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Synthesis and Reactivity of Silyl and Silylene Ligands in the Coordination Sphere of the 14-Electron Fragment $Cp^*(^iPr_3P)Os^+$

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Oxidative addition reactions of the 16-electron half-sandwich osmium complex $Cp^*(^iPr_3P)$-OsBr (**2**) with SiH_4 and primary and secondary hydrosilanes were examined. Compared to the previously studied ruthenium complex $Cp(^iPr_3P)RuCl$ (**1**), **2** exhibits a greater tendency to add hydrosilanes to afford stable, isolable silyl complexes. Using an abstraction−migration methodology, in which abstraction of a labile metal halide ligand is followed by 1,2-H migration from silicon to the metal center, new osmium silylene complexes were prepared. Thus, silyl complexes derived from **2** were combined with $LiB(C_6F_5)_4$ to afford cationic osmium silylene complexes of the type $[Cp^*(^iPr_3P)(H)_2Os{=}SiRR'][B(C_6F_5)_4]$ (R = aryl, silyl; R′ = aryl, H). The silylene complexes exhibit downfield ^{29}Si chemical shifts ranging from 316 ppm (R = 2,4,6-$^iPr_3C_6H_2$, R′ = H; **18**) to 417 ppm (R = $Si(SiMe_3)_3$, R′ = H; **19**). Complexes with a hydride substituent at silicon feature downfield shifts for this proton (e.g., 12.06 ppm for **19**). The reaction of $Cp^*(^iPr_3P)Os(H)(Br)SiH_2SiPh_3$ (**11**) with $LiB(C_6F_5)_4$ provided the unexpected rearrangement product $[Cp^*(^iPr_3P)(H)_2Os{=}Si(Ph)SiPh_2H][B(C_6F_5)_4]$ (**22**). Reaction of **2** with $KB(C_6F_5)_4$ produced the metalated complex $\{Cp^*[^iPr_2P(\eta^2\text{-}MeC{=}CH_2)]OsH_2\}$-$[B(C_6F_5)_4]$ (**24**), which was shown to act as a synthon for the 14-electron species $Cp^*(^iPr_3P)$-Os^+. Thus, **24** reacted with Ph_2SiH_2 to afford $[Cp^*(^iPr_3P)(H)_2Os{=}SiPh_2][B(C_6F_5)_4]$ (**14**).

Introduction

Many important reactions of organosilanes, such as the hydrosilylation of olefins,[1,2] the Direct Process for the synthesis of chlorosilanes,[3] and Si−H/O−H coupling,[4,5] are promoted by transition metals. In the future, it is expected that transition metal silicon chemistry will play an even greater role in providing useful routes to silicon-based compounds and materials. Undoubtedly, this will require a better understanding of possible reaction pathways resulting from the interaction of organosilicon compounds with reactive transition metal centers.

A primary mode of initial silane activation by a transition metal complex involves the oxidative addition of an Si−H bond to a coordinatively unsaturated metal center to give a silyl hydride complex.[6] Subsequent reactions of the silyl hydride complexes with additional substrates, or further rearrangements of the new silicon ligand, may provide pathways to new products. In

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(1) (a) Marciniec, B., Guliniski, J. J., Urbaniak, W., Kornetka, Z. W., Eds. *Comprehensive Handbook on Hydrosilylation*; Pergamon: Oxford, 1992. (b) Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1993**, *446*, 15. (c) Marciniec, B. *Silicon Chem.* **2002**, *1*, 155. (d) Brook, M. A. *Silicon in Organic*, *Organometallic*, *and Polymer Chemistry*; Wiley: New York. (e) Ojima, I. *The Chemistry of Organic Silicon Compounds*, Wiley: Avon, 1989; Chapter 25. (f) Ojima, I.; Li, Z.; Zhu, J. *The Chemistry of Organic Silicon Compounds*; Wiley: Avon, 1998; Chapter 29.

(2) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Seitz, F.; Wrighton, M. S. *Angew. Chem.*, *Int. Ed. Engl.* **1988**, *27*, 289. (c) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90.

(3) (a) Lewis, K. M., Rethwisch, D. G., Eds. *Catalyzed Direct Reactions of Silicon*; Elsevier: Amsterdam, 1993. (b) Walter, H.; Roewer, G.; Bohmhammel, K. *J. Chem. Soc.*, *Faraday Trans.* **1996**, *92*, 4605. (c) Okamoto, M.; Onodera, S.; Okano, T.; Suzuki, E.; Ono, Y. *J. Organomet. Chem.* **1997**, *531*, 67. (d) Roewer, G.; Werkmeister, J.; Bohmhammel, K. In *Silicon for the Chemical Industry IV*; Geiranger, Norway, June 3−5, 1998, University of Science and Technology: Trondheim, Norway, 1998; p 239. (e) Acker, J.; Bohmhammel, K. *J. Phys. Chem. B.* **2002**, *106*, 5105. (f) Pachaly, B.; Weis, J. In *Organosilicon Chemistry III: From Molecules to Materials*, *Munich Silicon Days*; April 3, 1996, Wiley & Sons: New York, 1998; p 478. (g) Esteruelas, M. A.; Herrero, J.; López, F. M.; Martîn, M.; Oro, L. A. *Organometallics* **1999**, *18*, 1110. (h) Díaz, J.; Esteruelas, M. A.; Herrero, J.; Moralejo, L.; Oliván, M. *J. Catal.* **2000**, *195,* 187.

(4) (a) Lukevics, E.; Dzinatara, M. *J. Organomet. Chem.* **1985**, *295*, 265. (b) Corey, J. *Adv. Silicon Chem.* **1991**, *1*, 327. (c) Schubert, U.; Lorenz, C. *Chem. Ber.* **1995**, *128*, 1267. (d) Chalk, A. J. *Chem. Commun.* **1970**, 847. (e) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc.*, *Chem. Commun.* **1973**, 38. (f) Ojima, I.; Kogure, T.; Nihonyanigi, M.; Kono, H.; Inaba, S.; Nagai, Y. *Chem. Lett.* **1973**, 501. (g) Davies, J. A.; Hartley, F. R.; Murray, S. G.; Marshall, G. *J. Mol. Catal.* **1981**, *10*, 171. (h) Parish, R. V.; Dwyer, J.; Hilal, H. S. *J. Organomet. Chem.* **1982**, *228*, 191. (i) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *120*, 337. (j) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *114*, 135. (k) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1977**, *127*, 7. (l) Parish, R. V.; Blackburn, S. N.; Haszeldine, R. N.; Setchfield, J. H. *J. Organomet. Chem.* **1980**, *192*, 329. (m) Oehmichen, U.; Singer, H. *J. Organomet. Chem.* **1983**, *23*, 199. (n) Crabtree, R. H.; Luo, X.-L. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (o) Doyle, M. P.; High, K. G.; Bagheri, V.; Pieters, R. J.; Lewis, P. J.; Pearson, M. M. *J. Org. Chem.* **1990**, *55*, 6082. (p) Bedard, T. C.; Corey, J. Y. *J. Organomet. Chem.* **1992**, *428*, 315. (q) Barber, D. E.; Lu, Z.; Richardson, T.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4709. (r) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045. (s) Field, L. D.; Messerle, B. A.; Rehr, M.; Soler, L. P.; Hambley, T. W. *Organometallics* **2003**, *22*, 2387.

(5) Goikhman, R.; Aizenberg, M.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 10894.

(6) (a) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (b) Corey, J. Y. *Adv. Silicon Chem.* **1991**, *1*, 327. (c) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons: New York, 1989; Chapter 24. (d) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons: New York, 1991; Chapter 10.

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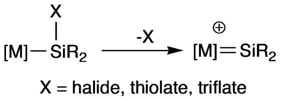
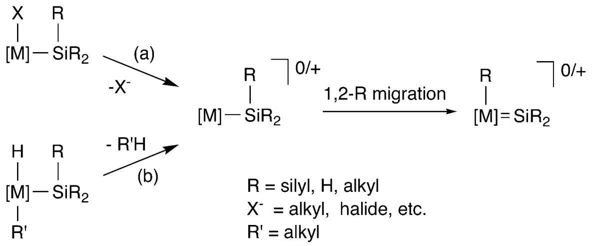
studies on transition metal-mediated reactions of organosilanes, considerable speculation has centered on the possible role of transition metal silylene complexes in observed reactivity. Such silylene species have been proposed as intermediates in processes such as the redistribution of substituents on silicon,[7] transfer of silylene fragments to an unsaturated carbon−carbon bond,[8] and the Direct Process.[3] Consequently, studies with isolated silylene complexes should contribute important information regarding their possible roles in observed, metal-mediated transformations.

For the conversion of silyl to silylene complexes, two reaction pathways have been observed. These are anion metathesis, in which a labile substituent on silicon, such as a halide, triflate, or thiolate, is replaced with a noncoordinating anion (eq 1),[9] and 1,2-migration of a substituent, such a hydride, silyl, or alkyl group, from silicon to an unsaturated metal center (eq 2).[10,11]



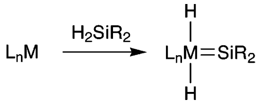
(1)



(2)

The open coordination site required for the latter pathway may be created by abstraction of an anionic group from the metal center (path a),[10a] reductive C−H bond elimination (path b),[10b−e] or ligand dissociation.[11] For example, abstraction of the methyl ligand from the platinum complex $(\kappa^2\text{-}{}^iPr_2PCH_2CH_2P^iPr_2)Pt(Me)SiHMes_2$ afforded the cationic silylene complex $[(\kappa^2\text{-}{}^iPr_2PCH_2CH_2P^iPr_2)(H)Pt{=}SiMes_2][MeB(C_6F_5)_3]$ via a 1,2 hydride migration from silicon to the unsaturated metal center.[10a]

While the synthesis of silylene complexes via multistep routes involving silyl complexes has provided important data concerning the nature of these species, synthesis of silylene complexes directly from silanes remains an important goal. Furthermore, transformations of the latter type may play a role in the development of new catalytic cycles involving silicon. In principle, the activation of two Si−H bonds at a metal center would seem to require a 14-electron metal fragment or its synthetic equivalent (eq 3). Along these lines, unsaturated iridium complexes have been employed in the conversion of secondary silanes to silylene ligands via two sequential Si−H bond activations.[10b,c] The future development of this reactivity and its use in new catalytic pathways is likely to hinge upon the availability of a range of metal species capable of activating silanes in this manner.



(3)

Previous studies involving the coordinatively unsaturated ruthenium species $Cp^*(R_3P)RuCl$ (R = cyclohexyl, ${}^iPr$ (**1**)) demonstrated that these complexes are useful precursors to a variety of electron-rich silyl and silene complexes.[12] Similarly, preliminary investigations with the related osmium complex $Cp^*({}^iPr_3P)OsBr$ (**2**) demonstrated that it also oxidatively adds small molecules such as H_2 and $PhSiH_3$ to form stable Os(IV) species.[13] The presence of a potentially labile bromide substituent in complexes derived from **2** suggested the use of the abstraction−migration route outlined above for the generation of new osmium silylene complexes. In particular, it seemed that the established ability of electron-rich osmium fragments to stabilize unsaturated ligands[14−19] might facilitate the isolation of stable silylene complexes. For this reason, we have begun to explore the oxidative addition reactions of **2** with various hydrosilanes and have investigated conversions of the resulting osmium silyl derivatives to silylene complexes. Generation of a 14-electron fragment of the type $Cp^*({}^iPr_3P)Os^+$, as a means to effect the direct conversion of silanes to silylene ligands (eq 3), was also targeted.

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(7) (a) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213. (b) Kumada, M. *J. Organomet. Chem.* **1975**, *100*, 127.

(8) (a) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57. (b) Cirakovic, J.; Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 9370. (c) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824. (d) Bodnaryl, P. M.; Palmer, W. S.; Ridgway, B. H.; Shaw, J. T.; Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 4737. (e) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 1097. (f) Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **1999**, *121*, 949. (g) Palmer, W. S.; Woerpel, K. A. *Organometallics* **2001**, *20*, 3691. (h) Yamamoto, K.; Okinoshi, H.; Kumada, M. *J. Organomet. Chem.* **1970**, *23*, C7. (i) Yamamoto, K.; Okinoshi, H.; Kumada, M. *J. Organomet. Chem* **1971**, *27*, C31. (j) Okinoshi, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (k) Kumada, M.; Ishikawa, M.; Okinoshi, H.; Yamamoto, K. *Ann. N. Y. Acad. Sci.* **1974**, *239*, 32. (l) Yamashita, H.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 403.

(9) (a) Straus, D. A.; Tilley, T. D.; Reingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673. (c) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801. (d) Grumbine, S. D.; Chadha, R. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1518. (e) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358. (f) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495. (g) Grumbine, S. K.; Straus, D. A.; Tilley, T. D. *Polyhedron* **1995**, *14*, 127. (h) Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 5607. (i) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884. (j) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, *21*, 4648. (k) Kobayashi, H.; Ueno, K.; Ogino, H. *Chem. Lett.*, **1999**, 239. (l) Glaser, P. B.; Wanandi, P. W.; Tilley, T. D. *Organometallics*, submitted. (m) Wanandi, P. W.; Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 972.

(10) (a) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Intl. Ed.* **1998**, *37*, 2524. (b) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4065. (c) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871. (d) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702. (e) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816.

(11) (a) Ogino, H. *Chem. Rec.* **2002**, *2*, 291. (b) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (c) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (d) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2797. (e) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369. (f) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (g) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (h) Sharma, H. K.; Pannell, K. H. *Organometallics* **2001**, *20*, 7.

(12) (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1992**, 1201.

(13) Glaser, P. B.; Tilley, T. D. *Eur. J. Inorg. Chem.* **2001**, 2747.

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Table 1. NMR Spectroscopic Data for Silyl Complexes 3−11

$RSiH_3$	product		δ ^1H (Si−*H*)	δ ^{29}Si (Os−*Si*)
SiH_4	$Cp^*(^iPr_3P)Os(H)(Br)SiH_3$	(**3**)	3.59	−73.0
$PhSiH_3$	$Cp^*(^iPr_3P)Os(H)(Br)SiH_2Ph$	(**4**)	6.60, 4.71	−26.0
$MesSiH_3$	$Cp^*(^iPr_3P)Os(H)(Br)SiH_2Mes$	(**5**)	4.90, 4.90	−49.9
$dippSiH_3$	$Cp^*(^iPr_3P)Os(H)(Br)SiH_2dipp$	(**6**)	5.05, 4.91	−53.1
$tripSiH_3$	$Cp^*(^iPr_3P)Os(H)(Br)SiH_2trip$	(**7**)	4.96, 4.83	−53.0
$(C_6F_5)SiH_3$	$Cp^*(^iPr_3P)Os(H)(Br)SiH_2(C_6F_5)$	(**8**)	5.49, 3.98	−62.2
$HexSiH_3$	$Cp^*(^iPr_3P)Os(H)(Br)SiH_2Hex$	(**9**)	5.38, 4.39	−30.5
$(Me_3Si)_3SiSiH_3$	$Cp^*(^iPr_3P)Os(H)(Br)SiH_2Si(SiMe_3)_3$	(**10**)	5.12, 3.62	−83.5
Ph_3SiSiH_3	$Cp^*(^iPr_3P)Os(H)(Br)SiH_2SiPh_3$	(**11**)	4.84, 3.19	−78.3

Results and Discussion

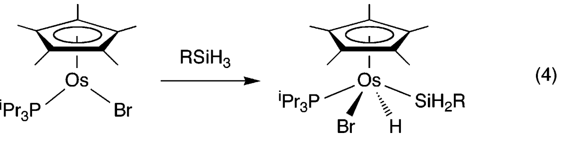
As described below, oxidative additions of hydrosilanes to **2** are substantially more general in scope than corresponding reactions of hydrosilanes with related ruthenium species such as $Cp^*(^iPr_3P)RuCl$ (**1**). While intermolecular oxidative addition reactions of hydrosilanes with **1** are limited to primary silanes such as $PhSiH_3$ and $MesSiH_3$,[12] secondary silanes such as Me_2SiH_2 and Ph_2SiH_2 add to **2** to form stable silyl complexes (vida infra). The underlying reasons for this observed difference in reactivity may include a higher metal−silicon bond strength for the osmium complexes and the greater stability of osmium(IV) versus analogous ruthenium(IV) complexes.[20]

Reactions of 2 with Hydrosilanes. Despite being the simplest hydrosilane, SiH_4 has been employed in few syntheses of transition metal silyl complexes.[6a,21] The paucity of such reports may be attributed to the difficulty in safely handling this pyrophorric reagent and to the instability of the resulting products toward further reactions.[6a]

Exposure of a solution of **2** to an atmosphere of 15% SiH_4 in N_2 resulted in immediate formation of the bright yellow silyl complex $Cp^*(^iPr_3P)Os(H)(Br)SiH_3$ (**3**), which was isolated as a yellow microcrystalline solid. When **2** was treated with excess SiH_4 in an NMR tube at room temperature, only **3** and unreacted SiH_4 were observed. The stability of the Si−H bonds in **3** to further oxidative addition may be attributed to the steric protection afforded by the Cp* and P^iPr_3 ligands. The bimetallic complex $Cp^*(^iPr_3P)(H)(Br)Os(SiH_2)Os(Br)(H)(P^iPr_3)Cp^*$, in which two osmium centers are bridged by a single silicon atom, would presumably be too sterically crowded.

A ^1H-coupled ^{29}Si INEPT NMR spectrum in which the ^{29}Si resonance appeared as a quartet of doublets of doublets ($^1J_{SiH} = 176$ Hz, $^2J_{SiH} = 10$ Hz, $^2J_{PSi} = 10$ Hz) conclusively demonstrated the presence of three intact Si−H bonds in **3**. The presence of diastereotopic methyl groups on the P^iPr_3 ligand indicated that the complex is stereochemically rigid on the NMR time scale at room temperature. The osmium-bound hydride ligand exhibits a $^2J_{SiH}$ coupling constant of 6.2 Hz, suggesting that oxidative addition of the Si−H bond to osmium is complete in **3** and that there are no "nonclassical" interactions present.

Reactions of **2** with the primary silanes $PhSiH_3$, $MesSiH_3$, $dippSiH_3$ (dipp = 2,4-$^iPr_2C_6H_3$), $tripSiH_3$ (trip = 2,4,6-$^iPr_3C_6H_2$), $(C_6F_5)SiH_3$, $HexSiH_3$, $(Me_3Si)_3SiSiH_3$, and Ph_3SiSiH_3 proceeded smoothly to afford the corresponding Os(IV) silyl complexes **4**−**11** (eq 4, Table 1).



(4)

R = H (**3**), Ph (**4**), Mes (**5**), dipp (**6**), trip (**7**),
C_6F_5 (**8**), Hex (**9**), $Si(SiMe_3)_3$ (**10**), $SiPh_3$ (**11**)

The complexes were isolated as moderately air-sensitive yellow to yellow-orange microcrystalline solids. As determined by NMR spectroscopy, yields were essentially quantitative (>95%) in all cases. The most important spectroscopic data for these complexes were obtained from ^1H and ^{29}Si NMR spectroscopy. In each case, the two silicon hydrides are rendered diastereotopic by the chiral osmium center. Each complex exhibits a single, upfield-shifted, ^{31}P-coupled resonance for the osmium hydride ligand. For silyl hydride complexes of this type, the possibility exists for "nonclassical" hydrogen−silicon interactions. Species featuring such interactions, including η^2 silane complexes, often display values for $^2J_{SiH}$ in excess of 20 Hz.[6a,22] In the silyl complexes discussed here, coupling between the osmium hydride ligand and the silicon center, when

---

(14) (a) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939. (b) Brumaghim, J. L.; Girolami, G. S. *Chem. Commun.* **1999**, 953. (c) Roder, K.; Werner, H. *J. Organomet. Chem.* **1989**, *367*, *321.* (d) Huang, D.; Spivak, G. J.; Caulton, K. G. *New J. Chem.* **1998**, *22*, 1023. (e) Werner, H.; Stuer, W.; Wolf, J.; Laubender, M.; Weberndorfer, B.; Herbst-Irmer, R.; Lehmann, C. *Eur. J. Inorg. Chem.* **1999**, *11*, 1889

(15) (a) Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205. (b) Elliott, G. P.; Roper, W. R.; Waters, J. M. *Chem. Commun.* **1982**, 811.

(16) (a) Bin Wen, T.; Zhou, Z. Y.; Jia, G. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 1951. (b) Roper, W. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2440.

(17) (a) Baya, M.; Crochet, P.; Esteruelas, M. A.; Lopez, A. M.; Modrego, J. *Organometallics* **2001**, *20*, 4291. (b) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *195*, 977. (c) Bin Wen, T.; Yang, S. Y.; Zhou, Z. Y.; Lin, Z. Y.; Lau, C. P.; Jia, G. C. *Organometallics* **2000**, *19*, 3757.

(18) (a) Collins, T. J.; Roper, W. R.; Town, K. G. *J. Organomet. Chem.* **1976**, *121*, C41. (b) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 1206.

(19) (a) Collins, T. J.; Roper, W. R. *Chem. Commun.* **1976**, 1044. (b) Collins, T. J.; Roper, W. R. *J. Organomet. Chem* **1978**, *159*, 73.

(20) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley-Interscience: New York, 1980. (b) Sánchez-Delgado, R. A.; Rosales, M.; Esteruelas, M. A.; Oro, L. A. *J. Mol. Catal. A* **1995**, *96*, 231.

(21) (a) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648 (b) Woo, H. G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698. (c) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (d) Luo, X. L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159. (e) Herrmann, W. A.; Voss, E.; Guggolz, E.; Ziegler, M. *J. Organomet. Chem.* **1985**, *284*, 47. (f) Anema, S. G.; Barris, G. C.; MacKay, K. M.; Nicholson, B. K. *J. Organomet. Chem.* **1988**, *350*, 207. (g) Anema, S. G.; MacKay, K. M.; Nicholson, B. K.; Van Tiel, M. *Organometallics* **1990**, *9*, 2436. (h) Mackay, K. M.; Cham Chee, T. *J. Chem. Res., Synop.* **1982**, 229 (i) Ebsworth, E. A. V.; Fraser, T. E.; Henderson, S. G.; Leitch, D. M.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1010. (j) Ebsworth, E. A. V.; Marganian, V. M.; Reed, F. J. S.; Gould, R. O. *J. Chem. Soc., Dalton Trans.* **1978**, 1167. (k) Atheaux, I.; Donnadieu, B.; Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Hussein, K.; Barthelat, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 5664. (l) Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1. (m) Lebuis, A. M.; Harrod, J. F. *J. Chem. Soc., Chem. Commun.* **1998**, 1089.

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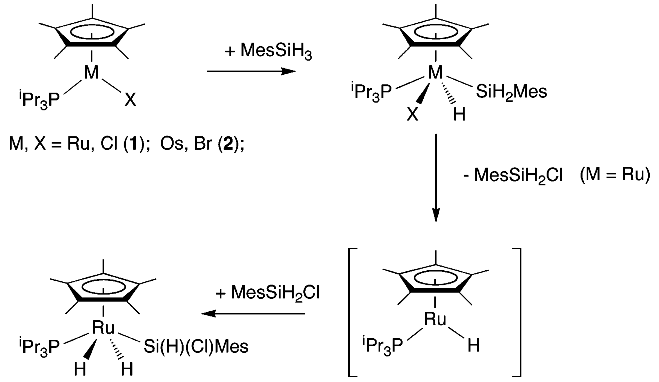
Scheme 1



observable, was found to be below 6 Hz. For example, the value for $^2J_{SiH}$ is 5.3 Hz for **5** and is too small to be resolved in **10**.[23] These low values are inconsistent with a significant Si−H interaction.

As previously reported,[12b] the reaction of **1** and MesSiH$_3$ afforded the chlorosilyl complex Cp*($^iPr_3P$)(H)$_2$RuSi(H)(Cl)Mes instead of a dihydridosilyl complex analogous to **5**. In this reaction, it appears that the initial product Cp*($^iPr_3P$)Ru(H)(Cl)RuSiH$_2$Mes reductively eliminates MesSiH$_2$Cl, which then adds to Cp*($^iPr_3P$)RuH to afford the observed product (Scheme 1). The observed difference in reactivity between **1** and **2** may be attributed to the inherently greater lability of ruthenium complexes compared to analogous osmium species and to the greater thermodynamic driving force for the formation of a Si−Cl versus a Si−Br bond.

Reaction of (C$_6$F$_5$)SiH$_3$ with **5** (2-fold molar excess, CD$_2$Cl$_2$ solution) quantitatively afforded **8** after 7 h at room temperature. This indicates that the oxidative addition of MesSiH$_3$ to **2** is reversible and that **8** is thermodynamically more stable than **5**.

Reactions of secondary silanes with **1** have so far not provided isolable silyl complexes.[12] For example, in the presence of a large excess of Me$_2$SiH$_2$, **1** was found to exist in rapid equilibrium with the corresponding oxidative addition product, precluding isolation of the product in this case.[24]

In contrast to the behavior of **1** toward secondary silanes, **2** reacts with Me$_2$SiH$_2$ and Ph$_2$SiH$_2$ to afford Cp*($^iPr_3P$)Os(H)(Br)SiMe$_2$H (**12**) and Cp*($^iPr_3P$)Os(H)(Br)SiPh$_2$H (**13**), respectively, as isolable, crystalline compounds. It is reasonable to assume that greater Os−H and Os−Si bond strengths, as well as the stability of the Os(IV) oxidation state, are responsible for this pronounced difference in reactivity. The spectroscopic properties of these complexes are similar to those resulting from the oxidative additions of primary silanes. In both **12** and **13**, the two organic groups bound to silicon are diastereotopic (by NMR spectroscopy).

The steric limitations of this oxidative addition are reached with more bulky secondary silanes such as $^iPr_2SiH_2$, Mes$_2$SiH$_2$, and $^tBu_2SiH_2$, which do not react with **2** to afford isolable silyl complexes. Consistent with a steric explanation for this lack of reactivity, **2** was also found to be unreactive toward tertiary hydrosilanes such as Me$_3$SiH and Et$_3$SiH. Esteruelas and co-workers have previously shown that upon loss of a phosphine ligand, Cp($^iPr_3P$)$_2$OsCl adds Et$_3$SiH and Ph$_3$SiH, an observation consistent with the smaller steric impact of the Cp ligand versus Cp*.[25]

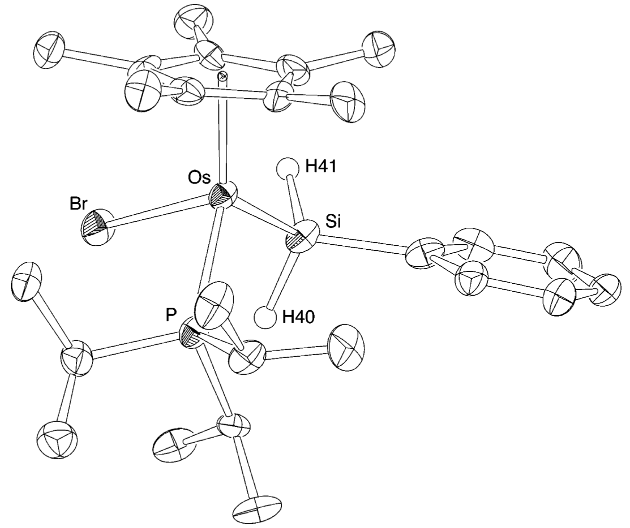


Figure 1. ORTEP drawing of **4** with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C$_5$Me$_5$ centroid): Os−P 2.368(3), Os−Br 2.568(1), Os−Si 2.398(3), Os−Cp* 1.9369(4) Br−Os−P 86.51(7), Br−Os−Si 79.56(7), P−Os−Si 101.0(1), Si−Os−Cp* 120.58(8), P−Os−Cp* 136.29(7), Br−Os−Cp* 112.15(3).

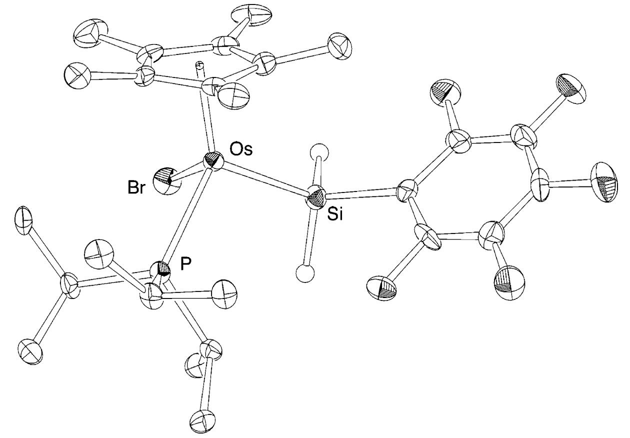


Figure 2. ORTEP drawing of **8** with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C$_5$Me$_5$ centroid): Cp*−Os 1.9379(1), Os−Si 2.389(2), Os−P 2.393(2), Os−Br 2.562(7), Cp*−Os−Br 112.87(2), Cp*−Os−Si 122.93(5), Cp*−Os−P 134.41(4), P−Os−Si 101.46(6), P−Os−Br 85.47(4), Br−Os−Si 76.24(5).

X-ray Structures of Osmium Silyl Complexes. Complexes **4**, **8**, **11**, **12**, and **13** were characterized by X-ray crystallography (Figures 1−5). In each case, the complex was found to adopt a geometry in which the

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[22] (a) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (b) Crabtree, R. H. *Angew. Chem.*, *Int. Ed. Engl.* **1993**, *35*, 789. (c) Dubberley, S. R.; Ignatov, S. K.; Rees, N. H.; Razuvaev, A. G.; Mountford, P.; Nikonov, G. I. *J. Am. Chem. Soc.* **2003**, *125*, 642.

[23] A ^{29}Si filtered ^{1}H NMR spectrum showed that the coupling present in this complex was on the order of the Os−H line width of 2 Hz.

[24] Glaser, P. B.; Tilley, T. D. Unpublished results.

[25] Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Ruiz, N. *Organometallics* **1999**, *18*, 5034.

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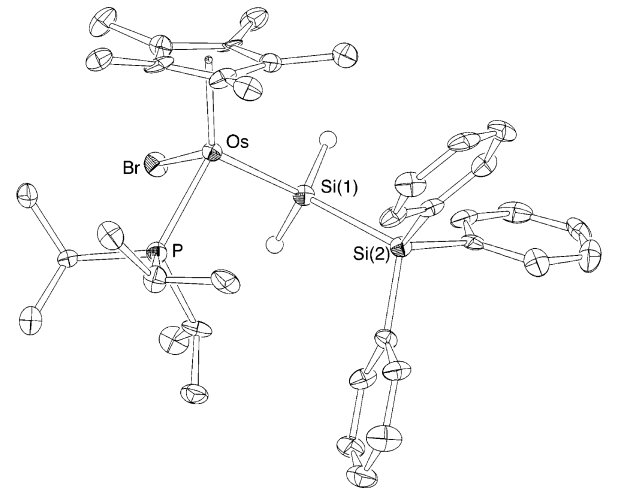

Figure 3. ORTEP drawing of **11** with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C_5Me_5 centroid): Cp*—Os 1.9414(3), Os—Si(1) 2.406(3), Os—P 2.382(3), Os—Br 2.567(1), Si(1)—Si(2) 2.378(4), Cp*—Os—Si 110.26(3), Cp*—Os—Br 112.19(7), Cp*—Os—P 136.43(7), Os—Si(1)—Si(2) 126.1(1), P—Os—Si 100.00(9), P—Os—Br 85.60(7), Br—Os—Si 80.01(7).

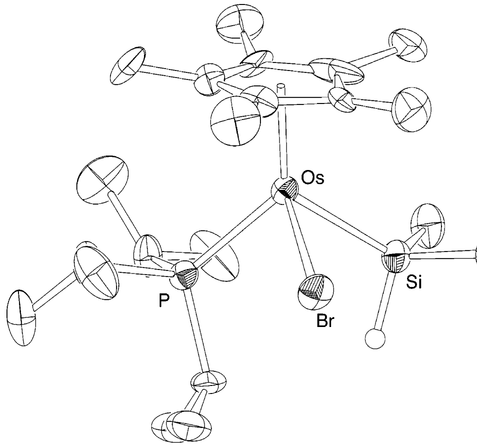

Figure 4. ORTEP drawing of **12** with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C_5Me_5 centroid): Cp*—Os 1.9471(8), Os—Si 2.431(6), Os—P 2.379(5), Os—Br 2.574(2), Cp*—Os—Si 115.15(6), Cp*—Os—Br 126.7(1), Cp*—Os—P 130.6(1), P—Os—Si 99.8(2), P—Os—Br 87.1(1), Br—Os—Si 78.6(2).

phosphine, hydride, bromide, and silyl substituents form the "legs" of a "four-legged piano stool", in which the triisopropylphosphine and the silyl substituents are in mutually *transoid* positions.[26] Whereas the silyl groups derived from primary silanes and small secondary silanes can adopt a conformation in which steric interactions with the Cp* and P^iPr_3 ligands are minimized, this is not possible for large secondary or tertiary silyl groups.

The bond lengths and angles for this series of complexes are all relatively similar (Table 2). The Os—Si bond lengths range from 2.389(2) Å in **8** to 2.431(6) Å in **12**.

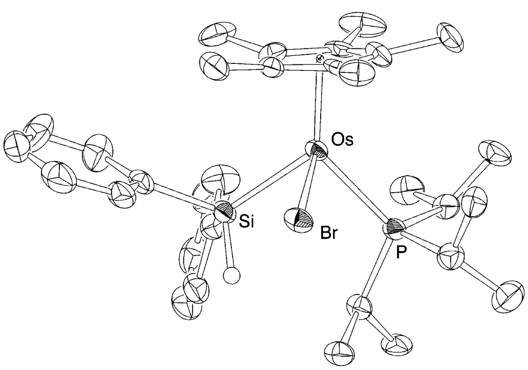

Figure 5. ORTEP drawing of one of the two similar molecules of **13** in the asymmetric unit with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C_5Me_5 centroid): Cp*—Os 1.9409(3), Os—Si 2.414(2), Os—P 2.382(2), Os—Br 2.5655(8), Cp*—Os—Si 111.63(2), Cp*—Os—Br 127.21(5), Cp*—Os—P 135.56(5), P—Os—Si 94.78(7), P—Os—Br 85.83(5), Br—Os—Si 81.25(5).

Osmium Silylene Complexes via 1,2-Hydrogen Migrations. It was reasoned that abstraction of the bromide substituent of an osmium silyl species might promote a hydride migration process and allow access to cationic osmium silylene complexes (Scheme 2).

Treatment of **13** with the anion metathesis reagent $LiB(C_6F_5)_4 \cdot 3Et_2O$ in CD_2Cl_2 afforded a product having C_s symmetry (on the NMR time scale) and formulated as the osmium dihydride silylene complex $[Cp^*(^iPr_3P)(H)_2OsSiPh_2][B(C_6F_5)_4]$, as determined by ^1H and ^{13}C NMR spectroscopy. A ^{29}Si resonance could not be detected for this species (23 °C, CD_2Cl_2 solution), possibly because of a dynamic interaction with Et_2O or LiBr in solution. Such a process could dramatically broaden the ^{29}Si resonance of the silylene complex. Unfortunately, attempts to separate the organometallic product from LiBr and Et_2O by crystallization or precipitation were unsuccessful and resulted in either the recovery of starting material or decomposition (apparently, small amounts of Et_2O efficiently solubilize LiBr in CH_2Cl_2 and fluorobenzene). Removal of volatile materials from reaction mixtures containing Et_2O under high vacuum and subsequent workup afforded only impure products that retained Et_2O. This behavior contrasts with that of the previously described bis-phosphine silylene complexes $[Cp^*(Me_3P)_2MSiR_2][B(C_6F_5)_4]$ (M = Ru, Os), which can be recrystallized as base-free complexes from solutions containing ethereal solvents.[9h–j,l,m]

Use of the ether-free borate reagent $LiB(C_6F_5)_4$ facilitated preparation of the pure silylene complex $[Cp^*(^iPr_3P)(H)_2Os{=}SiPh_2][B(C_6F_5)_4]$ (**14**). In the absence of Et_2O, LiBr precipitates from CH_2Cl_2 solution and can be removed by filtration. The resulting complex has effective C_s symmetry on the NMR time scale and exhibits a single set of resonances for the triisopropylphosphine methyl groups, one upfield resonance integrating to two protons for two mutually *transoid* osmium hydrides, and a sharp, ^{31}P-coupled ^{29}Si resonance at 313 ppm. The observed value for $^2J_{SiH}$ (5.5 Hz) is inconsistent with a significant silicon—hydrogen interaction in **14**.

Exhaustive attempts to crystallize **14** and the other osmium silylene complexes described below were unsuc-

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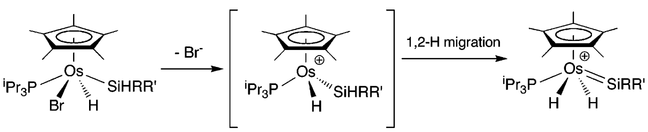
[26] The position of the osmium hydride ligand in these complexes could not be reliably located by X-ray crystallography and is inferred from the positions of the other ligands on osmium and by spectroscopic measurements.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Crystallographically Characterized Osmium Silyl Complexes Derived from 1

	4	**8**	**11**	**12**	**13**[b]		**15**
Cp*-Os[a]	1.9369(4)	1.9378(1)	1.9414(3)	1.9471(8)	1.9409(3)	1.9534(3)	1.9348(3)
Os−Si	2.398(3)	2.389(2)	2.406(3)	2.431(6)	2.414(2)	2.412(2)	2.355(2)
Os−P	2.368(3)	2.393(2)	2.382(3)	2.379(5)	2.382(2)	2.382(2)	2.358(2)
Os−Br	2.568(1)	2.5627(7)	2.567(1)	2.574(2)	2.5655(8)	2.5723(8)	
Cp*−Os−Br	112.15(3)	112.87(2)	110.26(3)	115.15(6)	111.63(2)	111.45(2)	
Cp*−Os−Si	120.58(8)	122.93(5)	112.19(7)	126.7(1)	127.21(5)	127.92(5)	123.98(5)
Cp*−Os−P	136.29(7)	134.41(4)	136.43(7)	130.6(1)	135.56(5)	134.76(5)	131.72(4)
P−Os−Si	101.0(1)	101.46(6)	100.00(9)	99.8(2)	94.78(7)	94.98(7)	104.24(6)
P−Os−Br	86.51(7)	85.47(4)	85.60(7)	87.1(1)	85.83(5)	86.34(5)	
Br−Os−Si	79.56(7)	76.24(5)	80.01(7)	78.6(2)	81.25(5)	80.71(6)	
Os−Si−C	120.3(3)	118.3(2)	126.1(1)[c]	116.6(7)	118.1(3)	118.7(3)	121.2(2)
				117.7(8)	116.7(3)	116.7(3)	119.9(2)
C−Si−C				103(1)	104.4(4)	103.2(4)	105.2(3)

[a] Cp* = C_5Me_5 centroid. [b] Two crystallographically independent molecules in the unit cell. [c] Os−Si−Si.

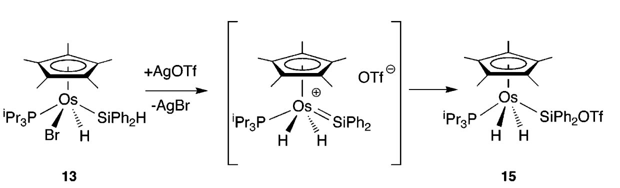
Scheme 2



cessful. Cooling concentrated CH_2Cl_2 or C_6H_5F solutions failed to afford solid products, and various hydrocarbon−halocarbon and fluoroether−halocarbon solvent mixtures led primarily to phase separation and precipitation of the products as viscous orange oils. Difficulties in crystallizing ionic species containing large, very weakly coordinating anions such as $B(C_6F_5)_4^-$ are often attributed to the low lattice energies of such substances.[27] Attempts to increase the crystallinity of the silylene complexes by employing the $\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}^-$ anion were unsuccessful and led to decomposition. This anion is known to be more susceptible than $B(C_6F_5)_4^-$ to electrophilic attack by a Lewis acidic silicon species.[28]

Removal of solvent from solutions of the silylene complexes described here, including **14**, afforded dark yellow oils which solidified as foams after prolonged exposure to vacuum. These foams tenaciously retained small quantities of solvent, making combustion analyses unreliable. The silylene complexes decomposed over the course of days in the solid state to afford complicated mixtures of products. For these reasons, the silylene complexes (other than **18**) were characterized in solution using multinuclear NMR spectroscopy.

The reaction of **13** with AgOTf gave the silyltriflate complex $Cp^*(^iPr_3P)(H)_2OsSiPh_2OTf$ (**15**; eq 5).



(5)

In contrast to the silylene complex $[Cp^*(Me_3P)(H)IrSiMes_2][OTf]$,[9j] the triflate group in **15** remains coordinated to the silicon center both in CD_2Cl_2 solution, as determined by NMR spectroscopy, and in the solid state, as determined by X-ray crystallography (Figure 6). The Os−Si bond in **15** is significantly shorter than the corresponding bond in **13** (Table 2), and the sum of the Os−Si−C and the C−Si−C bond angles in **15** is 346.3° (for comparison, this sum is 339.2° for **13**). These observations are consistent with a greater amount of silylene character at the silicon center of **15**.

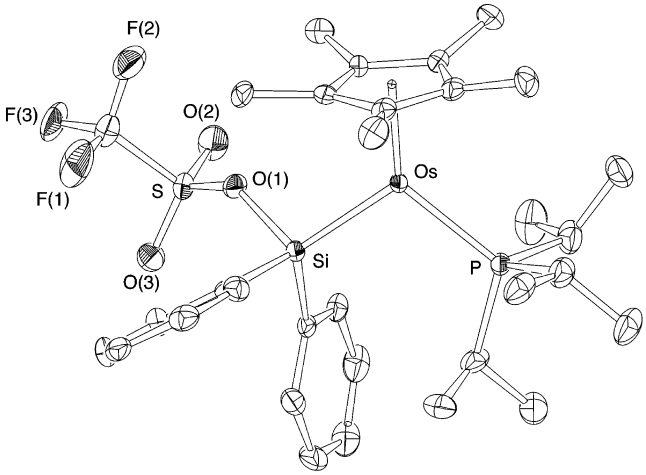


Figure 6. ORTEP drawing of **15** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C_5Me_5 centroid): Cp*−Os 1.9348(3), Os−Si 2.355(2), Os−P 2.358(2), Si−O(1) 1.847(5), Cp*−Os−Si 123.98(5), Cp*−Os−P 131.72(4), P−Os−Si 104.24(6), Os−Si−O(1) 107.6(2).

Silylene Complexes of the Type $[Cp^*(^iPr_3P)(H)_2Os{=}Si(H)R]^+$. Silylene complexes derived from dihydrosilyl derivatives, $L_nM\text{-}SiH_2R$, are of particular interest, as silylene complexes possessing an Si−H bond represent a very rare structure type with relatively unexplored reactivity and spectroscopic properties.[10b,29]

In an attempt to synthesize a cationic silylene complex of the type $[L_nM{=}SiH_2]^+$, **3** was treated with $LiB(C_6F_5)_4$ in CD_2Cl_2. This reaction afforded a single major product that featured resonances in the ^1H NMR spectrum consistent with a highly fluxional structure.

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(27) (a) Bond, D. R.; Jackson, G. E.; Joao, H. C.; Hofmeyer, M. N.; Modro, T. A.; Nassimbein, L. R. *J. Chem. Soc.*, *Chem. Commun.* **1989**, 1910. (b) Hunter, R.; Haueisan, R. H.; Irving, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 566. (c) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1996**, *15*, 3859. (d) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001.

(28) (a) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325.

(29) (a) Simons, R. S.; Gallucci, J. C.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2002**, *654*, 224. (b) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 218. (c) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428.

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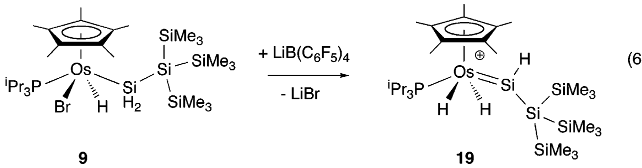
In the ^1H NMR spectrum, the Cp* and P^iPr_3 peaks of the product are sharp, but the resonances associated with the presumed SiH_2 silylene group ($\delta(^1H) = 6.2$ ppm) and the metal-bound hydride ($\delta(^1H) = -14.8$ ppm) were broad and featureless. A ^{29}Si resonance could not be detected for this species. The identities of the species in solution are unclear, but low-temperature NMR data are consistent with reversible aggregation to a low-symmetry complex tentatively formulated as $\{[Cp^*(^iPr_3P)(H)_2Os{=}SiH_2][B(C_6F_5)_4]\}_n$ (**16**).

Various reactions of $LiB(C_6F_5)_4$ with $Cp^*(^iPr_3P)Os(H)(Br)SiH_2R$ did not cleanly generate silylene complexes when R = Ph (**4**), Mes (**5**), or Hex (**9**). However, reaction of $LiB(C_6F_5)_4$ with silyl complexes possessing more sterically demanding substituents on silicon afforded cationic osmium silylene species of the type $[Cp^*(^iPr_3P)(H)_2Os{=}Si(H)R][B(C_6F_5)_4]$. These silylene complexes are distinguished by C_s symmetry on the NMR time scale and downfield ^{29}Si and ^1H shifts for the silylene center and the silicon-bound proton, respectively. For example, for R = trip (**17**), the Si−H resonance appears at 11.56, and δ (^{29}Si) = 315 ppm. These values parallel the downfield ^{13}C and ^1H chemical shifts observed in metal carbene complexes of the type $M{=}C(H)R$[30] and reflect sp^2 hybridization at silicon. As demonstrated by $^{13}C\{^1H\}$ NMR spectroscopy, the large aryl groups in **16** (R = dipp) and **17** rotate freely about their Si−C bonds, rendering the *ortho*-isopropyl methyl groups equivalent on the NMR time scale.

The silylene complex derived from **9**, $[Cp^*(^iPr_3P)(H)_2Os{=}Si(H)Si(SiMe_3)_3][B(C_6F_5)_4]$ (**19**; eq 6),



(6)

exhibits a downfield ^1H chemical shift for the Si−H group at 12.05 ppm and a very downfield-shifted ^{29}Si resonance at 417.5 ppm. Surprisingly, the $^1J_{SiH}$ coupling constant for **19** is 147 Hz, a value approximately 30 Hz lower than the $^1J_{SiH}$ values in **9**. The steric demands of the $Si(SiMe_3)_3$ group bound to silicon should favor a large Os−Si−Si angle in **19**, which would, in turn, decrease the amount of s-character in the Si−H bond, causing a decreased value for $^1J_{SiH}$. For comparison, the values for $^1J_{SiH}$ in **17** (188 Hz) and **18** (184 Hz) are essentially identical to those in the corresponding silyl complexes. It is interesting to note that the β-silicon atom in **19** has a ^{29}Si chemical shift of −74.9 ppm. Consequently, ^{29}Si chemical shifts spanning nearly 500 ppm are found in a single molecule.

Reaction of **8** with $LiB(C_6F_5)_4$ in CD_2Cl_2 afforded $[Cp^*(^iPr_3P)(H)_2Os{=}Si(H)(C_6F_5)]$ $[B(C_6F_5)_4]$ (**20**), as determined by NMR spectroscopy. While the ^{29}Si resonance of **20** appears at 318 ppm, the silicon-bound hydride appears at only 6.75 ppm. The origin of the disparity between the chemical shifts of the Si−H resonances in **17**−**19** and that of **20** is not entirely clear. The ^{29}Si chemical shift of **20** is inconsistent with a four-coordinate silicon center that might result from intramolecular donation by an aryl C−F group to the silylene silicon center. The ^{19}F NMR spectrum of **20** exhibits three resonances for the cation in **20**, but the *ortho*-F resonances are significantly broader than the *meta* and *para* resonances. Fluorocarbons are known to be exceedingly poor hydrogen bond acceptors,[31] but the close proximity of the C_6F_5 group to the silicon-bound hydrogen, the relatively organized structure of **20**, and the inductive effect of the electrophilic silylene center on the Si−H bond could favor an unusual interaction between an *ortho*-fluorine and the silicon-bound hydrogen in **20**.

Treatment of $Cp^*(^iPr_3P)Os(H)(Br)SiH_2SiPh_3$ (**11**) with $LiB(C_6F_5)_4$ in CD_2Cl_2 afforded a single product displaying two equivalent osmium hydride resonances and a single Si−H resonance having a chemical shift of 5.78 ppm, a value that would seem to be inconsistent with an $Os{=}Si(H)R^+$ structure. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum indicates that the $SiPh_3$ group of the starting material is not intact in the presumed silylene product. A ^{29}Si−^1H HMQC NMR experiment demonstrated that the hydrogen resonating at 5.78 ppm is bound to the β-silicon in the product, instead of the metal-bound silicon. It was therefore concluded that a nascent silylene complex formulated as $[Cp^*(^iPr_3P)(H)_2Os{=}Si(H)(SiPh_3)][B(C_6F_5)_4]$ (**21**) undergoes an isomerization involving the exchange of a phenyl group with the silylene hydrogen to afford $[Cp^*(^iPr_3P)(H)_2Os{=}Si(Ph)(SiPh_2H)][B(C_6F_5)_4]$ (**22**). Related 1,2-migrations between silicon and electrophilic centers have been previously observed and studied with theoretical methods.[32] Reaction of **11** with $LiB(C_6F_5)_4$ in the presence of the strongly coordinating base 4-(dimethylamino)pyridine (DMAP) afforded a single product that contained an intact $SiPh_3$ group and a single Si−H bond, as determined by multinuclear NMR spectroscopy. This new product was formulated as the "intercepted" silylene complex $[Cp^*(^iPr_3P)(H)_2Os{=}Si(H)(SiPh_3)\cdot(DMAP)][B(C_6F_5)_4]$ (**21·DMAP**) (Scheme 3). This product is not formed upon reaction of **22** with DMAP.

Upon monitoring the reaction of **11** with $LiB(C_6F_5)_4$ in CD_2Cl_2 at low temperature by NMR spectroscopy, an intermediate (**23**) was observed. This intermediate reached a maximum concentration of approximately 70% after 2 min at 0 °C. Thereafter, the intensities of the resonances associated with this species rapidly decreased as the concentration of **22** increased. The intermediate exhibited two inequivalent osmium hydride resonances ($\delta(^1H) = -13.97$ and -14.37 ppm) and a single broad Si−H peak at 5.98 ppm in its ^1H NMR spectrum. The observation of two inequivalent hydride ligands in **23** suggests the presence of a chiral silicon center bound to osmium. Thus, the conversion of **21** to **22** appears to proceed by the 1,2-migration of a phenyl group from the β-silicon atom of **21** its silylene center to generate **23**. A 1,2 hydrogen migration would then complete the formation of **22** (Scheme 3).

A Metalated Triisopropylphosphine Complex as a Formal Synthon for the 14-Electron Cation

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[30] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 2001

[31] Plenio, H.; Diodone, R. *Chem. Ber.* **1997**, *130*, 633. (b) Plenio, H.; Hermann, J.; Diodone, R. *Inorg. Chem.* **1997**, *36*, 5722. (c) Takemura, H. *J. Synth. Org. Chem., Jpn.* **2002**, *60*, 963. (d) Mele, A.; Vergani, B.; Viani, F.; Meille, S. V.; Farina, A.; Bravo, P. *Eur. J. Org. Chem.* **1999**, 187.

[32] (a) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1987**, *109*, 272. (b) Cho, S. G. *J. Organomet. Chem.* **1996**, *510*, 25. (c) Lickiss, P. D In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons: New York, 1998; Vol. 2, Chapter 11.

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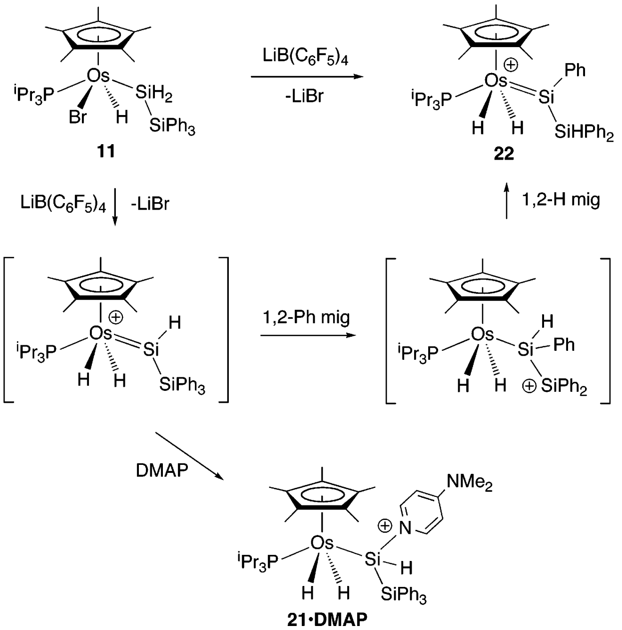
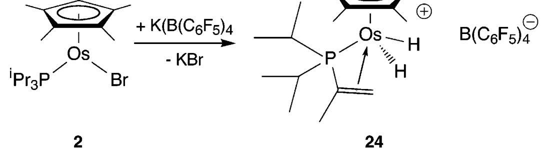
Scheme 3



Cp*(^{i}Pr$_3$P)Os$^+$. As demonstrated by the studies described above, coordinatively unsaturated osmium complexes are potentially very useful in the synthesis of silylene complexes. From the 16-electron complex **2**, silylene complexes are obtained in two steps involving oxidative addition of a silane followed by a bromide abstraction. In principle, the formally 14-electron complex Cp*(^{i}Pr$_3$P)Os$^+$ could serve as a more direct precursor to cationic [Cp*(^{i}Pr$_3$P)(H)$_2$Os=SiRR′]$^+$ silylene complexes via the double Si−H bond activation of a hydrosilane (eq 3). To investigate a possible route to Cp*(^{i}Pr$_3$P)Os$^+$ (or a synthon thereof), the metathesis of the bromide in **2** with the noncoordinating B(C$_6$F$_5$)$_4^-$ anion was attempted.

Reaction of **2** with 1 equiv of KB(C$_6$F$_5$)$_4$ in THF/CH$_2$Cl$_2$ afforded the unexpected cationic species {Cp*[^{i}Pr$_2$P(η^2-MeC=CH$_2$)]OsH$_2$}[B(C$_6$F$_5$)$_4$] (**24**; eq 7).



(7)

Presumably, exchange of the bromide substituent with the noncoordinating B(C$_6$F$_5$)$_4^-$ anion affords a transient, formally 14-electron intermediate Cp*(^{i}Pr$_3$P)Os$^+$, which then activates two of the C−H bonds in the triisopropylphosphine ligand (Scheme 4).[33] The solid-state structure of **24** is shown in Figure 7. The metalated isopropyl group is planar within error, indicating sp^2 hybridization of the phosphorus-bound carbon atom. Recently reported examples of metalated triisopropylphosphine ligands have also been described as chelating α-alkenylphosphine ligands. The ^{1}H NMR spectrum of **24** is consistent with its solid-state structure and features two distinct osmium hydride resonances and five intact and magnetically inequivalent isopropyl methyl groups.

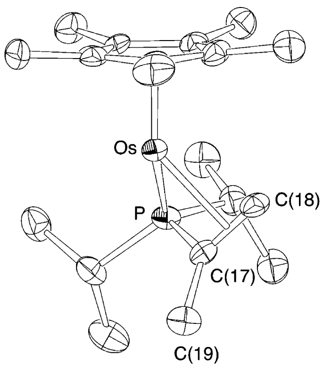
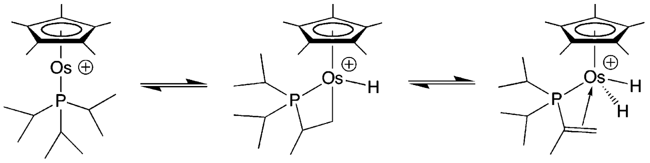
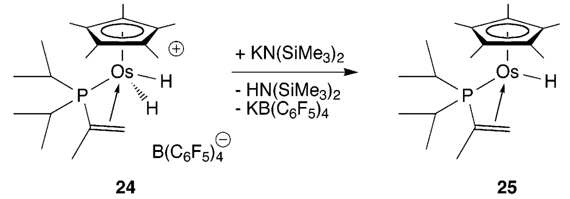


Figure 7. ORTEP drawing of **24** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the B(C$_6$F$_5$) counterion are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C$_5$Me$_5$ centroid, CC = midpoint of C(17) and C(18)): Os−P 2.320(2), Os−Cp* 1.8958(3), Os−CC 2.0680(3), C(17)−C(18) 1.43(1), C(17)−C(19) 1.49(1). Cp*−Os−P 134.02(5), Cp*−Os−CC 136.59(2), P−Os−CC 67.09(5), P−C(17)−C(18) 109.9(5), P−C(17)−C(19) 126.0(6), C(18)−C(17)−C(19) 124.1(7).

Scheme 4



Complex **24** was deprotonated with KN(SiMe$_3$)$_2$ to afford the neutral, hydrocarbon-soluble species Cp*[^{i}Pr$_2$P(η^2-MeC=CH$_2$)]OsH (**25**; eq 8).



(8)

This reaction is conveniently carried out in benzene, a solvent in which **24** forms a dense, insoluble oil and KB(C$_6$F$_5$)$_4$ is insoluble. Complex **25** is a viscous oil that is exceedingly soluble in common solvents such as hydrocarbons and Et$_2$O, and for this reason, it could not be crystallized. Thus, this compound was only characterized by multinuclear NMR spectroscopy.

Although complexes **24** and **25** are both coordinatively saturated 18-electron complexes, it was thought that they might function as synthons for 14-electron Cp*(^{i}Pr$_3$P)Os$^+$ via reductive elimination processes (Scheme 4). In fact, the reaction of **24** with Ph$_2$SiH$_2$ in CD$_2$Cl$_2$ at 80 °C in a sealed NMR tube for 48 h afforded the diphenylsilylene complex **14** as the major component of a mixture of products, as determined by NMR spectroscopy (eq 9). Although the generation of **14** from **24** is a demonstration of double Si−H activation by a

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[33] (a) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Onate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316. (b) Esteruelas, M. A.; Lopez, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657. (c) Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oliván, M.; Oñate, E.; Tajada, M. A.; Tomàs, J. *Organometallics* **2003**, 22, 2087. (d) Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E.; Tajada, M. A.; Ujaque, G. *Organometallics* **2003**, *22*, 3753. (e) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1416.

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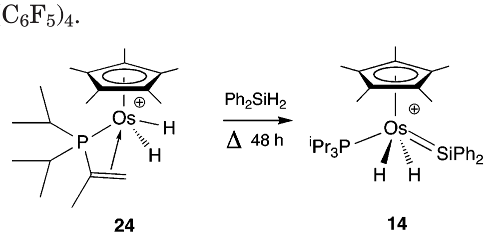
$Cp^*(^iPr_3P)Os^+$ surrogate, the synthesis of **14** is accomplished more rapidly and with fewer byproducts from the reaction of the isolable silyl complex **13** with $LiB(C_6F_5)_4$.



(9)

Concluding Remarks

The 16-electron complex **2** is a useful starting precursor to a series of stable osmium silyl complexes derived from hydrosilanes. Compared to the similar ruthenium complex **1**, **2** reacts with a wider variety of silanes, including secondary silanes such as Ph_2SiH_2 and Me_2SiH_2. This enhanced reactivity is attributed to the greater strength of bonds to osmium and the stability of Os(IV) versus Ru(IV) in analogous complexes.

The successful reactions of $LiB(C_6F_5)_4$ with these silyl complexes to afford silylene complexes under relatively mild conditions are examples of the utility of the abstraction−migration route to silylene complexes. Since the silyl complexes used in this method are derived from relatively simple hydrosilanes, the abstraction−migration route for the synthesis of silylene complexes may have greater versatility than previously employed routes to silylenes that require more complex silicon starting materials, such as alkylchlorohydridosilanes or thiolatosilanes. The successful preparation of a series of complexes featuring the M=Si(H)R structural motif should provide greater insight into the reactivity modes of this class of silylene complexes.

Attempted generation of the 14-electron complex $Cp^*(^iPr_3P)Os^+$ via reaction of $KB(C_6F_5)_4$ with **2** instead afforded the 18-electron complex $\{Cp^*[^iPr_2P(\eta^2\text{-}MeC{=}CH_2)]OsH_2\}[B(C_6F_5)_4]$. This complex features an unusual orthometalated alkylphosphine ligand resulting from the double C−H activation of an isopropyl group. The complex was shown to slowly react with Ph_2SiH_2 to afford the diphenylsilylene complex **14**, demonstrating the ability of a 14-electron synthon to convert hydrosilanes directly to silylene ligands through double Si−H activation. Improved understanding of the conversion of hydrosilanes to silylenes may contribute to the understanding of previously observed reactions believed to operate through mechanisms including silylene intermediates.

We are currently exploring the potential utility of cationic silylene complexes of the type $L_nM{=}Si(H)R^+$ for use as catalysts in a variety of organic transformations. Initial results have shown that such silylene complexes catalyze the selective hydrosilylation of alkenes by an unexpected mechanism.[34] It is hoped that new systems can be identified in which double Si−H activation processes are rapid enough for incorporation into useful catalytic cycles.

Experimental Section

Manipulations involving air-sensitive compounds were conducted using standard Schlenk techniques under a purified N_2 atmosphere or in a Braun Uni-Lab drybox. Nondeuterated solvents were distilled under N_2 from appropriate drying agents and stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotopes) were dried with appropriate drying agents, vacuum-transferred before use, and stored over molecular sieves.

Previously described methods were used to prepare $Cp^*(^iPr_3P)OsBr$,[13] $Li[B(C_6F_5)_4]\cdot 3Et_2O$,[35] $Cp^*(^iPr_3P)Os(H)(Br)(SiH_2Ph)$,[13] $(C_6F_5)SiH_3$,[36] and $KN(SiMe_3)_2$.[37] Both $Li[B(C_6F_5)_4]$ and $K[B(C_6F_5)_4]$ were generous gifts of Boulder Scientific Co. The silanes $(Me_3Si)_3SiSiH_3$, Ph_3SiSiH_3, $PhSiH_3$, dippSiH_3, and tripSiH_3 were prepared by the $LiAlH_4$ reduction of the corresponding silyl chlorides.[38] Liquid silanes were fractionally distilled under N_2 and stored over molecular sieves. Solid silanes were recrystallized from Et_2O and dried in vacuo. Hexylsilane and Ph_2SiH_2 were purchased from Gelest Co., degassed, and stored over molecular sieves. Dimethylsilane and 15% SiH_4 in N_2 were purchased from Gelest Co. and used as received.

NMR spectra were acquired on a Bruker DRX-500 spectrometer equipped with a 5 mm BBI probe or a Bruker AVB-400 spectrometer equipped with a 5 mm gradient BB probe. Spectra were recorded at room temperature and were referenced to protio-impurities in the deuterated solvent for ^1H, solvent peaks for ^{13}C, $CFCl_3$ for ^{19}F, $SiMe_4$ for ^{29}Si, and 85% H_3PO_4 for ^{31}P. Multiplets that appear as virtual triplets or quartets are denoted as "vt" or "vq", respectively. Resonances assignable to the $B(C_6F_5)_4$ anion are not reported. When necessary, DEPT and $^1H-^{13}C$ gHMQC detection schemes were employed in the assignment of ^{13}C and ^1H resonances. The gHMBC experiment used for ^{29}Si detection has a nominal resolution of approximately 1 ppm under standard conditions. Combustion analyses were performed by the University of California, Berkeley College of Chemistry Microanalytical Facility.

$Cp^*(^iPr_3P)Os(H)(Br)SiH_3$ (3). WARNING: *At concentrations of 15% in N_2, SiH_4 is pyrophoric and should only be handled by qualified individuals with adequate safety precautions in place.* A heavy-walled 100 mL reaction vessel equipped with an 8 mm PTFE valve and a 24/40 ground glass joint was charged 312 mg of **2** and a small magnetic stirbar. The solid was dissolved in approximately 15 mL of Et_2O to afford a purple solution. The vessel was attached directly to a Schlenk line, and the solution was degassed through a series of freeze−pump−thaw cycles. The vessel was then cooled to −78 °C and charged with 1 atm of SiH_4 (15% in N_2). The color of the vigorously stirred solution rapidly changed from purple to orange. The cooling bath was removed, and the solution was allowed to warm to room temperature. Stirring was continued until the solution had become a uniform banana-yellow color and a fine yellow precipitate had formed. Unreacted SiH_4 was then vented to the atmosphere with a N_2 cross-purge and allowed to inflame. The solution was stirred under an atmosphere of N_2 for an additional 10 min, and solvent was then removed in vacuo. The powdery yellow residue was extracted with two 5 mL portions of 3:1 Et_2O/CH_2Cl_2. The combined filtrates were cooled slowly to −80 °C over 16 h to afford well-formed orange-yellow crystals (192 mg). Removing the solvents from the filtrates afforded an additional 61 mg of analytically pure **3** as a fine yellow powder. Yield: 253 mg (76%). ^1H NMR (CD_2Cl_2, δ): 3.59 (s, 3 H, $^1J_{SiH} = 174.6$ Hz, $OsSiH_3$), 2.51 (m, 3 H, $P(CHMe_2)_3$), 1.74 (d, 15 H, $J_{PH} = 1.5$ Hz, C_5Me_5), 1.12−

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(34) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, 125, 13640.

(35) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

(36) Molander, G. F.; Corrette, C. P. *Organometallics* **1998**, *17*, 5504.

(37) (a) Barash, E. H.; Coan, P. S.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1993**, 32, 497. (b) Drouiche, Y.; Lickiss, P. D. *J. Organomet. Chem.***1991**, *407*, 41.

(38) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156. (b) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1980**, *225*, 1. (c) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1993**, *12*, 2584. (d) Woo, H. G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198.

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1.20 (2 overlapping vq, 18 H, P(CH*Me*$_2$)$_3$), −15.35 (d, 1 H, $^2J_{PH}$ = 32 Hz, Os*H*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 94.11 (d, J_{PH} = 2 Hz, *C*$_5$Me$_5$), 28.03 (d, $^2J_{PH}$ = 27.1, P(*C*HMeMe)$_3$), 20.28, 19.86 (P(CH*Me*$_2$)$_3$), 10.19 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 12.19. $_{29}$Si NMR (coupled INEPT, δ): −72.97 (qdd, $^1J_{SiH}$ = 176 Hz, $^2J_{SiH}$ = 10 Hz, $^2J_{PSi}$ = 10 Hz). Anal. Calcd: C, 38.18; H; 6.75. Found: C, 38.51; H, 6.98.

Cp*(^{i}Pr$_3$P)Os(H)(Br)SiH$_2$Mes (5). To a stirred solution of 500 mg (0.881 mmol) of **2** in approximately 25 mL of Et$_2$O was added slowly by cannula at room temperature 145 mg (0.97 mmol) of MesSiH$_3$ in 10 mL of Et$_2$O. The mixture's color quickly turned from purple to golden yellow-orange. The solution was concentrated in vacuo to approximately 15 mL and slowly cooled to −80 °C. After 1 day, a microcrystalline precipitate had formed. The product was isolated by filtration and dried in vacuo. Yield: 475 mg (75%). ^{1}H NMR (CD$_2$Cl$_2$, δ): 6.78 (s, 2 H, aryl), 4.9 (br s, 2 H, $^1J_{SiH}$ = 176 Hz, Si*H*$_2$Mes), 2.68 (s, 3 H, 4-*Me*), 2.52 (s, 6 H, 2,6-*Me*), 2.44 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.63 (s, 15 H, C$_5$*Me*$_5$), 1.11−1.16 (vq, 9 H, P(CH*Me*Me)$_3$), 1.07−1.11 (vq, 9 H, P(CHMe*Me*)$_3$), −15.04 (d, 1 H, $^2J_{PH}$ = 29.4 Hz, Os*H*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 144.5, 136.8, 136.5, 127.5 (aryl), 94.2 (*C*$_5$Me$_5$), 28.2 (d, $^1J_{CP}$ = 25.8 Hz, P(*C*H*Me*$_2$)$_3$) 23.9, 20.7 (C$_6$H$_2$*Me*$_3$), 19.8 (d, $^2J_{CP}$ = 3.1 Hz, P(CHMe*Me*)$_3$), 19.7 (P(CH*Me*Me)$_3$), 10.2 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 3.9. ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, HMBC, δ): −49.9 (d, $^2J_{SiP}$ = 9.8 Hz). Anal. Calcd for C$_{28}$H$_{50}$BrOsPSi: C, 46.98; H, 7.04. Found: C, 47.29; H, 7.24.

Cp*(^{i}Pr$_3$P)Os(H)(Br)SiH$_2$dipp (6). To a stirred solution of 175 mg (308 mmol) of **2** in approximately 25 mL of pentane was added slowly by cannula at room temperature 61 mg (0.32 mmol) of dippSiH$_3$ in 10 mL of pentane. The mixture's color quickly turned from purple to golden yellow-orange. The solution was concentrated in vacuo to approximately 10 mL and slowly cooled to −80 °C. After 1 day, a microcrystalline precipitate had formed. The product was isolated by filtration, washed with two 10 mL portions of pentane at −78 °C, and dried in vacuo. Yield: 131 mg (56%). ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.20 (t, 1 H, $^3J_{HH}$ = 8 Hz, *p*-aryl), 7.09 (d, 2 H, $^3J_{HH}$ = 8 Hz, *m*-aryl), 5.05 (d, 1 H, $^2J_{HH}$= 4.8 Hz, $^1J_{SiH}$ = 178 Hz, Si*H*H), 4.91 (d, 1 H, $^2J_{HH}$ = 4.8 Hz, $^1J_{SiH}$ = 181 Hz SiH*H*), 3.73 (sept, 2 H, $^3J_{HH}$ = 7 Hz, *m*-C*H*Me$_2$), 2.52 (m, 3 H, P(C*H*Me$_2$)$_3$, 1.68 (s, 15 H, C$_5$*Me*$_5$), 1.26 (d, 12 H, 7 Hz, *m*-CH*Me*$_2$), 1.21 (vq, 9 H, P(CH*Me*Me)$_3$, 1.09 (vq, 9 H, P(CH*Me*Me)$_3$), −15.00 (d, 1 H, $^2J_{PH}$ = 29.3 Hz, Os−H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 156.1 (*m*-aryl) 138.1, (ipso-aryl), 128.5, 122.0 (aryl), 94.6 (*C*$_5$Me$_5$), 33.4 (*o*-CHMe2), 28.7 (d, $^1J_{PC}$ = 27 Hz, P(*C*HMe$_2$)$_3$) 25.3, 24.8 (*o*-CH*Me*$_2$), 20.2, 20.0 (P(CH*Me*$_2$)$_3$), 10.8 (C$_5$Me$_5$). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, δ): −53.1. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 4.31. Anal. Calcd for C$_{31}$H$_{56}$BrOsPSi: C, 49.12; H, 7.45. Found: C, 49.33; H, 7.65.

Cp*(^{i}Pr$_3$P)Os(Br)(H)SiH$_2$trip (7). To a stirred solution of 600 mg (1.06 mmol) of **1** in approximately 25 mL of pentane was added slowly by cannula at room temperature 367 mg (1.48 mmol) of tripSiH$_3$ in 10 mL of pentane. The mixture's color quickly turned from purple to golden yellow-orange. The solution was concentrated in vacuo to approximately 10 mL and slowly cooled to −80 °C. After 1 day, a microcrystalline precipitate had formed. The product was isolated by filtration, washed with two 10 mL portions of pentane at −78 °C, and dried in vacuo. Yield: 715 mg (85.1%). ^{1}H NMR (CD$_2$Cl$_2$, δ): 6.92 (s, 2 H, aryl H), 4.96 (d, 1 H, $^2J_{HH}$ = 4 Hz, $^1J_{SiH}$ = 178 Hz, Os−Si*H),* 4.83 (d, 1 H $^2J_{HH}$ = 4 Hz, $^1J_{SiH}$ = 179 Hz, Os−Si*H)*, 3.70 (sept, 2 H, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 2.82 (sept, 1 H, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 2.46 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.64 (d, 15 H, J_{PH} = 0.8 Hz, C$_5$*Me*$_5$), 1.23 (d, 12 H, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 1.21 (d, 6 H, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 1.16 (vq, 9 H, P(CH*Me*Me)$_3$) 1.03 (vq, 9 H, P(CHMe*Me*)$_3$), −15.07 (d, 1 H, $^2J_{PH}$ = 29.4 Hz, Os*H*). ^{13}C{^{1}H} NMR: 155.6, 148.5, 134.4, 119.7 (Ar), 94.1 (d, *C*$_5$Me$_5$, $^2J_{PC}$ = 2.5 Hz), 34.19, 32.98, (*C*HMe$_2$) 28.32 (d, $^1J_{C-P}$ = 23.5 Hz, P(*C*HMe$_2$)$_3$), 24.90, 24.39, 23.79, 23.70, 19.73, 19.50 (CH*Me*$_2$), 10.29 (C$_5$*Me*$_5$). ^{29}Si NMR (CD$_2$Cl$_2$,δ): −53.0. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$,δ): 4.0. Anal. Calcd for C$_{34}$H$_{62}$BrOsPSi: C, 51.04; H, 7.81. Found: C, 51.17; H, 7.70.

Cp*(^{i}Pr$_3$P)Os(H)(Br)SiH$_2$(C$_6$F$_5$) (8). To a stirred solution of **2** (253 mg, 0.440 mmol) in CH$_2$Cl$_2$ (10 mL) was added 100 mg (0.505 mmol) of (C$_6$F$_5$)SiH$_3$ in CH$_2$Cl$_2$ (approximately 5 mL) by cannula, causing a rapid color change from purple to yellow-orange. The volume of the solution was reduced by half, and the flask was slowly cooled to −80 °C. After 24 h, well-formed orange crystals of **8** had formed. These crystals were isolated by filtration. Yield: 260 mg (77%). ^{1}H NMR (CD$_2$Cl$_2$, δ): 5.48 (dd, 1 H, *J* = 5 Hz, $^1J_{SiH}$ = 200 Hz), 3.98 (dd, 1 H, *J* = 5 Hz, $^1J_{SiH}$ = 201 Hz), 2.06 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.71 (s, 15 H, C$_5$*Me*$_5$), 1.22−1.15 (2 overlapping vq, 18 H, P(CH*Me*$_2$)$_3$), −15.05 (d, 2 H, $^2J_{PH}$ = 31.7 Hz, $^2J_{SiH}$ = 5 Hz) Os(*H*)). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 95.1 (d, J_{PC} = 1 Hz, *C*$_5$Me$_5$), 27.9 (d, $^1J_{PC}$ = 26.0 Hz, P(*C*HMe$_2$)$_3$), 20.21, 19.95 (P(CH*Me*$_2$)$_3$), 10.42 (C$_5$*Me*$_5$). ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, δ): −125.00 (m, *o*-C$_6$F$_5$), −155.85 (t, *p*-C$_6$F$_5$), −62.89 (m, *m*-C$_6$F$_5$). ^{29}Si{^{1}H} NMR (INEPT, CD$_2$Cl$_2$, δ): −62.2 (d, $^2J_{PSi}$ = 13.5 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 6.68. Anal. Calcd for C$_{25}$H$_{39}$BrF$_5$OsPSi: C, 39.31; H 5.15. Found: C, 39.16; H, 5.20.

Cp*(^{i}Pr$_3$P)Os(H)(Br)SiH$_2$Hex (9). To a stirred solution of **2** (210 mg, 0.370 mmol) in C$_5$H$_{12}$ (10 mL) was added 52 mg (0.447 mmol) of HexSiH$_3$ in 20 mL of pentane. The solution immediately became a golden yellow. The volume of the solution was reduced to approximately 5 mL in vacuo, and the reaction vessel was slowly cooled to −80 °C. After 24 h at −80 °C, a fine, yellow, microcrystalline precipitate had formed. This product was isolated by filtration and dried in vacuo. Yield: 148 mg (58%). ^{1}H NMR (C$_6$D$_6$, δ): 5.38 (m, 1 H, $^1J_{SiH}$ = 183 Hz, OsSi*H*H), 4.39 (m, 1 H, $^1J_{SiH}$ = 167 Hz, OsSiH*H*), 2.48 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.90 (m, 2 H, C*H*$_2$), 1.69−1.58 (m, overlapping, 2 H, C*H*$_2$), 1.42−1.36 (2 overlapping m, 4 H, C*H*$_2$), 1.38−1.35 (overlapping m, 1 H, Si(H)$_2$C*H*H), 1.18 (m, 1 H, Si(H)$_2$C*H*H), 1.09−1.02 (2 overlapping vq, P(CH*Me*$_2$)$_3$), 0.91 (t, $^3J_{HH}$ = 7 Hz, CH$_2$C*H*$_3$), −15.36 (d, $^2J_{PH}$ = 32.4 Hz, 1 H, Os*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 93.64 (d, J_{CP} = 1.8 Hz, *C*$_5$Me$_5$), 33.69, 32.36, 31.27 (*C*H$_2$), 28.01 (d, $^1J_{CP}$ = 26.8 Hz, P(*C*HMe$_2$)$_3$), 23.18 (*C*H$_2$), 20.36, 21.17, (P(CH*Me*$_2$)$_3$), 17.73 (SiH$_2$*C*H$_2$), 14.45, (CH$_2$*Me*), 10.44 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 8.50. ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, δ): −30.49 (d, $^2J_{PSi}$ = 9 Hz). Anal. Calcd for C$_{25}$H$_{52}$BrOsPSi: C, 44.04; H, 7.69. Found: C, 44.17; H, 7.90.

Cp*(^{i}Pr$_3$P)Os(H)(Br)SiH$_2$Si(SiMe$_3$)$_3$ (10). To a solution of 479 mg of **2** (0.844 mmol) in Et$_2$O (15 mL) was added 239 mg (0.86 mmol) of (Me$_3$Si)$_3$SiSiH$_3$ in 20 mL of Et$_2$O by cannula, causing a rapid color change from purple to yellow and the precipitation of a microcrystalline solid. The heterogeneous mixture was stirred for an additional 5 min and then allowed to settle. The solid was collected by filtration and dried in vacuo. Yield: 581 mg (81%). ^{1}H NMR (C$_6$D$_6$, δ): 5.12 (s, 1 H, $^1J_{SiH}$ = 179 Hz, SiH*H*), 3.62 (s, 1 H, $^1J_{SiH}$ = 171 Hz, Si*H*H), 2.41 (m, 3 H, P(C*H*Me$_2$)$_3$) 1.62 (s, 15 H, C$_5$*Me*$_5$), 1.05 (vq, 9 H, P(CH*Me*Me)$_3$), 0.98 (vq, 9 H, P(CHMe*Me*)$_3$), 0.49 (s, 27 H, Si(Si*Me*$_3$)$_3$, −14.91 (d, 1 H $^2J_{PH}$ = 30.8 Hz). ^{13}C{^{1}H} NMR: 94.04 (*C*$_5$Me$_5$), 28.48 (d, $^1J_{CP}$ = 28.1 Hz, P(*C*HMe$_2$)$_3$), 20.48, 20.34, (P(CH*Me*$_2$)$_3$), 11.08 (C$_5$*Me*$_5$), 3.49 (Si(SiMe$_3$)$_3$). ^{29}Si NMR (gHMBC, C$_6$D$_6$, δ): −8.3 (SiH$_2$Si(*Si*Me$_3$)$_3$), −83.5 (d, $^2J_{SiP}$ = 12 Hz, *Si*H$_2$Si(SiMe$_3$)$_3$), −134.0 (SiH$_2$*Si*(SiMe$_3$)$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 8.81.

Cp*(^{i}Pr$_3$P)Os(H)(Br)SiH$_2$SiPh$_3$ (11). To a solution of 143 mg of **2** (0.252 mmol) in toluene (10 mL) was added 75 mg (0.253 mmol) of Ph$_3$SiSiH$_3$ in toluene (5 mL) by pipet, causing a rapid color change from purple to yellow. The mixture was concentrated in vacuo to a volume of approximately 10 mL, layered with pentane (15 mL), and cooled to −80 °C, affording a microcrystalline precipitate (60 mg), which was isolated by filtration and dried in vacuo. Solvent was removed in vacuo from the filtrate, affording an additional 60 mg of **11** as an analytically pure, fine yellow powder. Yield: 120 mg (55%). ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.64 (m, 6 H, *o*-Ph), 7.32 (m, 9 H, *p*- and *m*-Ph), 4.84 (s, 1 H, $^1J_{SiH}$ = 178 Hz, Si*H*H), 3.19 (s, 1 H, $^1J_{SiH}$

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= 164 Hz, SiH*H*), 2.31 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.59 (d, 15 H, J_{PH} = 0.5 Hz, C$_5$*Me$_5$*), 1.06 (vq, 9 H, P(CHMe*Me*)$_3$), 0.94 (vq, 9 H, P(CH*Me*Me)$_3$), −14.66 (d, 1 H, $^2J_{\mathrm{PH}}$ = 31 Hz, Os−H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 138.9 (ipso-C), 136.4, 128.3, 127.4 (aryl), 94.53 (*C$_5$*Me$_5$), 28.73 (d, $^1J_{\mathrm{CP}}$ = 26.7 Hz, P(*C*HMe$_2$)$_3$), 19.82, 19.64 (P(CH*Me$_2$*)$_3$), 9.92 (C$_5$*Me$_5$*). ^{29}Si NMR (gHMBC, CD$_2$Cl$_2$, δ): −78.3 (d, $^2J_{\mathrm{SiP}}$ = 9 Hz, Os−*Si*H$_2$SiPh$_3$), −21.0 (Os−SiH$_2$*Si*Ph$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 10.10. Anal. Calcd: C, 51.91; H, 6.36. Found: C, 52.63; H, 6.46.

Cp*(^{i}Pr$_3$P)Os(H)(Br)SiMe$_2$H (12). A solution of 113 mg (0.199 mmol) of **2** in Et$_2$O (15 mL) was degassed with a freeze−pump−thaw cycle. An atmosphere of Me$_2$SiH$_2$ was admitted to the reaction flask, causing the stirred solution to change immediately from a purple to a yellow color. The volatile components of the mixture were removed in vacuo to afford **12** as an analytically pure yellow-orange foam. Yield: 125 mg (92%). ^{1}H NMR (C$_6$D$_6$, δ): 6.16 (m, 1 H, $^1J_{\mathrm{SiH}}$ = 178 Hz, Si*H*) 2.41 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.56 (d, 15 H, *J* = 1 Hz, C$_5$*Me$_5$*), 1.03 (vq, 9 H, P(CHMe*Me*)$_3$), 1.07 (vq, 9 H, P(CH*Me*Me)$_3$), 0.93 (d, 3 H, $^3J_{\mathrm{HH}}$ = 4 Hz, Si(H)*Me*Me), 0.91 (d, 3 H, $^3J_{\mathrm{HH}}$ = 4 Hz, Si(H)Me*Me),* −15.23 (d, 1 H, $^2J_{\mathrm{PH}}$ = 31.9 Hz, Os−*H*). ^{1}H NMR (CD$_2$Cl$_2$, δ): 5.50 (m, 1 H, $^1J_{\mathrm{SiH}}$ = 178 Hz, Si*H*), 2,48 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.74 (d, 15 H, *J* = 1 Hz, C$_5$*Me$_5$),* 1.22−1.16, (2 overlapping vq, 18 H, (P(CH*Me$_2$*)$_3$). 0.49 (d, 3 H, $^3J_{\mathrm{HH}}$ = 4 Hz, Si(H)*Me*Me), 0.39 (d, 3 H, $^3J_{\mathrm{HH}}$ = 4 Hz, Si(H)Me*Me),* −15.24 (d, 1 H, $^2J_{\mathrm{PH}}$ = 31.7 Hz, Os*H).* ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 94.06 (C$_5$Me$_5$), 28.16 (d, $^1J_{\mathrm{PC}}$ = 26.5 Hz), 20.74, 20.48 (P(CHMe$_2$)$_3$), 10.94 (C$_5$*Me$_5$*), 4.26, 0.94 (Si*Me$_2$*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 5.66. ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, HMBC, δ): −23.9. Anal. Calcd: C, 40.31, H 7.09. Found: C 40.44; H, 7.24

Cp*(^{i}Pr$_3$P)Os(H)(Br)SiPh$_2$H (13). To a stirred solution of 452 mg of **2** in pentane (40 mL) was added 157 mg (0.853 mmol) of Ph$_2$SiH$_2$ in pentane (5 mL) by cannula, causing a rapid color change from purple to yellow. The solution was filtered, concentrated to 2/3 its original volume, and cooled to −80 °C, affording a microcrystalline solid. Yield: 375 mg (78%). IR: ν_{SiH} 2080 cm^{-1}, ν_{OsH} 2199 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, δ): 8.11 (d, 2 H, $^3J_{\mathrm{HH}}$ = 7.8 Hz, *o*-Ph), 8.07 (d, 2 H, $^3J_{\mathrm{HH}}$ = 7.8 Hz, *o*-Ph), 7.31−7.17 (m, overlapping, 9 H, aryl, Si*H*), 2.38 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.47 (s, 15 H, C$_5$*Me$_5$*), 1.04 (vq, 9 H, P(CHMe*Me*)$_3$), 0.87 (vq, 9 H, P(CH*Me*Me)$_3$), −14.15 (d, 1 H, $^2J_{\mathrm{PH}}$ = 32 Hz, Os*H*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 145.7, 144.6, 137.4, 137.2, 127.4, 127.3, 127.0, 126.6 (aryl), 94.96 (C$_5$*Me$_5$*) 28.28 (d, $^1J_{\mathrm{PC}}$ = 26.6 Hz, P(*C*HMe$_2$)$_3$), 20.48, 20.33 (P(CH*Me$_2$*)$_3$), 10.76 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 3.79. ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, δ): −10.65 (d, $^2J_{\mathrm{SiP}}$ = 9 Hz). Anal. Calcd: C, 49.65; H, 6.45. Found: C, 49.47; H, 6.48.

[Cp*(^{i}Pr$_3$P)(H)$_2$Os=SiPh$_2$][B(C$_6$F$_5$)$_4$] (14). To a CD$_2$Cl$_2$ solution (1 mL) of **13** (25 mg, 33 μmol) was added 1.1 equiv of LiB(C$_6$F$_5$)$_4$ (26 mg, 38 μmol) in CD$_2$Cl$_2$ (0.75 mL) by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was then filtered through a fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **14** to be the major (>95%) product in solution. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.86 (d, 4 H, *o*-Ph, $^3J_{\mathrm{HH}}$ = 7 Hz), 7.67 (t, 2 H, *p*-Ph, $^3J_{\mathrm{HH}}$ = 8 Hz), 7.61 (m, 4 H, *m*-Ph), 2.07 (s, 15 H, C$_5$*Me$_5$*), 1.88 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.05 (vq, 18 H, P(CH*Me$_2$*)$_3$) −11.65 (d, 2 H, $^2J_{\mathrm{PH}}$ = 28.4 Hz, Os(H)$_2$). ^{13}C{^{1}H} NMR: 143.0, 136.2, 133.8, 128.7 (aryl), 96.1 (*C$_5$*Me$_5$), 28.8 (d, $^1J_{\mathrm{CP}}$ = 30 Hz, (P(C*H*Me$_2$)$_3$), 19.33 (P(C*H*Me$_2$)$_3$, 11.34 (C$_5$*Me$_5$*). ^{29}Si NMR (INEPT, CD$_2$Cl$_2$, δ): 313.6 (d, $^2J_{\mathrm{SiP}}$ = 7 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 39.6.

Cp*(^{i}Pr$_3$P)Os(H)$_2$SiPh$_2$OTf (15). To a stirred pentane solution of 324 mg (0.394 mmol) of **13** cooled in a CO$_2$/^{i}PrOH bath was added slowly an Et$_2$O (25 mL) solution of 114 mg (0.445 mmol) of AgOTf by cannula. The reaction vessel was protected from light and allowed to slowly come to room temperature. After 3 h, a dark, extremely fine precipitate had formed. The solution was filtered through a combination of Whatman #50 paper and glass fiber to afford an orange solution. Volatile components of the mixture were removed in vacuo to afford a yellow-orange foam. NMR spectroscopy showed that the desired product was consistently contaminated with varying amounts (5−20%) of a second, unidentified species and unreacted starting material that was not removed by crystallization from pentane/Et$_2$O. Employing a molar excess of AgOTf (1.25 equiv) in the reaction did not increase the proportion of **15** in the product mixture. ^{1}H NMR (C$_6$D$_6$, δ): 8.17 (d, 4 H, $^3J_{\mathrm{HH}}$ = 7 Hz, *o*-aryl), 7.29 (m, 4 H, $^3J_{\mathrm{HH}}$ = 7 Hz, *m*-aryl), 7.16 (m, 2 H, *p*-aryl), 1.61 (m, 3 H, P(C*H*Me$_2$)$_3$) 1.59 (s, 15 H, C$_5$*Me$_5$*), 0.87 (vq, 18 H, P(CH*Me$_2$*)$_3$), −14.34 (d, 2 H, $^2J_{\mathrm{PH}}$ = 28 Hz, Os*H).* ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 30.0. ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, δ): 64.1 (d, $^2J_{\mathrm{PSi}}$ = 24.6 Hz).

{[Cp*(^{i}Pr$_3$P)(H)$_2$Os=SiH$_2$][B(C$_6$F$_5$)$_4$]}$_n$ (16). To a CD$_2$Cl$_2$ solution (1 mL) of **3** (20 mg, 33 μmol) was added 1.1 equiv of LiB(C$_6$F$_5$)$_4$ (25 mg, 36 μmol) in CD$_2$Cl$_2$ by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was filtered through a fine glass fiber, affording a clear yellow solution. ^{1}H NMR spectroscopy showed **16** to be the major (>95%) product in solution. NMR (^{1}H, CD$_2$Cl$_2$, δ): 6.2 (br s, LW = 500 Hz, fwhh), 1.79 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.77 (s, 15 H, C$_5$*Me$_5$*), 0.87 (vq, 18 H, P(CH*Me$_2$*)$_3$), −14.77 (br s, LW = 100 Hz, fwhh, 2 H, Os*H*). ^{31}P{^{1}H} (CD$_2$Cl$_2$, δ): 32.5 (LW = 150 Hz, fwhh).

[Cp*(^{i}Pr$_3$P)(H)$_2$Os=Si(H)dipp][B(C$_6$F$_5$)$_4$] (17). To a CD$_2$Cl$_2$ solution (1 mL) of **6** (31 mg, 40 μmol) was added LiB(C$_6$F$_5$)$_4$ (30 mg, 44 μmol) in 0.75 mL of CD$_2$Cl$_2$ by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was then filtered through a fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **17** to be the major (>95%) product in solution. ^{1}H NMR (CD$_2$Cl$_2$, δ): 11.61 (s, 1 H, $^1J_{\mathrm{SiH}}$ = 188 Hz OsSi(H)), 7.35 (t, 1 H, $^3J_{\mathrm{HH}}$ = 8 Hz, *p*-aryl), 7.26 (d, 2 H, $^3J_{\mathrm{HH}}$ = 8 Hz, *m*-aryl), 2.73 (sept, 2 H, $^3J_{\mathrm{HH}}$ = 6.4 Hz, *m*-C*H*Me$_2$), 2.07 (m, 3H, P(C*H*Me$_2$)$_3$), 2.04 (s, 15 H, C$_5$Me$_5$), 1.34 (d, 12 H, $^3J_{\mathrm{HH}}$ = 6.4 Hz, *m*-CH*Me$_2$*), 1.14 (vq, 18 H, P(C*H*Me$_2$)$_3$), −12.72 (d, 2 H, 2*J*PH = 27.9 Hz, Os−H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 151.2, 136.5, 133.1 123.3 (aryl), 97.4 (C$_5$Me$_5$), 37.4 (*m*-*C*HMe$_2$), 28.3 (d, $^1J_{\mathrm{CP}}$ = 29 Hz, P(*C*HMe$_2$)$_3$), 24.1 (*m*-CH*Me$_2$*), 18.6 ((P(CH*Me$_2$*)$_3$), 10.89 (C$_5$Me$_5$). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, δ): 314 (d, $^2J_{\mathrm{SiP}}$ = 15 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 32.4.

[Cp*(^{i}Pr$_3$P)(H)$_2$Os=Si(H)trip][B(C$_6$F$_5$)$_4$] (18). To a solution of 310 mg (0.387 mmol) of **7** in 10 mL of fluorobenzene was added a solution of 275 mg (0.401 mmol) of Li[B(C$_6$F$_5$)$_4$] in 10 mL of fluorobenzene. The solution immediately turned from golden yellow-orange to pale lemon yellow. A fine white precipitate formed at the same time. The mixture was filtered and the volatile material was removed in vacuo to afford a pale yellow foam, which was then dried in vacuo. Yield: 373 mg (73%). ^{1}H NMR (CD$_2$Cl$_2$, δ): 11.56 (s, 1 H, $^1J_{\mathrm{SiH}}$ = 183 Hz, Os=Si(*H*)trip), 7.06 (s, 2 H, Ar), 2.92 (sept, 1 H, $^3J_{\mathrm{HH}}$ = 7 Hz, C*H*Me$_2$), 2.72 (sept, 2 H, $^3J_{\mathrm{HH}}$ = 7 Hz, C*H*Me$_2$), 2.0−2.1 (m, 3 H, P(C*H*Me$_2$)$_3$), 2.04 (s, 15 H, C$_5$*Me$_5$*), 1.34 (d, 12 H, $^3J_{\mathrm{HH}}$ = 7 Hz, CH*Me$_2$*), 1.25 (d, 6 H, $^3J_{\mathrm{HH}}$ = 7 Hz, CH*Me$_2$*), 1.13 (vq, 18 H, P(CH*Me$_2$*)$_3$), −12.74 (d, 2 H, $^2J_{\mathrm{PH}}$ = 27 Hz, $^2J_{\mathrm{SiH}}$ = 5.5 Hz Os−H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 155.3, 151.8, 134.2, 121.9 (Ar), 97.81 (d, *C$_5$*Me$_5$, $^2J_{\mathrm{PC}}$ = 2.5 Hz), 37.86, 35.06 (*C*HMe$_2$), 28.79 (d, $^1J_{\mathrm{CP}}$ = 30.0 Hz, P(*C*HMe$_2$)$_3$), 24.57, 23.94, 19.08 (CH*Me$_2$*), 11.31 (C$_5$*Me$_5$*). ^{29}Si (HMBC expt, CD$_2$Cl$_2$, δ): 315 (dd, $^2J_{\mathrm{SiP}}$ = 13.6 Hz, $^2J_{\mathrm{SiH}}$ = 5.5 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 32.5. Anal. Calcd for C$_{58}$H$_{62}$BF$_{20}$OsPSi: C, 49.79; H, 4.47. Found: C, 50.04; H, 4.31.

[Cp*(^{i}Pr$_3$P)(H)$_2$Os=Si(H)Si(SiMe$_3$)$_3$][B(C$_6$F$_5$)$_4$] (19). To a CD$_2$Cl$_2$ solution (0.75 mL) of **10** (28 mg, 33 μmol) was added LiB(C$_6$F$_5$)$_4$ (25 mg, 36 μmol) in CD$_2$Cl$_2$ (0.75 mL) by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was then filtered through a

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fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **19** to be the major (>95%) product in solution. ^{1}H NMR (CD$_2$Cl$_2$, δ): 12.05 (t, 1 H, $^2J_{HH}$ = 2.5 Hz, $^1J_{SiH}$ = 147.6 Hz, OsSiH), 2.18 (s, 15 H, C$_5$*Me*$_5$) 1.76 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.22 (vq, 18 H, P(CH*Me*$_2$)$_3$) 0.40 (s, $^2J_{SiH}$ = 5.9 Hz, 27 H, Si(Si*Me*$_3$)$_3$), −9.90 (d, $^2J_{PH}$ = 27.5 Hz, Os*H*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 96.43 (*C*$_5$Me$_5$), 31.07 (d, $^1J_{PH}$ = 29 Hz, P(*C*HMe$_2$)$_3$), 19.45 (P(CH*Me*$_2$)$_3$), 12.17 (C$_5$Me$_5$), 3.20 (SiMe$_3$). ^{29}Si NMR (HMBC): 417.5 (d, $^2J_{PSi}$ = 9 Hz, Os*Si*(H)Si(SiMe$_3$)$_3$), −5.9 (OsSi(H)Si(*Si*Me$_3$)$_3$), −74.9 (OsSi(H)*Si*(SiMe$_3$)$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 40.88.

[Cp*(^{i}Pr$_3$P)(H)$_2$Os=Si(H)(C$_6$F$_5$)][B(C$_6$F$_5$)$_4$] (20). To a CD$_2$Cl$_2$ solution (0.75 mL) of **8** (22 mg, 29 μmol) was added LiB(C$_6$F$_5$)$_4$ (22 mg, 32 μmol) in CD$_2$Cl$_2$ (0.75 mL) by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and filtered through a fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **20** to be the major (>95%) product in solution. ^{1}H NMR (CD$_2$Cl$_2$, δ): 6.75 (br s, 1 H, $^1J_{SiH}$ = 185 Hz), 1.92−2.20 (m, 3 H, P(C*H*Me$_2$)$_3$), 2.05 (s, 15 H, C$_5$Me$_5$), 1.08−1.18 (vq, 18 H, P(CH*Me*$_2$)$_3$), −14.09 (d, $^2J_{PH}$ = 27.9 Hz). ^{13}C{^{1}H} NMR: 95.50 (*C*$_5$Me$_5$), 28.95 (d, $^1J_{PC}$ = 27.7 Hz, P(*C*HMe$_2$)$_3$), 18.92 (P(CH*Me*$_2$)$_3$), 11.20 (C$_5$*Me*$_5$). ^{19}F{^{1}H} NMR: −128.8 (br, *o*-C$_6$F$_5$), −150.9, 160.8, (C$_6$*F*$_5$). ^{29}Si NMR (HMBC expt, CD$_2$Cl$_2$, δ): 318 br. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 29.9.

[Cp*(^{i}Pr$_3$P)(H)$_2$Os=Si(H)SiPh$_3$·DMAP][B(C$_6$F$_5$)$_4$] (21·DMAP). To a CD$_2$Cl$_2$ solution (1 mL) of **11** (19 mg, 22 μmol) and DMAP (3 mg, 25 μmol) was added a CD$_2$Cl$_2$ solution (0.75 mL) of LiB(C$_6$F$_5$)$_4$ (17 mg, 25 μmol) by pipet, causing a color change from golden yellow to very pale yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was then filtered through a fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **21**·DMAP to be the major (>95%) product in solution with excess DMAP. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.81 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, DMAP) 7.46 (m, 6 H, aryl), 7.40 (m, 3 H, aryl), 7.32 (m, 6 H, aryl), 6.47 (d, 1 H, *J* = 2.5 Hz, $^1J_{SiH}$ = 169 Hz, Si−H), 6.35 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, DMAP), 3.10 (s, 6 H, N*Me*$_2$), 2.09 (m, 3 H, P(C*H*Me$_2$)$_3$), 1.84 (s, 15 H, C$_5$*Me*$_5$), 1.02 (vq, 9 H, P(CHMe*Me*)$_3$), 0.93 (vq, 9 H, P(CHMe*Me*)$_3$), −14.65 (d, 1 H, $^2J_{PH}$ = 29 Hz, Os−H), −14.71 (d, 1 H, $^2J_{PH}$ = 28 Hz, Os−H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 145.8 (DMAP aryl), 136.4, 136.3, 129.7, 128.4 (aryl), 106.8 (DMAP aryl), 94.4 (*C*$_5$Me$_5$), 39.9 (N*Me*$_2$), 26.8 (d, $^1J_{PC}$ = 29.7 Hz, P(*C*HMe$_2$)$_3$), 18.8 (P(CH*Me*$_2$)$_3$), 11.62 (C$_5$*Me*$_5$).

[Cp*(^{i}Pr$_3$P)(H)$_2$Os=Si(Ph)SiPh$_2$H][B(C$_6$F$_5$)$_4$] (22). To a CD$_2$Cl$_2$ solution (1 mL) of **11** (26 mg, 30 μmol), a CD$_2$Cl$_2$ solution (0.75 mL) of LiB(C$_6$F$_5$)$_4$ (23 mg, 34 μmol) was added by pipet, causing a color change from golden yellow to pale lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and filtered through a fine glass fiber. NMR spectroscopy showed **22** to be the major (>95%) product in solution. ^{1}H NMR (CD$_2$Cl$_2$, δ): 8.24 (d, 2 H, *o*-PH, $^3J_{HH}$ = 8 Hz), 7.72−7.44 (overlapping m, 13 H, aryl), 5.79 (s, 1 H, $^1J_{SiH}$ = 198 Hz, $^2J_{SiH}$ = 7 Hz, Si*H*), 1.99 (s, 15 H, C$_5$*Me*$_5$), 1.70 (m, 3 H, P(C*H*Me$_2$)$_3$), 0.94 (vq, 18H, P(CH*Me*$_2$)$_3$), −10.58 (d, 2 H, $^2J_{PH}$ = 28.2 Hz, $^2J_{SiH}$ = 13.5 Hz, Os−*H*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 136.3, 135.9, 135.7, 134.0, 130.4, 129.8, 128.8, 128.5 (aryl), 95.7 (d, J_{PC} = 1 Hz, *C*$_5$Me$_5$), 28.5 (d, $^1J_{PC}$ = 29.8 Hz, P(*C*HMe$_2$)$_3$), 18.8 (P(CHMe$_2$)$_3$), 11.0 (C$_5$*Me*$_5$). ^{29}Si NMR (HMBC, CD$_2$Cl$_2$, δ): 379, −18. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 41.4.

{Cp*[^{i}Pr$_2$P(η^2-MeC=CH$_2$)]OsH$_2$}[B(C$_6$F$_5$)$_4$] (24). Solid **2** (545 mg, 0.94 mmol) and solid KB(C$_6$F$_5$)$_4$ (750 mg, 1.04 mmol) were combined in a Schlenk tube and cooled to −78 °C with a dry ice/^{i}PrOH bath. THF (10 mL) was added, and the mixture was stirred for 5 min at −78 °C and then allowed to come to room temperature. After 1 h at room temperature, solvent was removed in vacuo. The dark residue was extracted with 3 × 10 mL of 1:1 CH$_2$Cl/Et$_2$O. The combined filtrates were cooled slowly to −80 °C, affording a crop of well-formed taupe crystals. Yield: 540 mg (46%). ^{1}H NMR (CD$_2$Cl$_2$, δ): 3.12 (d, 1 H, J_{PH} = 35 Hz, MeC=C*H*H), 2.54 (d, 3 H, J_{PH} = 8 Hz, *Me*C=CHH), 2.37 (m, 1 H, P(C*H*Me$_2$)), 2.24 (s, 15 H, C$_5$*Me*$_5$), 2.24 (d, overlapping, 1 H, J_{PH} = 12 Hz, MeC=CH*H*), 1.60−1.53 (3 overlapping vq, 9 H, P(CHMe*Me*)), 1.55−1.52 (m, overlapping, 1 H, P(C*H*Me$_2$), 1.41 (vq, 3 H, P(CHMe*Me*), −13.74 (d, 1 H, OsH, $^2J_{PH}$ = 23.1 Hz), −15.10 (d, 1 H, Os*H*, $^2J_{PH}$ = 20.6 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 98.28 (*C*$_5$Me$_5$), 57.79 (d, $^2J_{PH}$ = 20.3 Hz, Me*C*=CH$_2$), 33.42 (d, $^2J_{PH}$ = 37.5 Hz, P(*C*HMe$_2$), 32.70 (s, MeC=*C*H$_2$), 26.55 (s, *Me*C=CH$_2$), 24.92, 22.55 (s, P(CH*Me*Me), 22.08 (d, $^2J_{PH}$ = 22.3 Hz, P(*C*HMe$_2$)), 19.81, 18.73 (s, P(CH*Me*Me), 11.73 (s, *C*$_5$Me$_5$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): −4.62. Anal. Calcd: C, 44.34; H, 3.12. Found: C, 44.06; H, 3.29.

Cp*[^{i}Pr$_2$P(η^2-MeC=CH$_2$)]OsH (25). A 468 mg (0.377 mmol) sample of **9** was treated with 10 mL of C$_6$H$_6$, affording a dense, mobile oil at the bottom of the vessel. The mixture was stirred, forming a heterogeneous suspension. This suspension was treated with KN(SiMe$_3$)$_2$ (80 mg, 0.40 mmol) in C$_6$H$_6$ (30 mL). The solution rapidly became homogeneous as the cationic species reacted, and a white precipitate, presumably KB(C$_6$F$_5$)$_4$, formed. The solution was allowed to settle and was filtered to afford a pale yellow solution. Removal of solvent from the filtrate afforded a dense, gelatinous oil that did not solidify upon prolonged exposure to vacuum or treatment with pentane. Attempts to isolate this compound as a solid suitable for elemental analysis were unsuccessful. NMR tube reactions and spectroscopy of the viscous oil both demonstrated that **25** is formed in greater than 95% yield from **24** in C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$, δ): 2.27 (m, 1 H, MeC=C*H*H), 2.05 (s, 15 H C$_5$*Me*$_5$), 1.98 (m, 1 H, MeC=CH*H*), 1.71 (m, 1 H, P(C*H*Me$_2$)), 1.56 (m, 3 H, P(C*H*Me$_2$)), 1.52 (d, 3 H, $^3J_{PH}$ = 6 Hz, *Me*C=CHH), 1.19 (vq, 3 H, P(CHMe*Me*)), 1.11 (vq, 1 H, P(CHMe*Me*)), 0.91−0.85 (2 overlapping vq, 6 H, P(CHMe*Me*), −16.18 (dd, 1 H J_{HH} = 8 Hz, $^2J_{PH}$ = 26 Hz, Os*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 88.11 (d, J_{PH} = 0.8 Hz, *C*$_5$Me$_5$), 27.08 (d, $^1J_{PH}$ = 31 Hz, P(*C*HMe$_2$)), 23.10 (d, $^2J_{PH}$ = 6.7 Hz, P(CH*Me*Me)), 20.84 (d, $^2J_{PH}$ = 21 Hz, Me*C*=CH$_2$), 20.62 (d, $^2J_{PH}$ = 4 Hz, P(CH*Me*Me)), 20.39 (d, $^2J_{PH}$ = 6.7 Hz, P(CH*Me*Me)), 19.84 (d, $^2J_{PH}$ = 2.4 Hz, P(CH*Me*Me)), 18.88 (d, $^2J_{PH}$ = 4.5 Hz, P(CH*Me*Me)), 16.95 (d, $^3J_{PH}$ = 21.2 Hz, P(*C*HMe$_2$)), 12.30 (C$_5$*Me*$_5$), 12.15 (d, $^2J_{PH}$ = 15 Hz, MeC=*C*H$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 4.82.

X-ray Crystallography. General Considerations. Crystallographic analyses were carried out at the University of California, Berkeley CHEXRAY crystallographic facility.[39] All measurements were made on a Bruker SMART CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Crystals were mounted on capillaries with Paratone-N hydrocarbon oil and held in a low-temperature N$_2$ stream during data collection. Frames were collected using ω scans at 0.3° increments, using exposures of 10 s (**4**, **8**, **11**, **15**, and **24**) or 20 s (**12** and **13**). Data were integrated with the program SAINT,[40] corrected for Lorentz and polarization effects, and analyzed for agreement and possible absorption using XPREP.[41] Empirical absorption corrections were made with either SADABS[42] or XPREP. A *p*-factor of 0.030 was employed to downweight intense reflections. Structures were solved by direct methods and expanded using Fourier techniques.[43] The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)$, where w is the weight of a given observation. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were

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(39) http://xray.cchem.berkeley.edu.

(40) *SAINT*: *SAX Area-Detector Integration Program*, version 4.024; Bruker, Inc.: Madison, WI, 1995.

(41) *XPREP v. 5.03*, Part of the *SHELXTL* Crystal Structure Determination Package; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

(42) Sheldrick, G. M. *SADABS*, Siemens Area Detector Absorption Correction Program; 1996. Advance copy, private communication.

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Table 3. Experimental Details for X-ray Crystallography

	4	**8**	**11**·C_6H_6	**12**·$(C_6H_5F)_{0.5}$
empirical formula	$C_{25}H_{44}BrOsSiP$	$C_{25}H_{39}F_5SiPOsBr$	$C_{43}H_{60}OsPSi_2Br$	$C_{24}H_{43}OsSiBrPF_{0.50}$
fw	673.79	763.74	934.20	670.27
cryst color and habit	yellow blade	orange shard	yellow plate	yellow block
cryst size (mm)	0.29 × 0.1 × 0.02	0.20 × 0.09 × 0.05	0.15 × 0.10 × 0.07	0.11 × 0.09 × 0.07
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
lattice type	primitive	primitive	C-centered	primitive
space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	Cc (#9)	$P2_1/n$ (#14)
a (Å)	9.242(1)	15.5293(1)	9.364(2)	9.0114(1)
b (Å)	17.895(2)	9.1041(1)	28.9855(5)	20.7564(9)
c (Å)	16.121(2)	19.8726(3)	15.5909(3)	14.876(3)
α (deg)	90	90	90	90
β (deg)	95.507	99.319(1)	104.671(1)	91.25(1)
γ (deg)	90	90	90	90
volume (Å^3)	2653.9(4)	2772.51(5)	4093.7(5)	2781.9(3)
orientation refln, 2θ range (deg)	3.4−51.3	3.4−50.9	3.4−51.2	3.4−51.2
Z	4	4	4	4
D_{calc} (g/cm^3)	1.69	1.830	1.516	1.600
F_{000}	1336	1496	1888	1326
μ(Mo Kα) (cm^{-1})	64.38	61.89	42.18	61.39
temperature (°C)	−112	−109	−119	−105
data collected, 2θ_{max} (deg)	51.3	50.9	51.1	50.9
no. of reflns measd, total	11 889	12 218	10 796	5495
no. of reflns measd, unique	4531	4874	5115	4074
R_{int}	0.057	0.036	0.035	.034
transmn factors, T_{min}/T_{max}	0.15/0.88	0.41/0.65	0.50/0.72	0.50/0.61
no. of obsd data $I > 3\sigma$	2911	3608	4540	2925
no. of params refined	262	307	431	242
refln/param ratio	11.11	11.75	10.53	12.09
final residuals R; R_w; R_{all}[a]	0.042, 0.049, 0.065	0.034; 0.041; 0.044	0.038; 0.044; 0.043	0.064; 0.096; 0.078
goodness of fit indicator[b]	1.20	1.34	1.51	3.16
max. shift/error in final LS cycle	0.01	0.00	0.01	0.03
max.; min. peaks (e$^-$/Å^3)	2.91; −3.78	1.35; −2.63	1.72; −2.31	2.64; 4.46

	13·$(C_5H_{12})_2$	**15**	**24**
empirical formula	$Os_2Si_2P_2Br_2C_{74}H_{100}$	$OsPC_{35.5}F_3SSiO_3H_{48}Br_{0.05}$	$C_{43}F_{24}POsH_{36}B$
fw	1647.93	865.08	1240.70
cryst color and habit	yellow plate	yellow prism	amber block
cryst size (mm)	0.19 × 0.17 × 0.07	0.26 × 0.23 × 0.16	0.13 × 0.11 × 0.08
cryst syst	monoclinic	triclinic	monoclinic
lattice type	primitive	primitive	primitive
space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)
a (Å)	13.5150(3)	9.1510(2)	17.1214(6)
b (Å)	39.3983(9)	11.9720(3)	14.1558(6)
c (Å)	14.3453(3)	18.1370(1)	19.3014(6)
α (deg)	90	81.930(1)	90
β (deg)	98.738(1)	77.270(1)	114.089(1)
γ (deg)	90	76.040(1)	90
volume (Å^3)	7549.8(3)	1872.92(6)	4270.6(2)
orientation reflns, 2θ range (deg)	3.4−51.4	3.5−45.0	3.4−49.4
Z	4	2	4
D_{calc} (g/cm^3)	1.450	1.534	1.930
F_{000}	3296	869.5	2424
μ(Mo Kα) (cm^{-1})	45.28	36.33	31.61
temperature (°C)	−113	−127	−132
data collected, 2θ_{max} (deg)	51.5	50.8	49.4
no. of reflns measd, total	39 351	9183	18 809
no. of reflns measd, unique	13 103	5884	7343
R_{int}	0.058	0.036	0.055
transmn factors, T_{min}/T_{max}	0.43/0.67	0.20/0.59	0.52/0.78
no. of obsd data $I > 3\sigma$	8826	4986	4487
no. of params refined	723	400	475
refln/param ratio	12.21	12.46	9.45
final residuals R; R_w; R_{all}[a]	0.037; 0.045; 0.064	0.038; 0.046; 0.042	0.034; 0.038; 0.065
goodness of fit indicator[b]	1.17	1.43	1.06
max. shift/error in final LS cycle	0.04	0.02	0.03
max.; min. peaks in (e$^-$/Å^3)	2.74; 1.92	1.86; −2.78	0.92; −1.66

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [b] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

corrected for both the real and the imaginary components of anomalous dispersion. Calculations were performed using the teXsan crystallographic software package.[44] In each case, the calculated centroid of the Cp* ring was placed in a fixed position as a carbon atom with a partial occupancy of 0.0001 and a fixed B_{iso} of 0.2 and included in the final cycles of least-squares refinement. Osmium hydride ligands could not be reliably located in the Fourier difference maps and were not included in the refinement. Unless stated otherwise, non-hydrogen atoms were allowed to refine anisotropically, and carbon-bound hydrogen atoms were placed at calculated positions and not refined.

Selected experimental parameters for data collection and refinement are presented above in Table 3. Atomic coordinates,

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anisotropic thermal parameters, and selected bond lengths and angles are collected in the Supporting Information.

For 4. Crystals were grown by slow diffusion of pentane into a benzene solution. The relatively large residual peaks in the Fourier density map are a symptom of an imperfect absorption correction due to the bladelike morphology of the crystals. The largest peaks in the Fourier map are symmetrically disposed about osmium.

For 8. Crystals were grown by slow cooling of a concentrated CH_2Cl_2/Et_2O solution. The structure is of high quality, and no problems were encountered in the refinement. The largest peaks in the Fourier map were located close to osmium.

For 11. Crystals were grown by layering a concentrated C_6D_6 solution with pentane. There is one well-ordered molecule of benzene per molecule of **11**. The structure is of high quality, and no problems were encountered in the refinement. The correct choice of enantiomorph was verified by refinement to a low R value and a successful Bijvoet analysis. The largest peaks in the Fourier map were located close to osmium.

For 12. Crystals were grown from a concentrated fluorobenzene/pentane solution at -30 °C. After collection of the data set, careful inspection of the data showed that the crystal had fractured in the cold stream midway through collection. Data collected after this event were discarded, significantly reducing the redundancy of the data (total/unique data = 1.34). Despite this difficulty, the model refined to an acceptable R value, and bond lengths and angles were reasonable. The asymmetric unit contains half of a molecule of fluorobenzene located on an inversion center. This solvent molecule was refined isotropically. The largest peaks in the Fourier map were located close to osmium.

For 13. Crystals were grown by layering a concentrated C_6D_6 solution with pentane. The asymmetric unit contains two crystallographically independent molecules of **13** which have essentially identical metric parameters. The unit cell has sizable channel-shaped voids that are filled with disordered pentane. This disordered solvent was successfully modeled as a series of half-occupancy carbon atoms. The largest peaks in the Fourier map were located close to osmium.

For 15. Crystals were grown by layering a toluene solution containing **15** as the major constituent with pentane. The asymmetric unit contains half of a molecule of toluene on an inversion center. A large peak close to osmium was at the appropriate distance for an osmium-bound bromine atom and was modeled as such at 5% occupancy. The partial occupancy of bromine at this location can be attributed to cocrystallization of a small amount of the precursor material **13**. Other large peaks in the Fourier map were located close to osmium.

For 24. Crystals were grown by slow cooling of a CH_2Cl_2/Et_2O solution. The 24 carbon atoms of the $B(C_6F_5)_4$ anion were allowed to refine isotropically to maintain a high data/parameter ratio. A model in which these carbons were refined anisotropically did not provide significantly different metric parameters. Hydrogen atoms bound to the sp^2 carbon atom in the metalated P^iPr_3 ligand were located in the Fourier map and fixed in the final stages of refinement. The largest residual peaks in the Fourier difference map were close to osmium.

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Supporting Information Available: Tables of atomic coordinates, thermal displacement parameters, and selected bond lengths and angles for **4**, **8**, **11**, **12**, **13**, **15**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) (a) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *SIR92*. *J. Appl. Crystallogr.* **1993**, *26*, 343. (b) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *DIRDIF92*: *The DIRDIF Program System*, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

(44) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation, 1985 and 1992.