Metal-Dependent Stabilization of Si−S Bonds to Hydrolysis in Iridium and Rhodium Silyls. Hydrolyzability as a Probe for Si−H Reductive Elimination

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*Summary: The iridium (triethylthio)silyl complexes cis-$(PPh_3)_2(CO)IrH_2(Si(SEt)_3)$ (**5**), fac-$(PMe_3)_3Ir(CH_3)(H)(Si(SEt)_3)$ (**6**), and mer-$(PMe_3)_3Ir(C_6F_5)(H)(Si(SEt)_3)$ (**7**) were synthesized by oxidative addition of $HSi(SEt)_3$ (**1**) to $HIr(CO)(PPh_3)_3$ (**2**), $CH_3Ir(PMe_3)_4$ (**3**), and $C_6F_5Ir(PMe_3)_3$ (**4**), respectively. **4** was synthesized by the reaction between $Ir(PMe_3)_4Cl$ and C_6F_5MgBr. The rhodium analog of **7**, mer-$(PMe_3)_3Rh(C_6F_5)(H)(Si(SEt)_3)$ (**9**), was obtained similarly from $C_6F_5Rh(PMe_3)_3$, (**8**) and **1**. Unlike the extremely easily hydrolyzable parent silane **1**, compounds **5**-**7** are stable in H_2O/THF and even in NaOH/H_2O/THF solutions. This stabilization is attributed to the electron-donating capacity of the Ir centers, which efficiently reduces electrophilicity of the silicon. Reactivity of the rhodium complex **9** is strikingly different, cleanly producing in the presence of 5 equiv of H_2O the ethylthio-complex mer-$(PMe_3)_3Rh(C_6F_5)(H)(SEt)$ (**10**). Compound **10** was identified spectroscopically and was synthesized independently from **8** and HSEt. A plausible scheme accounting for the generation of **10** under the hydrolysis conditions is presented. The observed difference in the reactivities of **5**−**7** and **9** is explained in terms of their different tendencies to reductively eliminate H−Si(SEt)$_3$.*

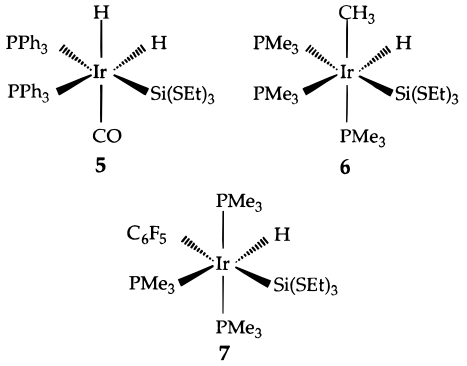
Introduction

Complexes that contain a metallo-silanol fragment, M−Si−OH, have been an object of considerable recent interest.[1−3] They were reported to be accessible from hydrolysis of Fe, Os, and Pt silyl complexes,[1] from oxyfunctionalization of M−Si−H compounds (M = Fe, W) by use of dimethyldioxirane,[1c,2] and from direct Si−H oxidative addition of secondary silanols to a low-valent electron-rich iridium(I) center.[3]

In the course of our studies of the approaches to synthesis of metallo-silanols and their derivatives, we tested several Ir^{III}−Si−X systems with regard to their succeptibility to selective hydrolysis of Si−X bonds. Preliminary experiments indicated that, in contrast to reported Os(II)[1b] and Fe(II)[2] chlorosilyls, triethoxysilyl complexes of Ir(III), such as *mer*-$(PEt_3)_3Ir(Cl)(H)(Si(OEt)_3)$ (**12**) and *trans*-$(PEt_3)_2Ir(H)(Cl)(Si(OEt)_3)$ (**13**), cannot be hydrolyzed selectively. Under mild conditions they are hydrolytically stable, while forcing conditions lead to cleavage of the metal-silicon bonds. This led us to examine the reactivity of derivatives of much more easily hydrolyzable silane, namely $HSi(SEt)_3$. In the present paper we report that coordination to Ir(III) centers causes remarkable stabilization of an (alkylthio)silyl group to hydrolysis. Moreover, this group becomes stable even to alkaline conditions. In striking difference, an exactly analogous Rh(III) complex undergoes facile hydrolysis. We show that this is a result of the reactivity of free $HSi(SEt)_3$. This hydrolyzability of thiosilyl ligands provides a simple tool to detect whether or not Si−H reductive elimination is operative, even when its formation equilibrium lies far to the left.

Results and Discussion

Addition of the silane $HSi(SEt)_3$[4] (**1**) to benzene solutions of $HIr(CO)(PPh_3)_3$[5a] (**2**), $CH_3Ir(PMe_3)_4$[6a] (**3**), and $C_6F_5Ir(PMe_3)_3$ (**4**) at room temperature yields the oxidative addition products **5**−**7**, respectively. The composition and stereochemistry of the complexes unequivocally follow from their NMR data and from their comparison with those of known fully characterized analogs.[5b,6b,7]



Complex **5** exhibits in the $^{31}P\{^1H\}$ NMR spectrum two mutually coupled doublets of equal intensity, indicating

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(1) (a) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219. (b) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9682. (c) 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.

(2) Adam, W.; Azzena, U.; Prechtl, F.; Hindahl. K.; Malisch, W. *Chem. Ber.* **1992**, *125*, 1409.

(3) Goikhman, R.; Aizenberg, M.; Kraatz, H.-B.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 5865.

(4) (a) Wolinski, L.; Tieckelmann, H.; Post, H. W. *J. Org. Chem.* **1951**, *16*, 395. (b) Lambert, J. B.; Shulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201.

(5) (a) Wilkinson, G. *Inorg. Synth.* **1972**, *13*, 126. (b) Reactions of **2** with other silanes were studied previously, and the fully characterized products exhibited ^1H NMR data completely analogous to those reported herein for **5**; see: Harrod, J. F.; Gilson, D. F. R.; Charles, R. *Can. J. Chem.* **1969**, *47*, 2205.

(6) (a) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (b) Ph_3Si, $(EtO)_3Si$, and Et_3Si analogs of **6** are fully characterized and exhibit completely analogous spectral data; see: Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1990**, *29*, 2017. Aizenberg, M.; Milstein, D. *Angew. Chem.* **1994**, *106*, 344; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 317. Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456.

(7) An analog of complexes **7** and **9**, namely *mer*-$(PMe_3)_3Rh(C_6F_5)(H)(Si(OEt)_3)$ (**11**), which was prepared similarly and was fully characterized, exhibited spectral data analogous to those reported herein for **7** and **9**; see: Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359.

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a cis-phosphine configuration. The signal at δ 1.9 ppm has characteristic ^{29}Si satellites with $^2J_{P-Si,trans} = 157$ Hz.[8] ^{1}H NMR clearly indicates the presence of two different hydrides whose signals are coupled to each other and are also split by two different phosphorus nuclei. The hydride signal at δ −10.21 ppm has a typical, large $^2J_{H-P,trans}$ value of 104.3 Hz. The carbonyl carbon gives rise to a doublet of doublets in the ^{13}C-{^{1}H} NMR spectrum at δ 179.8 ppm with two different $^2J_{C-P,cis}$ couplings of 7.4 and 4.2 Hz.

The facial configuration of complex **6** clearly follows from the presence of three mutually coupled signals in its ^{31}P{^{1}H} NMR spectrum. Its ^{1}H NMR spectrum contains appropriately split signals due to the iridium-bound methyl group at δ 0.51 ppm and due to the hydride at δ −12.35 ppm; the protons of the PMe_3 ligands give rise to three doublets.

Complex **7** exhibits in the ^{31}P{^{1}H} NMR spectrum two signals integrated as 2:1, the signal of the unique phosphine appearing as a doublet of doublets of triplets due to additional $^4J_{P-F}$ couplings. The ^{1}H NMR spectrum of **7** contains a signal of a hydride at δ −12.0 ppm which is also additionally split by one of the aromatic fluorines. The protons of the mutually trans PMe_3 ligands give rise to a virtual triplet, indicative of the meridional configuration. The presence of the C_6F_5 group is expressed in the ^{19}F{^{1}H} NMR spectrum as five multiplets of equal intensity. Two of them, which are due to ortho fluorines, are significantly shifted to lower field and appear at δ −95.5 and −102.4 ppm.[9]

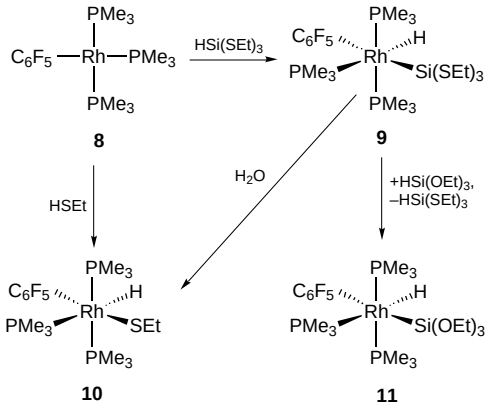
The ^{1}H NMR spectra of complexes **5**−**7** contain signals of appropriate intensity and multiplicity due to $Si(SCH_2CH_3)_3$ groups bound to the iridium centers.

Attempted hydrolysis of **5**−**7** did not result in the formation of silanol complexes. No reaction was observed with a 280-fold excess of H_2O in THF after 1 day. Moreover, even 3 equiv of NaOH in THF/H_2O solution did not affect the complexes after 10 h.[10] Similarly, the triethoxysilyl Ir(III) complexes **12** and **13**, obtained by oxidative addition of $HSi(OEt)_3$ to $Ir(PEt_3)_3Cl$ and $Ir(PEt_3)_2(C_2H_4)Cl$, respectively, are also stable at room temperature in the presence of an excess of H_2O in dioxane and can be recovered easily.

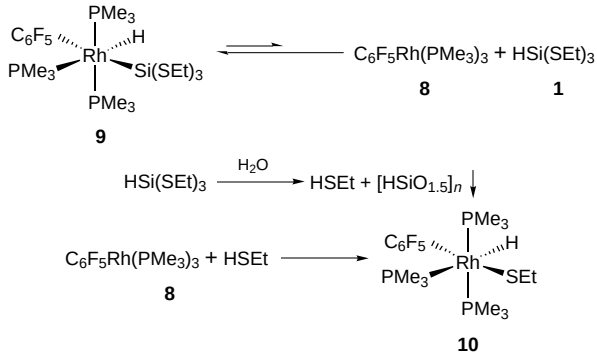
To test whether the nature of the metal center alone can influence the capability of the $MSi(SEt)_3$ fragment to hydrolyze, we prepared the exact analog of **7**, namely *mer*-$(C_6F_5)(H)(Si(SEt)_3)Rh(PMe_3)_3$ (**9**),[11] and examined its reactivity. This complex is readily accessible[7] from the reaction of $(C_6F_5)Rh(PMe_3)_3$ (**8**) with **1** (Scheme 1). The main features of the NMR spectra of complex **9** are the same as those of **7**.

Quite unexpectedly, **9** was completely consumed already after 3 h at room temperature in the presence of 5 equiv of H_2O in C_6D_6. At the same time,formation of a white precipitate (probably silica) was observed. However, the only organometallic product formed in the reaction was the ethylthio complex **10**, rather than the expected metallo-silanol.

Scheme 1. Formation of the Rhodium Complexes 9−11



Scheme 2. Reactivity of 9 in the Presence of H_2O



The ^{31}P{^{1}H} NMR spectrum of **10** exhibits two signals in a 1:2 ratio. The small value $^1J_{P-Rh} = 98.2$ Hz, observed for the mutually trans phosphines, is indicative of a Rh(III) complex. The signal due to the unique PMe_3 appears as a multiplet, undoubtedly because of additional couplings to the fluorines of the C_6F_5 group. The ^{1}H NMR spectrum contains a high-field hydride signal with a large H-trans-to-P coupling constant and (as in the cases of **7** and **9**) virtual triplet and doublet patterns for the protons of the PMe_3 ligands. Importantly, the signals of the SCH_2CH_3 group, which appear as a regular quartet and triplet ($^3J_{H-H} = 7.6$ Hz), are integrated as two and three protons, leaving no doubt about the presence of only one such group in the complex. The ^{19}F{^{1}H} NMR spectrum consists, again, of five different signals, two of which are significantly deshielded.[12] The identity of **10** was also confirmed by its independent synthesis from **8** and EtSH[13] (Scheme 1).

There are two important observations that require further explanation. The first is the striking difference in the reactivities of $HSi(SEt)_3$ and $Ir^{III}-Si(SEt)_3$ toward O-nucleophiles. The second is the major influence of

(8) Ozawa, F.; Hikida, T.; Hayashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2844.

(9) (a) Bruce, M. I. *J. Chem. Soc. A* **1968**, 1459. (b) Bennett, R. L.; Bruce, M. I.; Gardner, R. C. F. *J. Chem. Soc. Dalton Trans.* **1973**, 2653.

(10) We also checked reactivity of complex **7** toward water under acidic conditions. **7** slowly decomposes in a THF solution in the presence of 3 equiv of CF_3COOH and 100 equiv of H_2O at room temperature to a mixture of uncharacterized products, a major compound still remaining (42%, as judged by ^{31}P{^{1}H} NMR) after 2 days.

(11) Attempts to prepare rhodium analogs of **5** and **6** were unsuccessful.

(12) Restricted rotation of a pentafluorophenyl group, which gives rise to five instead of the usual three signals in ^{19}F NMR, is known. See, for example: (a) Bennett, R. L.; Bruce, M. I.; Goodfellow. R. J. *J. Fluorine Chem.* **1972/73**, *2*, 447. (b) Reference 9b.

(13) For RS−H oxidative additions see, for example: (a) Singer, H.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2516. (b) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 797. (c) Stiddard, M. H. B.; Townsend, R. E. *J. Chem. Soc. A* **1970**, 2719. (d) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 3386. (e) Collman, J. P.; Rothrock, R. K.; Stark, R. A. *Inorg. Chem.* **1977**, *16*, 437.

the nature of the metal center on the hydrolytic behavior of the completely analogous complexes **7** and **9**.

Mechanistically, the hydrolysis of the Si−SEt bond proceeds by nucleophilic attack of OH^- or H_2O at the Si center. The resulting species which would then contain Si−OH bonds are expected to be thermodynamically more stable than the precursor thiosilyl species. The fact that all the $Ir^{III}-Si(SEt)_3$ complexes studied are stable for hours in $NaOH/H_2O/THF$ medium, while free $HSi(SEt)_3$ hydrolyzes instantaneously even in the presence of traces of water, can be explained by the electronic influence of the Ir center. Its strong electron-donating capacity efficiently reduces the electrophilicity of the $Si(SEt)_3$ fragment and hence its susceptibility to nucleophilic attack. Steric factors may also play a role. It is noteworthy that a related phenomenon was observed for platinum(IV)−tin complexes, such as $PtMe_2Cl(bpy)(SnR_nCl_{3-n})$ (R = Ph, Me; n = 1, 2). No reaction between these complexes and water or other Lewis bases took place, and the starting compounds could be recovered at low temperatures.[14]

Regarding the hydrolytic reactivity of the rhodium complex **9**, we propose that complex **10** is a result of EtS−H oxidative addition to **8**. Complex **8** and EtSH are, in turn, available as products of reductive elimination of H−Si(SEt)$_3$ from **9** and of the hydrolysis of free **1**, respectively (Scheme 2). This hypothesis was verified not only by preparation of **10** from **8** and EtSH (see above) but also by silane exchange experiments. When $HSi(OEt)_3$ (10 equiv) was added to a C_6D_6 solution of complex **9** at room temperature, 80% conversion to the known *mer*-$(C_6F_5)(H)(Si(OEt)_3)Rh(PMe_3)_3$ (**11**)[7] and free $HSi(SEt)_3$ was observed by NMR after two days, thus establishing the equilibrium **9** ⇌ **8** + **1** (Scheme 2). It is noteworthy that this equilibrium lies far to the left, the equilibrium concentration of the undetected free **1** being very low. It is sufficient, however, for $HSi(SEt)_3$ to be efficiently removed by the irreversible hydrolysis. Importantly, under the same conditions neither **5** nor **7** undergoes such $Si(SEt)_3/Si(OEt)_3$ exchange, remaining unchanged at room temperature after 2 days as detected by NMR.

We believe that the observed difference in reactivity between the Rh complex **9** and the Ir complexes **5**−**7** originates from their different tendencies to reductively eliminate the Si−H bond,[15] rather than to hydrolyze. Although we are unaware of a direct comparison of Si−H reductive elimination from isostructural Ir(III) and Rh(III) complexes, trimethylphosphine Rh(III) complexes have a much higher propensity to undergo C−H reductive elimination than the analogous Ir(III) complexes,[16] as expected for a comparison between second- and third-row metals. However, it is worth noting that although the electron density at the Rh center in the PMe_3 complex **9** is definitely lower than that at the Ir centers in the PMe_3 complexes **6** and **7**, it may be comparable to that of the Ph_3P complex **5**. Still, **9** reductively eliminates **1**, while **5** does not,[17] as evidenced by its stability in the presence of H_2O.

Conclusions

The results presented here clearly demonstrate that (i) ligation to a late transition metal significantly reduces the succeptibility of an (alkylthio)silyl group to nucleophilic attack, making it hydrolytically stable, (ii) even completely analogous complexes of the second- and third-row transition metals, e.g. Rh and Ir, can exhibit strikingly different hydrolytic reactivities due to their different propensities for reductive elimination, (iii) use of extremely easily hydrolyzable silanes, such as $HSi(SEt)_3$, makes possible an indirect but efficient detection of Si−H reductive elimination.

Experimental Section

General Considerations. All the manipulations of air- and moisture-sensitive compounds were carried out using a nitrogen-filled Vacuum Atmospheres glovebox. The solvents used were purified by standard procedures, degassed, and stored over molecular sieves in the glovebox. All the reagents were of reagent grade. $HSi(SEt)_3$,[4] $HIr(CO)(PPh_3)_3$,[5a] $CH_3Ir(PMe_3)_4$,[6a] $C_6F_5Rh(PMe_3)_3$,[7] $Ir(PMe_3)_4Cl$,[18] $Ir(PEt_3)_3Cl$,[19] and $Ir(PEt_3)_2(C_2H_4)Cl$[3] were prepared according to the literature procedures. NMR spectra were obtained with a Bruker AMX 400 spectrometer at ambient probe temperature in C_6D_6 (99% D, Riedel-de Haën) solutions unless otherwise specified. 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), internal C_6D_6 at δ 128.00 (^{13}C NMR, 100 MHz), and external C_6F_6 at δ −162.9 (^{19}F NMR, 376 MHz). Abbreviations are as follows: d, doublet; t, triplet; q, quartet; m, multiplet; v, virtual; br, broad; app, apparent. IR spectra were recorded with a Nicolet 510 FT-IR spectrometer using NaCl plates. Elemental analyses were obtained from the Microanalysis Laboratory of The Hebrew University of Jerusalem.

Preparation of $(C_6F_5)Ir(PMe_3)_3$ (4). To a suspension of 100 mg (0.188 mmol) of $Ir(PMe_3)_4Cl$ in 7 mL of THF was dropwise added 2.1 mL of a 0.10 M solution of C_6F_5MgBr in THF/Et_2O (4:1) (1.12 equiv). After the addition was complete (ca. 20 min), the mixture was stirred for 10 min more and then the solvent was removed under vacuum. The residue was extracted with pentane (3 × 3 mL); the extract after filtration was evacuated to yield 71 mg (64%) of **4** as orange needles. Anal. Calcd for $C_{15}H_{27}F_5IrP_3$: C, 30.67; H, 4.63. Found: C, 30.95; H, 4.48. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −34.4 (m, 1P), −27.2 (d, J = 25.4 Hz, 2P). ^{1}H NMR (C_6D_6): δ 0.95 (vt, J = 3.0 Hz, 18H, CH_3−P), 1.16 (d, J = 7.1 Hz, 9H, CH_3−P). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −111.5 (m, 2F, ortho), −163.2 (m, 1F, para), −163.7 (m, 2F, meta).

Preparation of *cis*-$(PPh_3)_2(CO)IrH_2(Si(SEt)_3)$ (5). To a solution of 30 mg (0.03 mmol) of $HIr(CO)(PPh_3)_3$ in 1 mL of C_6D_6 was added 6 μL (6.3 mg, 0.03 mmol) of $HSi(SEt)_3$. The initial greenish color of the reaction mixture slowly disappeared during 15 min. NMR analysis of the resulting colorless solution indicated quantitative formation of **5** and liberation of 1 equiv of PPh_3. The solvent was removed under vacuum to yield 36 mg of the 1:1 mixture of **5** and PPh_3. Anal. Calcd for $C_{61}H_{62}IrOP_3S_3Si$ ($C_{43}H_{47}IrOP_2S_3Si$ + 1 ($C_6H_5)_3P$): C, 60.03;

(14) Kuyper, J. *Inorg. Chem.* **1977**, *16*, 2171.

(15) The reductive elimination of Si−H bonds is well-known, and its kinetics was investigated. See for example: (a) Haszeldine, R. N.; Parish, R. V.; Taylor, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2311. (b) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 8621. (c) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 65. (d) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531. (e) Hays, M. K.; Eisenberg, R. *Inorg. Chem.* **1991**, *30*, 2623. (f) Cleary, B. P.; Mehta, R.; Eisenberg, R. *Organometallics* **1995**, *14*, 2297 and references therein.

(16) See, for example: Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.

(17) The $Si(OEt)_3$ analog of **5** was reported to be extremely stable with regard to loss of $HSi(OEt)_3$. The Ir−D/H−$Si(OEt)_3$ exchange reactions of its monodeuterido isotopomer were, therefore, proposed to proceed by concerted bimolecular mechanism, rather than by a reductive elimination−oxidative addition sequence.[5b]

(18) Herskovitz, T. *Inorg. Synth.* **1982**, *21*, 99.

(19) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738.

H, 5.12. Found: C, 60.00; H, 5.14. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.9 (d, J = 13.8 Hz, 1P), 5.4 (d, J = 13.8 Hz, 1P), −4.8 (s, 1P, free PPh_3). ^1H NMR (C_6D_6): δ −10.21 (ddd, $^2J_{H-P,trans}$ = 104.3 Hz, $^2J_{H-P,cis}$ = 19.6 Hz, $^2J_{H-H}$ = 4.4 Hz, 1H, Ir−*H*), −9.23 (ddd, $^2J_{H-P,cis}$ = 14.1 Hz, $^2J_{H-P,cis}$ = 21.8 Hz, $^2J_{H-H}$ = 4.4 Hz, 1H, Ir−*H*), 1.33 (t, $^3J_{H-H}$ = 7.4 Hz, 9H, C*H*$_3$−CH_2S), 2.91 (m, 6H, C*H*$_2$S), 6.8−7.6 (several m, 30H, C_6H_5−P).$^{13}C\{^1H\}$ NMR (C_6D_6): δ 179.8 (dd, $^2J_{C-P,cis}$ = 7.4 Hz, $^2J_{C-P,cis}$ = 4.2 Hz, Ir−*C*O).

Preparation of *fac*-$(PMe_3)_3Ir(CH_3)(H)(Si(SEt)_3)$ (6). To a solution of 25 mg (0.05 mmol) of $CH_3Ir(PMe_3)_4$ in 1 mL of C_6H_6 was added 10 μL (0.05 mmol) of $HSi(SEt)_3$ at room temperature. The yellow color of the solution immediately disappeared. The reaction mixture was filtered from a small amount of a precipitate, and $^{31}P\{^1H\}$ NMR of the filtrate indicated clean formation of **6** and liberation of 1 equiv of PMe_3. The solvent was removed under vacuum to yield 26 mg (80%) of **6** as colorless plates. Anal. Calcd for $C_{16}H_{46}IrP_3S_3Si$: C, 29.66; H, 7.16. Found: C, 29.36; H, 7.17. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −61.0 (pseudo t, J = 20.2 Hz, 1P), −59.7 (dd, J_1 = 17.2 Hz, J_2 = 19.6 Hz, 1P), −57.1 (dd, J_1 = 17.2 Hz, J_2 = 20.7 Hz, 1P). ^1H NMR (C_6D_6): δ −12.35 (ddd, $^2J_{H-P,trans}$ = 124.5 Hz, $^2J_{H-P,cis}$ = 21.8 Hz, $^2J_{H-P,cis}$ = 13.6 Hz, 1H, Ir−*H*), 0.51 (dddd, $^3J_{H-P,trans}$ = 11.5 Hz, $^3J_{H-P,cis}$ = 10.2 Hz, $^3J_{H-P,cis}$ = 4.4 Hz, $^3J_{H-H}$ = 1.2 Hz, 3H, Ir−C*H*$_3$), 1.02 (d, $^2J_{H-P}$ = 7.7 Hz, 9H, C*H*$_3$−P), 1.33 (d, $^2J_{H-P}$ = 7.9 Hz, 9H, C*H*$_3$−P), 1.58 (d, $^2J_{H-P}$ = 8.0 Hz, 9H, C*H*$_3$−P), 1.48 (t, $^3J_{H-H}$ = 7.4 Hz, 9H, C*H*$_3$−CH_2S), 3.12 (m, 6H, C*H*$_2$S).

Preparation of *mer*-$(PMe_3)_3Ir(C_6F_5)(H)(Si(SEt)_3)$ (7) and *mer*-$(PMe_3)_3Rh(C_6F_5)(H)(Si(SEt)_3)$ (9). These complexes were prepared similarly to *mer*-$(PMe_3)_3Rh(C_6F_5)(H)(Si(OEt)_3)$ (**11**), which was fully characterized.[7]

Characterization of **7**: colorless solid, yield 95%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −65.4 (ddt, $^4J_{P-F}$ = 26.3 Hz, $^4J_{P-F}$ = 38.3 Hz, $^2J_{P-P}$ = 22.0 Hz, 1P), −53.7 (d, $^2J_{P-P}$ = 22.0 Hz, 2P). ^1H NMR (C_6D_6): δ −12.0 (app dq, $^2J_{H-P,trans}$ = 132 Hz, $^2J_{H-P,cis}$ = $^4J_{H-F}$ = 13 Hz, 1H, Ir−*H*), 1.33 (vt, J = 3.6 Hz, 18H, C*H*$_3$−P), 1.49 (d, $^2J_{H-P}$ = 7.6 Hz, 9H, C*H*$_3$−P), 1.40 (t, $^3J_{H-H}$ = 7.4 Hz, 9H, C*H*$_3$−CH_2S), 3.00 (q, $^3J_{H-H}$ = 7.4 Hz, 6H, C*H*$_2$S). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −95.5 (m, 1F, ortho), −102.4 (tt, J_1 = 9.6 Hz, J_2 = 37.6 Hz, 1F, ortho), −160.1 (t, J = 20.6 Hz, 1F, para), −160.4 (m, 1F, meta), −161.3 (m, 1F, meta). FD-MS: m/z 800 (M^+, ^{193}Ir).

Characterization of **9**: slightly yellow solid, yield 93%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −30.0 (dm, $^1J_{P-Rh}$ = 85.9 Hz, $^2J_{P-P}$ = 30.7 Hz, 1P), −11.0 (dd, $^1J_{P-Rh}$ = 94 Hz, $^2J_{P-P}$ = 30.8 Hz, 2P). ^1H NMR (C_6D_6): δ −9.77, (dm, $^2J_{H-P,trans}$ = 164.3 Hz, 1H, Rh−*H*), 1.17 (vt, J = 3.3 Hz, 18H, C*H*$_3$−P), 1.33 (br d, $^2J_{H-P}$ = 7.1 Hz, 9H, C*H*$_3$−P), 1.37 (t, $^3J_{H-H}$ = 7.5 Hz, 9H, C*H*$_3$−CH_2S), 3.00 (q, $^3J_{H-H}$ = 7.5 Hz, 6H, C*H*$_2$S). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −95.9 (m, 1F, ortho), −101.4 (tt, J_1 = 11.8 Hz, J_2 = 40.4 Hz, 1F, ortho), −159.5 (t, J = 20.7 Hz, 1F, para), −160.0 (m, 1F, meta), −160.9 (m, 1F, meta).

Preparation of *mer*-$(PMe_3)_3Rh(C_6F_5)(H)(SEt)$ (10). A bright yellow solution of 15 mg (0.03 mmol) of $C_6F_5Rh(PMe_3)_3$ in 0.5 mL of C_6D_6 was treated with 225 μL of a 0.135 M solution of HSEt in C_6D_6. The color of the solution changed to slightly yellow, and NMR analysis indicated quantitative formation of **10**, which was isolated after removal of the solvent under vacuum in 95% yield as a yellow solid. Anal. Calcd for $C_{17}H_{33}F_5P_3RhS$: C, 36.44; H, 5.94. Found: C, 36.14; H, 6.01. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −31.5 (m, $^2J_{P-P}$ = 28.0 Hz, 1P), −9.0 (dd, $^1J_{P-Rh}$ = 98.2 Hz, $^2J_{P-P}$ = 28.0 Hz, 2P). ^1H NMR (C_6D_6): δ −10.00 (dm, $^2J_{H-P,trans}$ = 194.3 Hz, 1H, Rh−*H*), 1.03 (d, $^2J_{H-P}$ = 7.5 Hz, 9H, C*H*$_3$−P), 1.05 (vt, J = 3.2 Hz, 18H, C*H*$_3$−P), 1.50 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, C*H*$_3$−CH_2S), 2.59 (q, $^3J_{H-H}$ = 7.6 Hz, 2H, C*H*$_2$S). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −97.2 (m, 1F, ortho), −107.2 (m, 1F, ortho), −162.1 (m, 1F, meta), −162.4 (t, J = 20.7 Hz, 1F, para), −163.0 (m, 1F, meta).

Preparation of *mer*-$(PEt_3)_3Ir(H)(Cl)(Si(OEt)_3)$ (12). To a red solution of 58 mg (0.100 mmol) of $Ir(PEt_3)_3Cl$ in 1 mL of pentane was added dropwise upon stirring a solution of 22 mg (0.134 mmol) of $HSi(OEt)_3$ in 2 mL of pentane. After 1 h the mixture became almost colorless and the solvent was removed under vacuum to afford **12** as an off-white powder. Yield: 72 mg (97%). IR (Nujol): ν_{Ir-H} 2123 cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −23.8 (t, $^2J_{P-P}$ = 17.8 Hz, 1P), −16.3 (d, $^2J_{P-P}$ = 17.8 Hz, 2P). ^1H NMR (C_6D_6): δ −11.27 (dt, $^2J_{H-P,trans}$ = 126.5 Hz, $^2J_{H-P,cis}$ = 19.0 Hz, 1H, Ir−*H*), 1.20 (t, $^3J_{H-H}$ = 7 Hz, 9H, C*H*$_3$−CH_2O), 3.80 (q, $^3J_{H-H}$ = 7 Hz, 6H, C*H*$_2$O), 1.12 (overlapped m, 27H, PCH_2−C*H*$_3$), 2.11 (app quin, J = 7.3 Hz, 6H, unique P−C*H*$_2$−CH_3), 2.15 and 2.30 (symmetrical pattern consisting of two 13-line multiplets, 6H each, mutually trans P−C*H*$_2$−CH_3). FD-MS: m/z 746 (M^+, ^{193}Ir).

Preparation of *trans*-$(PEt_3)_2Ir(H)(Cl)(Si(OEt)_3)$ (13). To an orange solution of 62 mg (0.126 mmol) of $Ir(PEt_3)_2(C_2H_4)$-Cl in 4 mL of pentane was dropwise added upon stirring a solution of 21 mg (0.128 mmol) of $HSi(OEt)_3$ in 2.5 mL of pentane. After 30 min the solution became yellow and the solvent was evacuated to yield 76 mg (96%) of **13** as a yellow-brownish oil. IR (Nujol): ν_{Ir-H} = 2200 cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 24.0 (s). ^1H NMR (C_6D_6): δ −21.62 (t, $^2J_{H-P,cis}$ = 12.7 Hz, 1H, Ir−*H*), 1.22 (t, $^3J_{H-H}$ = 7 Hz, 9H, C*H*$_3$−CH_2O), 3.92 (q, $^3J_{H-H}$ = 7 Hz, 6H, C*H*$_2$O), 1.06 (app quin, J = 7.6 Hz, 18H, PCH_2−C*H*$_3$), 1.97 (m, 12H, P−C*H*$_2$−CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.78 (s, PCH_2−C*H*$_3$), 17.85 (vt, J = 16.2 Hz, P−C*H*$_2$−CH_3), 18.39 (s, C*H*$_3$−CH_2O), 58.23 (s, CH_3−C*H*$_2$−O). FD-MS: m/z 628 (M^+, ^{193}Ir).

Procedures of Hydrolysis Experiments. The pure complexes were subjected to high vacuum prior to use to ensure that no traces of easily hydrolyzable silanes would be present at the next stage.

(a) Complexes **5**−**7** (0.02 mmol) were dissolved in a mixture containing 0.1 mL (about 280 equiv) of H_2O and 0.4 mL of THF. No changes were observed in ^{31}P NMR after 1 day. Then 3 equiv of NaOH as a 1 M solution in H_2O was added to every sample. After 10 h the reaction mixtures were checked by ^{31}P NMR again to show no observable changes.

(b) Complex **9** (0.02 mmol) was treated with 5 equiv of H_2O in 0.5 mL of C_6D_6. After 3 h of stirring, the white precipitate that was formed was filtered off and the filtrate containing pure **10** was identified by its ^{31}P and ^1H NMR. The solvent was removed under vacuum to afford **10** in almost quantitative yield.

(c) Complexes **12** and **13** (0.1 mmol) were dissolved in 1,4-dioxane (2 mL) and to the resulting solutions was added 50 μL of H_2O (about 28 equiv). ^{31}P NMR spectra of the mixtures showed no changes after 12 h. Then an additional 100 μL of H_2O was added to each of the samples, and the mixtures were heated in closed vessels at 80 °C for 12 h. Under these conditions white precipitates were formed. These were removed by filtration, the filtrates were evacuated, and the residues formed were redissolved in C_6D_6. NMR analysis showed clean formation of *mer*,*cis*-$(PEt_3)_3IrH_2Cl$ (**14**)[20] in the case of **12**, while **13** decomposed to a complicated mixture, containing **14** along with some other unidentified compounds. The systems were not investigated further.

Silane Exchange Experiments. Complexes **5**, **7**, and **9** were all treated as described below. To a solution of the complex (0.02 mmol) in 0.5 mL of C_6D_6 was added by a microsyringe 0.2 mmol of $HSi(OEt)_3$. The reaction mixture was kept at room temperature and was periodically monitored by ^{31}P and ^1H NMR spectroscopy. No change in the NMR spectra was detected after 2 days for complexes **5** and **7**, while in the case of complex **9** 80% conversion to the known *mer*-$(C_6F_5)(H)(Si(OEt)_3)Rh(PMe_3)_3$ (**11**)[7] along with formation of free $HSi(SEt)_3$ was observed.

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(20) Complex **14** was easily identified by its ^{31}P and ^1H NMR, see: Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582 and references therein.