11556 *Inorg. Chem.* **2010**, *49*, 11556–11572
DOI: 10.1021/ic1017196

Inorganic Chemistry
Article

Multiple Silicon−Hydrogen Bond Activations at Adjacent Rhodium and Iridium Centers

Md Hosnay Mobarok,[†] **Okemona Oke,**[†] **Michael J. Ferguson,**[†,‡] **Robert McDonald,**[†,‡] **and Martin Cowie***[,†]

[†]*Department of Chemistry, University of Alberta, Edmonton, AB, Canada, T6G 2G2, and*
[‡]*X-ray Crystallography Laboratory*

Received August 24, 2010

The reaction of 1 equiv of primary silanes, SiH_3R (R = Ph, Mes), with $[RhIr(CO)_3(dppm)_2]$ yields mono(silylene)-bridged complexes of the type $[RhIr(H)_2(CO)_2(\mu\text{-}SiHR)(dppm)_2]$ (R = Ph or Mes), while for R = Ph the addition of 2 equiv yields the bis(silylene)-bridged complexes, $[RhIr(CO)_2(\mu\text{-}SiHPh)_2(dppm)_2]$. The kinetic isomer of this bis(silylene)-bridged product has the phenyl substituent axial on one silylene unit and equatorial on the other, and in the presence of excess silane this rearranges to the thermodynamically preferred "axial−axial" isomer, in which the phenyl substituents on each bridging silylene unit are axial and parallel to one another. The reaction of 1 equiv of diphenylsilane with $[RhIr(CO)_3(dppm)_2]$ produces the mono(silylene)-bridged product, $[RhIr(H)_2(CO)_2(\mu\text{-}SiPh_2)(dppm)_2]$, and the subsequent addition of silane in the presence of CO yields the silyl/silylene product $[RhIr(H)(SiPh_2H)(CO)_3(\kappa^1\text{-}dppm)(\mu\text{-}SiPh_2)(dppm)]$. The reaction of $[RhIr(CO)_3(dppm)_2]$ with 2 equiv of SiH_2Me_2 yields the analogous product $[RhIr(H)(SiMe_2H)(CO)_3(\kappa^1\text{-}dppm)(\mu\text{-}SiMe_2)(dppm)]$. Low-temperature NMR spectroscopic observation of some key intermediates, such as $[RhIr(H)(SiH_2Ph)(CO)_2(\mu\text{-}CO)(dppm)_2]$, formed during the formation of the mono(silylene)-bridged species provides evidence for a mechanism involving initial Si−H bond activation at Rh, followed by the subsequent Si−H bond activation at Ir. The Si−H bond activation of a second equivalent of silane seems to be initiated by dissociation of the Rh-bound end of one diphosphine. The reaction of diphenylsilane with the cationic complex $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ gives rise to a different reactivity pattern in which Si−H bond activation is initiated at Ir. In this case, the cationic silyl-bridged species, $[RhIr(CH_3)(CO)_2(\kappa^1{:}\eta^2\text{-}SiHPh_2)(dppm)_2][CF_3SO_3]$, contains an agostic Si−H interaction with Rh. In solution, at ambient temperature, this complex converts to two species, $[RhIr(H)(COCH_3)(CO)(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2][CF_3SO_3]$ and $[RhIr(CO)_2(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2]$ $[CF_3SO_3]$, formed by the competing methyl migration to CO and reductive elimination of methane, respectively. In the diphenylsilylene dihydride product, a weak interaction between the bridging silicon and the terminal Ir-bound hydride is proposed on the basis of NMR evidence.

Introduction

The chemistry of transition-metal complexes containing metal−silicon bonds occupies a prime position in a number catalytic transformations including olefin and ketone hydrosilylation,[1] silane alcoholysis,[2] silane redistribution,[3] silane reduction of haloarenes,[4] and dehydrogenative silane oligomerization.[5] One of the most versatile methods for generating Si-containing complexes is by the oxidative addition of Si−H bonds in silanes. From the perspective of dehydrogenative silane oligomerization, the incorporation of two or more Si-containing fragments into metal complexes is of particular importance, potentially leading to the coupling of these fragments. Multinuclear complexes can play an important role in Si−Si coupling, since two or more metals have a greater capacity for silane oxidative addition and for the concomitant incorporation of multiple Si-containing fragments than does a single metal. This has been amply demonstrated by the early work of Graham,[6a] and more recently as described in reviews by Tobita and Ogino,[6b] Corey and Braddock-Wilking,[6c] and

---

*To whom correspondence should be addressed. Tel.: 017804925581. Fax: 017804928231. E-mail: martin.cowie@ualberta.ca.

(1) (a) Marciniec, B. *Silicon Chem.* **2002**, *1*, 155. (b) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000. (c) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 11161. (d) Ojima, I.; Kogure, T.; Nihonyanagi, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 938. (e) Ojima, I.; Nihonyanagi, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3506. (f) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Gierz, V.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2008**, *27*, 224.

(2) (a) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (b) Biffis, A.; Basato, M.; Brichese, M.; Ronconi, L.; Tubaro, C.; Zanella, A.; Graiff, A; Tiripicchio, A. *Adv. Synth. Catal.* **2007**, *349*, 2485.

(3) (a) Hashimoto, H.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1995**, *499*, 205. (b) Radu, N. S.; Hollander, F. J.; Tilley, T. D.; Rheingold, A. L. *Chem. Commun.* **1996**, 2459. (c) Gavenonis, J.; Tilley, T. D. *Organometallics* **2004**, *23*, 31.

(4) (a) Boukherroub, R.; Chatgiliaoglu, C.; Manuel, G. *Organometallics* **1996**, *15*, 1508. (b) Esteruelas, M. A.; Herrero, J.; Lopez, F. M.; Martin, M.; Oro, L. A. *Organometallics* **1999**, *18*, 1110. (c) Diaz, J.; Esteruelas, M. A.; Herrero, J.; Moralejo, L.; Olivan, M. *J. Catal.* **2000**, *195*, 187.

(5) (a) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (b) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (c) Rosenberg, L.; Davis, C. W.; Yao, J. Z. *J. Am. Chem. Soc.* **2001**, *123*, 5120. (d) Fontaine, F.-G.; Zargarian, D. *J. Am. Chem. Soc.* **2004**, *126*, 8786. (e) Corey, J. Y. *Adv. Organomet. Chem.* **2004**, *51*, 1.

(6) (a) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81 and references therein. (b) Ogino, H.; Tobita, H. *Adv. Organomet. Chem.* **1998**, *42*, 223 and reference therein. (c) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175 and references therein. (d) Shimada, S.; Tanaka, M. *Coord. Chem. Rev.* **2006**, *250*, 991. (e) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

Tanaka and Shimada[6d] in which a variety of complexes have been reported incorporating bis-silylene,[7−18] silyl/silylene,[19−22] bis-silyl,[10−12,15,16,18,23] and silane/silyl[15] combinations of groups.

Binuclear late-metal complexes have played a dominant role in the chemistry of Si-bridged species and within the group of bis-silylene-bridged products; two structural classes have emerged in which the M_2Si_2 framework is either planar[7,11−14,16−19,23] or folded in a butterfly-type arrangement.[7b,8,10,22] The strongest structural evidence for Si−Si interactions in these species has been found in the planar M_2Si_2 arrangement, in which the Si centers at opposite corners of a parallelepiped are in close contact.[24−26] Si−Si bond formation should also be possible in the folded arrangement, having the Si atoms at the "wingtips", since such a geometry allows the Si centers to approach within bonding distance. Si−Si bond formation has also been reported between silyl and silylene-bridged moieties in a binuclear species.[22]

In previous work on silane activation by pairs of adjacent metals, we had investigated a diiridium system in which, under the conditions investigated, the incorporation of only a single silicon-containing group had been achieved.[9] In contrast, Eisenberg and Wang, investigating closely related Rh_2 systems, had observed the incorporation of up to two Si-containing fragments, to give folded Rh_2Si_2 cores.[8] The difference in reactivity of these two systems can be rationalized by the greater lability of Rh, which more readily allows coordinative unsaturation to be achieved after double Si−H bond activation of the first silane. Although silane activation by a number of homodinuclear late metals (Pt,[7,12,13,18,19,22b,27] Pd,[14,17,28] Rh,[8,11,20,21] Ir,[9] Fe,[29] Ru,[10,15,16,23,30] and Ni[22a]) has been studied, only a few examples involving mixed-metal complexes have been reported.[31] In order to learn more about the stepwise incorporation of silanes and the roles of the adjacent meatals in the activation process by the group 9 metals, we have investigated the Rh/Ir combination of metals in anticipation that the greater tendency for Ir to undergo oxidative addition combined with the greater lability of Rh might lead to chemistry that differs from that observed with the homobinuclear analogues. These results are reported herein.

Experimental Section

General Comments. All solvents were dried (using appropriate drying agents), distilled before use, and stored under dinitrogen. Reactions were performed under an argon atmosphere using standard Schlenk techniques. Ph_2SiH_2 and $PhSiH_3$ were purchased from Aldrich and Alfa-Aesar, respectively, while $MesSiH_3$,[32a] $C_6H_3F_2SiH_3$,[32b] and Ph_2SiD_2[32c] were prepared according to the literature methods. $PhSiD_3$ was prepared according to a modified literature method (overnight reflux in diethyl ether instead of at room temperature).[33] Silanes were dried over CaH_2 and distilled under Ar before use. ^{13}C-enriched CO (99.4%) and $LiAlD_4$ were purchased from Cambridge Isotope Laboratories; ^{13}C-enriched methyl-triflate and ^2H-enriched methyl triflate were purchased from Sigma-Aldrich. $[RhIr(CO)_3(dppm)_2]$ (**1**)[34] and $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**)[35] were prepared as previously reported. NMR spectra were recorded on Bruker AM-400, Varian Inova-400, or Varian Unity-500 spectrometers operating at 400.0, 399.8, or 499.8 MHz, respectively, for ^1H; at 161.9, 161.8, or 202.3 MHz, respectively, for ^{31}P; and at 100.6, 100.6, or 125.7 MHz, respectively, for ^{13}C nuclei. $^{29}Si\{^1H\}$ NMR spectra were acquired on the Varian Inova-400 spectrometer operating at 79.5 MHz according to a combination of DEPT, 2D $^1H-^{29}Si$ HSQC, and 2D $^1H-^{29}Si$ HMBC. The ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were referenced internally to residual solvent proton signals relative to tetramethylsilane,

---

(7) (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 577.

(8) Wang, W. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 1833.

(9) McDonald, R.; Cowie, M. *Organometallics* **1990**, *9*, 2468.

(10) Suzuki, H.; Takao, T.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 476.

(11) Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Organometallics* **1999**, *18*, 958.

(12) Sanow, L. M.; Chai, M.; McConnville, D. B.; Galat, K. J.; Simons, R. S.; Rinaldi, P. L.; Youngs, W. J.; Tessier, C. A. *Organometallics* **2000**, *19*, 192.

(13) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Organometallics* **2001**, *20*, 474.

(14) Fürstner, A.; Krause, H.; Lehmann, C. W. *Chem. Commun.* **2001**, 2372.

(15) Hashimoto, H.; Hayashi, Y.; Aratani, I.; Kabuto, C.; Kira, M. *Organometallics* **2002**, *21*, 1534.

(16) Takao, T.; Amako, M. A.; Suzuki, H. *Organometallics* **2003**, *22*, 3855.

(17) Tanabe, M.; Mawatari, A.; Osakada, K. *Organometallics* **2007**, *26*, 2937.

(18) Tanabe, M.; Ito, D.; Osakada, K. *Organometallics* **2008**, *27*, 2258.

(19) Shimada, S.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8289.

(20) Osakada, K.; Koizumi, T.; Yamamoto, T. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 349.

(21) Koizumi, T. A.; Osakada, K.; Yamamoto, T. *Organometallics* **1998**, *19*, 5721.

(22) (a) Shimada, S.; Rao, M. L. N.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 213. (b) Shimada, S.; Li, Y.-H.; Rao, M. L. N.; Tanaka, M. *Organometallics* **2006**, *25*, 3796.

(23) Takao, T.; Yoshida, S.; Suzuki, H. *Organometallics* **1995**, *14*, 3855.

(24) (a) Anderson, A. B.; Shiller, P.; Zaraten, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *Organometallics* **1989**, *8*, 2320. (b) Aullón, G.; Alemany, P.; Alvarez, S. *J. Organomet. Chem.* **1994**, *478*, 75.

(25) Sakaki, S.; Yamaguchi, S.; Musashi, Y.; Sugimoto, M. *J. Organomet. Chem.* **2001**, *635*, 17.

(26) Nakajima, S.; Yokogawa, D.; Nakao, Y.; Sato, H.; Sakaki, S. *Organometallics* **2004**, *23*, 4672.

(27) (a) Brittingham, K. A.; Gallaher, T. N.; Schreiner, S. *Organometallics* **1995**, *14*, 1070. (b) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917.

(28) (a) Yamada, T.; Mawatari, A.; Tanabe, M.; Osakada, K.; Tanase, T. *Angew. Chem., Int. Ed. Engl.* **2009**, *48*, 568. (b) Herrmann, W. A.; Härter, P.; Gstöttmayr, C. W. K.; Bielert, F.; Seeboth, N.; Sirsch, P. *J. Organomet. Chem.* **2002**, *649*, 141.

(29) (a) Tobita, H.; Kawano, Y.; Ogino, H. *Chem. Lett.* **1989**, 2155. (b) Kawano, Y.; Tobita, H.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 843. (c) Kawano, Y.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1994**, *116*, 8575. (d) Ohki, Y.; Kojima, T.; Oshima, M.; Suzuki, H. *Organometallics* **2001**, *20*, 2654.

(30) (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1992**, *11*, 3918. (b) Takao, T.; Suzuki, H.; Tanaka, T. *Organometallics* **1994**, *13*, 2554. (c) Takao, T.; Amako, M. A.; Suzuki, H. *Organometallics* **2001**, *20*, 3406. (d) Takao, T.; Yoshida, S.; Suzuki, H. *Chem. Lett.* **2001**, *11*, 1100. (e) Takao, T.; Yoshida, S.; Suzuki, H. *Organometallics* **2005**, *24*, 521.

(31) (a) Powell, J.; Sawyer, J. F.; Shiralian, M. *Organometallics* **1989**, *8*, 557. (b) Sakaba, H.; Ishida, K.; Horino, H. *Chem. Lett.* **1998**, 149. (c) Bodensieck, U.; Braunstein, P.; Deck, W.; Faure, T.; Knorr, M.; Stern, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2440. (d) Knorr, M.; Strohmann, C.; Braunstein, P. *Organometallics* **1996**, *15*, 5653. (e) Braunstein, P.; Morise, X. *Organometallics* **1998**, *17*, 540. (f) Braunstein, P.; Durand, J.; Morise, X.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **2000**, *19*, 444. (g) Braunstein, P.; Durand, J.; Knorr, M.; Strohmann, C. *Chem. Commun.* **2001**, 211. (h) Braunstein, P.; Clerc, G.; Morise, X. *Organometallics* **2001**, *20*, 5036. (i) Tanabe, M.; Osakada, K. *Inorg. Chim. Acta* **2003**, *350*, 201. (j) Yamada, T.; Tanabe, M.; Osakada, K.; Kim, Y.-J. *Organometallics* **2004**, *23*, 4771. (k) Braunstein, P.; Faure, T.; Knorr, M. *Organometallics* **1999**, *18*, 1791. (l) Shelby, Q. D.; Lin, W.; Girolami, G. S. *Organometallics* **1999**, *18*, 1791.

(32) (a) Minge, O.; Nogai, S.; Schmidbaur, H. *Z. Naturforsch. B* **2004**, *59*, 153. (b) Molander, G. A.; Corrette, C. P. *Organometallics* **1998**, *17*, 5504. (c) Prince, P. D.; Bearpark, M. J.; McGrady, G. S.; Steed, G. W. *Dalton. Trans.* **2008**, 271.

(33) Benkeser, R. A.; Landesman, H.; Foster, D. J. *J. Am. Chem. Soc.* **1952**, *74*, 648.

(34) McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564.

(35) Oke, O. Ph.D. Thesis, University of Alberta, Alberta, Canada, 1999; p 24.

whereas $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ and $^{19}\mathrm{F}\{^{1}\mathrm{H}\}$ NMR spectra were referenced relative to external standard 85% $\mathrm{H_3PO_4}$ and $\mathrm{CCl_3F}$, respectively. In the $^{1}\mathrm{H}$ NMR spectral results, the aromatic protons in the range δ 8.50−6.20 are not reported. The $^{13}\mathrm{C}$ NMR resonances involving the CO and $\mathrm{CH_3}$ ligands were acquired using $^{13}\mathrm{CO}$- and $^{13}\mathrm{CH_3}$-enriched samples. The $^{13}\mathrm{C}$ NMR resonances for the dppm methylene groups (which were not $^{13}\mathrm{C}$-enriched) are not reported for those complexes which are either in low NMR yield (**6** and **11**), were only observed at low temperature (**3**, **14**, and **15**), or were unstable at room temperature (**16** and **17**) and therefore unsuitable for extended data acquisition times. The $^{13}\mathrm{C}$ NMR resonances for the aryl carbons (in the range of δ 125−135) are not reported, since they appear in the typical region and give no structural information. The yields of all nonisolable complexes were determined by the integration of their resonances in $^{31}\mathrm{P}$ NMR spectra, taking all resonances present as 100% in a sealed NMR tube. For compounds **3**−**6**, **8a**, **8d**, and **11**, the labeling of the phosphorus resonances is as shown later in the manuscript for compound **11** in Figure 7. For compounds **7**, **10**, and **12**, the numbering is as shown for compound **10** in the same figure. Coupling constants tagged with an asterisk appeared as additional coupling when the respective ligands (either CO or $\mathrm{CH_3}$) were $^{13}\mathrm{C}$-enriched and therefore were not included in the description of the multiplicity. All spectra were recorded at 27 °C unless otherwise noted. Infrared spectra were obtained on a Nicolet Avatar 370 DTGS spectrometer. The elemental analyses were performed by the Microanalytical Laboratory in the department.

Preparation of Compounds. (a). [RhIr(H)(SiH₂Ph)(CO)₂(μ-CO)(dppm)₂] (3). In a sealed NMR tube under an $\mathrm{Ar_{(g)}}$ atmosphere, $[\mathrm{RhIr(CO)_3(dppm)_2}]$ (**1**) (30 mg 0.026 mmol) was dissolved in 0.7 mL of $\mathrm{CD_2Cl_2}$ at ambient temperature, producing a dark orange solution, then cooled to −78 °C. The addition of $\mathrm{PhSiH_3}$ (3.2 μL, 0.026 mmol) using a microliter syringe resulted in a lightening of the solution color. Compound **3** was formed quantatively after 30 min, as made evident by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (−78 °C; $\mathrm{CD_2Cl_2}$, 161.9 MHz): δ 40.0 ($\mathrm{P_A}$, 1P, ddd, $^{1}J_{\mathrm{RhP(A)}} = 107$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 241$ Hz, $^{2}J_{\mathrm{P(A)P(C)}} = 31$ Hz), 25.2 ($\mathrm{P_C}$, 1P, ddd, $^{1}J_{\mathrm{RhP(C)}} = 89$ Hz, $^{2}J_{\mathrm{P(C)P(D)}} = 152$ Hz), −3.3 ($\mathrm{P_B}$, 1P, dd, $J_{\mathrm{P(B)P(D)}} = 18$ Hz), −11.5 ($\mathrm{P_D}$, 1P, dd). $^{1}\mathrm{H}$ NMR (−78 °C; $\mathrm{CD_2Cl_2}$, 399.8 MHz): δ 4.66 ($\mathrm{CH_2}$, m, 1H), 4.23 (Si−H, m, 1H), 4.14 ($\mathrm{CH_2}$, m, 1H), 4.07 ($\mathrm{CH_2}$, m, 1H), 4.05 (Si−H, m, 1H), 2.50 ($\mathrm{CH_2}$, m, 1H), −11.50 (Ir−H, ddd, 1H, $^{2}J_{\mathit{trans}\mathrm{P-H}} = 125.0$ Hz, $^{2}J_{\mathit{cis}\mathrm{P-H}} = 15.0$ Hz, $^{4}J_{\mathrm{distal}(\mathit{trans})\mathrm{P-H}} = 27.0$ Hz). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (−78 °C; $\mathrm{CD_2Cl_2}$, 100.5 MHz): δ 229.0 (μ-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 34.0$ Hz), 199.0 (Rh-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 70.0$ Hz), 178.0 (Ir-CO, t, 1C, $^{2}J_{\mathrm{PC}} = 9.8$ Hz). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (−78 °C; $\mathrm{CD_2Cl_2}$, 78.5 MHz, DEPT): δ − 18.0 (dddd, $^{1}J_{\mathrm{Rh-Si}} = 37.0$ Hz, $^{2}J_{\mathrm{Si-P}} = 137.0$ Hz, $^{2}J_{\mathrm{Si-P}} = 18.0$ Hz, $^{4}J_{\mathrm{Si-P}} = 18.0$ Hz).

(b). [RhIr(H)₂(CO)₂(μ-SiHPh)(dppm)₂] (4). In a 100 mL Schlenk tube, under anhydrous conditions and an Ar atmosphere, $[\mathrm{RhIr(CO)_3(dppm)_2}]$ (**1**; 46 mg, 0.040 mmol) was dissolved in 5 mL of benzene at ambient temperature. Phenylsilane (7.4 μL, 0.060 mmol) was then added to the solution by syringe, resulting in an immediate color change from dark orange to light yellow. The reaction was allowed to stir for 1 h, followed by the reduction of solvent volume to approximately 1 mL *in vacuo*. The subsequent slow addition of pentane gave a pale yellow powdery solid. The compound was recrystallized by layering the concentrated benzene solution of the compound with pentane at −20 °C. Yield: 35 mg (71%). Anal. Calcd for $\mathrm{C_{58}H_{52}IrO_2P_4RhSi\cdot C_6H_6}$: C, 58.79; H, 4.44. Found: C, 58.53; H, 4.58. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (27 °C; $\mathrm{C_6D_6}$, 161.9 MHz): δ 29.0 ($\mathrm{P_A}$, 1P, bm), 15.9 ($\mathrm{P_C}$, 1P, bm), −8.2 ($\mathrm{P_B}$, 1P, bm), −14.0 ($\mathrm{P_D}$, 1P, bm). $^{1}\mathrm{H}$ NMR (27 °C; $\mathrm{CDCl_2}$, 499.8 MHz): δ 5.30 ($\mathrm{CH_2}$, m, 2H), 3.10 ($\mathrm{CH_2}$, m, 2H), −9.60 (Rh−H, bm, 1H), −10.90 (Ir−H, bm, 1H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (27 °C; $\mathrm{CD_2Cl_2}$, 100.5 MHz): δ 194.1 (Rh-CO, dt, 1C, $J_{\mathrm{Rh-C}} = 70.0$ Hz, $^{2}J_{\mathrm{PC}} = 10.0$ Hz), 181.1(Ir-CO, t, 1C, $^{2}J_{\mathrm{PC}} = 9.8$ Hz), 49.5 ($\mathrm{CH_2}$, 1C, m), 44.8 ($\mathrm{CH_2}$, 1C, m). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (−40 °C; $\mathrm{CD_2Cl_2}$, 161.9 MHz): δ 29.0 ($\mathrm{P_A}$, 1P, ddd, $^{1}J_{\mathrm{RhP(A)}} = 101$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 131$ Hz, $^{2}J_{\mathrm{P(A)P(C)}} = 11$ Hz), 15.9 ($\mathrm{P_C}$, 1P, ddd, $^{1}J_{\mathrm{RhP(C)}} = 107$ Hz, $^{2}J_{\mathrm{P(C)P(D)}} = 129$ Hz), −8.2 ($\mathrm{P_B}$, 1P, dd, $^{2}J_{\mathrm{P(B)P(A)}} = 131$ Hz, $^{2}J_{\mathrm{P(B)P(D)}} = 9$ Hz), −14.0 ($\mathrm{P_D}$, 1P, dd). $^{1}\mathrm{H}$ NMR (−40 °C; $\mathrm{CD_2Cl_2}$, 399.8 MHz): δ 6.70 (Si−H, bs, 1H, $^{1}J_{\mathrm{SiH}} = 190.0$ Hz), 5.50 ($\mathrm{CH_2}$, m, 1H), 5.25 ($\mathrm{CH_2}$, m, 1H), 3.10 ($\mathrm{CH_2}$, m, 1H), 2.80 ($\mathrm{CH_2}$, m, 1H), −9.50 (Rh−H, ddm, 1H, $^{2}J_{\mathit{trans}\mathrm{P-H}} = 145.0$ Hz, $^{1}J_{\mathrm{Rh-H}} = 11.2$ Hz), −11.0 (Ir−H, dm, 1H, $^{2}J_{\mathit{trans}\mathrm{P-H}} = 123.0$ Hz). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (−40 °C; $\mathrm{CD_2Cl_2}$, 78.5 MHz, DEPT): δ 142.9 (dt, $^{1}J_{\mathrm{Si-Rh}} = 30.1$ Hz, $^{2}J_{\mathrm{P-Si}} = 72.2$ Hz). IR: $\nu_{\mathrm{SiH}} = 2045\ \mathrm{cm^{-1}}$, $\nu_{\mathrm{CO}} = 1962\ \mathrm{cm^{-1}}$, $1942\ \mathrm{cm^{-1}}$.

(c). [RhIr(H)₂(CO)₂(μ-SiHC₆H₂Me₃)(dppm)₂] (5). A total of 52 mg (0.045 mmol) of $[\mathrm{RhIr(CO)_3(dppm)_2}]$ (**1**) in a Schlenk flask under Ar was dissolved in 5 mL of benzene. The addition of 30 μL (0.132 mmol) of mesitylsilane by syringe to the continuously stirring solution of complex **1** resulted in a slow color change from orange to light yellow over the course of 3 h. After 6 h, the solution volume was reduced to 2 mL under vacuum conditions. the slow addition of 10 mL of pentane gave a pale yellow compound. Yield: 42 mg (73%). Anal. Calcd for $\mathrm{C_{61}H_{58}IrO_2P_4RhSi}$: C, 57.64; H, 4.57. Found: C, 57.89; H, 4.89. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (27 °C; $\mathrm{CD_2Cl_2}$, 161.9 MHz): δ 21.3 (bm), −12.1 (bm). $^{1}\mathrm{H}$ NMR (27 °C; $\mathrm{CD_2Cl_2}$, 399.8 MHz): δ 6.70 (Si−H, b, 1H), 5.30 ($\mathrm{CH_2}$, m, 2H), 3.10 ($\mathrm{CH_2}$, m, 2H), 2.97 (*o*-$\mathrm{CH_3}$, s, 6H), 2.37 (*p*-$\mathrm{CH_3}$, s, 3H), −9.30 (Rh−H, bm, 1H), −11.0 (Ir−H, bm, 1H). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (−40 °C; $\mathrm{CD_2Cl_2}$, 161.9 MHz): δ 26.9 ($\mathrm{P_A}$, 1P, ddd, $^{1}J_{\mathrm{RhP(A)}} = 102$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 130$ Hz, $^{2}J_{\mathrm{P(A)P(C)}} = 11$ Hz), 15.5 ($\mathrm{P_C}$, 1P, ddd, $^{1}J_{\mathrm{RhP(C)}} = 105$ Hz, $^{2}J_{\mathrm{P(C)P(D)}} = 129$ Hz), −9.4 ($\mathrm{P_B}$, 1P, dd, $^{2}J_{\mathrm{P(B)P(A)}} = 130$ Hz, $^{2}J_{\mathrm{P(B)P(D)}} = 9$ Hz), −14.8 ($\mathrm{P_D}$, 1P, dd). $^{1}\mathrm{H}$ ($\mathrm{CD_2Cl_2}$, 399.8 MHz): δ 6.70 (Si−H, bs, 1H), 5.40 ($\mathrm{CH_2}$, m, 1H), 5.20 ($\mathrm{CH_2}$, m, 1H), 3.10 ($\mathrm{CH_2}$, m, 1H), 2.90 ($\mathrm{CH_2}$, m, 1H), 2.97 (*o*-$\mathrm{CH_3}$, s, 6H), 2.37 (*p*-$\mathrm{CH_3}$, s, 3H), −9.30 (Rh−H, ddm, 1H, $^{2}J_{\mathit{trans}\ \mathrm{P-H}} = 140.0$ Hz, $^{1}J_{\mathrm{Rh-H}} = 11.0$ Hz), −11.05 (Ir−H, dm, 1H, $^{2}J_{\mathit{trans}\mathrm{P-H}} = 125.0$ Hz). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (−40 °C; $\mathrm{CD_2Cl_2}$, 100.5 MHz): δ 194.0 (Rh-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 68.0$ Hz), 181.7 (Ir-CO, bs, 1C), 44.5 ($\mathrm{CH_2}$, m, 1C), 48.3 ($\mathrm{CH_2}$, m, 1C), 26.1 (*o*-$\mathrm{CH_3}$, s, 2C), 20.1 (*p*-$\mathrm{CH_3}$, s, 1C). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (−40 °C; $\mathrm{CD_2Cl_2}$, 78.5 MHz, DEPT): δ 110.4 (dt, $^{1}J_{\mathrm{Si\text{-}Rh}} = 30.0$ Hz, $^{2}J_{\mathrm{Si-P}} = 67.0$ Hz).

(d). [RhIr(CO)₂(μ-SiHPh)(μ-CO)(dppm)₂] (6). In an NMR tube, $[\mathrm{RhIr(H)_2(CO)_2}(\mu\text{-}\mathrm{SiHPh})\mathrm{(dppm)_2}]$ (**4**; 30 mg, 0.024 mmol) was dissolved in 0.7 mL of $\mathrm{C_6D_6}$, and the tube was pressurized to 1 atm with CO followed by heating the reaction tube at 60 °C for 2 h. Compound **6** appeared in approximately 10% yield according to $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. During the course of this reaction, some portion of **4** was also converted to $[\mathrm{RhIr(CO)_3}(\mu\text{-}\mathrm{dppm})_2]$ (**1**) in approximately 5% yield, as confirmed by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR, while 85% of compound **4** remained unconverted in the mixture. Complex **6** also appeared in approximately the same quantity when the reaction was carried out for longer times (up to 24 h) at room temperature. An attempt to isolate complex **6**, by the addition of pentane to the concentrated benzene solution of the abovementioned mixture, failed, presumably due to its low concentration. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (27 °C; $\mathrm{CD_2Cl_2}$, 202.1 MHz): δ 43.9 ($\mathrm{P_A}$, 1P, ddd, $^{1}J_{\mathrm{RhP(A)}} = 109$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 240$ Hz, $^{2}J_{\mathrm{P(A)P(C)}} = 29$ Hz), 23.4 ($\mathrm{P_C}$, 1P, ddd, $^{1}J_{\mathrm{RhP}} = 109$ Hz, $^{2}J_{\mathrm{P(C)P(D)}} = 142$ Hz, $^{2}J_{\mathrm{P(A)P(C)}} = 29$ Hz), 8.1 ($\mathrm{P_B}$, 1P, dd, $^{2}J_{\mathrm{P(B)P(D)}} = 20$ Hz), −8.2 ($\mathrm{P_D}$, 1P, dd). $^{1}\mathrm{H}$ NMR (27 °C; $\mathrm{CD_2Cl_2}$, 498.1 MHz): δ 4.73 ($\mathrm{CH_2}$, m, 1H), 4.35 ($\mathrm{CH_2}$, m, 1H), 3.50 ($\mathrm{CH_2}$, m, 1H), 2.48 ($\mathrm{CH_2}$, m, 1H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (27 °C; $\mathrm{CD_2Cl_2}$, 100.5 MHz): δ 229.2 (μ-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 31.9$ Hz), 199.9 (Rh-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 78.8$ Hz), 183.4 (bs, 1C).

(e). [RhIr(CO)₃(κ¹-dppm)(μ-SiHPh)₂(dppm)] (7). Method 1. In an NMR tube, under an Ar atmosphere, $[\mathrm{RhIr(H)_2(CO)_2}(\mu\text{-}\mathrm{SiHPh})\mathrm{(dppm)_2}]$ (**4**) (30 mg, 0.024 mmol) was dissolved in 0.7 mL of $\mathrm{CD_2Cl_2}$. The tube was then evacuated and filled to a pressure of 1 atm with CO. A total of 3.0 μL (1 equivalent) of $\mathrm{PhSiH_3}$ was added via a microliter syringe to the NMR tube. After 18 h, complex **7** formed almost quantitatively (97%) according to $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. During that time, the color of the solution changed from golden yellow to lemon yellow. The transfer of complex **7** from the NMR tube to a 100 mL Schlenk flask and the subsequent addition of 5 mL of pentane resulted in the precipitation of a light yellow solid. However, attempts to remove the solvent either under high vacuum conditions or an Ar flow resulted in the conversion of **7** to [RhIr(CO)$_2$(μ-SiHPh)$_2$(dppm)$_2$] (**8a**) in variable amounts (up to 20%) while still retaining some solvent. As a result, satisfactory microanalytical analysis could not be obtained for this complex. Under the conditions noted above, the reaction of compound **4** with PhSiD$_3$ and CO resulted in deuterium scrambling in the product, [RhIr(CO)$_3$(κ^1-dppm)(μ-SiH(D)Ph)$_2$(dppm)] (**7$_\mathbf{d}$**).

Method 2. The reaction of **1** with 2 equiv of PhSiH$_3$ at ambient temperature in a well-sealed NMR tube yielded **7** (NMR yield, 70%) and **8a** (NMR yield, 30%) after 24 h. ^{31}P{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 202.1 MHz): δ 15.6 (P$_A$, 1P, ddd, $^1J_{\mathrm{RhP(A)}}$ = 105 Hz, $^2J_{\mathrm{P(A)P(B)}}$ = 108 Hz, $^3J_{\mathrm{P(A)P(D)}}$ = 5 Hz), 3.4 (P$_D$, 1P, dddd, $^2J_{\mathrm{P(C)P(D)}}$ = 41 Hz, $^3J_{\mathrm{RhP(D)}}$ = 6 Hz, $^2J_{\mathrm{P(B)P(D)}}$ = 13 Hz), −10.5 (P$_B$, 1P, ddd, $^4J_{\mathrm{P(B)P(C)}}$ = 4 Hz), −24.5 (P$_C$, 1P, dd). ^{1}H NMR (27 °C; CD$_2$Cl$_2$, 399.8 MHz): δ 6.20 (Si−H, dd, 1H, $^1J_{\mathrm{Si-H}}$ = 190.0 Hz, $^3J_{\mathrm{P(D)H}}$ = 24.0 Hz, $^3J_{\mathrm{P(A)H}}$ = 19.0 Hz), 5.80 (Si−H, dd, 1H, $^1J_{\mathrm{Si-H}}$ = 190.0 Hz, $^3J_{\mathrm{P(D)H}}$ = $^3J_{\mathrm{P(A)H}}$ = 5.3 Hz), 4.21 (CH$_2$, m, 1H), 3.73 (CH$_2$, m, 1H), 3.10 (CH$_2$, m, 1H), 2.80 (CH$_2$, m, 1H). ^{2}H{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 61.4 MHz): δ 6.24 (b, Si-D, 1D), 5.75 (b, Si-D, 1D). ^{13}C{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 100.5 MHz): δ 198.0 (Rh-CO, dd, 1C, $^1J_{\mathrm{RhC}}$ = 57.0 Hz, $^2J_{\mathrm{PC}}$ = 10.0 Hz), 195.0 (Rh-CO, dd, 1C, $^1J_{\mathrm{RhC}}$ = 75.0 Hz, $^2J_{\mathrm{PC}}$ = 22.0 Hz), 186.0 (Ir-CO, bs, 1C), 37.6 (CH$_2$, m, 1C), 34.2 (CH$_2$, m, 1C). ^{29}Si{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 78.5 MHz, DEPT, gHSQC): δ 101.8 (m), 136.6 (m).

(f). [RhIr(CO)$_2$(μ-SiHPh)$_2$(dppm)$_2$] (8a). A total of 50 mg (0.041 mmol) of [RhIr(H)$_2$(CO)$_2$(μ-SiHPh)(dppm)$_2$] (**4**) in a Schlenk tube was dissolved in 5 mL of CH$_2$Cl$_2$. A total of 5.5 μL (0.044 mmol) of PhSiH$_3$ was dissolved in 1 mL of CH$_2$Cl$_2$ in another flask and slowly transferred via cannula to the Schlenk flask containing the solution of **4**. Leaving the solution at ambient temperature for 24 h resulted in lightening of the yellow color. Removal of the solvent under vacuum conditions, redissolving in 2 mL of CH$_2$Cl$_2$, and subsequent slow addition of pentane yielded a pale yellow precipitate of **8a**. Yield: 33 mg (56%). Anal. Calcd. for C$_{64}$H$_{56}$IrO$_2$P$_4$RhSi$_2$: C, 57.66; H, 4.20. Found: C, 57.90; H, 4.35. Under the conditions noted above, the reaction of compound **4** with PhSiD$_3$ resulted in deuterium scrambling in both silylene groups, yielding [RhIr(CO)$_2$(μ-SiH(D)Ph)$_2$(dppm)$_2$] (**8a$_\mathbf{d}$**). ^{31}P{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 202.1 MHz): δ 29.3 (P$_A$, 1P, ddd, $^1J_{\mathrm{RhP}}$ = 104 Hz, $^2J_{\mathrm{P(A)P(B)}}$ = 108 Hz, $^2J_{\mathrm{P(A)P(C)}}$ = 33 Hz), 21.5 (P$_C$, 1P, ddd, $^1J_{\mathrm{RhP}}$ = 105 Hz, $^2J_{\mathrm{P(C)P(D)}}$ = 139 Hz), 2.6 (P$_B$, 1P, dd, $^2J_{\mathrm{P(B)P(D)}}$ = 25 Hz), −7.8 (P$_D$, 1P, dd). ^{1}H NMR (27 °C; CD$_2$Cl$_2$, 399.8 MHz): δ 5.66 (Si−H, ddm, 1H, $^1J_{\mathrm{Si-H}}$ = 180.0 Hz, $^3J_{\mathrm{PH}}$ = 32.0 Hz, $^3J_{\mathrm{HH}}$ = 2.3 Hz), 5.52 (Si−H, dm, 1H, $^1J_{\mathrm{Si-H}}$ = 180.0 Hz, $^3J_{\mathrm{HH}}$ = 2.3 Hz), 5.27 (CH$_2$, m, 1H), 4.62 (CH$_2$, m, 1H), 3.10 (CH$_2$, m, 1H), 2.95 (CH$_2$, m, 1H). ^{13}C{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 100.5 MHz): δ 198.9 (Rh-CO, dm, 1C, $^1J_{\mathrm{RhC}}$ = 73.6 Hz), 186.6 (Ir-CO, bs, 1C), 39.3 (CH$_2$, dd, 1C, $^1J_{\mathrm{PC}}$ = 34.7 and 23.2 Hz), 37.1 (CH$_2$, dd, 1C, $^1J_{\mathrm{PC}}$ = 30.5 and 21.8 Hz). ^{29}Si{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 78.5 MHz, DEPT, gHSQC): δ 129.2 (m), 113.9 (m).

(g). [RhIr(CO)$_2$(μ-SiHPh)$_2$(dppm)$_2$] (8b). Method 1. Under an atmosphere of Ar, 70 mg (0.061 mmol) of [RhIr(CO)$_3$(dppm)$_2$] (**1**) in a 100 mL Schlenk tube was dissolved in 10 mL of benzene. A total of 30 μL (0.24 mmol, 4 equiv) of phenylsilane dissolved in 0.5 mL of benzene in a 10 mL Schlenk tube was slowly transferred to the 100 mL Schlenk tube. The reaction was set in an oil bath at 60 °C for 24 h. Within 3 h, the solution became cloudy, and the product began to precipitate. After 24 h, the yellow supernatant was removed through a cannula, and the white precipitate was washed with pentane and recrystallized from CH$_2$Cl$_2$/pentane. Yield: 35 mg (43%). Anal. Calcd for C$_{64}$H$_{56}$IrO$_2$P$_4$RhSi$_2$: C, 57.66; H, 4.20. Found: C, 57.81; H, 4.15.

Method 2: Under the conditions noted above, **8b** can also be prepared by the reaction of **8a** (50 mg, 0.038 mmol) with PhSiH$_3$ (4.7 μL, 0.038 mmol). When **8a** (50 mg, 0.038 mmol) was reacted with PhSiD$_3$ under similar reaction conditions, deuterium was found to be scrambled over both silylene groups of **8b** to give **8b$_\mathbf{d}$**. ^{31}P{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 161.9 MHz): δ 28.6 (P$_A$P$_{A'}$, 2P, dm, $^1J_{\mathrm{RhP}}$ = 105 Hz), 0.3 (P$_B$P$_{B'}$, 2P, m). ^{1}H NMR (27 °C; CD$_2$Cl$_2$, 399.8 MHz): δ 6.00 (Si−H, m, 2H, $^1J_{\mathrm{Si-H}}$ = 180.0 Hz), 5.20 (CH$_2$, m, 2H), 3.30 (CH$_2$, m, 2H). ^{2}H{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 61.4 MHz): δ 6.05 (b, Si-D). ^{13}C{^{1}H} NMR (27 °C; CD$_2$Cl$_2$ 100.5 MHz): δ 200.0 (Rh-CO, dm, 1C, $^1J_{\mathrm{RhC}}$ = 75.0 Hz), 187.0 (Ir-CO, bs, 1C), 43.5 (CH$_2$, m, 2C). ^{29}Si{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 79.5 MHz, DEPT): δ 127.0 (m). IR: ν_{SiH} = 2197 cm^{-1}, ν_{CO} = 1945 cm^{-1}, 1928 cm^{-1}.

(h). [RhIr(CO)$_2$(μ-SiHC$_6$H$_3$F$_2$)$_2$(dppm)$_2$] (8c). Under Ar, 50 mg (0.044 mmol) of [RhIr(CO)$_3$(dppm)$_2$] (**1**) in a 50 mL Schlenk tube was dissolved in 5 mL of benzene. A total of 29 μL (0.176 mmol, 4 equiv) of 3,5-difluorophenylsilane dissolved in 0.5 mL of benzene in a 10 mL Schlenk tube was slowly transferred to the 50 mL Schlenk tube. The reaction was set in an oil bath at 60 °C for 24 h. Colorless crystals were separated from the reaction mixture by removing the solvent via a cannula, and these were recrystallized from CH$_2$Cl$_2$/ether. Yield: 29 mg (47%). Anal. Calcd for C$_{64}$H$_{52}$F$_4$IrO$_2$P$_4$RhSi$_2$: C, 54.69; H, 3.70. Found: C, 54.85; H, 3.73. ^{31}P{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 161.9 MHz): δ 28.0 (P$_A$P$_{A'}$, 2P, dm, $^1J_{\mathrm{RhP}}$ = 108 Hz), 0.3 (P$_B$P$_{B'}$, 2P, m). ^{1}H NMR (27 °C; CD$_2$Cl$_2$, 399.8 MHz): δ 5.82 (Si−H, m, 2H, $^1J_{\mathrm{Si-H}}$ = 180.0 Hz), 5.25 (CH$_2$, m, 2H), 3.26 (CH$_2$, m, 2H). ^{13}C{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 100.5 MHz): δ 199.0 (Rh-CO, 1C, dm, $^1J_{\mathrm{RhC}}$ = 70.0 Hz), 187.0 (Ir-CO, 1C, bs), 43.8 (CH$_2$, m, 2C). ^{29}Si{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 79.5 MHz, DEPT): δ 125.0 (m). ^{19}F NMR (27 °C; CD$_2$Cl$_2$, 376.1 MHz): δ −113.5 (m).

(i). [RhIr(CO)$_2$(μ-SiHPh)(μ-SiHC$_6$H$_3$F$_2$)(dppm)$_2$] (8d). Method 1. Under an atmosphere of Ar, 50 mg (0.041 mmol) of [RhIr(H)$_2$(CO)$_2$(μ-SiHPh)(dppm)$_2$] (**4**) in an NMR tube was dissolved in 0.7 mL of C$_6$D$_6$. A total of 13.0 μL (0.082 mmol, 2 equiv) of 3,5-difluorophenylsilane was added to the NMR tube via a microlitre syringe. The tube was set in an oil bath at 60 °C for 24 h under a dynamic Ar atmosphere, during which time a white precipitate formed. The precipitated product (**8d**) was separated from the reaction mixture by removing solvent via cannula and was recrystallized from CH$_2$Cl$_2$/pentane. Yield: 25 mg (45%). Anal. Calcd for C$_{64}$H$_{54}$F$_2$IrO$_2$P$_4$RhSi$_2$: C, 56.13; H, 3.95. Found: C, 56.37; H, 3.98.

Method 2: Under similar conditions to those noted above, 20 mg (0.022 mmol) of [RhIr(CO)$_2$(μ-SiHPh)$_2$(dppm)$_2$] (**8a**) was reacted with 7.8 μL (0.044 mmol, 2 equiv) of 3,5-difluorophenylsilane. Multinuclear NMR analysis confirmed the complete conversion of **8a** to a mixture of **8b** (NMR yield, 50%), **8c** (NMR yield, 16.7%), and **8d** (NMR yield, 33.3%). ^{31}P{^{1}H} NMR for **8d** (27 °C; CD$_2$Cl$_2$, 201.6 MHz): δ 27.6 (P$_A$, 1P, dm, $^1J_{\mathrm{RhP}}$ = 107 Hz), 26.2 (P$_C$, 1P, dm, $^1J_{\mathrm{RhP}}$ = 105 Hz), −1.1 (P$_B$, 1P, m), −1.6 (P$_D$, 1P, m). ^{1}H NMR for **8d** (27 °C; CD$_2$Cl$_2$, 498.1 MHz): δ 5.95 (Si−H, m, 1H, $^1J_{\mathrm{Si-H}}$ = 180.0 Hz), 5.82 (Si−H, m, 1H, $^1J_{\mathrm{Si-H}}$ = 180.0 Hz), 5.26 (CH$_2$, m, 1H), 5.28 (CH$_2$, m, 1H), 3.28 (CH$_2$, m, 1H), 3.25 (CH$_2$, m, 1H). ^{13}C{^{1}H} NMR for **8d** (27 °C; CD$_2$Cl$_2$, 100.5 MHz): δ 199.5 (Rh−CO, dm, 1C, $^1J_{\mathrm{RhC}}$ = 70.0 Hz), 187.0 (Ir-CO, bs, 1C), 43.5 (CH$_2$, m, 1C), 43.1 (CH$_2$, m, 1C). ^{29}Si{^{1}H} NMR for **8d** (27 °C; CD$_2$Cl$_2$, 79.5 MHz, DEPT): δ 126.3 (m), 125.2 (m). ^{19}F NMR for **8d** (27 °C; CD$_2$Cl$_2$, 376.1 MHz): δ −111.9 (m).

(j). [RhIr(H)$_2$(CO)$_2$(μ-SiPh$_2$)(dppm)$_2$] (9). Under an Ar atmosphere, 50 mg of [RhIr(CO)$_3$(μ-dppm)$_2$] (**1**) (0.044 mmol) in a Schlenk tube was dissolved in 4 mL of benzene. A total of 12.2 μL (1.5 equiv) of Ph$_2$SiH$_2$ was added by syringe to the vigorously stirred solution of **1**, and the reaction was left for 6 h. During this time, the color of the solution lightened, accompanied by the formation of a pale yellow solid. The solvent was evaporated under vacuum conditions, and the residue was redissolved in 2 mL of C$_6$D$_6$. The slow addition of 6 mL of pentane resulted in the precipitation of complex **9** in 69% (40 mg) yield. Anal. Calcd for C$_{64}$H$_{56}$IrO$_2$P$_4$RhSi: C, 58.88; H, 4.29. Found: C, 59.19; H, 4.35. ^{31}P{^{1}H} NMR (27 °C; CD$_2$Cl$_2$, 161.9 MHz): δ 21.5 (bm), −11.7 (bm). ^{1}H (CD$_2$Cl$_2$, 399.8 MHz): δ 4.83 (CH$_2$, m, 2H), 3.14 (CH$_2$, m, 2H), −9.73 (bm), −11.50 (bm, 1H). ^{13}C{^{1}H} (CD$_2$Cl$_2$, 100.5 MHz): δ 198.7 (Rh-CO, dt, 1C, $^1J_{\mathrm{RhC}}$ = 69.0 Hz, $^2J_{\mathrm{PC}}$ = 9.0 Hz), 182.9 (Ir-CO, t, 1C, $^2J_{\mathrm{PC}}$ = 10.0 Hz), 50.2 (CH$_2$, m, 1C), 45.8 (CH$_2$, m, 1C). ^{31}P{^{1}H} NMR (−78 °C; CD$_2$Cl$_2$, 161.9 MHz): δ 24.3 (P$_A$, 1P, ddd,

$^{1}J_{\mathrm{RhP(A)}} = 101$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 132$ Hz, $^{2}J_{\mathrm{P(A)P(C)}} = 10$ Hz), 15.4 (P_C, 1P, ddd, $^{1}J_{\mathrm{RhP(C)}} = 105$ Hz, $^{2}J_{\mathrm{P(C)P(D)}} = 130$ Hz), −5.8 (P_B, 1P, dd, $^{2}J_{\mathrm{P(B)P(D)}} = 8$ Hz),−19.5 (P_D, 1P, dd). ^{1}H NMR (−78 °C; CD_2Cl_2, 399.8 MHz): δ 5.35 (CH_2, m, 1H), 4.94 (CH_2, m, 1H), 3.13 (CH_2, bm, 1H), 2.94 (CH_2, m, 1H), −9.76 (Rh−H, ddd, 1H, $^{1}J_{\mathrm{Rh-H}} = 15.0$ Hz, $^{2}J_{trans\mathrm{P-H}} = 120.0$ Hz, $^{2}J_{cis\mathrm{P-H}} = 14.0$ Hz), −11.09 (Ir−H, dd, 1H, $^{2}J_{trans\mathrm{P-H}} = 114.0$ Hz, $^{2}J_{cis\mathrm{P-H}} = 14.0$ Hz). IR: $\nu_{\mathrm{CO}} = 1980$ cm^{-1}, 1937 cm^{-1}.

(k). [RhIr(CO)$_4$(κ^1-dppm)(μ-SiHPh)(dppm)](10) and [RhIr(CO)$_2$(μ-CO)(μ-SiHPh)(dppm)$_2$] (11). A total of 20 mg of [RhIr(H)$_2$(CO)$_2$(μ-SiPh$_2$)(dppm)$_2$] (**9**) was dissolved in 0.5 mL of CD_2Cl_2 in an NMR tube and pressurized with CO (1.0 atm). After 18 h, the ^{31}P{^{1}H} NMR spectrum showed the presence of tetracarbonyl species, **10**, in about 75% yield, together with [RhIr(CO)$_3$(dppm)$_2$] (**1**) generated in 25% yield from **9** by the loss of silane. The reaction mixture was then transferred to a 10 mL Schlenk flask, and the solvent was removed under high vacuum conditions. The deep orange residue was redissolved in 0.7 mL of CD_2Cl_2, and the NMR analysis of this mixture indicated the formation of tricarbonyl silylene species, **11**, in approximately 10% yield (according to NMR), leaving the solution as a mixture of **1**, **10**, and **11** in a 2.5:1:6.5 ratio. The addition of CO to **11** generates **10**. Attempts to isolate analytically pure samples of **10** and **11** failed. ^{31}P{^{1}H} NMR for **10** (27 °C; CD_2Cl_2, 161.9 MHz): δ 18.1 (P_A, 1P, ddd, $^{1}J_{\mathrm{RhP(A)}} = 101$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 125$ Hz, $^{3}J_{\mathrm{P(A)P(D)}} = 5$ Hz), −10.3 (P_D, 1P, dddd, $^{2}J_{\mathrm{P(C)P(D)}} = 40$ Hz, $^{2}J_{\mathrm{RhP(D)}} = 12$ Hz), −10.4 (P_B, 1P, ddd, $^{2}J_{\mathrm{P(B)P(D)}} = 6$ Hz, $^{4}J_{\mathrm{P(B)P(C)}} = 5$ Hz), −26.2 (P_C, 1P, dd). ^{1}H NMR for **10** (27 °C; CD_2Cl_2, 399.8 MHz): δ 3.17 (CH_2, m, 2H), 2.84 (CH_2, m, 2H). ^{13}C{^{1}H} NMR for **10** (27 °C; CD_2Cl_2, 100.5 MHz): δ 212.4 (semibridging CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 5.6$ Hz), 201.7 (Rh-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 71.8$ Hz), 201.6 (Rh-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 73.6$ Hz), 185.3 (Ir-CO, bs, 1C), 60.3 (CH_2, m, 1C), 37.9 (CH_2, m, 1C).

^{31}P{^{1}H} NMR for **11** (27 °C; CD_2Cl_2, 161.9 MHz): δ 37.8 (P_A, 1P, ddd, $^{1}J_{\mathrm{RhP(A)}} = 107$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 255$ Hz, $^{2}J_{\mathrm{P(A)P(C)}} = 30$ Hz), 27.5 (P_C, 1P, ddd, $^{1}J_{\mathrm{RhP(C)}} = 98$ Hz, $^{2}J_{\mathrm{P(C)P(D)}} = 156$ Hz), 1.5 (P_B, 1P, dd, $^{2}J_{\mathrm{P(B)P(D)}} = 22$ Hz), −5.3 (P_D, 1P, dd). ^{1}H NMR NMR (27 °C; CD_2Cl_2, 399.8 MHz): δ 4.37 (CH_2, m, 1H), 3.98 (CH_2, m, 1H), 2.66 (CH_2, m, 1H), 2.32 (CH_2, m, 1H). ^{13}C{^{1}H} NMR for **11** (27 °C; CD_2Cl_2, 100.5 MHz): δ 227.6 (μ-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 40.7$ Hz), 201.3 (Rh-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 70.0$ Hz), 186.0 (Ir-CO, bs, 1C).

(l). [RhIr(H)(SiPh$_2$H)(CO)$_3$(κ^1-dppm)(μ-SiPh$_2$)(dppm)] (12). Method 1. A total of 30 mg of [RhIr(H)$_2$(CO)$_2$(μ-SiPh$_2$)(dppm)$_2$] (**9**; 0.023 mmol) in a Schlenk tube was dissolved in 4 mL of benzene, and the tube was pressurized with 1 atm of CO followed by the addition of 4.25 μL (1 equiv) of Ph_2SiH_2. The reaction flask was sealed and left for 24 h, after which the solvent was removed under high vacuum conditions, and the solid redissolved in 1 mL of benzene. The slow addition of pentane resulted in the formation of a lemon yellow precipitate, which was again recrystallized from the benzene/pentane to give analytically pure compound **12**.

Method 2. In a Schlenk tube, 200 mg of [RhIr(CO)$_3$(dppm)$_2$] (**1**; 0.174 mmol) was dissolved in 10 mL of benzene. Three freeze−pump−thaw cycles were applied to the solution, followed by the addition of 128 μL (4 equiv) of Ph_2SiH_2. The reaction was stirred for 48 h in the sealed Schlenk tube. The solution was concentrated to 2 mL and layered with pentane. After 24 h, orange crystals were separated by the removal of solvent. Yield: 202 mg (76.8%). Anal. Calcd for $C_{77}H_{66}IrO_3P_4RhSi_2 \cdot 1.5C_6H_6$: C, 63.25; H, 4.59. Found: C, 63.16; H, 4.60. Under the conditions noted in method 1, the reaction of compound **9** with $PhSiD_3$ resulted in deuterium scrambling in the silyl and hydride positions of **12** to give **12$_{\mathbf{d}}$**. ^{31}P{^{1}H} NMR (27 °C; CD_2Cl_2, 161.9 MHz): δ 3.1 (P_A, 1P, ddd, $^{1}J_{\mathrm{RhP(A)}} = 94$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 103$ Hz, $^{3}J_{\mathrm{P(A)P(D)}} = 6$ Hz), −2.5 (P_D, 1P, dddd, $^{2}J_{\mathrm{P(C)P(D)}} = 36$ Hz, $^{3}J_{\mathrm{RhP(D)}} = 5$ Hz), −9.5 (P_B, 1P, ddd, $^{2}J_{\mathrm{P(B)P(D)}} = 9$ Hz, $^{4}J_{\mathrm{P(B)P(C)}} = 8$ Hz), −27.9 (P_C, 1P, dd). ^{1}H NMR (27 °C; CD_2Cl_2, 399.8 MHz): δ 5.45 (CH_2, m, 1H), 5.30 (Si−H, d, 1H, $^{1}J_{\mathrm{Si-H}} = 180$ Hz $^{3}J_{\mathrm{PH}} = 7.1$ Hz), 3.80 (CH_2, m, 1H), 3.20 (CH_2, m, 1H), 2.70 (CH_2, m, 1H), −10.50 (Ir−H, dd, 1H, $^{2}J_{\mathrm{PH}} = 19.1$ Hz, $^{2}J_{\mathrm{PH}} = 15.0$ Hz). ^{2}H{^{1}H} NMR (27 °C; CD_2Cl_2, 61.4 MHz): δ 5.29 (b, Si-D, 1D), −10.44 (b, Si-D, 1D). ^{13}C{^{1}H} (CD_2Cl_2, 100.5 MHz): δ 203.9 (Rh-CO, ddd, 1C, $^{1}J_{\mathrm{RhC}} = 55.8$ Hz, $^{2}J_{\mathrm{PC}} = 24.1$ Hz, $^{3}J_{\mathrm{PC}} = 8.6$ Hz, $^{2}J_{\mathrm{CC}}* = 29.1$ Hz), 199.8 (Rh-CO, ddd, 1C, $^{1}J_{\mathrm{RhC}} = 55.6$ Hz, $^{2}J_{\mathrm{PC}} = 22.3$ Hz, $^{3}J_{\mathrm{PC}} = 9.4$ Hz), 186.1 (Ir-CO, bs, 1C), 59.2 (CH_2, m, 1C), 37.3 (CH_2, m, 1C). ^{29}Si{^{1}H} NMR (27 °C; CD_2Cl_2, 78.5 MHz, DEPT, gHSQC): δ −2.3 (dd, $^{1}J_{\mathrm{Rh-Si}} = 18.0$ Hz, $^{2}J_{\mathrm{P-Si}} = 18.0$ Hz), 146.0. IR: $\nu_{\mathrm{SiH}} = 2077$ cm^{-1}, $\nu_{\mathrm{CO}} = 2032$, 1943, 1972 cm^{-1}.

(m). [RhIr(H)(SiMe$_2$H)(CO)$_3$(κ^1-dppm)(μ-SiMe$_2$)(dppm)] (13). A static atmosphere of dimethylsilane was placed over a solution of [RhIr(CO)$_3$(dppm)$_2$] (**1**; 40 mg, 0.035 mmol in 3 mL of CH_2Cl_2), and the reaction mixture was stirred for 1 h. The addition of 10 mL of pentane caused the precipitation of a dull orange powdery solid which was washed twice with 5 mL portions of pentane and dried under Ar (44 mg, 88%). Anal. Calcd for $C_{57}H_{58}IrO_3P_4RhSi_2$: C, 53.96; H, 4.57. Found C, 53.84; H, 4.24. ^{31}P{^{1}H} NMR (27 °C; CD_2Cl_2, 161.9 MHz): δ 6.6 (P_A, 1P, ddd, $^{1}J_{\mathrm{RhP(A)}} = 100$ Hz, $^{2}J_{\mathrm{P(A)P(B)}} = 111$ Hz, $^{3}J_{\mathrm{P(A)P(D)}} = 6$ Hz), 0.1 (P_D, 1P, dddd, $^{2}J_{\mathrm{P(C)P(D)}} = 50$ Hz, $^{3}J_{\mathrm{RhP(D)}} = 5$ Hz), −9.9 (P_B, 1P, ddd, $^{2}J_{\mathrm{P(B)P(D)}} = 9$ Hz, $^{4}J_{\mathrm{P(B)P(C)}} = 6$ Hz), −26.7 (P_C, 1P, dd). ^{1}H NMR (27 °C; CD_2Cl_2, 399.8 MHz): δ 4.84 (CH_2, m, 1H), 4.40 (CH_2, m, 1H), 4.20 (Si−H, d, 1H, $^{3}J_{\mathrm{PH}} = 7.9$ Hz), 2.92 (CH_2, m, 2H), 0.84 (CH_3, m, 3H), 0.75 (CH_3, m, 3H), 0.24 (CH_3, m, 3H), 0.17 (CH_3, m, 3H), −11.20 (Ir−H, dd, 1H, $^{2}J_{\mathrm{P-H}} = 15.0$ Hz, $^{2}J_{\mathrm{P-H}} = 14.0$ Hz). ^{13}C{^{1}H} NMR (27 °C; CD_2Cl_2, 100.5 MHz): δ 204.5 (Rh-CO, ddd, 1C, $^{1}J_{\mathrm{RhC}} = 55.0$ Hz, $^{2}J_{\mathrm{PC}} = 19.1$ Hz, $^{3}J_{\mathrm{PC}} = 6.3$ Hz, $^{2}J_{\mathrm{CC}}* = 22.3$ Hz), 203.4 (Rh-CO, ddd, 1C, $^{1}J_{\mathrm{RhC}} = 55.0$ Hz, $^{2}J_{\mathrm{PC}} = 19.0$ Hz, $^{3}J_{\mathrm{PC}} = 8.9$ Hz), 187.4 (Ir-CO, bs, 1C). IR: $\nu_{\mathrm{CO}} = 1999$, 1977 cm^{-1}.

(n). [RhIr(CH$_3$)(SiHPh$_2$)(CO)(μ-H)(μ-CO)(dppm)$_2$][CF$_3$SO$_3$] (14). Under Ar, 28 mg (0.022 mmol) of [RhIr(CH$_3$)(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] (**2**) was taken into an NMR tube, dissolved in 0.7 mL of CD_2Cl_2, and cooled to −78 °C in an acetone−dry ice bath. A total of 4.1 μL (0.022 mmol) of diphenylsilane was added using a microliter syringe, and the reaction was observed by low-temperature NMR. Immediately after the addition of diphenylsilane, the dark orange color of the solution lightened. Between −80 and −60 °C, NMR analysis indicates the formation of [RhIr(CH$_3$)(SiHPh$_2$)(CO)(μ-H)(μ-CO)(μ-dppm)$_2$][CF$_3$SO$_3$] (**14**) as the major product (95%) in the solution. No attempts were made to isolate this product at this temperature. ^{13}C-enriched compound **14** was prepared under similar conditions to those noted above, by reacting ^{13}C-enriched [RhIr(^{13}CH$_3$)(^{13}CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] (**2**) with Ph_2SiH_2. ^{31}P{^{1}H} NMR (−78 °C; CD_2Cl_2, 161.9 MHz): δ 29.0 (P_AP_C, 2P, dm, $^{1}J_{\mathrm{RhP}} = 140$ Hz), −6.1 (P_B, br, 1P), −8.6 (P_D, br, 1P). ^{1}H NMR (−78 °C; CD_2Cl_2, 399.8 MHz): δ 5.50 (Si−H, td, 1H, $^{1}J_{\mathrm{SiH}} = 170.0$ Hz, $^{3}J_{\mathrm{PH}} = 13.5$ Hz, $^{3}J_{\mathrm{HH}} = 2.0$ Hz), 4.12 (CH_2, m, 2H), 3.59 (CH_2, m, 2H), 0.49 (CH_3, t, 3H, $^{3}J_{\mathrm{P-H}} = 6.9$ Hz), −8.44 (μ-H, ddm, 1H, $^{1}J_{\mathrm{RhH}} = 13.8$ Hz, $^{3}J_{\mathrm{HH}} = 2.0$ Hz, $^{2}J_{\mathrm{CH}(trans)}* = 24.0$ Hz). ^{13}C{^{1}H} NMR (−78 °C; CD_2Cl_2, 100.5 MHz): δ 216.6 (Rh-CO, dm, 1C, $^{1}J_{\mathrm{RhC}} = 31.2$ Hz), 173.8 (Ir-CO, t, 1C, $^{2}J_{\mathrm{PC}} = 9.8$ Hz, $^{2}J_{\mathrm{CH}(trans)}* = 24.0$ Hz), 14.8 (CH_3, dt, 1C, $^{1}J_{\mathrm{RhC}} = 29.0$ Hz, $^{2}J_{\mathrm{PC}} = 6.0$ Hz). ^{29}Si{^{1}H} NMR (−78 °C; CD_2Cl_2, 79.5 MHz, DEPT, gHSQC): δ −25.7 (t, $^{2}J_{\mathrm{Si-P}} = 10.0$ Hz).

(o). [RhIr(CH$_3$)(CO)$_2$(μ-H)(η^1:η^2-SiHPh$_2$)(dppm)$_2$][CF$_3$SO$_3$] (15). Method 1. As the solution of **14**, as discussed above, warmed to −20 °C, the color of the solution turned yellow from light orange. ^{31}P{^{1}H} NMR spectroscopy showed that compound **15** was formed in 83% yield, with 17% of **14** still present in the solution.

Method 2. A total of 40 mg of [RhIr(CH$_3$)(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] (**2**) in a Schlenk tube was dissolved in 2 mL of CH_2Cl_2, and the reaction was carried out as described above at −15 °C (ethylene glycol/dry ice bath). The addition of 5 mL of ether precipitated a yellow solid. The solvent was removed by cannula, and the solid was dried under vacuum conditions at 0 °C. The solid was again washed with 1 mL of CH_2Cl_2 at −15 °C, which preferentially removed species **14** (which had precipitated with **15**), leaving **15** as a pure product. The compound was stable at room temperature in the solid state; however, in solution, it decomposed within 30 min.

Yield: 32 mg (70%). Anal. Calcd for $C_{66}H_{59}F_3IrO_5P_4RhSiS$: C, 53.97; H, 4.02; S, 2.18. Found: C, 53.50; H, 3.91; S, 2.19. ^{13}CO- and $^{13}CH_3$-enriched compound **15** was prepared under similar conditions to those noted above, by reacting ^{13}C-enriched $[RhIr(^{13}CH_3)(^{13}CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with Ph_2SiH_2. $^{31}P\{^1H\}$ NMR (−20 °C; CD_2Cl_2, 161.9 MHz): δ 22.7 ($P_AP_{A'}$, 2P, dm, $^1J_{RhP} =$ 100 Hz), −13.4 ($P_BP_{B'}$, 2P, m). ^1H NMR (−20 °C; CD_2Cl_2, 399.8 MHz): δ 4.10 (CH_2, m, 2H), 3.25 (CH_2, m, 2H), 0.73 (t, 3H, $^2J_{PH} =$ 11.0 Hz), −0.65 (μ−Si-H, dddd, 1H, $^1J_{Si-H} =$ 84.0 Hz, $^1J_{RhH} =$ 24.0 Hz, $^2J_{H-H} =$ 6.0 Hz, $^3J_{P(Ir)\text{-}H(Si)} =$ 9.0 Hz, $^3J_{P(Rh)\text{-}H(Si)} =$ 8.0 Hz), −9.2 (μ-H, ddm, 1H, $^1J_{Rh-H} =$ 19.0 Hz, $^2J_{H-H} =$ 6.0 Hz, $^2J_{CH(trans)}{}^* =$ 24.3 Hz). $^{13}C\{^1H\}$ NMR (−20 °C; CD_2Cl_2, 100.5 MHz): δ 193.2 (Rh-CO, dt, 1C, $^1J_{RhC} =$ 78.4 Hz, $^2J_{PC} =$ 15.0 Hz), 178.0 (Ir-CO, bt, 1C, $^2J_{PC} =$ 10.0 Hz, $^2J_{CC}{}^* =$ 2.0 Hz, $^2J_{CH(trans)}{}^* =$ 24.3 Hz), −22.6 (CH_3, bt, 1C, $^2J_{PC} =$ 7.0 Hz). $^{29}Si\{^1H\}$ NMR (−20 °C; CD_2Cl_2, 79.5 MHz, DEPT): δ 6.3 (m).

(p). $[RhIr(H)(COCH_3)(CO)(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2][CF_3SO_3]$ (16) and $[RhIr(H)(CO)_2(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2$ (17). As the CD_2Cl_2 solution of **15**, as discussed above, was warmed to ambient temperature, a mixture of two products, **16** and **17**, was formed at a 1:1 ratio. Both of these complexes slowly decomposed at ambient temperature to unidentified products over 12 h; so attempts to isolate analytically pure samples failed. ^{13}CO- and $^{13}CH_3$-enriched compounds **16** and **17** were prepared under similar conditions to those mentioned above, by reacting ^{13}C-enriched $[RhIr(^{13}CH_3)(^{13}CO)_2(dppm)_2][CF_3SO_3]$ (**2**) with Ph_2SiH_2. $^{31}P\{^1H\}$ NMR for **16** (27 °C; CD_2Cl_2, 161.9 MHz): δ 26.5 ($P_AP_{A'}$, 2P, dm, $^1J_{RhP} =$ 118 Hz), 2.8 ($P_BP_{B'}$, 2P, m). ^1H NMR for **16** (27 °C; CD_2Cl_2, 400 MHz): δ 4.28 (CH_2, m, 2H), 3.49 (CH_2, m, 2H), 1.23 (CH_3CO, s, 3H), −8.86 (Ir−H, t, 1H, $^1J_{Si-H} =$ 32.0 Hz, $^2J_{PH} =$ 13.2 Hz), −14.98 (μ-H, ddd, 1H, $^1J_{RhH} =$ 22.0 Hz, $^2J_{P(Ir)H} =$ 13.2 Hz, $^2J_{P(Rh)H} =$ 10.9 Hz). $^{13}C\{^1H\}$ NMR for **16** (27 °C; CD_2Cl_2, 100.5 MHz): δ 280.0 (CH_3CO, s, $^1J_{CC}{}^* =$ 26.0 Hz), 193.7 (Rh-CO, dt, $^1J_{Rh-C} =$ 70.0 Hz, $^2J_{PC} =$ 9.0 Hz), 46 (CH_3CO, s, $^1J_{CC}{}^* =$ 26.0 Hz). $^{29}Si\{^1H\}$ NMR for **16** (27 °C; CD_2Cl_2, 79.5 MHz, gHSQC): δ 20.0. $^{31}P\{^1H\}$ NMR for **17** (27 °C; CD_2Cl_2, 161.9 MHz): δ 24.3 ($P_AP_{A'}$, 2P, dm, $^1J_{RhP} =$ 105 Hz), 9.9 ($P_BP_{B'}$, 2P, m). ^1H NMR for **17** (27 °C; CD_2Cl_2, 399.8 MHz): δ 4.42 (CH_2, m, 2H), 4.40 (CH_2, m, 2H), −10.22 (μ-H, dm, 1H, $^1J_{RhH} =$ 15.0 Hz). $^{13}C\{^1H\}$ NMR for **17** (27 °C; CD_2Cl_2, 100.5 MHz): δ 187.6 (Rh-CO, dm, 1C, $^1J_{RhC} =$ 77.3 Hz), 176.8 (Ir-CO, bt, 1C, $^2J_{PC} =$ 10.0 Hz).

X-ray Data Collection and Structure Determination. a. General Considerations. Single crystals suitable for X-ray diffraction were obtained either by the slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compounds (**4**, **5**, **8a**, **8c**) or by the diffusion of *n*-pentane into THF (**8b**) or benzene (**12**) solutions. Data were collected on either a Bruker D8/APEX II CCD diffractometer[36] (**4**, **5**, **8a**, **8b**, **8c**) at −100 °C using Mo Kα radiation or on a Siemens P4/RA diffractometer[36] (**12**) at −60 °C using graphite monochromated Cu Kα radiation. Data were corrected for absorption through the use of Gaussian integration from indexing of the crystal faces. The structures were solved using direct methods (*SIR97*[37b] (**4**, **8a**, **8c**), *SHELXS-97*[37d] (**8b**), *SHELXS-86*[37c] (**12**)) or Patterson location of heavy atoms followed by structure expansion (*DIRDIF-2008*[37a]) (**5**). Refinement was completed using the program *SHELXL-97*[37d] (**4**, **5**, **8a**, **8b**, **8c**) or *SHELXL−93*[38] (**12**). Hydrogen atoms attached to carbons were assigned positions on the basis of the sp^2 or sp^3 hybridization geometries of their parent atoms and were given isotropic displacement parameters 20% greater than the U_{eq}'s of their parent carbons. Metal hydrides for **4**, **5**, and **12** and silicon-bound hydrogens for **4**, **5**, **8a**, **8b**, and **8c** were located from difference Fourier maps and treated as detailed below. See the Supporting Information (Table S1 and S2) for a listing of crystallographic experimental data and for selected bond lengths and angles (Tables S3−S7) for all structures. Additional information is given in the CIF file.

b. Special Refinement Conditions. i. Compound 4. Metal atoms were refined with a site occupancy of either $Ir_{0.60}Rh_{0.40}$ or $Ir_{0.40}Rh_{0.60}$. The hydrido ligands were refined with fixed Ir−H or Rh−H distances (1.55 Å) and with isotropic displacement parameters 120% of the U_{eq} for their attached metals. The silyl hydrogens were included with fixed Si−H distances (1.35 Å) and isotropic displacement parameters 120% of the U_{eq} for their attached silicons.

ii. Compound 5. Metal atoms were refined with a site occupancy of either $Ir_{0.80}Rh_{0.20}$ or $Ir_{0.20}Rh_{0.80}$ (molecule A) or with a site occupancy of either $Ir_{0.75}Rh_{0.25}$ or $Ir_{0.25}Rh_{0.75}$ (molecule B). Cl atoms of dichloromethane solvent were refined with an occupancy factor of 0.5. Cl(1S) and C(1S) were refined with common anisotropic displacement parameters (due to these atoms occupying near-inversion-related positions as generated by the crystallographic inversion center ($^1/_2$, 0, $^1/_2$)). The positions and isotropic displacement parameters of the metal hydrides were freely refined. The positions of the silyl hydrogens (H(1SI) and H(2SI)) were freely refined, with these atoms assigned a common isotropic displacement parameter.

iii. Compound 8a. Metal atoms were refined with a site occupancy of either $Ir_{0.55}Rh_{0.45}$ or $Ir_{0.45}Rh_{0.55}$. The carbon atoms of one phenyl group of the silylene bridge were refined as two sets of positions, one set with an occupancy of 0.80 and with anisotropic displacement parameters, the other set with an occupancy of 0.20, fixed C−C bond lengths of 1.39 Å, and a common isotropic displacement parameter. The positions of the silyl hydrogens were freely refined, with these atoms assigned isotropic displacement parameters 120% of the U_{eq} for their attached silicons

iv. Compound 8b. Metal atoms were refined with a site occupancy of either $Ir_{0.60}Rh_{0.40}$ or $Ir_{0.40}Rh_{0.60}$. Disordered phenyl rings were refined with an occupancy of 0.50. The silyl hydrogens were included with fixed Si−H distances (1.40 Å) and isotropic displacement parameters 120% of the U_{eq} for their attached silicons. Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent tetrahydrofuran oxygen or carbon atoms were unsuccessful. The data were corrected for disordered solvent electron density through the use of the SQUEEZE procedure,[39a] as implemented in *PLATON*.[39b,c] A total solvent-accessible void volume of 1150 Å^3 with a total electron count of 350 (consistent with eight molecules of solvent tetrahydrofuran or two molecules per formula unit of the $[RhIr(CO)_2(\mu\text{-}SiHPh)_2(\mu\text{-}dppm)_2]$ molecule) was found in the unit cell.

v. Compound 8c. Metal atoms were refined with a site occupancy of either $Ir_{0.52}Rh_{0.48}$ or $Ir_{0.48}Rh_{0.52}$. The positions and isotropic displacement parameters of the silyl hydrogens were freely refined.

vi. Compound 12. The hydrido ligand was refined with a fixed Ir−H(1) distance (1.65 Å) and with a fixed isotropic displacement parameter.

Results and Compound Characterization

a. Reactions of $[RhIr(CO)_3(dppm)_2]$ with Primary Silanes. i. Monosilylene-Bridged Products. The reaction of $[RhIr(CO)_3(dppm)_2]$ (**1**) with 1 equiv of the primary silanes, $PhSiH_3$ and $MesSiH_3$ (Mes = mesityl), proceeds as shown in

---

(36) Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by (a) Bruker and (b) Siemens.

(37) (a) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M; Garcia-Granda, S.; Gould, R. O. *DIRDIF-2008*; Crystallography Laboratory, Radboud University Nijmegen: The Netherlands, 2008. (b) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119. (c) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473. (d) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(38) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993.

(39) (a) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201. (b) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34. (c) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13. *PLATON*; Utrecht University: Utrecht, The Netherlands.

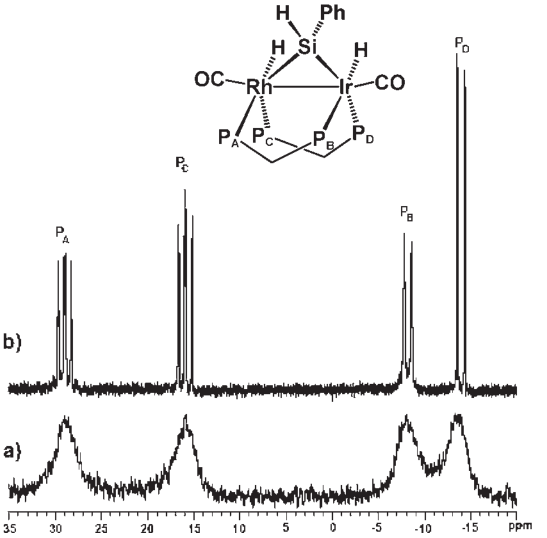
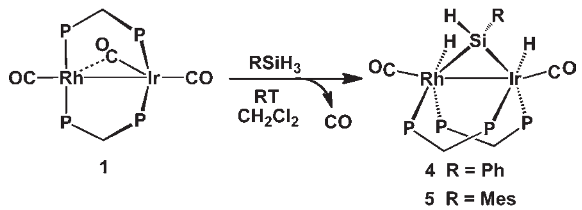


Figure 1. $^{31}P\{^1H\}$ NMR spectra of complex **4** (a) at 20 °C and (b) at −40 °C.

Scheme 1



Scheme 1, to give the silylene-bridged dihydride complexes, $[RhIr(H)_2(CO)_2(\mu\text{-}SiHR)(dppm)_2]$ (R = Ph (**4**) and R = Mes (**5**)), both of which were characterized by multinuclear NMR spectroscopy and X-ray crystallography. The NMR spectra of compounds **4** and **5** are closely comparable, so only those of **4** will be discussed.

At ambient temperature, compound **4** displays four broad unresolved resonances in the $^{31}P\{^1H\}$ NMR spectrum (Figure 1a), while at the same temperature the ^1H NMR spectrum displays the expected resonances for the dppm and silylene aryl groups. The dppm methylene protons of **4** appear as two multiplets at δ 5.30 and 3.10, while the broad silylene proton resonance (*ca.* δ 6.7) is buried beneath the aromatic protons as was confirmed by an HSQC experiment. Both rhodium- and iridium-bound hydride ligands appear as very broad resonances, barely resolved above the baseline, at *ca.* δ −9.6 and −10.9, respectively (Figure 2a). The $^{31}C\{^1H\}$ NMR spectrum at this temperature shows a doublet of triplets at δ 194.1 ($^1J_{RhC}$ = 70 Hz) and a triplet at δ 181.1, attributed to Rh- and Ir-bound carbonyls, respectively. Cooling both samples results in substantial sharpening in both the $^{31}P\{^1H\}$ NMR and ^1H NMR spectra, demonstrating the fluxional nature of these species. Upon cooling to −40 °C, the $^{31}P\{^1H\}$ NMR resonances of **4** resolve into sharp multiplets at δ 29.0, 15.9, −8.2, and −14.0, consistent with an ABCDX spin system (Figure 1b). The assigned peaks for the phosphorus nuclei were established on the basis of the magnitude of the coupling to Rh and by ^{31}P homonuclear decoupling experiments. The downfield pair of resonances are assigned to the Rh-bound ^{31}P nuclei on the basis of their coupling (101 and 107 Hz) to ^{103}Rh.

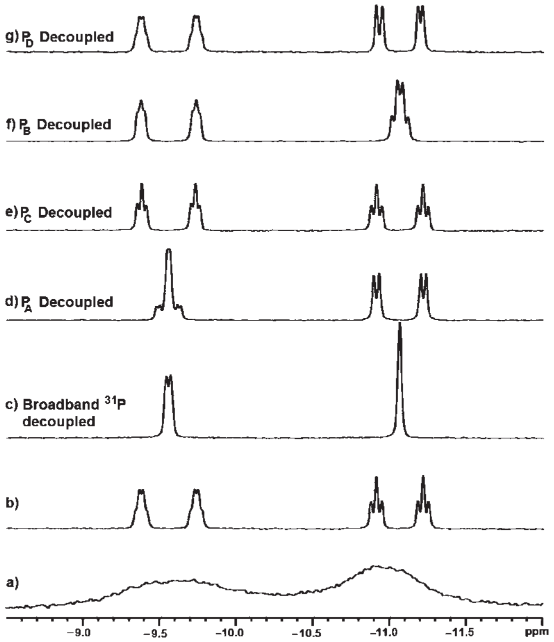


Figure 2. The metal−hydride region of the ^1H NMR spectrum of complex **4**: (a) at 25 °C and (b) at −40 °C. spectra c−g show different ^{31}P-decoupling experiments at −40 °C.

In the ^1H NMR spectrum at −40 °C, four multiplets appear for the dppm-methylene protons, consistent with the structure shown for **4**, while the silicon- and metal-bound hydrogens all sharpen. The Si-bound proton appears as a broad singlet at δ 6.70, while the metal−hydride resonances appear at typically high fields (see Figure 2). Each of the hydride resonances displays strong coupling to the ^{31}P nucleus in the *trans* position ($^2J_{HP(A)}$ = 145 Hz; $^2J_{HP(B)}$ = 123 Hz, see Figure 1 for labeling) and additional, approximately equal coupling to the distal ^{31}P nucleus at the other end of the diphosphine group that occupies the position *trans* to this hydride, and to the ^{31}P nucleus in the *cis* position (see Figure 2 for decoupling experiments). The Rh-bound hydride also displays 11.2 Hz coupling to this metal, as is obvious upon broadband ^{31}P decoupling (Figure 2c).

The ^{29}Si NMR spectrum shows an approximate doublet of triplets at δ 142.9 with coupling to phosphorus and rhodium of 72 and 30 Hz, respectively. The P−Si coupling constant lies intermediate between the values reported for typically *trans* (*ca.* 183 Hz)[40] and *cis* (*ca.* 7.4 Hz)[41] arrangements, in agreement with the intermediate arrangement obtained in the X-ray structure (*vide infra*).

Although the structures of both **4** and **5** were determined, only that of the latter is presented here, owing to a disorder in the silylene phenyl ring of **4** and the overall similarities in both structures (see the Supporting Information for the structural information on compound **4**). Figure 3 shows the ORTEP diagram of one of the two crystallographically independent molecules of compound **5**. This structure very much resembles the diiridium analogs, $[Ir_2(H)_2(CO)_2(\mu\text{-}SiRR')(dppm)_2]$ (RR′ = PhH, Ph$_2$).[9] In this species, as in all related dppm and silylene-bridged complexes, the metals

---

(40) Aizenberg, M.; Ott, J.; Elsevier, C. J.; Milstein, D. *J. Organomet. Chem.* **1998**, *551*, 81.

(41) Nishihara, Y.; Takemura, M.; Osakada, K. *Organometallics* **2002**, *21*, 825.

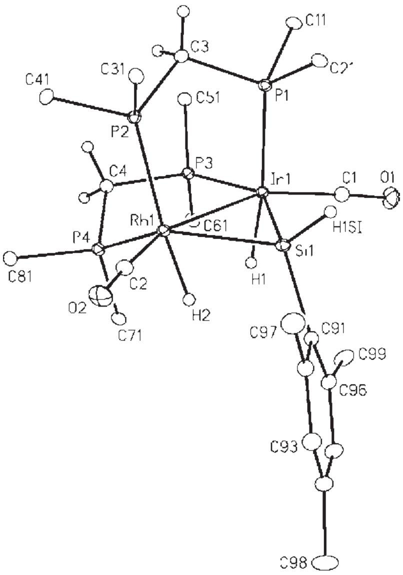


Figure 3. Perspective view of compound **5** showing the numbering scheme. Non-hydrogen atoms are represented by the Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown arbitrarily small except for the mesityl protons, which are not shown. For the dppm phenyl groups, only the ipso carbons are shown. Numbering for the aryl rings starts at the ipso carbon and works sequentially around the rings which are numbered from 1 to 8.

are bridged by the silylene group while the diphosphines are bent back in a mutually *cis* "cradle arrangement". Both metals adopt distorted octahedral coordination geometries in which the hydride ligand on each metal is *trans* to one end of a diphosphine and *cis* to another, as suggested by the NMR spectral results. These hydrides do not show any significant *trans* influence, as indicated by the closely comparable metal−phosphorus distances. Both hydride ligands and the silylene hydrogen were located and refined, yielding bond lengths (Ir−H(1) = 1.56(3) and 1.54(2) Å; Rh−H(2) = 1.48(3) and 1.52(3); and Si−H(SI) = 1.52(2) and 1.45(2) Å for the two independent molecules) that are typical for X-ray determinations.[9] The silylene bridge is pseudo-*trans* at each metal to different ends of the same diphosphine, with P(3)−Ir−Si angles of 145.08(2)° and 145.63(2)° and P(4)−Rh−Si angles of 129.52(2)° and 133.82(2)°.

As noted earlier, the Si−P coupling constant of 72 Hz, obtained in the ^{29}Si NMR spectrum, is consistent with the significant deviation from a rigorously *trans* arrangement. A twist of the Rh coordination sphere with respect to that of Ir (P(1)−Ir−Rh−P(2) and P(3)−Ir−Rh−P(4) torsion angles ranging from 18.21(2)° to 21.41(2)°) is responsible for the greater deviation at Rh from a *trans* phosphine−silylene arrangement. This twisting of the coordination spheres at both metals forces the Rh-bound hydride into significantly closer contact with Si (2.19(3) and 2.24(3) Å) than that of Ir-bound hydride (2.60(3) and 2.63(3) Å). Whether these H···Si interactions correspond to a significant degree of bonding between these two nuclei is not clear. They lie beyond the 2.0 Å distances that Schubert has suggested as the upper limit of a Si−H agostic interaction,[6e] and consistent with this, we see no evidence of such an interaction in the NMR spectra. However, recent investigations indicate that a weak secondary interaction is possible between silicon and hydrogen when they lie within *ca.* 2.1 to 2.5 Å of each other.[42,43] If there is a weak Si−H interaction in the solid for the "Rh-bound" hydrides, it is merely a solid-state effect, since there is a 3:2 disorder of the metals in the structure with the Rh position actually comprised of a 3:2 mix of Rh/Ir and the opposite being the case for the Ir position.

In order to gain a better understanding of the fluxionality in species **4**, saturation-transfer NMR experiments were carried out at lower temperatures. When the Rh-bound hydride resonance was selectively saturated at −50 °C, resonances due to the Si-bound proton and the Ir-bound hydride collapse. A similar collapse was observed in the Si-bound proton and Rh-bound hydride resonances when the Ir-bound proton was saturated, confirming the exchange among the three Si−H, Rh−H, and Ir−H positions. However, accurately measuring the intensity change in the silicon-bound proton resonance upon saturation of either metal-hydride resonance is not straightforward, owing to the overlap of this former signal with those of the phenyl groups. Alternatively, information about the differing exchange rates at Rh and Ir (which are expected to differ owing to the inherently different labilities of the metals) can, in principle, be obtained by saturation of the Si-bound proton resonance and observation of the relative intensities resulting from different rates of saturation transfer to the pair of hydride resonances, which are well resolved. However, saturation of the Si−H resonance is not possible without simultaneous saturation of at least some of the phenyl proton resonances (due to their close proximity to Si−H in the ^{1}H NMR spectrum), and we were concerned that saturation transfer via NOE effects between these phenyl protons and the metal-hydrides could bias the exchange results. We therefore, carried out saturation transfer difference (STD) experiments, in which the difference between a normal ^{1}H NMR spectrum minus the spectrum resulting from the saturation transfer experiment is obtained, allowing the influence of saturating the metal-hydride resonances on the Si-bound hydrogen to be more readily determined. At −50 °C, STD experiments suggest that the exchange process is approximately twice as fast at Rh than at Ir, as indicated by the intensity of the Si-bound proton peak, which is twice as intense when the Rh−H resonance is irradiated (indicating more saturation transfer) compared to the intensity when the Ir-hydride resonance saturated (see Figure S3 in the Supporting Information). The metal-hydride signals also display saturation transfer in much the same way, as each one of the Rh−H or Ir−H resonances is saturated.

In the dirhodium analog, $[Rh_2(CO)_2(H)_2(\mu\text{-SiHPh})(dppm)_2]$,[8] fluxionality, similar to that noted above, was attributed to rapid oxidative addition and reductive elimination of the Si−H bonds at both metal centers, while no such fluxionality was observed in analogous diiridium species, $[Ir_2(CO)_2(H)_2(\mu\text{-SiHPh})(dppm)_2]$,[9] indicating the importance of at least one labile Rh center to facilitate the exchange process.

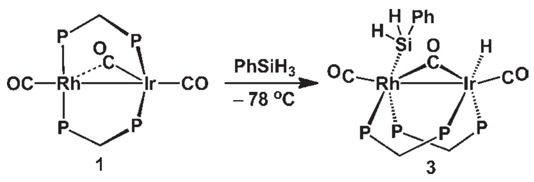
We suggest at least two mechanisms that would explain the differing exchange rates involving the Rh- and Ir-bound hydrides with the silylene hydrogen. First, sequential oxidative-addition/reductive elimination (OA/RE) of a Rh- and

---

(42) (a) Nikonov, G. I; Kuzmina, L. G.; Vyboishchikov, S. F.; Lemenovskii, D. A.; Howard, J. A. K. *Chem.—Eur. J.* **1999**, *5*, 2947. (b) Nikonov, G. I. *J. Organomet. Chem.* **2001**, *635*, 24.

(43) (a) Lachaize, S.; Sabo-Etienne, S. *Eur. J. Inorg. Chem.* **2006**, 2115. (b) Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 2578.

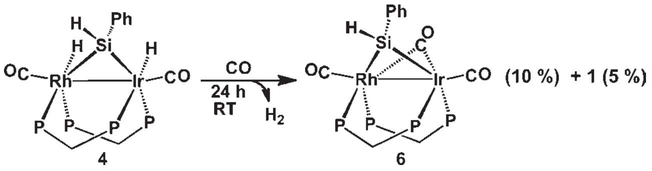
Scheme 2



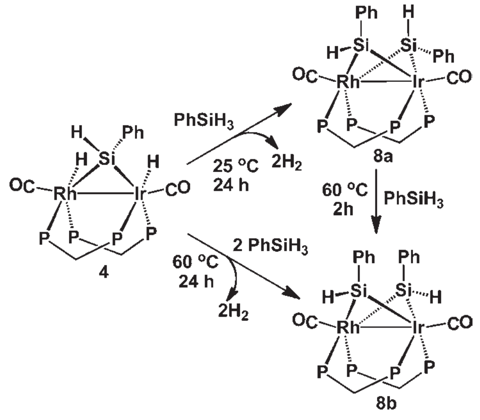
Ir-bound silyl group at the adjacent metal could be occurring, as proposed for the Rh_2 analog. Faster exchange at the more labile Rh center would rationalize the observed difference in exchange rates at lower temperatures. Alternatively, OA/RE could be occurring only at the more labile Rh center, accompanied by migration of the hydrides between the metals. Unfortunately, not enough data are available to establish whether either or both exchange mechanisms are involved.

If the addition of 1 equiv of $PhSiH_3$ to a CD_2Cl_2 solution of **1** is carried out at −78 °C, almost quantitative formation of the first Si−H activation product, a silyl/hydride complex, $[RhIr(H)(SiH_2Ph)(CO)_2(\mu\text{-}CO)(dppm)_2]$ (**3**), occurs (Scheme 2). This species was fully characterized by multinuclear NMR spectroscopy (see Figure S4 in the Supporting Information for selected NMR spectra). At this temperature, the $^{31}P\{^1H\}$ NMR spectrum shows four multiplets, at δ 40.0, 25.2, −3.3, and −11.5, and again the two downfield resonances are assigned to Rh-bound ^{31}P nuclei on the basis of their large Rh−P couplings. The ^1H NMR spectrum shows a doublet of doublets of doublets for the hydride at high field with one large *trans* P−H coupling (125 Hz) and two smaller couplings due to two other ^{31}P nuclei, as described earlier for complex **4**. This signal collapses to a singlet upon broadband ^{31}P-decoupling, with no resolvable coupling to Rh, confirming that it is Ir-bound. Selectively decoupling the ^{31}P signal at δ −3.3 results in loss of the large *trans* $^2J_{PH}$ coupling. The two diastereotopic Si-bound hydrogens show two multiplet resonances at δ 4.23 and 4.05 in the ^1H NMR spectrum. SST NMR spectroscopy shows no sign of exchange between Si- and Ir-bound hydrogens at this temperature. $^{29}Si\{^1H\}$ NMR spectroscopy shows a well resolved multiplet (dddd) at δ −18.0 having a large *trans* Si−P coupling constant (137 Hz), indicating a *trans* disposition of the silyl group to one of the Rh-bound ^{31}P nuclei. The other couplings are due to Rh, the *cis*-^{31}P, and the distal-^{31}P nucleus at the other end of diphosphine that is bound *trans* to the silyl group. It is also worth noting that due to the strong *trans* influence of the silyl ligand, the ^{31}P nucleus *trans* to this group exhibits a reduced $^1J_{Rh-P}$ value (89 Hz) compared to the coupling of the ^{31}P nuclei *cis* to the silyl group (107 Hz).[11] The position of the silyl group on Rh was also confirmed by a $^{13}C-^1H$ HMBC NMR experiment in which the Si-bound protons show a three-bond correlation to both the Rh-bound and the bridging carbonyls whereas the Ir-bound CO displays a two-bond correlation to the Ir-bound hydride. Three resonances at δ 178.0 (t), 199.0 (dm, $^1J_{Rh-C}$ = 70 Hz), and 229.0 (dm, $^1J_{Rh-C}$ = 34 Hz), in the $^{13}C\{^1H\}$ NMR can be assigned to the Ir-bound, Rh-bound, and bridging CO ligands, respectively. When a solution of **3** is warmed to −40 °C, this species begins to disappear, being replaced by compound **4**, resulting from the oxidative addition of the second Si−H bond, and at −20 °C, compound **4** is the sole species remaining, as indicated by NMR.

Scheme 3



Scheme 4



The reaction of species **4** with 1.0 atm of CO either at 60 °C over 30 min or at ambient temperature for 24 h results in the formation of the silylene- and carbonyl-bridged species $[RhIr(CO)_2(\mu\text{-}SiPhH)(\mu\text{-}CO)(dppm)_2]$ (**6**) in approximately 10% yield (by $^{31}P\{^1H\}$ NMR spectroscopy) by the reductive elimination of H_2 and CO addition (Scheme 3). Some of the tricarbonyl species, $[RhIr(CO)_3(dppm)_2]$ (**1**) (5%), also forms during the course of this reaction, indicating some silane loss from **4** in the presence of excess CO. The low yield of **6** is in contrast to the Rh_2 analog, $[Rh_2(CO)_2(\mu\text{-}SiPhH)(\mu\text{-}CO)(dppm)_2]$, which forms quantitatively under similar conditions[8] and also contrasts with the analogous Ir_2 dihydrides,[9] which are unreactive to CO. The $^{31}P\{^1H\}$ NMR and ^1H NMR spectra of **6** display the typical resonances expected for an ABCDX system. The bridging CO appears as a downfield doublet of multiplets in the $^{13}C\{^1H\}$ NMR spectrum at δ 229.2 ($^1J_{RhC}$ = 31.9 Hz) along with two other resonances at δ 199.9 ($^1J_{RhC}$ = 78.8 Hz) and 183.4, assignable to Rh- and Ir-bound carbonyls, respectively. The formation of **6** in the presence of CO by the elimination of H_2 from **4** implies the possibility of incorporating other substrates, such as additional silane, into this silylene-bridged core.

ii. Bis-Silylene-Bridged Products. Further reaction of **4** with 1 equiv of phenylsilane or the reaction of **1** with 2 equiv of phenylsilane at ambient temperature yields the bis(silylene)-bridged complex, $[RhIr(CO)_2(\mu\text{-}SiPhH)_2(dppm)_2]$ (**8a**), in which one silylene phenyl substituent is axial while the other is equatorial, as shown in Scheme 4. At ambient temperature, in the presence of excess silane, compound **8a** slowly converts, over a period of several days, to isomer **8b**, in which both silyl phenyl groups are axial (see Figure S5c in the Supporting Information for the ^{31}P NMR spectrum for the isomeric conversion from **8a** to **8b**). This conversion takes only 2 h if heated to 60 °C. In the absence of excess silane, complex **8a** is stable even at elevated temperature (60 °C), with no isomerization to **8b** observed.

The identities of isomers **8a** and **8b** were unambiguously established by their X-ray structure determinations, which

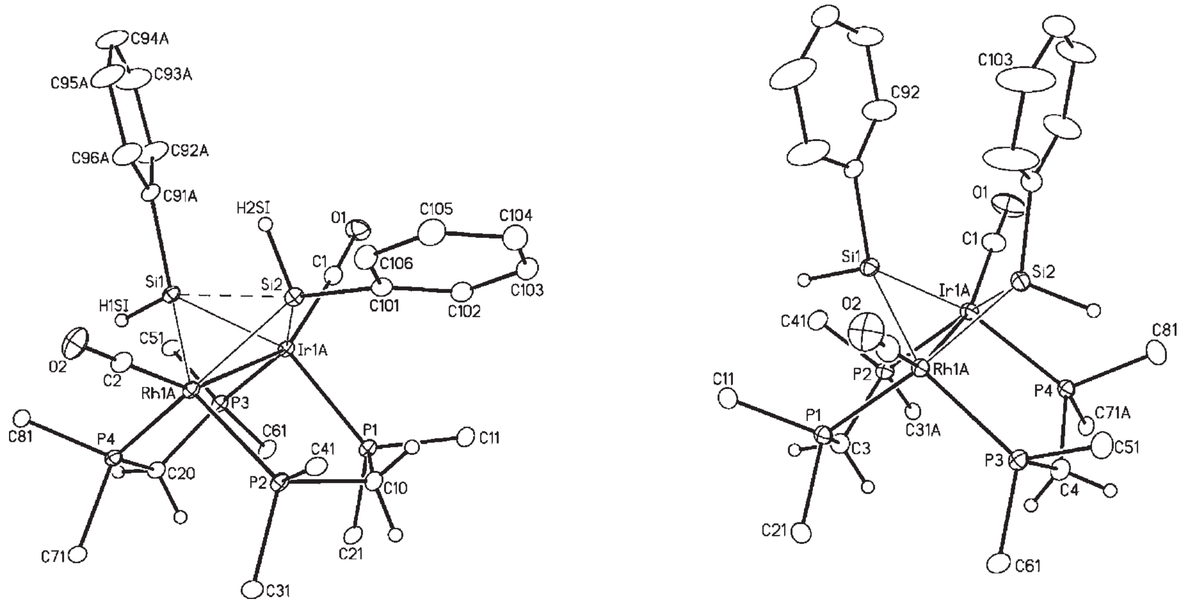


Figure 4. Perspective view of **8a** (left) and **8b** (right) showing the numbering scheme. Silylene-hydrogen positions of **8a** have been refined, but these atoms were assigned thermal parameters 20% greater than those of their attached atoms. All hydrogens are shown artificially small in the figure. Other thermal parameters are shown as described in Figure 3. Only the ipso carbons of the dppm phenyl groups are shown.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **8a** and **8b**

bond distances	**8a**	**8b**	bond angles	**8a**	**8b**
Ir−Rh	2.7957(3)	2.8207(3)	Rh(1)−Ir(1)−Si(1)	53.88(3)	53.19(3)
Ir−Si(1)	2.364(1)	2.367(1)	Rh(1)−Ir(1)−Si(2)	54.44(3)	53.23(3)
Ir−Si(2)	2.367(1)	2.369(1)	Ir(1)−Rh(1)−Si(1)	53.70(2)	53.49(3)
Rh−Si(1)	2.369(1)	2.358(1)	Ir(1)−Rh(1)−Si(2)	53.60(3)	53.52(3)
Rh−Si(2)	2.392(1)	2.360(1)	Si(1)−Ir(1)−Si(2)	71.51(4)	74.37(4)
Si(1)−Si(2)	2.764(1)	2.862(1)	Si(1)−Rh(1)−Si(2)	70.97(4)	74.71(4)
Si(1)−H2SI	2.81(4)		Rh(1)−Si(1)−Ir(1)	72.42(3)	73.31(3)
			Rh(1)−Si(2)−Ir(1)	71.96(3)	73.24(3)

are shown in Figure 4, with a summary of metrical parameters given in Table 1. Although superficially very similar, the significant difference in these two structures is, as noted above, the orientation of the silylene substituents. In **8b**, the phenyl ring on each silylene group is axial such that the pair has an almost parallel π-stacking type of arrangement in which the distance between the *ipso* carbons is 3.291(5) Å, while the distance between the centroid of both groups is 3.736 Å, close to the sum of the van der Waals radii for such groups (*ca.* 3.70 Å). Surprisingly perhaps, isomer **8b**, in which both bulky phenyl groups are adjacent, is favored. However, in this axial/axial arrangement, both groups avoid more serious repulsive interactions with the dppm phenyl groups, while adopting the relatively favorable π-stacking arrangement noted above. Nevertheless, the mutual repulsion of these groups is obvious in the Si(1)−Ir−Si(2) and Si(1)−Rh−Si(2) angles in the two species (71.51(4)° and 70.97(4)°, respectively, in **8a**, 74.37(4) and 74.71(4)°, respectively, in **8b**) demonstrating an opening up of the Rh(μ-SiHR)$_2$Ir "wing-tip" arrangement of the pair of μ-silylene groups, for the diaxial arrangement. This repulsion is more clearly demonstrated by the increase in Si−Si separation from 2.764(1) Å in **8a** to 2.862(1) Å in **8b**. Although it is tempting to attribute this difference to a weakly attractive interaction between two Si atoms in the former (in which the Si−Si separation is close to the longest known Si−Si bond distance of *ca.* 2.70 Å),[44a] it is difficult to rule out a purely steric origin to these differences.

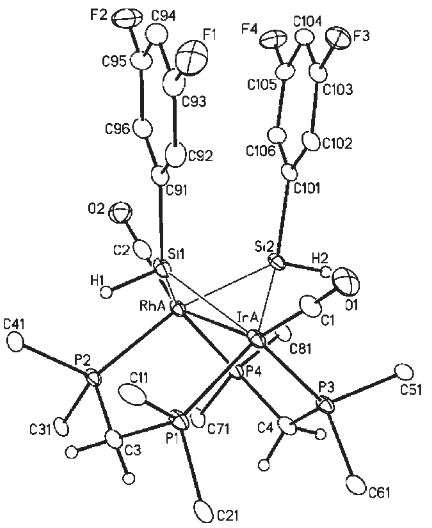


Figure 5. Perspective view of [RhIr(CO)$_2$(μ-SiHC$_6$H$_3$F$_2$)$_2$(dppm)$_2$] (**8c**) showing the numbering scheme. Thermal parameters are shown as described in Figure 3. Only the *ipso* carbons of the dppm phenyl groups are shown.

As a further indication that Si−Si contacts display little direct bonding interaction, the analogous species, [RhIr(CO)$_2$(μ-SiHC$_6$H$_3$F$_2$)$_2$(dppm)$_2$] (**8c**), having fluoro substituents in the meta position of the phenyl groups, was synthesized. As anticipated, the aryl rings in **8c**, having the electron-withdrawing fluorines attached (Figure 5), have a closer approach than in **8b**[45] and display a separation between the *ipso* carbons of 3.233 Å and between the

---

[44] (a) Wiberg, N.; Schuster, H.; Simon, A.; Peter, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 79. (b) Corey, J. Y.; Kraichely, D. M.; Huhmann, J. L.; Braddock-Wilking, J.; Lindeberg, A. *Organometallics* **1995**, *14*, 2704.

[45] Cozzi, F.; Ponzini, F.; Annunziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1019.

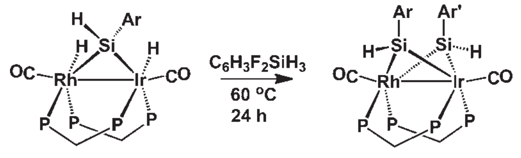
aryl-group centroids of 3.551 Å, yet the Si−Si separation (2.873(1) Å) is larger in this fluoro-substituted case, indicating that the closer approach of Si atoms in **8c** is not inhibited by aryl-group repulsion.

Consistent with the X-ray structures, in which all phosphorus environments are chemically inequivalent, the ^{31}P-{^{1}H} NMR spectrum of **8a** shows four resonances at δ 29.3, 21.5, 2.6, and −7.8 (see Figure S5a in the Supporting Information). The absence of symmetry in **8a** is also obvious in the ^{1}H NMR spectrum in which four multiplets appear for the inequivalent methylene protons and two resonances, a doublet of doublets of multiplets at δ 5.66 ($^3J_{PH}$ = 32 Hz, $^3J_{HH}$ = 2.3 Hz) and a doublet of multiplets at δ 5.52 (with no observable $^3J_{PH}$ coupling), for two chemically inequivalent silicon-bound protons are observed. ^{29}Si{^{1}H} NMR shows two multiplets at δ 129.2 and δ 113.9 for **8a** indicating two different environments for the Si atoms. Interestingly, the two Si-bound protons show mutual coupling of 2.3 Hz, which is clearly demonstrated by 2D COSY and homonuclear ^{1}H{^{1}H} NMR experiments. Although coupling of this magnitude could arise from four-bond coupling through the di-metal-*bis*-silylene framework, it is significant that comparable three-bond H−Si−Si−H coupling values between 2.2 and 2.5 Hz have been reported in a number of disilanes.[44b] This coupling together with the relatively short Si−Si contact is suggestive of significant Si−Si interaction in this species, suggesting that the origin of the short contact may not arise exclusively from steric influences. Another explanation for the observed coupling between these silylene protons is the presence of a secondary Si−H interaction[42,43] involving the axial Si−H bond and the adjacent silylene group (see Figure 4). This possibility had previously been suggested for an analogous Rh$_2$ species on the basis of NMR studies,[8] and now the structure determination of **8a** demonstrates the orientation of the axial hydrogen toward the adjacent Si atom, although the contact (2.81(4) Å) appears to be long for such an interaction.[43a]

The higher symmetry of **8b** is manifested in an AA′BB′X-type pattern in ^{31}P{^{1}H} NMR spectrum in which only two multiplets at δ 28.6 (dm; $^1J_{RhP}$ = 105 Hz) and 0.3 (m) appear (see Figure S5b in the Supporting Information). Also consistent with the higher symmetry, the ^{1}H NMR spectrum of **8b** shows two peaks for two types of dppm methylene protons (aimed toward or away from the μ-SiHPh groups) and one peak representing the Si-bound protons, all integrating equally as 2:2:2. In the ^{29}Si{^{1}H} NMR spectrum, a multiplet at δ 127.0 is observed, having unresolved P−Si and Rh−Si coupling; this resonance lies slightly upfield compared to the monosilylene-bridged species **4** (δ 142.9). In both isomers (**8a** and **8b**), two ^{13}C{^{1}H} NMR resonance are observed for the carbonyls at *ca.* 187 and 200, with the latter displaying 74 Hz coupling to Rh in both compounds, confirming that for each species one carbonyl resides on each metal. The NMR spectra for **8c** very much resemble those of **8b**.

The reaction of complex **4** with 2 equiv of 3,5-difluorophenylsilane produces the mixed silylene-bridged complex [RhIr(CO)$_2$(μ-SiHPh)(μ-SiHC$_6$H$_3$F$_2$)(dppm)$_2$] (**8d**) in a moderate yield (45%; see Scheme 5), displaying two doublets of multiplets at δ 27.6 and 26.2 for the Rh-bound phosphorus nuclei and two muliplets at δ −1.1 and −1.6 for the Ir-bound ones in the ^{31}P{^{1}H} NMR spectrum. The Si-bound hydrogens appear as two multiplets at δ 5.95 and 5.82 in the ^{1}H NMR, and two multiplets appear at δ 126.3 and 125.2 in the ^{29}Si{^{1}H} NMR. The ^{19}F NMR spectrum displays a multiplet at δ −111.9, which is different from the ^{19}F chemical shift of **8c** (δ −113.5, measured in the same solvent and frequency), eliminating the possibility that the above-mentioned reaction is producing a 1:1 mixture of **8b** and **8c**.

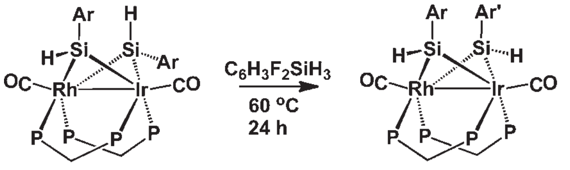
Scheme 5



4, Ar = Ph

8d, Ar = Ph, Ar' = C$_6$H$_3$F$_2$

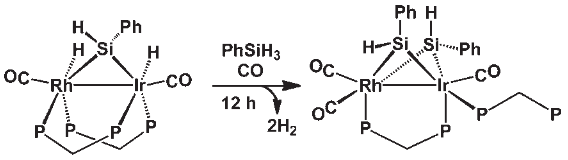
Scheme 6



8a, Ar = Ph

8b, Ar = Ar' = Ph (50 %)
8c, Ar = Ar' = C$_6$H$_3$F$_2$ (16.7 %)
8d, Ar = Ph, Ar' = C$_6$H$_3$F$_2$ (33.3 %)

Scheme 7



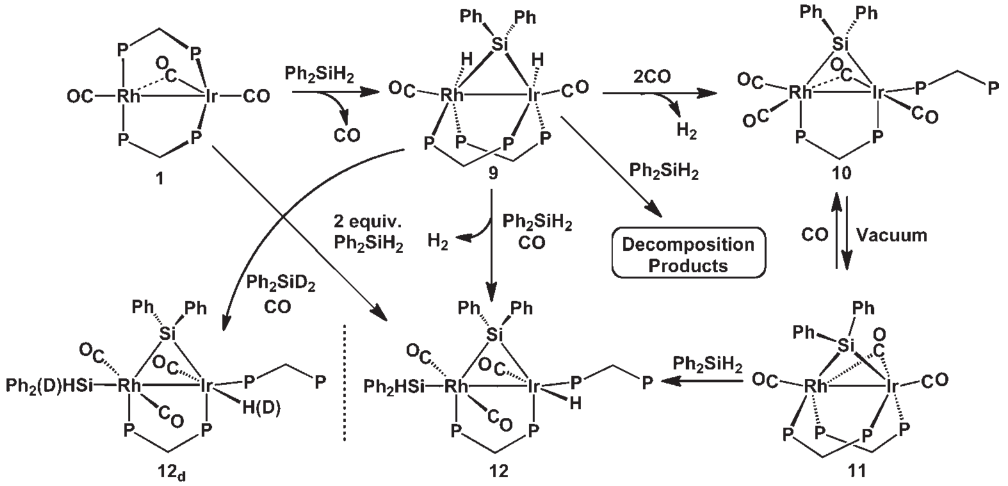
4

7

As noted earlier, the isomerization of **8a** to **8b** requires excess silane, implying the reversible incorporation of a third Si-containing fragment at the same stage of the isomerization. To test this possibility, compound **8a** was reacted with 3,5-difluorophenylsilane. This reaction with 2 equiv of 3,5-difluorophenylsilane (Scheme 6) produces a mixture of **8b** (50%), **8c** (16.7%), and **8d** (33.3%) (based on integration of the Si−H resonances of **8b**, **8c**, and **8d** with respect to the residual solvent peak). The formation of products **8c** and **8d**, containing the 3,5-difluorophenylsilylene moiety, confirms that the added silane has been incorporated, and the presence of **8b** indicates that this occurs before elimination of one of the original SiHPh groups.

The reaction of **4** with 1 equiv of PhSiH$_3$ in the presence of CO results in almost quantitative formation of a *bis*-(silylene)-bridged tricarbonyl complex [RhIr(CO)$_3$(κ^1-dppm)(μ-SiHPh)$_2$(dppm)] (**7**), in which one end of a diphosphine ligand is pendent, having been displaced from Rh by a carbonyl ligand (Scheme 7). The ^{31}P{^{1}H} NMR spectrum of **7** displays four resonances at δ 15.6, 3.4, −10.5, and −24.5, of which only the one at low field displays coupling to Rh (105 Hz). The high-field resonance is close to the value for free dppm (δ −23.0), consistent with the presence of the pendent group. The ^{1}H NMR spectrum displays two peaks for the two Si hydrogens at δ 5.80 (dd) and 6.20 (dd), indicating chemically inequivalent environments, presumably a result of their axial/equatorial orientation, as shown in **8a**. In this

Scheme 8



case, these inequivalent protons do not show mutual coupling. In the ^{29}Si{^{1}H} NMR spectrum, two resonances appear at δ 101.8 (m) and 136.6 (m) for the two inequivalent silylene groups. The downfield NMR shifts for these groups indicate that both of them are in bridging positions.[6b] Under high vacuum conditions, or at elevated temperatures, complex **7** converts exclusively to **8a** (in variable amounts, up to 20%) by the loss of one CO from Rh and subsequent recoordination of the pendent end of the diphosphine. The conversion of **7** to **8a** confirms an axial/equatorial alignment of silylene hydrogens in the former. Neither isomer **8a** nor **8b** reacts with H_2 to release disilane, as was the case in a previously reported dirhodium complex.[11]

b. Reactions of [RhIr(CO)$_3$(dppm)$_2$] with Secondary Silanes. The reaction of diphenylsilane with complex **1** yields the diphenylsilylene-bridged complex, [RhIr(H)$_2$(CO)$_2$(μ-SiPh$_2$)(dppm)$_2$] (**9**) (Scheme 8), analogous to the phenylsilylene-bridged species **4**. The formation of **9** is slower than that of **4**, requiring 6 h at ambient temperature, presumably due to the larger steric bulk of the more substituted silane. Like **4**, compound **9** is fluxional at 27 °C. The ^{31}P{^{1}H} NMR spectrum at this temperature appears as two broad peaks at *ca.* δ 21.5 and −11.7, and cooling to −40 °C causes each broad signal to split into two sets of peaks (with unresolved P−M−P coupling), indicating the different environments of all phosphorus nuclei. The ^{1}H NMR spectrum behaves similarly, with two sets of broad, unresolved resonances each for the hydrides (δ −9.73 and −11.50) and for the dppm methylene protons (δ 4.83 and 3.14) at ambient temperature, which resolve upon cooling to −40 °C with the hydride resonances each displaying similar *trans* and *cis* coupling, as was shown in complex **4** and with dppm methylene resonances appearing as four signals (δ 5.35, 4.94, 3.13, 2.94). Again, a saturation transfer NMR experiment at −20 °C indicates that the fluxionality of this species involves exchange of the metal-bound hydrides.

Upon further addition of diphenylsilane to **9**, incorporation of a second silylene group, as observed with primary silanes, was not observed; instead only decomposition products resulted. However, the addition of 1 equiv of diphenylsilane in the presence of 1 atm of CO quantitatively yields an unusual silyl(μ-silylene) complex, [RhIr(H)(SiPh$_2$H)(CO)$_3$(κ^1-dppm)(μ-SiPh$_2$)(dppm)] (**12**), by the loss of 1 equiv of H_2, dissociation of the Rh end of one dppm group to give a pendent Ir-bound diphosphine and the addition of the second equivalent of silane to Rh. This compound also resulted from the reaction of compound **1** with 2 equiv of Ph$_2$SiH$_2$ in a sealed tube (Scheme 8). Clearly, the presence of CO is necessary to stabilize this silyl(silylene) complex, which is too crowded to allow the pendent dppm to coordinate to alleviate the unsaturation.

The ^{31}P{^{1}H} NMR spectrum for compound **12** displays an ABCDX spin pattern with peaks at δ 3.1, −2.5, −9.5, and −27.9, in which the resonance at δ 3.1 displays strong Rh−P coupling (94 Hz) while the upfield doublet of doublets is close to that of free dppm (δ −23.0), suggesting that this latter ^{31}P resonance corresponds to the pendent end of the dppm group. This high-field resonance is also close to that reported earlier for compound **7**, the related dirhodium species [Rh$_2$(CO)$_3$(κ^1-dppm)(μ-CO)(μ-SiEt$_2$)(dppm)],[8] and for other metal complexes having κ^1-dppm ligands.[46] The Ir-bound ^{31}P nucleus of the pendent-dppm ligand exhibits a weak coupling of 5 Hz to Rh. Since this coupling is far less than expected for direct bonding to Rh, this weak coupling presumably occurs via the Rh−Ir bond, as this phosphine is almost *trans* to the Rh−Ir axis (see the X-ray structure in Figure 6). A satisfactory simulation of the ^{31}P NMR spectrum of **12** was obtained by employing the values $J_{\mathrm{RhP(A)}}$ = 94.4 Hz, $J_{\mathrm{RhP(D)}}$ = 5.1 Hz, $J_{\mathrm{P(A)P(B)}}$ = 103 Hz, $J_{\mathrm{P(A)P(D)}}$ = 5.6 Hz, $J_{\mathrm{P(B)P(C)}}$ = 8.3 Hz, $J_{\mathrm{P(B)P(D)}}$ = 9.0 Hz, and $J_{\mathrm{P(C)P(D)}}$ = 35.6 Hz.

The ^{13}C{^{1}H} NMR spectrum for **12** shows the presence of two carbonyl groups on Rh (δ 203.9 and $^1J_{\mathrm{RhC}}$ = 55.8 Hz and δ 199.8 Hz and $^1J_{\mathrm{RhC}}$ = 55.6 Hz) and one on Ir (δ 186.1), and the magnitude of the C−C couplings ($^2J_{\mathrm{CC}}$ = 29.1 Hz, determined for a ^{13}CO-enriched sample) between the pair of Rh-bound carbonyls is consistent with a mutually *trans* arrangement of these groups.[48] In the ^{1}H NMR

---

(46) (a) Bruce, M. I.; Cifuentes, M. P.; Grundy, K. R.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1988**, *41*, 603. (b) Brown, M. P.; Yavari, A.; Hill, R. H.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2421. (c) Azam, K. A.; Brown, M. P.; Hill, R. H.; Puddephatt, R. J.; Yavari, A. *Organometallics* **1984**, *3*, 697. (d) Car, S. W.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1763.

(47) Trepanier, S. J.; Dennett, J. N. L.; Sterenberg, B. T.; McDonald, R.; Cowie, M. *J. Am. Chem. Soc.* **2004**, *126*, 8046.

(48) (a) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 3342. (b) Vaartstra, B. A.; Xiao, J.; Jenkins, J. A.; Verhagen, R.; Cowie, M. *Organometallics* **1991**, *10*, 2708. (c) Mague, J. T.; De Vries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.

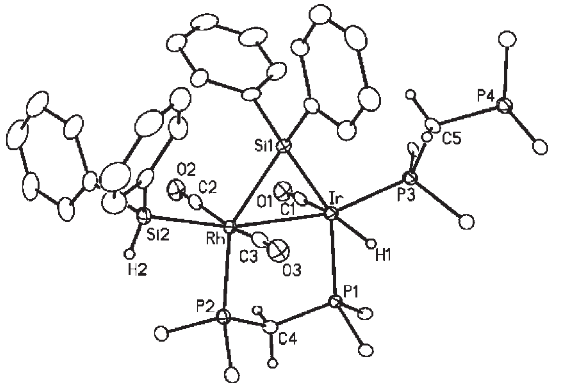
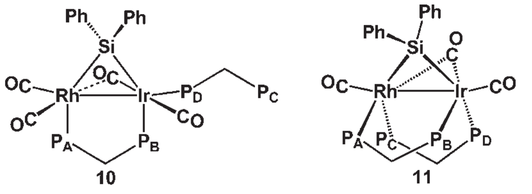


Figure 6. ORTEP drawing of **12** showing the atom labeling scheme. Thermal parameters are as described in Figure 3. Only the *ipso* carbons are shown for the dppm phenyl groups.

spectrum, the silyl hydrogen appears as a doublet at δ 5.30 ($^3J_{PH}$ = 7.1 Hz) with no resolvable coupling to Rh and collapses to a singlet only upon irradiation of the Rh-bound ^{31}P resonance, indicating that the silyl group is bound to Rh. The hydride ligand appears as doublet of doublets at δ −10.5 with approximately 15 and 19 Hz *cis* coupling to both Ir-bound ^{31}P nuclei as established by selective ^{31}P{^{1}H} decoupling experiments. The absence of Rh−H coupling further indicates that the hydride is terminally bound to Ir. The terminally bound silyl group appears at δ −2.3, as a doublet of doublets in the ^{29}Si{^{1}H} NMR spectrum with coincidentally equal coupling to both ^{103}Rh and the Rh-bound ^{31}P nucleus, whereas the bridging silylene group appears at δ 146.0. These chemical shifts are characteristic of silyl and silylene groups, respectively (*vide supra*).

An X-ray structure determination of **12,** shown in Figure 6, confirms the proposed structure. The geometry at each metal is distorted octahedral, in which the major distortions result from the strain imposed by the bridging $SiPh_2$ group, which lies almost opposite the bridging dppm group. This silylene-bridged complex also has an accompanying Rh-bound diphenylsilyl group. The Rh−Si(1) and Ir−Si(1) bond lengths of 2.427(2) Å and 2.338(2) Å, respectively, for the μ-silylene group are essentially equal to the Rh−Si(2) distance 2.398(2) Å) for the terminal silyl group, and all are comparable to previous determinations of related species.[19−22,49] As deduced from the NMR spectral data above, one dppm group is pendent and bound to Ir almost opposite the Rh−Ir bond, and opposite the silyl group on the adjacent metal. The mutually *trans* disposition of the two Rh-bound carbonyl groups, as deduced in the solution from the ^{13}C{^{1}H} NMR spectrum, is also present in the solid. The closely comparable solution NMR and X-ray results indicate that there is no significant difference in the solution and solid-state structures of **12**.

The reaction of 2 equiv of Me_2SiH_2 with complex **1**, in the presence of CO, yields the analogous species, [RhIr(H)(SiMe$_2$H)(CO)$_3$(η^1-dppm)(μ-SiMe$_2$)(dppm)] (**13**), having similar spectral parameters. In keeping with the much lower steric bulk of dimethylsilane, this reaction is much faster than that of diphenylsilane, taking 1 h as opposed to 24 h for the latter, although the lower steric bulk is not enough to allow the formation of a pair of silylene bridges, as seen for the primary silanes.



$J_{RhP(A)}$ = 100.8 Hz, $J_{RhP(D)}$ = 11.9 Hz
$J_{P(A)P(B)}$ = 124.7 Hz, $J_{P(A)P(D)}$ = 4.7 Hz
$J_{P(B)P(C)}$ = 5.0 Hz, $J_{P(C)P(D)}$ = 40.0 Hz

$J_{RhP(A)}$ = 106.7 Hz, $J_{RhP(C)}$ = 97.9 Hz
$J_{P(A)P(B)}$ = 254.9 Hz, $J_{P(A)P(C)}$ = 30.2 Hz
$J_{P(C)P(D)}$ = 155.6 Hz, $J_{P(B)P(D)}$ = 22.3 Hz

Figure 7. Coupling constants of **10** and **11** obtained from spectral simulation of the ^{31}P{^{1}H} spectra.

When the diphenylsilylene-bridged dihydride complex **9** is pressurized with CO in a sealed NMR tube at room temperature, the tetracarbonyl species, [RhIr(CO)$_4$(κ^1-dppm)(μ-SiPh$_2$)(dppm)] (**10**), results, in 75% yield (according to ^{31}P NMR), accompanied by the evolution of H_2 (see Scheme 8). Also present in the reaction mixture is [RhIr(CO)$_3$(dppm)$_2$] (**1**) resulting from the displacement of diphenylsilane by CO. The analogous tetracarbonyl complex was not observed during the reaction of **4** with CO, which gave only 10% of a tricarbonyl species (**6**) under similar conditions. The ^{13}C{^{1}H} NMR spectrum of this new species displays resonances at δ 212.4 ($^1J_{RhC}$ = 5.6 Hz), 201.7 ($^1J_{RhC}$ = 71.8 Hz), 201.6 ($^1J_{RhC}$ = 73.6 Hz), and 185.3, which are assignable to one weakly bridging and three terminally bonded carbonyl groups, respectively. The absence of hydride signals in the ^{1}H NMR spectrum, together with the ^{31}P{^{1}H} NMR spectrum, which is characteristic of an ABCDX spin system and the chemical shift for the free end of the pendent diphosphine group, which appears upfield at δ −26.2 in the ^{31}P NMR spectrum, is consistent with the formulation shown in Scheme 8, much like that described above for **7** and **12** and related dirhodium species.[8] Compound **10** loses CO reversibly to form the tricarbonyl species, [RhIr(CO)$_2$(μ-CO)(μ-SiPh$_2$)(dppm)$_2$] (**11**), in which the pendent dppm has recoordinated to Rh to form a cradle-like tricarbonyl species, similar to compound **6** and the related species [Rh$_2$(CO)$_2$(μ-CO)(μ-SiPh$_2$)(dppm)$_2$].[8] However, as with **6**, the formation of **11** is not complete, appearing as only approximately 10% of the mixture of **1** and **10**. The spectral parameters from the ^{31}P spectral simulations for compounds **10** and **11** are summarized in Figure 7.

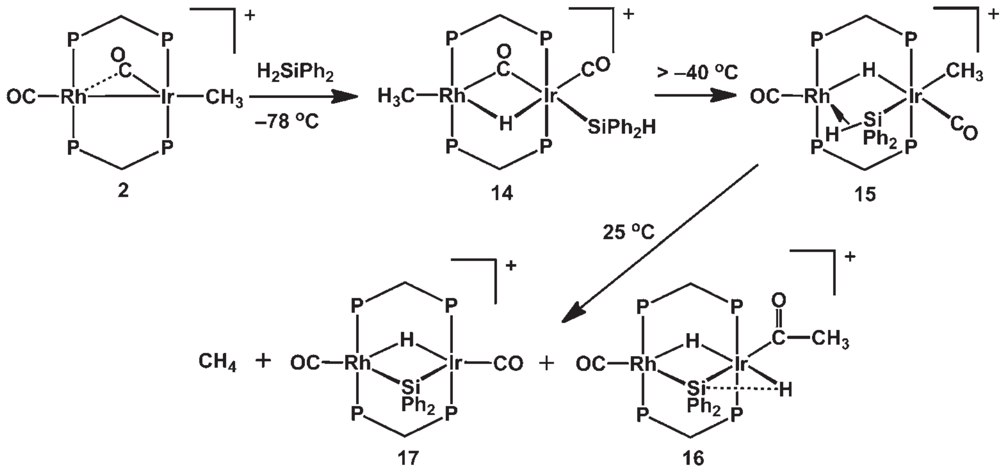
Not surprisingly, in the presence of excess diphenylsilane, the mixture of compounds **1**, **10**, and **11** yields **12** after 1 day. The reaction of **9** with Ph_2SiD_2 under 1 atm of pressure of CO gives rise to the deuterium scrambled product (**12$_d$**), having a D/H ratio of 4:1, as confirmed by ^{2}H NMR, in which two peaks at δ 5.29 and −10.44 appear for the silyl deuterium and Ir-bound deuteride, respectively. In the ^{1}H NMR spectrum, these two resonances appear at approximately 20% intensity compared to the dppm-methylene protons and with the same resonances in a nondeuterated sample. The scrambling of H/D indicates that H_2 loss does not precede silane activation.

Bimetallic silyl(silylene-bridged) complexes are not common in the literature, with only a few having been reported.[19−22,49] Silyl(silylene) complexes are of interest, as many transition-metal-mediated reactions of organosilicon compounds, such as Si−Si bond formation, isomerization,

---

(49) Pannell, K. H.; Sharma, H. K.; Kapoor, R. N.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **1997**, *119*, 9315.

Scheme 9



and redistribution of organosilicon compounds, are thought to proceed via such species.[49,50] More recently, a monometallic silyl(silylene) complex was shown to promote Si−Si bond formation by a 1,2-silyl migration from the metal to the silylene ligand in the presence of a strong donor.[51] Formation of the silyl(silylene-bridged) compounds (**12** and **13**), noted above, is also in contrast to the reaction of secondary silanes with the dirhodium analogue of **1**, in which a P−C bond of a dppm ligand was cleaved followed by the formation of a P−Si bond to give $[Rh_2(\mu\text{-}H)(CO)_2(dppm)(\mu\text{-}Ph_2PCH_2PPhSiEt_2)]$.[8] Attempts to promote Si−Si bond formation in **12** and **13** by heating and/or reaction with Lewis bases were not successful.

c. Reactions of $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ with Secondary Silanes. The addition of 1 equiv of Ph_2SiH_2 to a CD_2Cl_2 solution of the cationic complex, $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**), at −78 °C, yields the silyl/hydride complex, $[RhIr(CH_3)(SiPh_2H)(CO)(\mu\text{-}CO)(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**14**) (Scheme 9). Multinuclear NMR spectroscopy suggests that in this case Si−H bond activation has been initiated at Ir, in contrast to the reactivity of silanes with the neutral complex (**1**), described above, in which Si−H bond activation is presumed to be initiated at Rh. The formation of **14** is also accompanied by methyl migration from Ir to Rh. The ^1H NMR spectrum of **14** shows the silyl hydrogen as a triplet of doublets at δ 5.50 ($^3J_{P-H}$ = 13.5 Hz, $^3J_{H-H}$ = 2.0 Hz) in which the ^{29}Si satellites indicate $^1J_{Si-H}$ = 170 Hz, consistent with a classical Si−H bond, and a hydride signal at δ −8.44 as a doublet of doublets of multiplets ($^1J_{RhH}$ = 13.8 Hz, $^3J_{H-H}$ = 2.0 Hz). Resonances for the dppm methylene groups and all phenyl groups are as expected. Selective decoupling of the Ir-bound ^{31}P nuclei results in a collapse of the signal for the silyl hydrogen to a doublet, while decoupling of the Rh-bound ^{31}P nuclei has no affect on this resonance, establishing that the silyl group is bound to Ir. Broadband ^{31}P decoupling transforms the multiplet resonance for the hydride, described above, to a doublet of doublets, showing coupling to Rh and the silyl proton. The three-bond coupling of the bridging hydride to the silyl proton was confirmed by the homonuclear ($^1H\{^1H\}$) NMR decoupling experiments. In addition, the selective decoupling of both the Rh- and Ir-bound ^{31}P nuclei results in sharpening of the multiplets, confirming that the hydride is bridging the metals. The methyl protons appear as a triplet at δ 0.49 ($^3J_{P-H}$ = 6.9 Hz), which collapses to a broad singlet upon irradiation of the Rh-bound ^{31}P nuclei, indicating that this group has migrated from Ir to Rh. The absence of two-bond coupling between Rh and the methyl protons is not unusual.[47] In the $^{29}Si\{^1H\}$ NMR spectrum, a triplet is observed at δ −25.7, consistent with a terminally bound silyl group. Moreover, the small $^2J_{Si-P}$ coupling (10 Hz) implies a mutually *cis* disposition of Si and the adjacent ^{31}P nuclei. The $^{13}C\{^1H\}$ NMR spectrum exhibits resonances at δ 216.6 ($^1J_{RhC}$ = 31.2 Hz) due to a bridging carbonyl and at δ 173.8 for the terminally bound carbonyl on Ir. If $^{13}CH_3$-enriched compound **2** is used as a precursor, an additional doublet of triplets ($^1J_{RhC}$ = 29 Hz) appears in the $^{13}C\{^1H\}$ NMR at δ 14.8, due to the Rh-bound methyl group. The *trans* disposition of the Ir-bound CO and the bridging hydride was confirmed in the ^{13}C NMR spectrum by ^{13}CO enrichment of **14**, which shows *trans* $^2J_{C-H}$ coupling of 24 Hz in both $^1H\{^{31}P\}$ and $^{13}C\{^{31}P\}$ NMR spectra. Compound **14** is fluxional in solution, as revealed by the $^{31}P\{^1H\}$ NMR spectra. At ca. −80 °C, the Ir-bound ^{31}P nuclei appear as two broad peaks at δ −6.1 and −8.6, while the Rh-bound phosphines appear as a single sharp and well-resolved resonance at δ 29.0. At −60 °C, the former peaks coalesce to a broad unresolved peak centered at δ −7.3, and finally at −40 °C, this resonance resolves into a multiplet consistent with the BB′ part of an AA′BB′X spin system. The signals due to the Rh-bound ^{31}P nuclei, silyl hydrogen, and the bridging hydride ligand remain sharp and unaffected throughout the temperature range from −80 and −40 °C, indicating that these groups are not significantly affected by the fluxional process. The origin of this fluxionality is not clearly understood, although it might result from an asymmetry in the environments of the silyl phenyls, which renders both Ir-bound ^{31}P nuclei inequivalent in the static low-temperature structure.

Upon warming above −40 °C, a new species $[RhIr(CH_3)(CO)_2(\mu\text{-}H)(\mu\text{-}\kappa^1\text{:}\eta^2\text{-}SiPh_2H)(dppm)_2][CF_3SO_3]$ (**15**) begins to appear together with complex **14**, and at −20 °C compound **15** is the major product (83%, according to ^{31}P NMR) with 17% unconverted **14** (Scheme 9). This species,

---

(50) (a) Ogino, H. *Chem. Rec.* **2002**, *2*, 291. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351.

(51) Tobita, H.; Matsuda, A.; Hashimoto, H.; Ueno, K.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 221.

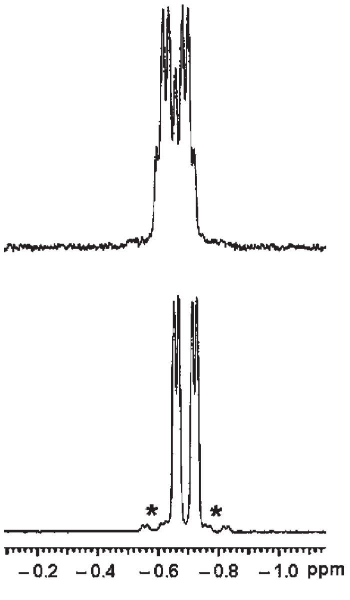


Figure 8. ^{1}H NMR resonance of the Si−H moiety (above) and with broadband ^{31}P decoupling (below) for compound **15** at −20 °C. ^{29}Si satellites marked by the asterisks.

like **14**, at this temperature, displays a pattern typical of an AA′BB′X spin system in the $^{31}P\{^{1}H\}$ NMR spectrum, and the ^{1}H NMR spectrum suggests migration of the methyl group back to Ir, as evidenced by its triplet resonance at δ 0.73 in the ^{1}H NMR, which, upon irradiation of the Ir-bound ^{31}P nuclei, collapses to a singlet. The resonance for this ligand in the $^{13}C\{^{1}H\}$ NMR spectrum appears as a triplet at δ −22.6 ($^{2}J_{P-C}$ = 7.0 Hz), showing no Rh coupling. The high-field chemical shift of this signal is also consistent with an Ir-bound methyl ligand in this system, in contrast to the Rh-bound methyl groups, which tend to resonate significantly downfield, as observed for **14**. The silicon−hydrogen moiety is bound to Rh in a nonclassical, agostic fashion, as shown by its ^{1}H NMR resonance, which appears as a multiplet (dddd) at δ −0.65 ($^{1}J_{Rh-H}$ = 24 Hz, $^{2}J_{H-H}$ = 6 Hz, $^{3}J_{P(Ir)-H(Si)}$ = 9 Hz, $^{3}J_{P(Rh)-H(Si)}$ = 8 Hz). The additional coupling shown by this hydrogen to the Ir-bound ^{31}P nuclei, as established by selective ^{31}P decoupling experiments, indicates that the silyl group is σ-bound to Ir. The chemical shift of this agostic proton is significantly upfield compared to the silyl hydrogen of **14**, which appears at δ 5.50, but still lies downfield from a classical metal hydride resonance in this system. Similar high-field signals for M−H−Si protons have been reported for $[Ir_2(H)(CO)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}SiPh_2H)(dppm)_2]$,[9] $[Cp_2Ti(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^2\text{-}HSiPhH)TiCp_2]$,[52a] and $[Mn_2(CO)_6(\mu\text{-}\eta^3\text{-}H_2SiPh_2)(dppm)_2]$.[52b] Furthermore, the small coupling constant (*ca.* 8 Hz.) between this hydrogen and the Rh-bound ^{31}P nuclei, compared to typical values for a terminal hydride on Rh (*ca.* 20 Hz), argues in support of a three-center Rh−H−Si interaction in **15**, consistent with inherently weaker Rh−H interaction. However, the most compelling evidence for the agostic nature of this Si−H bond is given by the observed Si satellites (Figure 8) in the ^{1}H NMR spectrum, demonstrating Si−H coupling of 84 Hz, typical of agostic or η^2-silane complexes,[8] which is significantly lower than the coupling constant for a classical Si−H bond, as was shown in complex **14** ($^{1}J_{Si-H}$ = 170 Hz). The ^{29}Si NMR of **15** also shows a significant downfield shift to δ 6.3 compared with the chemical shift (δ −25.7) for the terminally bonded Si in compound **14**.

The terminal nature of the two carbonyl ligands was confirmed by the $^{13}C\{^{1}H\}$ NMR spectrum, showing signals at δ 193.2 (dt, $^{1}J_{RhC}$ = 78.4 Hz, $^{2}J_{PC}$ = 15 Hz) and 178.0. Once again, the *trans* disposition of the Ir-bound CO and the hydride was established by the *trans* C−H coupling constant of 24.3 Hz, observed in the proton-coupled ^{13}C NMR spectrum. In a doubly enriched ($^{13}CH_3/^{13}CO$) sample of compound **15**, the mutually *cis* arrangement of the Ir-bound CO and CH_3 groups was established by their low mutual coupling of 2 Hz in the ^{13}C NMR spectrum. Compound **15** appears to be static in solution at −20 °C, displaying no observable exchange between the silyl hydrogen and the bridging hydride, as was confirmed by SST NMR experiments, which is in contrast with the report of such exchange for the related $[(dippe)_2(Rh)_2(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^2\text{-}SiPh_2H)]$.[11] Compound **15** is unstable at ambient temperatures in solution but was isolated analytically pure at −20 °C and found to be stable at ambient temperature in the solid state, as confirmed by redissolving the solid compound at −20 °C and subsequent NMR studies. The conversion of **14** to **15** was found to be irreversible, as cooling **15** to −78 °C did not produce **14**. Unfortunately, attempts to obtain single X-ray-quality crystals of **15** were unsuccessful.

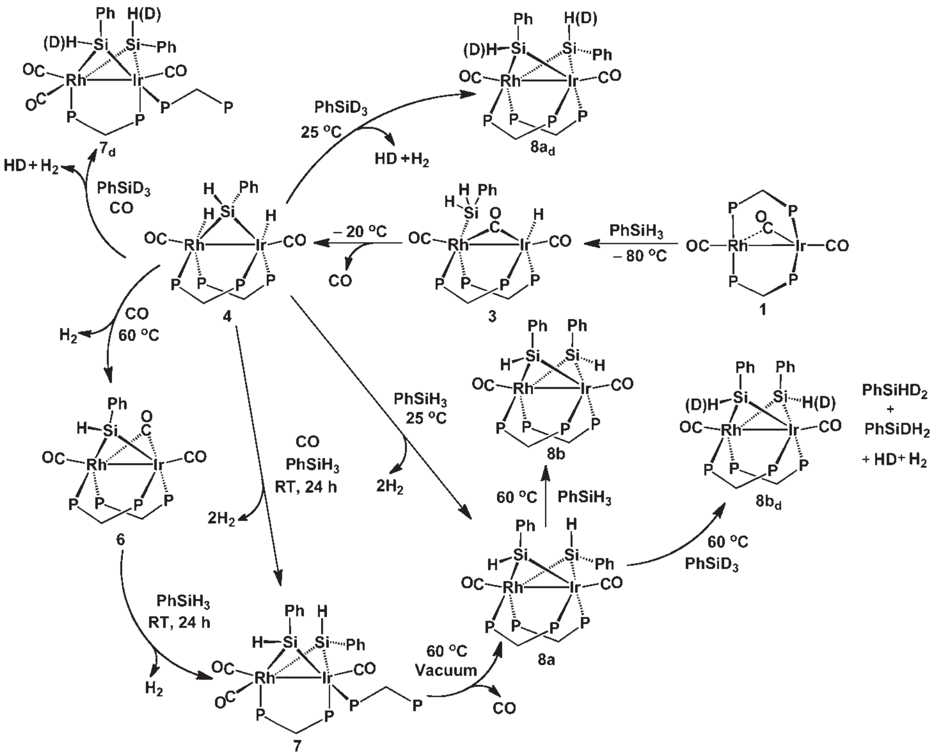
When allowed to warm to ambient temperature, compound **15** transforms into two new species in an approximate 1:1 ratio (Scheme 9). One of these products, the silylene-bridged acetyl dihydride complex, $[RhIr(H)(COCH_3)(CO)(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2][CF_3SO_3]$ (**16**), is the result of oxidative addition of the second Si−H bond, concomitant with migratory insertion of the methyl group and a carbonyl. The other product, identified as a silylene-bridged monohydride complex, $[RhIr(CO)_2(\mu\text{-}H)(\mu\text{-}SiPh_2)(dppm)_2][CF_3SO_3]$ (**17**), has resulted from oxidative addition of the second Si−H bond and accompanying reductive elimination of methane, identified by a singlet at δ 0.21 in the ^{1}H NMR spectrum. The $^{13}C\{^{1}H\}$ NMR spectrum of the crude product mixture also shows $^{13}CH_4$ as a singlet at δ −4.3, which disappears upon workup as the gas is lost.

The acetyl carbonyl of compound **16** appears as a singlet at δ 280.0 in the $^{13}C\{^{1}H\}$ NMR spectrum, and the methyl group gives rise to a singlet at δ 46.0, indicating that this group is not directly bonded to either metal. In addition, these signals appear as doublets in the doubly enriched ($^{13}CH_3/^{13}CO$) compounds, showing a mutual coupling of 26 Hz. The other carbonyl is shown to be Rh-bound (δ 193.7; $^{1}J_{Rh-C}$ = 70 Hz). The acetyl protons appear in the ^{1}H NMR spectrum as a singlet at δ 1.23. This spectrum also shows signals at −8.86 (triplet, $^{2}J_{P-H}$ = 13.2 Hz) and −14.98 (doublet of doublets of doublets, $^{1}J_{Rh-H}$ = 22 Hz, $^{2}J_{P(Ir)H}$ = 13.2 Hz, $^{2}J_{P(Rh)H}$ = 10.9 Hz) assigned to terminal (Ir) and bridging hydride ligands, respectively. When the Ir-bound ^{31}P nuclei are decoupled, the terminal hydride signal collapses to a singlet, showing ^{29}Si satellites with coupling of only 32 Hz, indicating a weak interaction of the hydrido group with Si. This interaction is further confirmed by the HSQC NMR experiment, which shows a peak for ^{29}Si at δ 20.0 (consistent with the bridging nature of the $SiPh_2$ group) displaying a correlation with the Ir-bound hydride.

---

(52) (a) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (b) Carreño, R.; Riera, V.; Ruiz, M. A; Jeannin, Y.; Philoche-Levisalles, M. *J. Chem. Soc., Chem. Commun.* **1990**, 15.

Scheme 10



The $^{13}C\{^{1}H\}$ NMR spectrum for compound **17** shows a doublet of multiplets at δ 187.6 with Rh coupling of *ca.* 77 Hz and a broad triplet at 176.8, assigned to terminal carbonyls on Rh and Ir, respectively. The ^{1}H NMR spectrum of this compound displays multiplets at δ 4.42 and 4.40 for the dppm methylenes and a doublet of multiplets with unresolved P−H coupling at δ −10.22 for the hydride, which integrates as approximately half of those of the dppm methylenes groups. Cooling the sample to −40 °C does not result in simplification of the hydride resonance; however, the broadband-decoupled $^{1}H\{^{31}P\}$ NMR spectrum gives a doublet with Rh coupling ($^{1}J_{Rh-H} = 15$ Hz). Compound **17** can also be generated from the reaction of the diphenylsilylene-bridged complex, $[RhIr(H)_2(CO)_2(\mu\text{-}SiPh_2)(dppm)_2]$ (**9**), with 1 equiv of trifluoromethane sulfonic acid, accompanied by H_2 evolution, further confirming its formulation.

Discussion

In the major part of this report, the reactivity of the neutral species $[RhIr(CO)_3(dppm)_2]$ (**1**) with a limited number of primary and secondary silanes was studied. Not surprisingly, the difference in steric bulk of these classes of silanes resulted in significant differences in their reactivities, with the smaller arylsilanes readily forming products in which two silylene groups bridged the metals. Upon the basis of the reactions carried out under various conditions, involving **1** and phenylsilane, a stepwise sequence of transformations leading to the final bis(silylene)-bridged product (**8b**) is proposed and is shown (for phenylsilane) in Scheme 10.

At −80 °C, the reaction of $PhSiH_3$ with **1** (shown at the upper right of Scheme 10) initially proceeds by activation of one Si−H bond to form the silyl/hydride complex **3**, having the silyl group on Rh and the hydride on Ir. Although this low-temperature intermediate does not conclusively establish at which metal center Si−H bond-activation is initiated, two possibilities can be proposed: either the Si−H bond oxidatively adds at Rh followed by hydride migration to Ir, or it adds at Ir followed by silyl migration to Rh. We feel that the much higher mobility of a hydride ligand favors addition at Rh followed by migration of the hydride. Although hydride migration at low temperatures is well precedented,[53] there are few examples of silyl migration reported in bimetallic complexes, even at ambient temperatures,[31c,e,k,l] and the migration of an aryl-silyl group in the presence of bulky dppm ligands would appear not to be facile. Furthermore, oxidative addition at Rh is consistent with the coordinative unsaturation at this metal, and the saturation at Ir. Upon warming the solution of **3** to −20 °C, conversion to the silylene-bridged dihydride species (**4**) occurs by the oxidative addition of the second Si−H bond. No intermediate was observed during this transformation; however, it is presumed to take place through a silyl-bridged agostic intermediate in which one Si−H bond of the Rh-bound silyl group interacts with Ir to form a σ complex. The unsaturation at Ir required for the agostic Si−H interaction and subsequent oxidative addition of the Si−H bond can occur by transfer of the bridging carbonyl to Rh concomitant with Rh−Ir bond cleavage. The loss of one of the Rh-bound carbonyls following the second Si−H bond cleavage is then accompanied by hydride migration from Ir to Rh to give **4**.

The reaction of **4** with another equivalent of $PhSiH_3$ at ambient temperatures yields the bis(silylene)-bridged product **8a**. As was the case for compound **3**, complex **4** is again coordinatively saturated, necessitating ligand loss in order to accommodate a second silane. The reaction of **4** with $PhSiD_3$ in the presence and the absence of CO (yielding deuterium scrambled $\mathbf{7_d}$ or $\mathbf{8a_d}$, respectively) eliminates the possibility

---

[53] Vaarstra, B. A.; O'Brien, K. N.; Eisenberg, R.; Cowie, M. *Inorg. Chem.* **1988**, *27*, 3668.

that H_2 loss from **4** precedes activation of the second silane, since both H_2 and HD are produced, accompanied by incorporation of both H and D into both silylene ligands. Unsaturation can also result from dissociation of one end of a diphosphine unit (probably from the more labile Rh center) or by reductive elimination of a hydride and one end of the μ-silylene bridge (again, probably from the Rh center) to yield a transient Ir-bound silyl group. The observation of the pendent-dppm species **7** and of the silyl/silylene product **12** supports phosphine dissociation. Furthermore, the recoordination of the pendent-dppm group at Rh upon carbonyl removal from **7** to give **8a** offers additional support for phosphine dissociation/reassociation steps.

A necessary intermediate in the transformation of **4** to **8a** is one containing the original bridging silylene group together with a terminal silyl group, resulting from the first Si−H activation of the added silane. Although no such species was observed in the reaction with primary silanes, a model species (stabilized by CO addition) was observed with diphenylsilane. This model silyl/silylene-bridged compound (**12**; see Scheme 8) confirms phosphine dissociation from Rh and concomitant silane addition at this metal. In the absence of the additional carbonyl ligand, the oxidative addition of one of the remaining Si−H bonds of the phenylsilyl group in the putative silyl/silylene intermediate occurs with H_2 elimination promoted by recoordination of the pendent phosphine at Rh.

In the case of the monosubstituted bis(silylene)-bridged products, the kinetic product (**8a**) in which the aryl substituent on one μ-silylene group is axial while the other is equatorial minimizes unfavorable interactions between these groups, while having unfavorable interactions between the equatorial substituent and the dppm phenyls (see Scheme 4). In the axial/axial isomer (**8b**), the unfavorable interactions between both axial substituents can be alleviated by an increase in the separation of these groups, which is permitted by the lower steric interactions with the dppm groups (having hydrogens in both equatorial sites on the Si atoms). This is not possible with doubly substituted silylene groups, for which repulsive interactions with each other and with dppm phenyl groups simultaneously result.

Although Scheme 10 offers a credible rationalization for the multiple Si−H activation processes leading to the bis(silylene)-bridged products, the observation that the axial/equatorial isomer of the bis(silylene)-bridged **8a** requires additional silane for isomerization to the axial/axial isomer (**8b**) to occur, and the deuterium/hydrogen scrambling that occurs points to additional complexities that are not fully understood. It appears that an unobserved transient, containing three Si-containing units, is involved at some stage. Such M_2Si_3 species have been reported.[54] This proposal is supported by the observation of a mixed phenylsilylene/difluorophenylsilylene product (**8d**) together with bis-phenylsilylene (**8b**) and bis-difluorophenylsilylene (**8c**) products in the reaction of the bis-phenylsilylene precursor (**8a**) with difluorophenylsilane.

In the second, minor part of this study, we investigated the reactivity of the related cationic precursor, $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**), with diphenylsilane. This species has two fewer electrons than the neutral tricarbonyl compound **1**, which leads to unsaturation at both metals in **2**, instead of only at Rh in **1**. This additional unsaturation is manifested in silane oxidative addition at Ir (see Scheme 9) instead of at Rh, as was proposed in the reaction of **1**.

In this cationic system, the agostic interaction of a silyl Si−H bond with the adjacent metal is observed. Although such species are presumably involved in the double Si−H activation by the neutral tricarbonyl precursor **1**, these intermediates were never observed in these neutral species. Presumably, the positive charge on **2** inhibits the second Si−H activation step, allowing the bridged agostic species, in which the silyl group is σ-bound to Ir while involved in an agostic interaction with Rh, to be observed. Warming slightly leads to a subtle rearrangement, which brings about further weakening of this remaining Si−H bond. This transformation can be viewed as resulting from migration of the diphenylsilyl group from Ir to Rh and of the agostic interaction to Ir. The greater tendency of Ir to cleave the Si−H bond is evident in the ^1H NMR spectrum, which displays a very weak one-bond Si−H coupling of only 32 Hz, indicative of a weak Si−H interaction, lying close to the silylene-bridged hydride extreme.

Conclusions

In this Rh/Ir system, we were able to observe species not observed in the Rh_2 and Ir_2 systems giving us a clearer picture of the roles of the adjacent metals in the different steps leading to the eventual activation of up to four Si−H bonds and the incorporation of two Si-containing fragments. Evidence has been obtained for interactions between pairs of adjacent bridging silylene groups, although the nature of these interactions is not clear. This and the observation of a silyl/silylene unit in the Rh/Ir core suggest the possibility of Si−Si coupling at these centers.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support for this research and NSERC for funding the Siemens P4/RA diffractometer, the Bruker D8/APEX II CCD diffractometer, and the Nicolet Avatar IR spectrometer. We thank the Department's Analytical and Instrumentation Laboratory and NMR Spectroscopy Laboratory for their outstanding support. Lindsay J. Hounjet is thanked for help during manuscript preparation.

Supporting Information Available: Tables of crystallographic experimental details (for compounds **4**, **5**, **8a**, **8b**, **8c**, and **12**) and selected bond lengths and angles (for compounds **4**, **5**, **8c**, and **12**). The STD NMR spectrum for compound **4** and selected NMR spectra for compounds **3**, **8a**, and **8b** in PDF format. Atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for these compounds in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(54) Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Inorg. Chim. Acta* **1994**, *222*, 345.