated complex $(PP_2)IrCl$ (**7**), which was prepared from $[(COE)_2IrCl]_2$ and the PP_2 ligand in THF at room temperature, did not exhibit reactivity with $HSi(SEt)_3$. This is remarkable, considering the normally high propensity of electron-rich Ir(I) for Si−H oxidative addition. $(PP_2)IrMe$ (**8**), which was synthesized from **7** analogously to the Rh methyl complex **3**, *selectively* adds the Si−H bond of $HSi(SEt)_3$ at room temperature, yielding the stable Ir(III) complex *fac*-$(PP_2)Ir(Me)(H)(Si(SEt)_3)$ (**9**) (Scheme 3). As expected, C−H reductive elimination from Ir(III) is more difficult than from Rh(III), resulting in a stable hydrido methyl complex. Interestingly, in contrast to the addition of $HSi(SEt)_3$ to the rhodium complex **3**, no Si−S activation was observed with **8**.

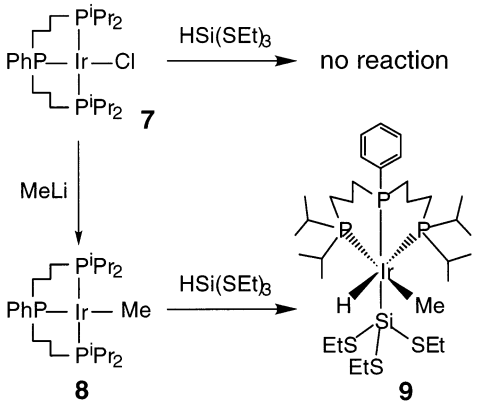
(9) Christoph, G.; Blum, P.; Liu, W.; Elia, A.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 894.

(10) (a) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 8249. (b) For a recent review on silane reactions with transition-metal complexes, including other Si−X bond additions, see: Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (c) We believe that an alternative mechanism, involving addition of the Si−H bond followed by intramolecular activation of the Si−S bond, is unlikely because of the highly favored spontaneous elimination of methane from the intermediate $[(PP_2)Rh(Me)(H)(Si(SEt)_3)]$. Additionally, intramolecular bond activation in this saturated 18e$^-$ intermediate is expected to be unfavorable.

Scheme 2



Scheme 3



Complex **9** was characterized by multinuclear NMR, including ^{31}P, ^{31}P{^{1}H}, ^{1}H, ^{13}C{^{1}H}, and ^{31}P−^{1}H 2D correlation. A proton-coupled ^{31}P NMR spectrum defined the signal of P trans to hydride. This signal is cross-linked only with the isopropyl signals in a ^{31}P−^{1}H 2D correlation (besides the hydride). Another ^{31}P signal is cross-linked only with the aromatic protons and was assigned as trans to the silyl ligand. The third ^{31}P signal is cross-linked with both the isopropyl and methyl signals in the ^{1}H spectrum, being trans to the Me ligand. It is noteworthy that the Me signal of the Ir(I) complex **8** appears in the ^{13}C{^{1}H} NMR spectrum at −5.7 ppm as a doublet of triplets ($^2J_{CPtrans}$ = 60 Hz, $^2J_{CPcis}$ = 11 Hz), whereas the Me signal of the Ir(III) complex **9** is strongly high field shifted and appears at −33.6 ppm (dt, $^2J_{CPtrans}$ = 55 Hz, $^2J_{CPcis}$ = 8 Hz).

In summary, a number of (PP$_2$)RhX complexes with a new tridentate phosphine ligand were synthesized. The reactivity of the new Rh(I) complexes toward tris(ethylthio)silane was investigated. It was demonstrated that the reaction pathway strongly depends on the X ligand, showing lack of reactivity when X = Cl, formation of a Rh(III) adduct as a result of Si−H oxidative addition when X = H, and both Si−H and Si−S bond activation when X = Me, resulting in Rh(I) products. A rare example of an X-ray-characterized Rh(I)−silyl complex was presented. Reactivities of the Rh(I) and Ir(I) complexes toward the thiosilane were compared. In contrast to the rhodium analogue, (PP$_2$)IrMe oxidatively added the Si−H bond of HSi(SEt)$_3$, giving rise to a stable Ir(III) adduct with no evidence of Si−S activation.

Experimental Section

General Considerations. All the manipulations of air- and moisture-sensitive compounds were carried out using a nitrogen-filled Vacuum Atmospheres glovebox. Solvents were purified by standard procedures, degassed, and stored over molecular sieves in the glovebox. All the reagents were of reagent grade. HSi(SEt)$_3$[5] was prepared according to a literature procedure. NMR spectra were obtained with a Bruker AMX 400 spectrometer at ambient probe temperature in C_6D_6 solutions unless otherwise specified. NMR chemical shifts are reported in ppm and are referenced to internal residual C_6D_5H at δ 7.15 (^{1}H NMR, 400 MHz), external 85% H_3PO_4 in D_2O at δ 0.0 (^{31}P NMR, 162 MHz), or internal C_6D_6 at δ 128.00 (^{13}C NMR, 100 MHz). Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; v, virtual; ov, overlapped; ap, apparent. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mulheim-an-der-Ruhr, Germany.

^{i}Pr$_2$P(CH$_2$)$_3$P(Ph)(CH$_2$)$_3$P^{i}Pr$_2$ (PP$_2$). This compound was synthesized in analogy to a literature procedure reported for $Cy_2P(CH_2)_3P(Ph)(CH_2)_3PCy_2$.[6] A 31 g amount (0.28 mol) of $PhPH_2$ in dry degassed hexane was treated under argon with 450 mL of 1.475 M BuLi (0.66 mol) in hexane at room temperature; this mixture was then refluxed for 1 h and cooled to room temperature. The resulting yellow mixture was filtered under argon, washed with dry pentane, and dried in vacuo to give 34 g of $PhPLi_2$ in quantitative yield. An 11.3 g amount (0.093 mol) of $PhPLi_2$ was suspended in 160 mL of freshly distilled and degassed ether, and the suspension was added under nitrogen over 1 h to 35.9 g (0.185 mol) of Cl(CH$_2$)$_3$P^{i}Pr$_2$, dissolved in 140 mL of ether, and cooled to 0 °C. The resulting mixture was refluxed overnight and then hydrolyzed with 300 mL of distilled degassed water. The water layer was extracted twice with 150 mL of ether, and the ether fractions were combined and dried with anhydrous Na_2SO_4. The volatile compounds and unreacted Cl(CH$_2$)$_3$P^{i}Pr$_2$ were removed under vacuum, and the residue was chromatographed over active neutral Al_2O_3, using benzene as eluent. Removal of the benzene in vacuo yielded 18 g (55%) of pure PP$_2$. NMR characterization ($CDCl_3$) was as follows. ^{31}P{^{1}H} NMR: 2.9 s (2P), −26.0 s (1P). ^{1}H NMR: 7.33 m (P−Ph, 2H), 7.15 m (P−Ph, 3H), 1.2−1.7 ov m (CH$_2$ and C*H*Me$_2$, 16H), 0.87 m (CH$_3$, 24H). ^{13}C{^{1}H} NMR: 138.33 d ($^1J_{C-P}$ = 14.8 Hz, Ph−P), 132.18 d ($^2J_{C-P}$ = 18.8 Hz, Ph−P), 128.98 d ($^4J_{C-P}$ = 0.7 Hz, Ph−P), 128.0 d ($^3J_{C-P}$ = 6.9 Hz, Ph−P), 29.90 vt (J_{C-P} = 11.8 Hz, CH$_2$), 24.33 dd ($^1J_{C-P}$ = 19.7 Hz, $^3J_{C-P}$ = 14.5 Hz, CH$_2$), 23.17 dd ($^1J_{C-P}$ = 17.7 Hz, $^3J_{C-P}$ = 11.3 Hz, CH$_2$), 22.96 d ($^2J_{C-P}$ = 12.1 Hz, CH$_3$), 19.89 d ($^1J_{C-P}$ = 15.7 Hz, CH), 19.83 d ($^1J_{C-P}$ = 15.5 Hz, CH), 18.56 d ($^2J_{C-P}$ = 9.5 Hz, CH$_3$).

(PP$_2$)RhCl (1). A solution of 222 mg (0.31 mmol) of [(C$_8$H$_{14}$)$_2$RhCl]$_2$ in 3 mL of THF was treated with 265 mg (0.62 mmol) of PP$_2$. The mixture was stirred for 2 h at room temperature, and then the solvent was removed under vacuum to yield quantitatively 350 mg of pure compound **1** as a yellow-brown solid. ^{31}P{^{1}H} NMR: 21.45 dt ($^1J_{P-Rh}$ = 173.0 Hz,

$^2J_{P-P}$ = 49 Hz, 1P), 15.72 dd ($^1J_{P-Rh}$ = 125.5 Hz, $^2J_{P-P}$ = 49 Hz, 2P). ^{1}H NMR: 8.17 m (Ph−P, 2H), 7.75 m (Ph−P, 1H), 7.17 m (Ph−P, 2H), 3.0 m (CH_2, 2H), 2.18 m (CH_2, 2H), 1.64 dvt (J = 7.2 Hz, CH_3CH−P, 6H), 1.49 dvt (J_H = 7.2 Hz, CH_3-CH−P, 6H), 1.03 dvt (J = 6.9 Hz, CH_3CH−P, 6H), 0.97 dvt (J = 6.2 Hz, CH_3CH−P, 6H), signals of other CH_2 and CH groups appear as overlapped multiplets at 0.9−1.7 ppm. ^{13}C-{^{1}H} NMR: 138.13 dd ($^1J_{C-P}$ = 35.8 Hz, $^2J_{C-Rh}$ = 1.5 Hz, Ph−P), 134.70 dd ($^2J_{C-P}$ = 11.5 Hz, $^3J_{C-Rh}$ = 1.3 Hz, Ph-P), 129.78 d ($^4J_{C-P}$ = 2.2 Hz, Ph−P), 127.59 d ($^3J_{C-P}$ = 9.0 Hz, Ph-P), 29.35 ddt ($^1J_{C-P}$ = 29.9 Hz, $^3J_{C-P}$ = 5.3 Hz, $^2J_{C-Rh}$ = 0.9 Hz, Ph−P−CH_2), 27.35 vt ($^1J_{C-P}$ = $^3J_{C-Ptrans}$ = 10.3 Hz, CH_3CH−P), 24.30 vt ($^1J_{C-P}$ = $^3J_{C-Ptrans}$ = 12.1 Hz, CH_3CH−P), 21.12 vt ($^2J_{C-P}$ = $^4J_{C-Ptrans}$ = 2.9 Hz, CH_3CH−P), 20.95 vt ($^2J_{C-P}$ = $^4J_{C-Ptrans}$ = 2.2 Hz, CH_3CH−P), 20.66 m (P−$CH_2CH_2CH_2$−P), 19.46 vt ($^2J_{C-P}$ = $^4J_{C-Ptrans}$ = 1.2 Hz, CH_3CH−P), 19.09 m (^{i}Pr−P−CH_2), 17.59 m (CH_3CH−P). Anal. Calcd for $C_{24}H_{45}ClP_3Rh$: C, 51.03; H 8.03. Found: C, 50.87; H, 7.91.

(PP$_2$)RhH (2). Complex **1** (113 mg, 0.2 mmol) was dissolved in dry THF and the solution treated with 0.125 mL of a 1.6 M ^{t}BuLi (0.2 mmol) solution in pentane at −30 °C and then warmed to room temperature. After the mixture stood at room temperature for 2 h, the solvents were evaporated in vacuo, the residue was redissolved in pentane, and the solution filtered. The filtrate was evaporated and dried in vacuo, affording complex **2** as a dark brown, slightly viscous substance in 88% yield (93 mg). ^{31}P{^{1}H} NMR: 44.2 dd ($^1J_{P-Rh}$ = 144.7 Hz, $^2J_{P-P}$ = 40.7 Hz, 2P), 9.2 dt ($^1J_{P-Rh}$ = 125.2 Hz, $^2J_{P-P}$ = 40.7 Hz, 1P). ^{1}H NMR: 8.04 m (Ph−P, 2H), 7.22 m (Ph−P, 2H), 7.12 m (Ph−P, 1H), 1.7−1.95 ov m (CH_2CH_2, 8H), 1.45 vdt. (J = 7.4 Hz, CH_3CH−P, 6H), 1.27 vdt (J = 7.1 Hz, CH_3-CH−P, 6H), 1.19 vdt (J = 6.7 Hz, CH_3CH−P, 6H), 1.10 vdt (J_H = 6.8 Hz, CH_3CH−P, 6H), −4.51 ap dq ($^2J_{H-Ptrans}$ = 108 Hz, $^1J_{H-Rh}$ = $^2J_{H-Pcis}$ = 20.0 Hz, H−Rh, 1H), signals of other CH_2 and CH groups appear as overlapped multiplets at 1.0−1.5 ppm. ^{13}C{^{1}H} NMR: 141.07 dd ($^1J_{C-P}$ = 21.2 Hz, $^2J_{C-Rh}$ = 0.8 Hz, Ph−P), 134.59 dd ($^2J_{C-P}$ = 13.9 Hz, $^3J_{C-Rh}$ = 0.8 Hz, Ph−P), 129.27 d ($^4J_{C-P}$ = 1.8 Hz, Ph−P), 127.60 d ($^3J_{C-P}$ = 8.4 Hz, Ph−P), 30.13 dt ($^1J_{C-P}$ = 20.6 Hz, $^3J_{C-P}$ = 4.9 Hz, Ph−P−CH_2), 28.52 vdt ($^1J_{C-P}$ = $^3J_{C-Ptrans}$ = 9.9 Hz, $^2J_{C-Rh}$ = 1.0 Hz, CH_3CH−P), 27.89 vddt ($^1J_{C-P}$ = $^3J_{C-Ptrans}$ = 13.1 Hz, $^3J_{C-Pcis}$ = 3.6 Hz, $^2J_{C-Rh}$ = 2.4 Hz, CH_3CH−P), 23.50 ap dq ($^1J_{C-P}$ = $^3J_{C-Ptrans}$ = $^3J_{C-Pcis}$ = 8.0 Hz, $^2J_{C-Rh}$ = 0.8 Hz, ^{i}Pr−P−CH_2), 21.58 m (P−$CH_2CH_2CH_2$−P), 21.45 vdt ($^2J_{C-P}$ = $^4J_{C-Ptrans}$ = 3.6 Hz, $^2J_{C-Rh}$ = 1.0 Hz, CH_3CH−P), 19.50 m (CH_3-CH−P), 19.32 m (CH_3CH−P), 18.79 ap q ($^2J_{C-P}$ = $^4J_{C-Ptrans}$ = $^3J_{C-Rh}$ = 1.7 Hz, CH_3CH−P). MS (ESI): m/z (%): 530 (30) [M$^+$], 529 (100) [M$^+$ − H].

(PP$_2$)RhMe (3). This complex was synthesized in analogy to **2**. A 170 mg amount (0.3 mmol) of **1** was dissolved in dry THF and the solution treated with 0.24 mL of a 1.4 M ether solution of MeLi (0.3 mmol) at −30 °C. This solution was warmed to room temperature, and the solvent was evaporated in vacuo. The residue was dissolved in pentane and filtered, and the filtrate was evaporated and dried in vacuo, affording complex **3** as a brown slightly viscous substance in 85% yield (140 mg). ^{31}P{^{1}H} NMR: 23.24 dd ($^1J_{P-Rh}$ = 145 Hz, $^2J_{P-P}$ = 46 Hz, 2P), 2.39 dt ($^1J_{P-Rh}$ = 118 Hz, $^2J_{P-P}$ = 46 Hz, 1P). ^{1}H NMR: 8.16 m (Ph−P, 2H), 7.19 m (Ph−P, 2H), 7.09 m (Ph−P, 1H), 2.39 m (CH_2, 2H), 2.04 m (CH_2, 2H), 1.8 ov m (CH_2, 4H), 1.45 vdt (J = 7.3 Hz, CH_3CH−P, 6H), 1.31 vdt (J = 6.9 Hz, CH_3CH−P, 6H), 1.05 vdt (J = 6.6 Hz, CH_3CH−P, 6H), 1.01 m (CH_3CH−P, 6H), 0.39 m (CH_3−Rh, 3H), signals of other CH_2 and CH groups appear as overlapped multiplets at 0.9−1.5 ppm. ^{13}C{^{1}H} NMR: 141.15 d ($^1J_{C-P}$ = 26.4 Hz, Ph−P), 134.6 d ($^2J_{C-P}$ = 12.5 Hz, Ph−P), 128.98 d ($^4J_{C-P}$ = 1.8 Hz, Ph−P), 127.34 d ($^3J_{C-P}$ = 8.3 Hz, Ph−P), 29.84 dvt ($^1J_{C-P}$ = 23.6 Hz, $^3J_{C-P}$ = $^2J_{C-Rh}$ = 4.3 Hz, Ph−P−CH_2), 27.66 dvt ($^1J_{C-P}$ = $^3J_{C-Ptrans}$ = 8.8 Hz, $^2J_{C-Rh}$ = 0.9 Hz, CH_3CH−P), 24.20 vtt ($^1J_{C-P}$ = $^3J_{C-Ptrans}$ = 11 Hz, $^2J_{C-Rh}$ = $^2J_{C-Pcis}$ = 1.4 Hz, CH_3CH−P), 21.55 m (^{i}Pr−P−CH_2), 20.9 m (^{i}Pr−P−CH_2), 20.90 s (CH_3-CH−P), 20.87 s (CH_3CH−P), 19.72 vt ($^2J_{C-P}$ = $^4J_{C-Ptrans}$ = 1.9 Hz, CH_3CH−P), 17.59 s (CH_3CH−P), −6.76 ddt ($^1J_{C-Rh}$ = 22.3 Hz, $^2J_{C-Ptrans}$ = 67 Hz, $^2J_{C-Pcis}$ = 13.7 Hz). Anal. Calcd for $C_{24}H_{48}P_3Rh$: C, 55.15; H, 8.89. Found: C, 55.25; H, 8.78.

***mer*-(PP$_2$)Rh(H$_2$)(Si(SEt)$_3$) (4).** A solution of 16 mg (0.03 mmol) of **2** in 0.5 mL of C_6D_6 was treated at room temperature with 6 μL (0.03 mmol) of HSi(SEt)$_3$, forming the complex *mer*-(PP$_2$)Rh(H)$_2$(Si(SEt)$_3$) (**4**) within minutes as the major product (85% by NMR). A brown viscous solid was formed after evaporation of the solvent. ^{31}P{^{1}H} NMR: 33.7 dd ($^1J_{P-Rh}$ = 93.5 Hz, $^2J_{P-P}$ = 36 Hz, 2P), 8.3 dt ($^1J_{P-Rh}$ = 85 Hz, $^2J_{P-P}$ = 36 Hz, 1P). ^{1}H NMR: 8.18 m (Ph−P, 2H), 7.37 m (Ph−P, 1H), 7.06 m (Ph−P, 2H), 3.13 q ($^3J_{H-H}$ = 7.3 Hz, S−CH_2, 6H), 3.09 m (CH_2, 4H), 1.50 t ($^3J_{H-H}$ = 7.3 Hz, S−CH_2CH_3, 9H), 1.45 vdt (J = 7.3 Hz, CH_3CH−P, 6H), 1.29 vdt (J = 7.3 Hz, CH_3-CH−P, 6H), 1.16 vdt (J = 6.9 Hz, CH_3CH−P, 6H), 1.04 vdt (J = 6.9 Hz, CH_3CH−P, 6H), −9.05 dddt ($^1J_{H-Rh}$ = 15.2 Hz, $^2J_{H-Ptrans}$ = 123 Hz, $^2J_{H-Pcis}$ = 11.5 Hz, $^2J_{H-H}$ = 1.9 Hz), −9.25 m ($^1J_{H-Rh}$ = 13.7 Hz, $^2J_{H-H}$ = 1.9 Hz), signals of other CH_2 and CH groups appear as overlapped multiplets at 0.9−2.0 ppm. Each hydride signal was observed in ^{1}H{^{31}P} decoupled measurements as a doublet of doublets (dd), and clear $^1J_{H-Rh}$ and $^2J_{H-H}$ values were obtained from this experiment, proving the dihydride structure.

The minor product (ca. 15%) formed in the synthesis of **4** had three different broad signals in ^{31}P NMR (26.9 br d ($^1J_{P-Rh}$ = 87 Hz, 1P), 13.7 br d ($^1J_{P-Rh}$ = 92 Hz, 1P), −0.8 dvt ($^1J_{P-Rh}$ = 92 Hz, $^2J_{P-P}$ = 30 Hz, 1P)), and two hydride (trans to P) signals in ^{1}H NMR (−9.8 dm ($^2J_{H-P}$ = 131 Hz, 1H), −10.7 dm ($^2J_{H-Ptrans}$ = 109 Hz, $^1J_{H-Rh}$ = 13 Hz, $^2J_{H-H}$ = 6 Hz, 1H)). The byproduct is likely to be a *fac* isomer of **4**, which was also supported by sufficient elemental analysis of the mixture. Anal. Calcd for $C_{30}H_{62}P_3RhS_3Si$: C, 48.50; H, 8.41. Found: C, 48.55; H, 8.04.

(PP$_2$)RhSi(SEt)$_3$ (5). A solution of 44 mg (0.08 mmol) of **3** in 1 mL of pentane was treated at −20 °C with 16 μL (0.08 mmol) of HSi(SEt)$_3$ and left standing at −20 °C. About 90% conversion was observed after 3 weeks. The major product was **5** (80%). Small amounts of complexes **3** (starting compound) and **4** were also observed. Methane and presumably MeSi-(SEt)$_3$ were detected by ^{1}H NMR (singlets at 0.14 and 0.63 ppm, respectively). Complex **5** was isolated in 25% yield (15 mg) as deep red crystals after standing in concentrated pentane solution at −20 °C for 1 month. The complex has a limited stability at room temperature.

A room-temperature reaction of equimolar amounts of **3** (30 mg) and HSi(SEt)$_3$ (11 μL) proceeded less selectively. Complexes **4** (10%), **5** (65%), and **6** (15%) and small amounts of several unidentified Rh(III) complexes were formed. New signals assigned to MeSiH(SEt)$_2$ were observed by ^{1}H NMR: 5.31 (q, $^3J_{H-H}$ = 3.3 Hz, H−Si); 0.41 (d, $^3J_{H-H}$ = 3.3 Hz, CH_3−Si).

NMR data for **5** are as follows. ^{31}P{^{1}H} NMR: 23.1 dd ($^1J_{P-Rh}$ = 131 Hz, $^2J_{P-P}$ = 50 Hz, 2P), −6.3 dt ($^1J_{P-Rh}$ = 119.6 Hz, $^2J_{P-P}$ = 50 Hz, 1P). ^{1}H NMR: 8.13 m (Ph−P, 2H), 7.23 m (Ph−P, 2H), 7.07 m (Ph−P, 1H), 3.67 m (CH_2, 2H), 3.26 m (CH_2, 2H), 3.16 q ($^3J_{H-H}$ = 7.4 Hz, CH_2−SSi, 6H), 1.50 t ($^3J_{H-H}$ = 7.4 Hz, CH_3CH_2−SSi, 9H), 1.54 vdt (J = 7.9 Hz, CH_3-CH−P, 6H), 1.27 vdt (J = 8.1 Hz, CH_3CH−P, 6H), 1.13 m (CH_3-CH−P, 6H), 1.07 m (CH_3CH−P, 6H), signals of other CH_2 and CH groups appear as overlapped multiplets at 0.8−1.7 ppm. Anal. Calcd for $C_{30}H_{60}P_3RhS_3Si$: C, 48.63; H 8.16. Found: C, 49.34; H, 7.95.

Crystal Structure Determination. Prismatic, red crystals of **5** were mounted on a glass fiber and coated with inert oil. They were then flash frozen in the liquid nitrogen gas stream. Data were collected at 110 K on a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) in the ω-scan mode. The unit cell parameters were obtained from least-squares refinement of

25 reflections, and all reflections in the range of $1.2° < 2\theta < 27.5°$ were collected. Table 2 summarized crystal and refinement data.

The structure was solved using direct methods and refined with the program SHELX-76. A full-matrix least-squares refinement with anisotropic temperature factors was used for all non-hydrogen atoms. Idealized hydrogen atoms were placed in calculated positions and refined in the riding mode.

(PP_2)RhSEt (6). A solution of 33 mg (0.06 mmol) of **3** in 1 mL of C_6D_6 was treated at room temperature with 4.5 μL (0.06 mmol) of HSEt. The reaction mixture was stirred for 30 min to give **6** in 95% yield. Formation of methane was detected by NMR. $^{31}P\{^1H\}$ NMR: 17.4 dd ($^1J_{P-Rh} = 132.7$ Hz, $^2J_{P-P} = 48.1$ Hz, 2P), 10.1 dt ($^1J_{P-Rh} = 147.5$ Hz, $^2J_{P-P} = 48.1$ Hz, 1P). ^1H NMR: 8.15 m (Ph−P, 2H), 7.12 ov m (Ph−P, 3H), 2.92 dq ($^3J_{H-H} = 7.3$ Hz, $^4J_{H-Ptrans} = 2.1$ Hz, S−CH_2, 2H), 2.67 m (CH_2, 4H), 1.78 t ($^3J_{H-H} = 7.4$ Hz, CH_3CH_2−S, 3H), 1.61 vdt ($J = 7.3$ Hz, CH_3CH−P, 6H), 1.38 vdt ($J = 7.3$ Hz, CH_3CH−P, 6H), 1.14 vdt ($J = 6.4$ Hz, CH_3CH−P, 6H), 1.00 vdt ($J = 6.3$ Hz, CH_3CH−P, 6H), signals of other CH_2 and CH groups appear as overlapped multiplets at 0.8−1.7 ppm. MS (ESI): *m*/*z* (%): 561 (86) [M^+ − Et], 529 (100) [M^+ − SEt].

[(Et_3P)$_2$Rh(Cl)(H)($Si(SEt)_3$)]. A solution of 15 mg (0.03 mmol) of (Et_3P)$_3$RhCl in 0.5 mL of C_6D_6 was treated at room temperature with 6 μL (0.03 mmol) of $HSi(SEt)_3$. The complex [(Et_3P)$_2$Rh(Cl)(H)($Si(SEt)_3$)] was formed within minutes, and 1 equiv of Et_3P was liberated. Evaporation of the solution gave 18 mg of the yellow-orange viscous compound. The yield is quantitative. The complex partially decomposes under high vacuum. $^{31}P\{^1H\}$ NMR: 26.5 d ($^1J_{P-Rh}$= 112 Hz). ^1H NMR: 3.03 q ($^3J_{H-H} = 7.5$ Hz, $SiS-CH_2$, 6H), 2.00 m (P−CH_2, 12H), 1.35 t ($^3J_{H-H} = 7.5$ Hz, $SiS-CH_2CH_3$, 9H), 1.06 dt ($^3J_{H-P} = 15.2$ Hz, $^3J_{H-H} = 7.6$ Hz, P−CH_2CH_3, 18H), −15.85 dt ($^1J_{H-Rh} = 23.7$ Hz, $^2J_{H-P} = 12.9$ Hz, Rh−H, 1H).

Reaction of (PP_2)RhSi(SEt)$_3$ (5) with HCl. A 9 mg amount (0.012 mmol) of compound **5** was dissolved in C_6D_6 and treated with an equivalent amount (3 μL) of 4 M HCl solution in 1,4-dioxane. Immediate quantitative formation of (PP_2)RhCl (**1**) and $HSi(SEt)_3$ was detected by NMR.

(PP_2)IrCl (7). A solution of 180 mg (0.2 mmol) of [(cyclooctene)$_2$IrCl]$_2$ in 4 mL of THF was treated with 171 mg (0.4 mmol) of PP_2. The mixture was stirred for 2 h at room temperature, and the solvent was removed under vacuum to yield quantitatively 262 mg of pure compound **7**. $^{31}P\{^1H\}$ NMR: 8.71 d ($^2J_{P-P} = 31$ Hz, 2P), −15.94 t ($^2J_{P-P} = 31$ Hz, 1P). ^1H NMR: 8.20 m (Ph−P, 2H), 7.19 m (Ph−P, 2H), 7.06 m (Ph−P, 1H), 3.14 m (CH_2, 2H), 2.27 m (CH_2, 2H), 1.94 m (CH_2, 2H), 1.63 dvt ($J = 7.5$ Hz, CH_3CH−P, 6H), 1.48 dvt ($J_H = 7.1$ Hz, CH_3CH−P, 6H), 1.07 dvt ($J = 7.0$ Hz, CH_3CH−P, 6H), 0.95 dvt ($J = 6.3$ Hz, CH_3CH−P, 6H), signals of other CH_2 and CH groups appear as overlapped multiplets at 1.2−1.7 ppm. MS (ESI): *m*/*z* (%): 697 (19) [M + K^+], 679 (13) [M + Na^+], 619 (100) [M^+ − Cl].

(PP_2)IrMe (8). This complex was synthesized in analogy to **3**. A 130 mg amount (0.2 mmol) of **7** was dissolved in dry THF and treated with 0.16 mL of a 1.4 M ether solution of MeLi (0.2 mmol) at −30 °C. The solution was warmed to room temperature, and the solvent was evaporated in vacuo. The residue was dissolved in pentane and the solution filtered. The filtrate was evaporated and dried in vacuo, affording orange viscous compound **8** in 89% yield (112 mg). $^{31}P\{^1H\}$ NMR: 9.62 d ($^2J_{P-P} = 30.3$ Hz, 2P), −17.62 t ($^2J_{P-P} = 30.3$ Hz, 1P). ^1H NMR: 8.24 m (Ph−P, 2H), 7.22 m (Ph−P, 2H), 7.08 m (Ph−P, 1H), 2.55 m (CH_2, 2H), 2.17 m (CH_2, 2H), 2.05 m (CH_2, 2H), 1.45 dvt ($J = 7.3$ Hz, CH_3CH−P, 6H), 1.30 dvt ($J_H = 6.9$ Hz, CH_3CH−P, 6H), 1.15 dt ($^3J_{H-Ptrans} = 5.5$ Hz, $^3J_{H-Pcis} = 7.2$ Hz, Ir−CH_3, 3H), 1.07 dvt ($J = 6.7$ Hz, CH_3CH−P, 6H), 0.98 dvt ($J = 6.0$ Hz, CH_3CH−P, 6H), signals of other CH_2 and CH groups appear as overlapped multiplets at 1.3−1.8 ppm. $^{13}C\{^1H\}$ NMR: −5.7 dt ($^2J_{C-Ptrans} = 60$ Hz, $^2J_{C-Pcis} = 11$ Hz, Ir−CH_3). MS (ESI): *m*/*z* (%): 634 (6) [M^+], 619 (92) [M^+ − CH_3].

***fac*-[(PP_2)Ir(H)(Me)($Si(SEt)_3$)] (9).** A solution of 19 mg (0.03 mmol) of **8** in 0.5 mL of C_6D_6 was treated at 6 °C with 6 μL (0.03 mmol) of $HSi(SEt)_3$. The complex *fac*-[(PP_2)Ir(H)(Me)-($Si(SEt)_3$)] (**9**) was readily formed. Removal of the solvent in vacuo gave an off-white residue of **9**. $^{31}P\{^1H\}$ NMR: −33.83 dd ($^2J_{P-P} = 19.1$ Hz, $^2J_{P-P} = 22.5$ Hz, 1P), −37.94 vt ($^2J_{P-P} = 19.1$ Hz, 1P), −41.07 dd ($^2J_{P-P} = 19.1$ Hz, $^2J_{P-P} = 22.5$ Hz, 1P). ^1H NMR: 8.21 m (Ph−P, 2H), 7.36 m (Ph−P, 2H), 7.17 m (Ph−P, 1H), 3.08 m ($SiS-CH_2$, 6H), 2.48 m (CH_2, 2H), 1.38 t ($^3J_{H-H} = 7.4$ Hz, $SiS-CH_2CH_3$, 9H), 0.81 m (Ir−CH_3, 3H), −12.38 ddd ($^2J_{H-Ptrans} = 116.9$ Hz, $^2J_{H-Pcis} = 21.6$ Hz, $^2J_{H-Pcis} = 9.3$ Hz), signals of other CH_3, CH_2, and CH groups appear as overlapped multiplets at 0.9−2.1 ppm. $^{13}C\{^1H\}$ NMR: −33.6 dt ($^2J_{C-Ptrans} = 55$ Hz, $^2J_{C-Pcis} = 8$ Hz, Ir−CH_3). MS (ESI): *m*/*z* (%) 869 (21) [M + Na^+], 769 (8) [M^+ − CH_4 − SEt], 619 (100) [M^+ − CH_4 − $Si(SEt)_3$].

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Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, all bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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