4020 *Organometallics* **2003,** *22,* 4020−4024

Iridium− and Rhodium−Silanol Complexes: Synthesis and Reactivity

Roman Goikhman, Michael Aizenberg, Linda J. W. Shimon, and David Milstein*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel 76100

Received January 21, 2003

Methods of metallo-silanol synthesis have been developed. The Ir(I) complex $(Et_3P)_2Ir(C_2H_4)Cl$ (**1**) oxidatively adds secondary silanols R_2SiHOH ($R = {}^iPr, {}^tBu$) to yield the iridium−silanol complexes $[(Et_3P)_2Ir(H)(Cl)(SiR_2OH)]$ ($R = {}^iPr$, **2**; $R = {}^tBu$, **3**). The crystal structure of **2** exhibits a trigonal-bipyramidal geometry, and *intermolecular* Si−O−H- - -Cl hydrogen bonding is present. Deprotonation of **2** results in the highly thermodynamically stable metallo-silanolate $[(Et_3P)_2Ir(H)(Cl)(Si^iPr_2OLi)]_2$ (**4**). Compound **4** has an almost planar core, consisting of two atoms each of iridium, silicon, chlorine, oxygen, and lithium. Upon treatment of $(Et_3P)_3RhCl$ with HSi^iPr_2OH, the first Rh−silanol complex, *trans*-$[(Et_3P)_2Rh(H)(Cl)(^iPrSi_2OH)]$, is formed in an equilibrium with the starting complex ($K_{eq} = 4 \times 10^{-3}$); hence, the reaction is dependent on the concentration of the silanol and Et_3P, an excess of the latter shifting the equilibrium to the starting compounds. Reaction of the bis-phosphine complex $[(Et_3P)_2RhCl]_2$ with the silanol, which does not generate free phosphine, results in 96% conversion to the adduct. On the other hand, the chelating bis-phosphine complex [(bis(diisopropylphosphino)propane)RhCl]$_2$ does not add the silanol even in the presence of a 10-fold excess of the silanol, indicating that the cis-phosphine configuration in the adduct is unfavorable. In contrast to the Et_3P-containing Ir complex, and similarly to the Rh complex, $(PPh_3)_3Ir(CO)H$ reacts with $^iPr_2SiHOH$ reversibly, leading to 60% conversion to the metallo-silanol $(PPh_3)_2Ir(CO)(H)_2(Si^iPr_2OH)$ (**6**). A stable PPh_3-containing Ir−silanol was prepared by starting from $(PPh_3)_2Ir(CO)(H)_2(Si(SEt)_3)$. Following reaction with $Et_3SiOSO_2CF_3$ to exchange one SEt substituent with OSO_2CF_3, reaction with NaOH generates the stable silanol complex $(PPh_3)_2Ir(CO)(H)_2(Si(SEt)_2OH)$ (**14**).

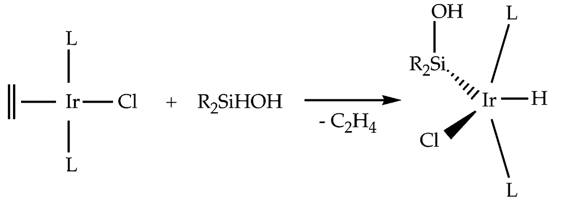
Introduction

Organic silanols have been extensively studied.[1] These compounds are intermediates in the formation of various organosilicon compounds, including important silicone polymers.[2] In contrast, metallo-silanols,[3−7] i.e., compounds that contain a M−Si−OH moiety, form a relatively new class of compounds which has attracted attention only recently. These complexes, being interesting as such, can also potentially be synthetically useful. For example, they may find applications in metallo-functionalized silica and organometallic polymers. Metallo-silanols, which are still limited in number, were reported to be formed either by hydrolysis of the corresponding silyl complexes or by oxyfunctionalization of a Si−H fragment bound to a metal center with dimethyldioxirane.[3−5]

We communicated the synthesis of metallo-silanol complexes by the direct oxidative addition of secondary silanols to transition-metal complexes.[6,7] In this paper we describe a complete study on the preparation of iridium− and rhodium−silanol complexes with different phosphine and silyl ligands.

Results and Discussion

Treatment of *trans*-$(Et_3P)_2Ir(C_2H_4)Cl$[8a] (**1**) (or its precursor $(Et_3P)_2Ir(C_2H_4)_2Cl$)[8b] with 1 equiv of R_2SiHOH ($R = {}^iPr$,[9] ^tBu[10]) at room temperature led to formation of the coordinatively unsaturated metallo-silanols $[(Et_3P)_2Ir(H)(Cl)(SiR_2OH)]$ (eq 1).



(1)

1, L =PEt$_3$ **2** , R = ^{i}Pr **3** , R =^{t}Bu

Complex **2** was characterized by X-ray analysis (see ref 6 for details). The fact that the coordinatively

---

* To whom correspondence should be addressed. Fax: 972-8-9344142. E-mail: david.milstein@weizmann.ac.il.

[1] Mittal, K. L., Ed. *Silanes and Other Coupling Agents;* VSP: Utrecht, The Netherlands, 1992.

[2] Noll, W. *Chemistry and Technology of Silicones*; VCH: Weinheim, Germany, 1968.

[3] Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219.

[4] Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9682.

[5] (a) Malisch, W.; Schmitzer, S.; Kaupp, G.; Hindahl, K.; Käb, H.; Wachtler, U. In *Organosilicon Chemistry. From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1994; p 185. (b) For recent publications on the subject see: Malisch, W.; Hofmann, M.; Kaupp, G.; Kab, H.; Reising, J. *Eur. J. Inorg. Chem.* **2002**, 3235 and references therein.

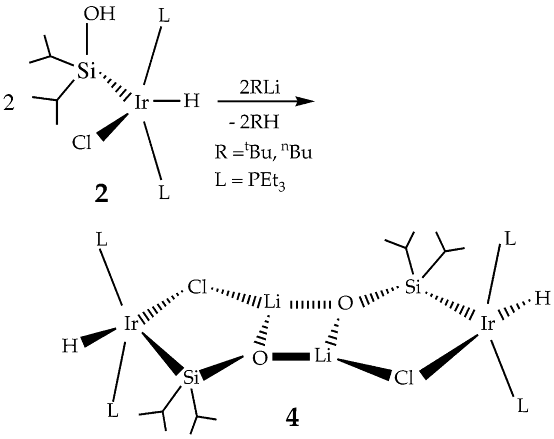
[6] Goikhman, R.; Aizenberg, M.; Kraatz, H. B.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 5865.

[7] Goikhman, R.; Aizenberg, M.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 10894.

10.1021/om0300427 CCC: $25.00
Publication on Web 08/30/2003

unsaturated 16-electron d^6 complex **2** has a trigonal-bipyramidal, rather than a square-pyramidal, configuration may be explained by the presence of the π-donor chloride ligand.[11] Surprisingly, an *inter*molecular rather than an *intra*molecular hydrogen bond between the chloride and the silanol hydrogen is observed.

Treatment of **2** with ^{t}BuLi or ^{n}BuLi resulted in deprotonation, generating the metallo-silanolate $[(Et_3P)_2Ir(H)(Cl)(Si^iPr_2OLi)]_2$ (**4**) (eq 2).



2

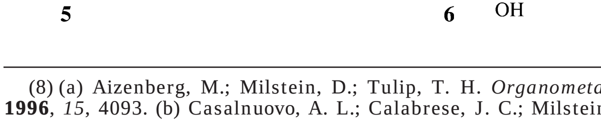
4

(2)

Complex **4** crystallizes as a centrosymmetric dimer with a near-planar core, consisting of two atoms each of iridium, silicon, chlorine, oxygen, and lithium (see ref 6 the for X-ray structure). The Li−O bond lengths and Li···Li contacts in the Li−O−Li−O square are among the shortest known.[12] The metallo-silanolate dimer **4** exhibites outstanding thermodynamic stability in solution, and remarkably, it is formed even at the expense of extraction of Li^+ from a crown ether. Thus, when $[Li(12\text{-crown-}4)_2][CHPh_2]$[13] was used as a base, the silanolate **4** and liberated 12-crown-4 were formed quantitatively. Complex **4** reacted instantaneously with water, yielding the parent compound **2**.

Whereas the triethylphosphine Ir(I) complexes form stable Ir(III) adducts with secondary silanols, triphenylphosphine monocarbonyl Ir(I) complexes show different reactivity.

Treatment of $(PPh_3)_3Ir(CO)H$ (**5**) with a stoichiometric amount of $^iPr_2SiHOH$ resulted in only a partial (60%) conversion to the metallo-silanol **6** (eq 3). Using a 10-fold excess of $^iPr_2SiHOH$ shifted the equilibrium to the right, resulting in 97% adduct formation.



5

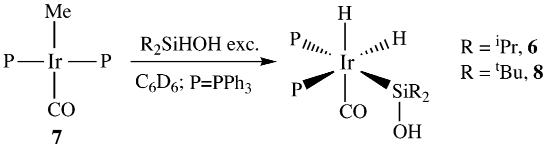
6

(3)

The NMR data of **6** are similar to those of other silyl complexes previously obtained with **5**.[14] Although the complex is stable in solution at room temperature in the presence of an excess of diisopropylsilanol, attempts to isolate it either by precipitation or by solvent evaporation resulted in decomposition to the starting compounds. Above 50 °C, slow decomposition of **6** to the starting complex **5** occurred as a result of condensation of the free silanol to form the inactive tetraisopropyldisiloxane, shifting the equilibrium (eq 3) to the left. The bulkier silanol $^tBu_2SiHOH$ did not give any observable adduct with **5**.

The more reactive unsaturated methyl complex *trans*-$(PPh_3)_2Ir(CO)Me$ (**7**) reacted with the silanols in a different manner. Reaction with 1 equiv of the silanol at room temperature required 1 day for $^iPr_2SiHOH$ and 5 days for $^tBu_2SiHOH$ and resulted in mixtures, the most significant product being the hydride complex **5**. Signals at 0.04 and −0.02 ppm, detected in the ^1H NMR of the reaction mixtures of **7** with $^iPr_2SiHOH$ and $^tBu_2SiHOH$, may be attributed respectively to $^iPr_2MeSiOH$ and $^tBu_2MeSiOH$. Apparently, Si−H oxidative addition to **7** was followed by Me-Si reductive elimination, resulting in the Ir(I) hydride complexes.[15] Competitive C−H and C−Si reductive elimination from Ir(III) was reported by our group.[15] It was shown that C−Si reductive elimination can occur when alkyl-substituted silyl ligands are employed, as observed here as well.

Addition of an *excess* of the silanols to **7** resulted in formation of dihydrido silyl complexes (eq 4). Reaction of **7** with a 4-fold excess of $^tBu_2SiHOH$ required 10 days at room temperature in C_6D_6 for completion and resulted in formation of the dihydride complex **8** as a major product (about 80% yield by NMR), which is the analogue of **6**.[16] Some amount of complex **5** was also formed as a byproduct, being a phosphine adduct of the intermediate Ir(I) hydride complex.



7

(4)

The fact that **8** was formed in reaction 4 while it was not formed in the reaction of $^tBu_2SiHOH$ with **5** (see above) can be explained by the presence of a free 1 equiv of phosphine in the latter case (compare with eq 3). As in the case of complex **6**, complex **8** is stable only in the presence of excess $^tBu_2SiHOH$.

Thus, the direct oxidative addition of two secondary dialkylsilanols to the *triphenyl*phosphine Ir(I) complexes **5** and **7** led to reversible formation of Ir(III)−silanol adducts, which were observed in solution in the presence of an excess of the silanol substrates. We then examined

---

(8) (a) Aizenberg, M.; Milstein, D.; Tulip, T. H. *Organometallics* **1996**, *15*, 4093. (b) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971.

(9) Gilman, H.; Clark, R. N. *J. Am. Chem. Soc.* **1947**, *69*, 1499.

(10) Barton, T. J.; Tully, C. R. *J. Organomet. Chem.* **1979**, *172*, 11.

(11) Stabilization of one configuration over another due to a partial multiple bond between the metal center and the π-donor was predicted by theoretical studies: Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. *Inorg. Chem.* **1994**, *33*, 1476 and references therein.

(12) Review on X-ray structures of organolithium compounds: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(13) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174.

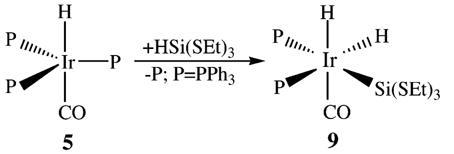
(14) Harrod, J. F.; Gilson, D. F. R.; Charles, R. *Can. J. Chem.* **1969**, *47*, 2205.

(15) Aizenberg, M.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 317.

(16) C−Si reductive elimination products were formed in less than equivalent amounts according to integration of signals in ^1H NMR. Parallel reactions leading to the same Ir products probably take place. These reactions are under investigation.

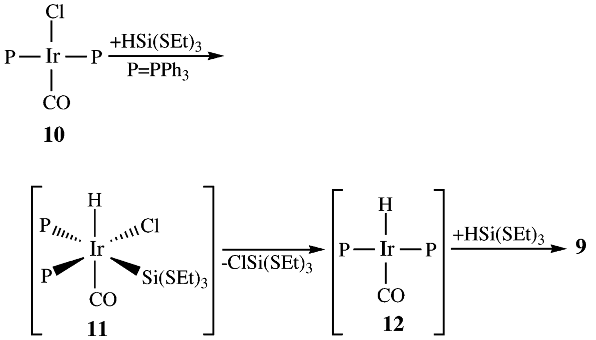
the possibility of synthesizing stable (triphenylphosphine)iridium−silanol species by a reaction of the silyl ligand.

As we have reported,[17] treatment of **5** with the tris(ethylthio)silane $(EtS)_3SiH$ resulted in the adduct **9** in quantitative yield (eq 5).



(5)

Complex **9** is stable in solution and in the solid state at room temperature. Interestingly, this compound may also be synthesized from Vaska's complex (**10**) and 2 equiv of the thiosilane. The route of the latter reaction (eq 6) involves most probably initial formation of the



(6)

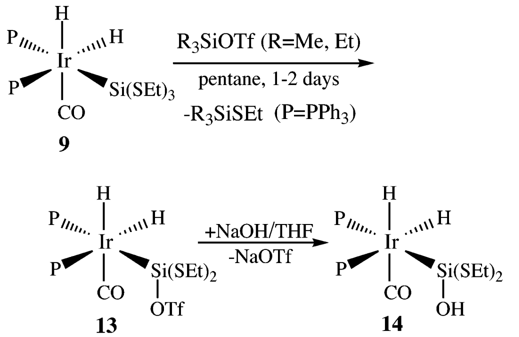
intermediate adduct **11**, which eliminates the $(EtS)_3SiCl$, giving rise to the unsaturated hydride complex **12** which, in turn, adds 1 equiv more of $HSi(SEt)_3$ to form the stable dihydride **9.** Apparently, the presence of the weak σ-donor chloride ligand in **11**, along with the high Si−Cl bond strength, makes Si−Cl reductive elimination favorable.[18] Formation of a new compound, which is believed to be $(EtS)_3SiCl$, was indicated by ^1H NMR; however, attempts to isolate this product failed.

Attempting to prepare a metallo-silanol from complex **9**, we first tried to substitute one SEt group for OH with NaOH in a water/THF solution, but no hydrolysis occurred.[17] Applying another approach, complex **9** was treated with a stoichiometric amount of Et_3SiOTf in pentane at room temperature, leading to selective substitution of one SEt group by the triflate anion (eq 7). An analogous reaction was demonstrated by Tilley with ruthenium and platinum thiosilyl complexes.[19] The reaction was slow but resulted in high yield and the product complex **13** precipitated from a pentane solution. An analogous, faster reaction took place with Me_3SiOTf, but the reaction was less selective, forming about 15% of byproducts.

Interestingly, while all the SEt groups in **9** are equivalent, the two SEt groups in complex **13** exhibit two different signals in ^1H NMR. Treatment of complex **13** with 1 equiv of NaOH in a THF/water solution resulted in the immediate formation of the new metallosilanol complex **14** (eq 7).

Table 1. ^{31}P NMR Chemical Shifts (δ) of PPh_3 Trans to Silyl Ligand

X in P−Ir−X				
$Si(^tBu)_2OH$	$Si(^iPr)_2OH$	$Si(SEt)_3$	$Si(SEt)_2OH$	$Si(SEt)_2OTf$
−0.53	1.60	1.88	1.98	2.72



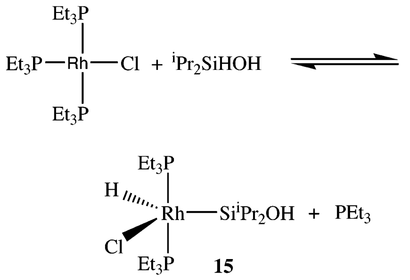
(7)

Complex **14** also has two nonequivalent SEt groups, according to ^1H NMR data. It is a stable colorless compound, which is completely inert toward an excess of water or NaOH, similarly to its precursor **9**.

It is worth noting that the ^{31}P NMR spectra of the new complexes indicate a downfield shift of the signals of the phosphine trans to the silyl group in the order depicted in Table 1. This dependence corresponds to the expected increase of electrophilicity of the silicon atom.

In order to compare Ir and Rh chemistry, $(Et_3P)_3RhCl$ was treated with HSi^iPr_2OH, producing the first Rh−silanol complex, $[(Et_3P)_2Rh(H)(Cl)(Si^iPr_2OH)]$ (**15**). The reaction is reversible, and addition of either silanol or triethylphosphine shifted the equilibrium to the products or to the starting compounds, respectively; $K_{eq} = 4 \times 10^{-3}$ (273 K). It is noteworthy that an excess of Et_3P caused breaking of the relatively strong Rh−H and Rh−Si bonds in favor of reductive elimination of the weak H−Si bond, undoubtedly driven by formation of a strong Rh(I)−PEt_3 bond.

The similar bis-phosphine complex $[(Et_3P)_2RhCl]_2$ reacted with a stoichiometric amount of the silanol, resulting in 96% conversion to the adduct **15**. Finally, no reaction was observed between the chelated bisphosphine complex $[(dippp)RhCl]_2$ (dippp = bis(diisopropylphosphino)propane) and the silanol, when either a stoichiometric amount or a 10-fold excess of the silanol was used. Considering the similarity of both bis-phosphine complexes from the electronic and steric points of view, it is likely that the thermodynamically stable configuration of the adduct is the trans-phosphine one (see eq 8), which is unavailable with dippp. This



(8)

---

[17] Aizenberg, M. Goikhman, R. Milstein, D. *Organometallics* **1996**, *15*, 1075.

[18] Formation of $ClSiR_3$ as a product of reaction of late-transition-metal chlorides with $HSiR_3$ is known. See for example: Haszeldine, R. N.; Malkin, L. S.; Parish, R. V. *J. Organomet. Chem.* **1979**, *182*, 323.

[19] Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 5607 and references therein.

structure was confirmed by ^{13}C NMR measurement of complex **15**. The P−CH_2 signal appears as a virtual triplet, in analogy to the P−CH_2 signal in the ^{13}C NMR spectrum of complex **2**. In addition, ^{29}Si NMR of **15** confirmed the cis orientation of the silyl ligand with regard to the two phosphines.[20]

In conclusion, a series of iridium−silanol complexes bearing different ligands were synthesized, using different approaches, and were fully characterized. The *PEt$_3$*-containing Ir(I) complexes reacted with secondary silanols to give stable Ir(III)−silanol complexes. The analogous reaction of silanols with PEt$_3$-containing Rh(I) complexes is reversible, whereas chelating bisphosphine Rh(I) complexes were unreactive. The Ir(III)−silanols can be converted to stable metallosilanolates by deprotonation with Li alkyls. The crystallographically characterized iridiasilanolate exhibits an interesting, very stable Li-bridged dimeric structure. Remarkably, this compound can be formed even by extraction of Li$^+$ from its crown ether complex. The less electron rich, similar *PPh$_3$*-containing iridium carbonyl adducts with bulky dialkylsilanols are unstable and exist only in the presence of an excess of the silanol substrate, similarly to the Rh silanols. A stable PPh$_3$ carbonyl iridium−silanol complex was synthesized by stepwise substitution of the SEt group in the Si(SEt)$_3$ ligand by a triflate group and then by hydroxide. In general, this stepwise substitution of suitable substituents at a silyl ligand seems to be a useful method for the preparation of metallo-silanol complexes, especially when the desired secondary silanols are not available, or in cases where they do not form stable adducts with metal complexes.

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. 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) or external 85% H_3PO_4 in D_2O at δ 0.0 (^{31}P NMR, 162 MHz). Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; v, virtual. IR spectra were measured with a Nicolet-510 FT-IR spectrometer. IR samples were prepared in the glovebox using cell holders featuring O-rings. They were measured as Nujol mulls on NaCl plates. Elemental analyses were performed at Kolbe Laboratorium, Mulheim, Germany. The following compounds were prepared according to reported procedures: ^{i}Pr$_2$SiHOH,[9] ^{t}Bu$_2$SiHOH,[10] HSi(SEt)$_3$,[21] **1**,[8] **5**,[22a] **7**,[22b] **9**,[17] **10**,[22c] (Et$_3$P)$_3$RhCl,[23a] [(Et$_3$P)$_2$RhCl]$_2$,[23b] [(dippp)RhCl]$_2$.[23c]

***trans*-[(Et$_3$P)$_2$(H)Ir(Cl)(Si^{i}Pr$_2$OH)] (2).** A solution of 40 mg (0.08 mmol) of (Et$_3$P)$_2$Ir(C$_2$H$_4$)(Cl) (**1**) in 0.5 mL of C_6D_6 was treated with 12.5 μL (0.08 mmol) of ^{i}Pr$_2$Si(H)OH at room temperature. A rapid change of color of the solution from orange to yellow was observed. Yellow crystals of **2** were obtained in quantitative yield after removal of the solvent in vacuo.

NMR (C_6D_6): ^{31}P{^{1}H}, 19.14 s; ^{1}H, 1.85 m (CH$_2$−P, 12H), 1.23 d, overlapped with 1.21 d (like quasi-t, $^3J_{H-H}$ = 7.2 Hz, CH_3CHSi, 12H total), 1.09 m (CHSi, 2H), 1.01 vtt (quasi-quin, $|J_{observed}|$ = 7.5 Hz, CH_3CH$_2$P, 18H), −20.82 t ($^2J_{H-Pcis}$ = 13.6 Hz; HIr, 1H) (the OH signal is obscured by other peaks); ^{2}D-{^{1}H} (after exchange with D$_2$O in benzene), 1.00 br s (IrSiOD), −20.8 br s (IrD, traces); ^{13}C{^{1}H}, 20.49 s (CHSi), 20.25 s (CH$_3$CHSi), 19.53 s (CH$_3$CHSi), 18.32 vt ($|^1J_{CP} + {}^3J_{CIrCP}|$ = 15.7 Hz, CH$_2$P), 8.77 s (CH$_3$CH$_2$P); ^{29}Si{^{1}H}, 19.57 t ($^2J_{Si-Pcis}$ = 26 Hz). IR data (Nujol): 3485 cm^{-1} (br, O−H). Anal. Calcd for C$_{18}$H$_{46}$ClIrOP$_2$Si: C, 36.26; H, 7.78. Found: C, 36.53; H, 8.15.

***trans*-(Et$_3$P)$_2$(H)Ir(Cl)(Si^{t}Bu$_2$OH) (3).** A solution of 40 mg (0.08 mmol) of **1** in 3 mL of pentane was treated with 13 mg (0.08 mmol) of ^{t}Bu$_2$Si(H)OH at room temperature. The reaction mixture was stirred overnight, and then the solvent was evaporated. The residue was washed with 2 × 0.5 mL of cold pentane. The metallo-silanol **3** was obtained in 62% yield (31 mg) as small orange crystals. NMR (C_6D_6): ^{31}P{^{1}H}, 19.7 and 10.6 (AB quartet, $^2J_{P-Ptrans}$ = 335 Hz); ^{1}H, 1.9 m (CH$_2$P, 12H), 1.36 br.s. (CH_3CSi, 9H), 1.18 m (OH, 1H) 1.08 br s (CH_3CSi, 9H), 1.0 m (CH_3CH$_2$P, 18H), −21.02 t ($|^2J_{H-Pcis}|$ = 14 Hz; H−Ir, 1H); ^{13}C{^{1}H}, 31.22 s (CH$_3$CSi), 30.49 s (CH$_3$CSi), 26.16 s (CSi), 25.61 s (CSi), 18.56 vt ($|^1J_{CP} + {}^3J_{CIrCP}|$ = 29 Hz, CH$_2$P), 8.88 s (CH$_3$CH$_2$P), 8.34 s (CH$_3$CH$_2$P).

[(Et$_3$P)$_2$(H)Ir(Cl)(Si^{i}Pr$_2$OLi)]$_2$ (4). A solution of 30 mg (0.05 mmol) of **2** in 1 mL of pentane was treated with 34 μL of a 15% pentane solution of ^{t}BuLi or ^{n}BuLi (0.05 mmol) at 0 °C. The resulting solution was carefully concentrated under vacuum to ~30% of the initial volume and cooled to −30 °C. Small yellow crystals of **4** precipitated over 1 day. They were separated from the solution in 90% yield. NMR (C_6D_6): ^{31}P{^{1}H}, 16.95 s; ^{1}H, 1.83 m (CH$_2$P, 12H), 1.60 d ($^3J_{H-H}$ = 7.5 Hz, CH_3CHSi, 6H), 1.35 d ($^3J_{H-H}$ = 7.5 Hz, CH_3CHSi, 6H), 1.06 vtt (quasi-quin, $|J_{observed}|$ = 7.5 Hz, CH_3CH$_2$P, 18H), 1.0 m (CHSi, 2H), −20.92 t ($^2J_{H-Pcis}$ = 15.7 Hz; HIr, 1H); ^{13}C{^{1}H}, 24.42 s (CH$_3$CHSi), 20.88 s (CH$_3$CHSi), 20.05 br s (CHSi), 18.02 vt ($|^1J_{CP} + {}^3J_{CIrCP}|$ = 15.0 Hz, CH$_2$P), 8.97 d ($^2J_{C-P}$ = 3.7 Hz, CH$_3$CH$_2$P); ^{29}Si{^{1}H}, 3.74 t ($^2J_{Si-Pcis}$ = 15 Hz); ^{7}Li{^{1}H}, 1.76 s. Anal. Calcd for C$_{18}$H$_{45}$ClLiIrOP$_2$Si: C, 35.90; H, 7.53. Found: C, 36.07; H, 7.91.

[(Ph$_3$P)$_2$(H)$_2$Ir(CO)(Si^{i}Pr$_2$OH)] (6). A solution of 30 mg (0.03 mmol) of **5** in 0.5 mL of C_6D_6 was treated with 46 μL (0.3 mmol) of ^{i}Pr$_2$Si(H)OH at room temperature. Under these conditions 97% conversion of **5** to **6** was observed (by NMR). The adduct **6** was characterized only in solution. Attempts to isolate this complex either by precipitation or by removal of solvents resulted in decomposition to starting compounds. NMR (C_6D_6): ^{31}P{^{1}H}, 8.5 d ($^2J_{P-P}$ = 13 Hz, PIrH, 1P), 1.6 d ($^2J_{P-P}$ = 13 Hz, PIrSi, 1P); ^{1}H, 7.50 m (PhP, 6H), 7.38 m (PhP, 6H), 7.03 m (PhP, 9H), 6.90 m (PhP, 9H), 1.65 m (CHSi, 1H), 1.51 d ($^3J_{H-H}$ = 7.3 Hz, CH_3CHSi, 3H), 1.45 d ($^3J_{H-H}$ = 7.1 Hz, CH_3CHSi, 3H), 1.38 m (CHSi, 1H), 1.28 d ($^3J_{H-H}$ = 7.0 Hz, CH_3CHSi, 3H), 1.15 d ($^3J_{H-H}$ = 7.0 Hz, CH_3CHSi, 3H), −9.33 ddd ($^2J_{H-Pcis}$ = 23 Hz; $^2J_{H-Pcis}$ = 15.7 Hz; $^2J_{H-H}$ = 4.2 Hz, HIrCO, 1H), −10.88 ddd ($^2J_{H-Ptrans}$ = 108.8 Hz; $^2J_{H-Pcis}$ = 18.7 Hz; $^2J_{H-H}$ = 4.2 Hz, HIrP, 1H) (the OH signal is obscured by other peaks).

[(Ph$_3$P)$_2$(H)$_2$Ir(CO)(Si^{t}Bu$_2$OH)] (8). A solution of 15 mg (0.02 mmol) of **7** in 0.5 mL of C_6D_6 was stirred for 10 days with 13 mg (0.08 mmol) of ^{t}Bu$_2$Si(H)OH at room temperature, resulting in a mixture of **8** and **5** in a ratio of 4:1. The metallo-silanol **8** was characterized only in solution for the same reasons mentioned for complex **6**. NMR data for **8** (C_6D_6): ^{31}P{^{1}H}, 5.64 d ($^2J_{P-P}$ = 9 Hz, PIrH, 1P), −0.34 d ($^2J_{P-P}$ = 9 Hz,

---

(20) The ^{29}Si NMR data of **15** are quite typical. For a recent ^{29}Si NMR report on Rh(III) silyl complexes see: Nishihara, Y.; Takemura, M.; Osakada, K. *Organometallics* **2002**, *21*, 825.

(21) (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.

(22) (a) Wilkinson, G. *Inorg. Synth.* **1972**, *13*, 126. (b) Rees, W. M.; Churchill, M. R.; Li, Y.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162. (c) Sears, J. C. T.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101.

(23) (a) Intille, G. M. *Inorg. Chem.* **1972**, *11*, 695. (b) Blekke, J. R.; Donaldson, A. J. *Organometallics* **1986**, *5*, 2401, (c) Fryzuk, M. D.; Piers, W. E.; Rettig, S. E.; Einstein, F. W. B.; Jones, T.; Albright, T. A. *J. Am. Chem. Soc.* **1989**, *111*, 5709.

PIrSi, 1P); ^{1}H, 7.51 m (PhP, 6H), 7.42 m (PhP, 6H), 6.91 m (PhP, 18H), 1.42 br s (CH_3CSi, 9H), 1.26 s (CH_3CSi, 9H), −9.38 ddd ($^2J_{H-Pcis} = 22.8$ Hz; $^2J_{H-Pcis} = 16.8$ Hz; $^2J_{H-H} = 4.7$ Hz, HIrCO, 1H), −10.95 ddd ($^2J_{H-Ptrans} = 106.8$ Hz; $^2J_{H-Pcis} = 18.0$ Hz; $^2J_{H-H} = 4.7$ Hz, HIrP, 1H) (the OH signal is obscured by other peaks).

[(Ph$_3$P)$_2$(H)$_2$Ir(CO)(Si(SEt)$_2$OTf)] (13). Complex **9** (20 mg, 0.02 mmol) was stirred with Et_3SiOTf (4.5 μL, 0.02 mmol) in a pentane solution for 2 days at room temperature to produce a colorless precipitate. Then the solvent was decanted and the residue was washed with pentane and dried, resulting in 16 mg (76%) of the pure complex **13** as a moisture-sensitive solid. **13** has limited stability at room temperature. NMR (C_6D_6): ^{31}P{^{1}H}, 4.45 d ($^2J_{P-P} = 15.7$ Hz, PIrH, 1P), 2.72 d ($^2J_{P-P} = 15.7$ Hz, PIrSi, 1P); ^{1}H, 7.47 m (PhP, 6H), 7.17 m (PhP, 6H), 6.97 m (PhP, 9H), 6.86 m (PhP, 9H), 2.98 m (CH_2S, 4H), 1.26 t ($^3J_{H-H} = 7.4$ Hz, CH_3CH_2S, 3H), 1.19 t ($^3J_{H-H} = 7.4$ Hz, CH_3CH_2S, 3H), −9.46 ddd ($^2J_{H-Pcis} = 18.8$ Hz; $^2J_{H-Pcis} = 13.6$ Hz; $^2J_{H-H} = 4.4$ Hz, HIrCO, 1H), −10.51 ddd ($^2J_{H-Ptrans} = 106$ Hz; $^2J_{H-Pcis} = 18.5$ Hz; $^2J_{H-H} = 4.4$ Hz, HIrP, 1H). Anal. Calcd for $C_{42}H_{42}F_3IrO_4P_2S_3Si$: C, 48.22; H, 4.05. Found: C, 49.03; H, 4.52.

[(Ph$_3$P)$_2$(H)$_2$Ir(CO)(Si(SEt)$_2$OH)] (14). Complex **13** (15 mg, 0.015 mmol) was dissolved in 0.5 mL of THF and treated with 60 μL of a 0.25 M aqueous solution of NaOH (0.015 mmol). The solvents were then removed in vacuo, the residue was extracted with benzene, and the extracts were filtered. The solvent was removed from the filtrate under vacuum, yielding 12 mg of the colorless compound **14** in 92% purity (by NMR). The pure compound was obtained by slow crystallization from pentane. NMR (C_6D_6): ^{31}P{^{1}H}, 6.89 d ($^2J_{P-P} = 15.1$ Hz, PIrH, 1P), 1.98 d ($^2J_{P-P} = 15.1$ Hz, PIrSi, 1P); ^{1}H, 7.56 m (PhP, 6H), 7.47 m (PhP, 3H), 7.31 m (PhP, 6H), 6.83−6.97 ov m (PhP, 15H), 2.97 m (CH_2S, 4H), 1.45 t ($^3J_{H-H} = 7.4$ Hz, CH_3CH_2S, 3H), 1.42 t ($^3J_{H-H} = 7.4$ Hz, CH_3CH_2S, 3H), −9.11 ddd ($^2J_{H-Pcis} = 22$ Hz, $^2J_{H-Pcis} = 14.8$ Hz, $^2J_{H-H} = 4.2$ Hz, HIrCO, 1H), −10.05 ddd ($^2J_{H-Ptrans} = 108$ Hz, $^2J_{H-Pcis} = 20.4$ Hz, $^2J_{H-H} = 4.2$ Hz, HIrP, 1H) (the OH signal is obscured by other peaks). IR (Nujol): 3260 cm^{-1}. Anal. Calcd for $C_{41}H_{43}IrO_2P_2S_2Si$: C, 53.87; H, 4.74. Found: C, 53.44; H, 4.60.

Reaction of Vaska's Complex (10) with HSi(SEt)$_3$. A solution of 15 mg (0.02 mmol) of **10** in 0.5 mL of C_6D_6 was treated with 8 μL (0.05 mmol) of $HSi(SEt)_3$. ^{31}P{^{1}H} NMR of the resulting solution showed formation of complex **9** as a single product. ^{1}H NMR (C_6D_6) exhibited signals of a new product, which is likely to be $ClSi(SEt)_3$: 2.61 q ($^3J_{H-H} = 7.4$ Hz, CH_2S, 6H), 1.10 t ($^3J_{H-H} = 7.4$ Hz, CH_3CH_2S, 3H).

[(Et$_3$P)$_2$(H)Rh(Cl)(Si^{i}Pr$_2$OH)] (15). A solution of 30 mg (0.04 mmol) of $[(Et_3P)_2RhCl]_2$ in 0.5 mL of C_6D_6 was treated with 12.5 μL (0.08 mmol) of $^iPr_2Si(H)OH$ at room temperature, resulting in 96% conversion in $^1/_2$ h. Complex **15** was characterized in solution. It slowly decomposes at room temperature. In an analogous reaction of $(Et_3P)_3RhCl$ with 1 equiv of $^iPr_2Si(H)OH$, just 3% conversion to **15** was observed. NMR (C_6D_6): ^{31}P{^{1}H}, 25.8 d ($^1J_{Rh-P} = 118.8$ Hz); ^{1}H, 1.82 m (CH_2P, 12H), 1.34 quasi-t ($^3J_{H-H} = 7.3$ Hz, CH_3CHSi, 12H), 1.2 m (CH_3CHSi, 2H), 1.09 br. t ($J = 7.5$ Hz, CH_3CH_2P, 18H), −16.49 dt ($^1J_{Rh-H} = 27.2$ Hz, $^2J_{H-P} = 14.6$ Hz, H−Rh, 1H) (the OH signal is obscured by other peaks); ^{13}C{^{1}H}, 21.83 s (CHSi), 20.12 s (CH_3CHSi), 19.54 s (CH_3CHSi), 17.93 vt ($|^1J_{CP} + ^3J_{CIrCP}| = 13.0$ Hz, CH_2P), 8.90 s (CH_3CH_2P); ^{29}Si{^{1}H}, 58.15 dt ($^1J_{Rh-Si} = 31.4$ Hz, $^2J_{P-Si} = 8.3$ Hz).

Acknowledgment. This work was supported by the Israel Science Foundation, Jerusalem, Israel, by the Minerva Foundation, Munich, Germany, and by the Helen and Martin Kimmel Center for Molecular Design. D.M. is the holder of the Israel Matz Professorial Chair of Organic Chemistry.

OM0300427