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Osmium Alkyl and Silyl Derivatives with Cyclopentadienyl(phosphine) and Pentamethylcyclopentadienyl(phosphine) Ligand Sets

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The preparation and characterization of new osmium(II) and osmium(IV) silyl derivatives containing the cyclopentadienyl(phosphine) and pentamethylcyclopentadienyl(phosphine) ligand sets are described. The osmium silyl complexes are prepared by thermal reactions of hydrosilanes with osmium(II) alkyl complexes of the type $Cp'(PR_3)_2OsCH_2SiMe_3$ (Cp' = Cp, R = Ph (**4**), Me (**5**); $Cp' = \eta^5\text{-}C_5Me_5$, R = Me (**7**)), which in turn are available via alkylation of the corresponding bromo complexes. The synthesis of alkyl derivatives of $Cp(PR_3)_2Os$ (R = Ph, Me) requires the use of dialkylmagnesium reagents, while alkylation of the more electron-rich $Cp^*(PMe_3)_2Os$ system can be achieved using Grignard reagents. Additionally, reaction of $Cp(PPh_3)_2OsBr$ with AgOTf ($Tf = SO_2CF_3$) affords the osmium(II) triflate complex $Cp(PPh_3)_2OsOTf$ (**2**), which possesses a labile triflate group. The structure of complex **2** was determined by X-ray crystallography. Similar to their ruthenium analogs, the osmium(II) alkyl complexes **4**, **5**, and **7** thermally activate arene C−H bonds. Reaction of **7** with $HSiR_2[S(p\text{-Tol})]$ (R = S(*p*-Tol), Me) provides metallacycle complexes of the type $Cp^*(PMe_3)(H)\overline{Os[C_6H_3(3\text{-}Me)(6\text{-}S)Si}R_2]$ (R = S(*p*-Tol) (**11**), Me (**13**)) via activation of both the Si−H and arene C−H bonds in the silanes. The X-ray structure of **13** is described. Alkyl complexes **4**, **5**, and **7** react with $HSiR_2Cl$ (R = Ph, Me) to give osmium(II) silyl and/or osmium(IV) bis(silyl) hydride species, depending on the reaction conditions and the strength of the Os−P bond. Reaction of **7** with $HSiMeCl_2$ or $HSiCl_3$ affords, exclusively, the osmium(II) silyl derivatives. Exchange reactions at silicon are used to synthesize $Cp^*(PMe_3)_2OsSiMe_2OTf$ (**24**) and $Cp^*(PMe_3)_2OsSiMe[S(p\text{-Tol})]_2$ (**25**) from the corresponding chloro(silyl) complexes $Cp^*(PMe_3)_2OsSiMe_2Cl$ (**17**) and $Cp^*(PMe_3)_2OsSiMeCl_2$ (**18**). The solution behavior and solid-state structure of **24** indicate that the compound may be described as a base-stabilized silylene complex.

Introduction

The burgeoning area of transition-metal silicon chemistry continues to generate considerable interest,[1] mainly due to the prominent role of metal−silicon bonded species in various catalytic processes, such as hydrosilation,[2] dehydrogenative coupling of hydrosilanes to polysilanes,[3] and the redistribution of silanes.[4] This growing interest in transition-metal−silicon bonded compounds has been further stimulated by the discovery of complexes containing reactive silicon species (e.g., silylenes, SiR_2; silenes, $R_2C{=}SiR'_2$; etc.) as ligands, especially since such complexes have often been invoked as key intermediates in numerous stoichiometric and catalytic reactions of organosilanes.[1,3c,4,5] In previous work, we demonstrated that a variety of ruthenium silyl complexes of the type $Cp^*(PMe_3)_2Ru(SiXX'X'')$ ($Cp^* = \eta^5\text{-}C_5Me_5$) are versatile precursors to ruthenium silylene[6] and base-stabilized silylyne[7] complexes.

On the basis of our previous work with ruthenium, we sought to develop the analogous silicon chemistry of osmium. Like ruthenium, osmium is an electron-rich metal that can serve as a strong π-donor, as evidenced by the wealth of osmium carbene and carbyne species

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that have been reported.[8] This, coupled with the fact that 5d transition metals inherently form strong bonds to ligands,[9] led us to expect that many silicon-based ligands might be stabilized by osmium. In addition, recent reports indicate that homogeneous catalysis by osmium silyl complexes may be a field with promising potential.[10]

While osmium silyl complexes have been known since the 1970s, very little reaction chemistry for Os−Si bonds has been developed. In a recent study, Esteruelas and co-workers showed that the hydrosilation of phenylacetylene, as catalyzed by $OsHCl(CO)(P^iPr_3)_2$, proceeds via the silyl dihydrogen intermediate $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$.[10a] Of the known osmium silyl complexes, the majority are derived from osmium carbonyl clusters (primarily $Os_3(CO)_{12}$)[1,11] and contain carbonyl ligands. The primary method of synthesis for monomeric osmium silyl complexes, such as $Os(SiMe_3)(Cl)(CO)(PPh_3)_2$,[12a] $Os(SiEt_3)(H)(CO)_2(PPh_3)_2$,[12b] and $OsH_3(CO)(SiHPh_2)(P^iPr_3)_2$,[13] involves oxidative addition of hydrosilanes to unsaturated metal centers.

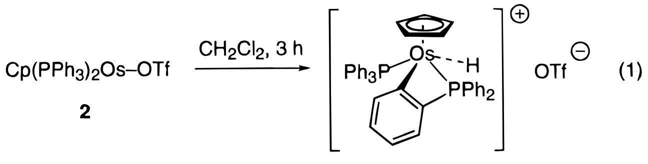
In this report, we describe synthetic routes to new osmium(II) and osmium(IV) silyl complexes containing cyclopentadienyl(phosphine) and pentamethylcyclopentadienyl(phosphine) ligand sets. These syntheses are modeled after our previously reported route to $Cp^*(PMe_3)_2RuSiX_3$ complexes, based on reactions of silanes with the corresponding ruthenium alkyls $Cp^*(PMe_3)_2RuR$.[6b] This strategy, therefore, required alkyl complexes of the type $Cp'(PR_3)_2OsR'$ ($Cp' = Cp, Cp^*$; $R' =$ alkyl), which we anticipated might be accessible via alkylation of the corresponding halide derivatives. To our knowledge, there have been no published reports on the synthesis of osmium alkyl complexes of this type, although the ^{187}Os NMR spectra of $Cp(PPh_3)_2OsMe$ and $Cp(PMe_3)_2OsR$ ($R = Me, Et, CH_2CMe_3, Ph$) have been reported.[14]

Results and Discussion

Synthesis of η^5-Cp and η^5-Cp* Osmium(II) Alkyl Complexes. Our interest initially focused on the starting material $Cp(PPh_3)_2OsBr$ (**1**), which was reported by Bruce *et al.* in 1977 as being available in high yield from reaction of hexabromoosmic acid (H_2OsBr_6), PPh_3, and cyclopentadiene in refluxing ethanol.[15] Initial attempts to repeat this synthesis using anhydrous ethanol gave mostly an insoluble red solid and only a very low yield (<10%) of the desired orange product **1**. NMR spectra of the red solid were consistent with a mixture of PPh_3-containing compounds, but Cp ligands were not detected. We found that the red solid could be efficiently converted to **1** by its reaction with cyclopentadiene in refluxing 95% ethanol. Apparently, the presence of water is essential for the formation of **1**, which involves the red solid as an intermediate. Subsequently, we obtained an improved procedure which gives **1** in 97% yield (see Experimental Section).[16] Recently, Jia *et al.* reported a modified synthesis of **1** using Zn as a reagent, but the yield of product is rather low (17%).[17]

Initial attempts to alkylate **1** with common alkylating agents met with little success. Thus, in contrast to the ruthenium alkyl complexes $Cp(PPh_3)_2RuR$ ($R = Me, CH_2SiMe_3, CH_2Ph$, etc.), which can be synthesized from $Cp(PPh_3)_2RuCl$ and an organolithium or Grignard reagent at room temperature,[18] **1** did not react with RMgCl ($R = CH_2SiMe_3, CH_2CMe_3, Ph, CH_2Ph$) or RLi ($R = Me, Ph, CH_2CMe_3$), even in refluxing toluene over a few days. Prolonged heating of these reaction mixtures led only to the decomposition of **1**.

We speculated that exchanging the bromide in **1** with a better leaving group might lead to a complex with greater reactivity toward alkylating agents. Treatment of **1** with AgOTf ($Tf = SO_2CF_3$) in arene solvents quantitatively produced the red-orange triflate complex $Cp(PPh_3)_2OsOTf$ (**2**) (by NMR spectroscopy). This compound crystallized from benzene or toluene as the arene solvate (1 equiv), as confirmed by ^1H NMR spectroscopy, elemental analysis, and X-ray crystallography (vide infra). The arene was not removed by prolonged exposure of **2** to a vacuum. The solid-state infrared spectrum of **2** contains a peak at 1311 cm^{-1}, which falls between the $\nu(SO_3)$ values normally associated with ionic (1280−1270 cm^{-1}) and covalently bound (1395−1365 cm^{-1}) triflates.[19] The lability of the triflate group in **2** was indicated by the facile isomerization of **2** to a new complex **2a**, both in solution and in the solid state (by NMR spectroscopy; eq 1). While solutions of **2** in arene solvents are indefinitely stable, a dichloromethane solution of **2** underwent orthometalation within a few hours at room temperature. Also, orthometalation of **2** occurred at room temperature in the solid state under nitrogen ($t_{1/2} \approx 1$ month).



2a

On the basis of its ^1H, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra, the new complex **2a** was formulated as an orthometalated osmium hydride cation with a triflate counterion. The ^1H NMR spectrum contains a doublet of doublets at δ −11.18 ($^2J_{PH} = 26, 34$ Hz) corresponding to an osmium hydride coupled to two inequivalent phosphorus atoms. The *cis* arrangement of the hydride

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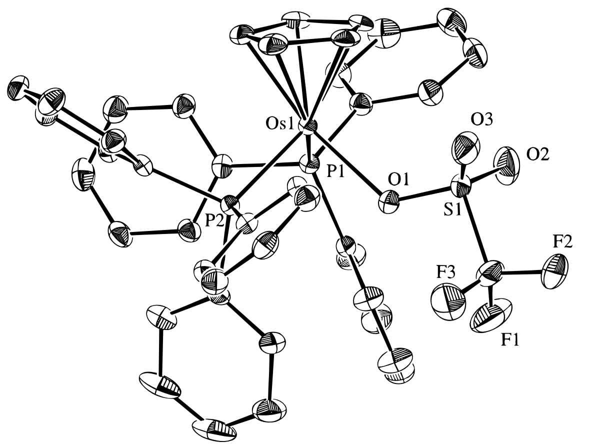

Figure 1. ORTEP drawing of $\mathrm{Cp(PPh_3)_2OsOSO_2CF_3}$ (**2**) with 40% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Os(1)−Cp 1.833; Os(1)−O(1) 2.221(2); Os(1)−P(1) 2.3206(7); Os(1)−P(2) 2.3424(7); P(1)−Os(1)−O(1) 92.64(5); P(2)−Os(1)−O(1) 84.79(5); P(1)−Os(1)−P(2) 101.80(2); Os(1)−O(1)−S(1) 126.7(1).

and phosphine ligands is suggested by the large $^2J_{\mathrm{PH}}$ coupling constants, since *trans* $^2J_{\mathrm{PH}}$ coupling constants in such four-legged piano-stool complexes are normally less than 10 Hz.[20] The two phosphines in **2a** are chemically inequivalent, as shown by the two doublet resonances in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum at δ 6.34 and −71.33 ($^2J_{\mathrm{PP}} = 21$ Hz). In addition, the sharp triflate resonance at δ −14.3 in the $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR spectrum of **2** was replaced in the spectrum of **2a** by a very broad resonance at δ −100. The $\nu(\mathrm{SO_3})$ band in the infrared spectrum of **2a** at 1275 $\mathrm{cm^{-1}}$ is consistent with an ionic triflate group.[19]

An ORTEP view of the molecular structure of **2** is shown in Figure 1. The three-legged piano-stool geometry about osmium and many of the corresponding distances and angles in **2** are similar to those found for the analogous halide complexes $\mathrm{Cp(PPh_3)_2OsX}$ (X = Cl, Br).[21] The Os−O(1) distance (2.221(2) Å) is shorter than the corresponding distances in two other structurally characterized complexes containing an Os−OTf bond, $\mathrm{Os(NAr)(CH_2{}^tBu)_2(OSiMe_3)(OTf)}$ (2.326(6) Å)[22] and $[\mathrm{Os(\equiv N)(terpy)(Cl)(OTf)}]^+$ (2.289(7) Å; terpy = 2,2′:6′,2″-terpyridine).[23] As expected from the analytical and spectroscopic data, each molecule of the compound in the unit cell is accompanied by one molecule of benzene. However, there is no chemically significant contact between the complex and benzene.

As expected, the triflate complex **2** is more reactive than its bromide precursor **1** toward alkylation. However, **2** readily exchanges its triflate group with the halide present in Grignard reagents. Thus, **2** reacted with $\mathrm{Me_3SiCH_2MgCl}$ in toluene at room temperature to give the corresponding alkyl and chloro complexes, $\mathrm{Cp(PPh_3)_2OsCH_2SiMe_3}$ (**3**) and $\mathrm{Cp(PPh_3)_2OsCl}$,[21a] in equimolar amounts (by NMR spectroscopy; eq 2). Upon treatment with organolithium reagents such as MeLi and $\mathrm{Me_3CCH_2Li}$, **2** reacted to give an inseparable mixture of the corresponding alkyl complex, a number of orthometalated species, and $\mathrm{Cp(PPh_3)_2OsCl}$ (<10%, presumably from trace amounts of halide present in the organolithium reagents).

$$\underset{\mathbf{2}}{2\mathrm{Cp(PPh_3)_2OsOTf}} \xrightarrow[-\mathrm{Mg(OTf)_2}]{\mathrm{Me_3SiCH_2MgCl}} \underset{\mathbf{3}}{\mathrm{Cp(PPh_3)_2OsCH_2SiMe_3}} + \mathrm{Cp(PPh_3)_2OsCl} \quad (2)$$

Clean alkylation was finally accomplished using a dialkylmagnesium reagent (eq 3). While the reaction of **2** with such reagents produced complex mixtures, **1** reacted cleanly to give the osmium alkyl derivative in high yield. Compound **1** reacts with bis(neopentyl)magnesium in benzene-d_6 at room temperature to give $\mathrm{Cp(PPh_3)_2OsCH_2CMe_3}$ (**3**) in >90% yield (by NMR spectroscopy). The trimethylsilylmethyl complex $\mathrm{Cp(PPh_3)_2OsCH_2SiMe_3}$ (**4**), prepared analogously, proved easier to isolate. Complex **4** is soluble in saturated hydrocarbons, from which it can be crystallized at −35 °C to give a bright-yellow, high-melting (225−226 °C) solid in 79% yield.

$$\underset{\mathbf{1}}{\mathrm{Cp(PPh_3)_2OsBr}} + {}^{1}/_{2}\mathrm{Mg(CH_2EMe_3)_2} \rightarrow \underset{\substack{\mathbf{3},\ \mathrm{E} = \mathrm{C}\\ \mathbf{4},\ \mathrm{E} = \mathrm{Si}}}{\mathrm{Cp(PPh_3)_2OsCH_2EMe_3}} \quad (3)$$

The complex $\mathrm{Cp(PMe_3)_2OsBr}$, synthesized from **1** by phosphine exchange at high temperature (190−200 °C),[24] was found to react analogously to **1**. Thus, while $\mathrm{Cp(PMe_3)_2OsBr}$ is inert toward Grignard and alkyllithium reagents, it reacts with $\mathrm{Mg(CH_2SiMe_3)_2}$ to form $\mathrm{Cp(PMe_3)_2OsCH_2SiMe_3}$ (**5**). This complex is quite soluble in hydrocarbons and can be crystallized from diethyl ether at −35 °C to give a low-melting (72−73 °C), pale-yellow solid in moderate (60%) yield. Compound **5** may also be sublimed at 50−65 °C under vacuum.

Given our success with preparing (pentamethylcyclopentadienyl)ruthenium silyl complexes, it was of interest to extend this work to the analogous osmium systems. Recently, Girolami *et al.* reported the synthesis of $[\mathrm{Cp^*OsBr_2}]_2$[20a] which, like the ruthenium dimer $[\mathrm{Cp^*RuCl_2}]_2$,[25] is a versatile starting material for the preparation of new complexes. Reaction of a dichloromethane solution of $[\mathrm{Cp^*OsBr_2}]_2$ with excess $\mathrm{PMe_3}$ at room temperature afforded the osmium(II) species $\mathrm{Cp^*(PMe_3)_2OsBr}$ (**6**) as orange plates in 54% isolated yield. The ^{1}H NMR spectrum of **6** consists of a triplet for the $\mathrm{C_5Me_5}$ ligand (δ 1.65, $^4J_{\mathrm{PH}} = 1.0$ Hz), as well as the filled-in doublet ("virtual triplet") for the $\mathrm{PMe_3}$ protons (at δ 1.37) expected for such compounds. A similar synthesis of **6** was recently reported by Girolami.[26]

Unlike $\mathrm{Cp(PPh_3)_2OsBr}$ and $\mathrm{Cp(PMe_3)_2OsBr}$, the bromide complex **6** reacts cleanly with $\mathrm{Me_3SiCH_2MgCl}$ in toluene at room temperature to form the alkyl complex $\mathrm{Cp^*(PMe_3)_2OsCH_2SiMe_3}$ (**7**) as a pale-yellow, high-melting (220−222 °C) solid in high yield (98%, eq 4).

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$$\underset{\textbf{6}}{Cp^*(PMe_3)_2OsBr} \xrightarrow[-MgClBr]{Me_3SiCH_2MgCl} \underset{\textbf{7}}{Cp^*(PMe_3)_2OsCH_2SiMe_3} \quad (4)$$

Compound **7** is very soluble in common organic solvents and is stable at room temperature for long periods in both the solid state and in solution under nitrogen.

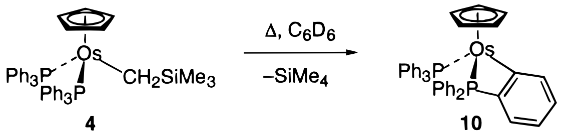
Interestingly, the $^{31}P\{^1H\}$ NMR spectra of the bromo and alkyl osmium complexes contain low-intensity satellites resulting from coupling to ^{187}Os in natural abundance ($I = {}^1/_2$, 1.64% abundance), with $^1J_{OsP}$ coupling constants ranging from 300 to 313 Hz. This observation is unusual because its low natural abundance makes ^{187}Os one of the most insensitive nuclei in NMR spectroscopy.[27] Similar coupling has been observed in osmium carbonyl cluster complexes[28] and more recently has been measured by indirect heteronuclear 2D NMR spectroscopy for a number of $Cp(PR_3)_2OsL$[14] and (η^6-arene)Os(II)[29] complexes.

C−H Activations by Osmium(II) Alkyl Complexes. Ruthenium(II) alkyl complexes of the type $Cp^*(PMe_3)_2RuR$ react with arene C−H or Si−H bonds at elevated temperatures.[6bc,30] For example, $Cp^*(PMe_3)_2RuCH_2SiMe_3$ reacts cleanly over 3 h with benzene at 100 °C to give $Cp^*(PMe_3)_2RuPh$ and $SiMe_4$.[30] The rate-determining step for this process was shown to be initial phosphine loss to generate the coordinatively unsaturated, 16-electron intermediate $Cp^*(PMe_3)RuR$, which oxidatively adds arene C−H bonds. In the presence of a large excess of arene, this 16-electron intermediate is selectively intercepted by near-stoichiometric quantities of hydrosilane. To analyze the behavior of the analogous osmium complexes under these conditions, we examined the reactions of the alkyl complexes **4**, **5**, and **7** with arenes.

Complex **7** was cleanly converted to $Cp^*(PMe_3)_2OsC_6D_5$ (**8**-d_5) and Me_3SiCH_2D in benzene-d_6 at 115 °C over 10 h, as monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (eq 5). An authentic sample of the phenyl derivative $Cp^*(PMe_3)_2OsC_6H_5$ (**8**) was prepared from $Cp^*(PMe_3)_2OsBr$ (**6**) and PhMgBr. The conversion of **7** to **8** required a higher temperature and a longer reaction time than for the analogous ruthenium complexes, as might be expected from periodic trends in reaction rates.[9]

$$\underset{\textbf{7}}{Cp^*(PMe_3)_2OsCH_2SiMe_3} \xrightarrow{\Delta,\ C_6D_6} \underset{\textbf{8}\text{-}d_5}{Cp^*(PMe_3)_2OsC_6D_5} + Me_3SiCH_2D \quad (5)$$

On the basis of the ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, $Cp(PMe_3)_2OsCH_2SiMe_3$ (**5**) also reacts with benzene-d_6 to form the deuterated phenyl derivative $Cp(PMe_3)_2OsC_6D_5$ (**9**-d_5). However, this reaction requires higher temperatures (160−170 °C) and a much longer reaction time (10 days). In contrast, thermolysis of $Cp(PPh_3)_2OsCH_2SiMe_3$ (**4**) in benzene-d_6 proceeded at much lower temperatures (60−67 °C) in 48 h to cleanly give $SiMe_4$ and a species whose ^1H and $^{31}P\{^1H\}$ NMR spectra are consistent with the orthometalated complex $Cp(PPh_3)Os(2-C_6H_4PPh_2)$ (**10**, eq 6). The behavior of **4** upon thermolysis is not surprising given the tendency of PPh_3 ligands to orthometallate.[31] A proposed mechanism for the observed C−H activation reactions, as illustrated for the intermolecular process, is given in Scheme 1.



(6)

We assume that phosphine loss from the alkyl complexes is rate determining, as shown in the analogous ruthenium systems[6b,30,32,33] and in the thermolysis of *cis*-$(PMe_3)_4Os(H)R$ ($R = CH_2CMe_3$, CH_2SiMe_3, Me).[34] Presumably, the large range of reaction temperatures reflects differences in the Os−P bond strengths for complexes **4**, **5**, and **7**; that is, the $Os-PMe_3$ bond in **5** is stronger than that in **7**, and the $Os-PMe_3$ bond is stronger than the $Os-PPh_3$ bond. Nolan *et al.* have recently determined the enthalpies of formation for a series of $Cp'(PR_3)_2RuCl$ ($Cp' = Cp$, Cp^*) complexes from the corresponding cyclooctadiene complexes.[35] Their results indicate that the $Ru-PMe_3$ bond is stronger than the $Ru-PPh_3$ bond by 7−8 kcal/mol and that replacing a Cp group with a Cp* group decreases the strength of the $Ru-PMe_3$ bond by 2−3 kcal/mol. Our results suggest that the same trend exists in the analogous osmium compounds.

Synthesis of Osmium Silyl Complexes. Ruthenium(II) silyl complexes of the type $Cp'(PR_3)_2RuSiX_3$ ($Cp' = Cp$, Cp^*; R = Ph, Me) were synthesized by heating the corresponding alkyl complexes $Cp'(PR_3)_2RuCH_2SiMe_3$ with the appropriate hydrosilane in toluene at 100 °C.[6b,c,33] Under certain conditions, ruthenium(IV) bis(silyl) hydride complexes are obtained along with the mono(silyl) products. However, the Ru(IV) products are readily converted to the corresponding bis(phosphine) Ru(II) complexes by reaction with excess phosphine at elevated temperatures. The proposed mechanism for the formation of the ruthenium silyl complexes is analogous to that by which the ruthenium and osmium alkyl complexes activate arenes (Scheme 2).

Initial attempts to synthesize osmium silyl complexes from $Cp^*(PMe_3)_2OsCH_2SiMe_3$ (**7**) and various silanes, using the same conditions employed in the ruthenium system, were unsuccessful. For example, reaction of **7** with $HSi(SEt)_3$ or $HSi(OEt)_3$ at 115 °C in benzene-d_6 gave an intractable mixture of products, the major one being $Cp^*(PMe_3)_2OsC_6D_5$ (**8**-d_5), which resulted from

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[27] (a) *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987. (b) Mason, J. *Chem. Rev.* **1987**, *87*, 1299.

[28] Gallop, M. A.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1831.

[29] Bell, A. G.; Kozminski, W.; Linden, A.; von Philipsborn, W. *Organometallics* **1996**, *15*, 3124.

[30] (a) Tilley, T. D.; Togni, A.; Paciello, R. A.; Bercaw, J. E.; Grubbs, R. H. Unpublished results. (b) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379. (c) Lehmkuhl, H.; Bellenbaum, M.; Grundke, J.; Mauermann, H.; Krüger, C. *Chem. Ber.* **1988**, *121*, 1719.

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[33] Lemke, F. R.; Chaitheerapapkul, C. *Polyhedron* **1996**, *15*, 2559.

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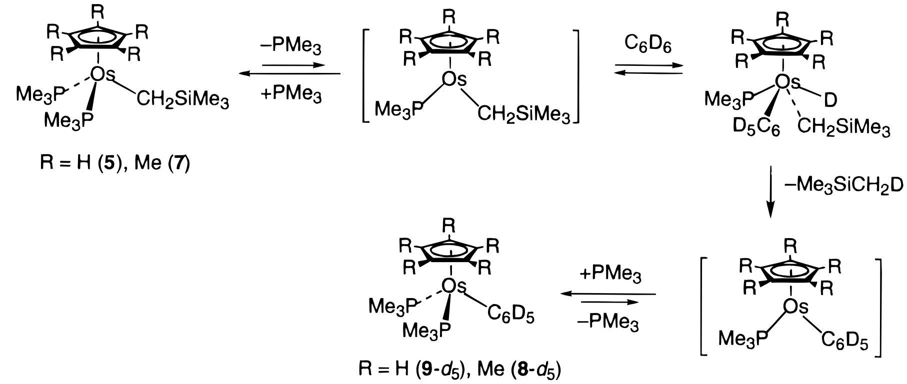
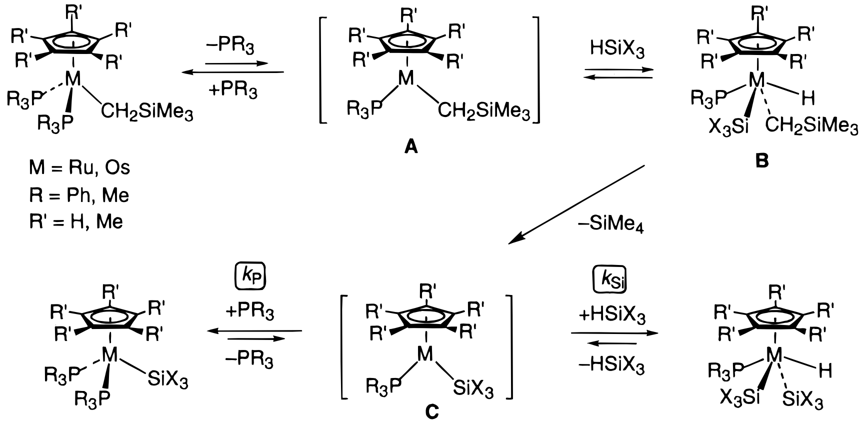
[35] (a) Cucullu, M. E.; Luo, L.; Nolan, S. P.; Fagan, P. J.; Jones, N. L.; Calabrese, J. C. *Organometallics* **1995**, *14*, 289. (b) Luo, L.; Nolan, S. P.; Fagan, P. J. *Organometallics* **1993**, *12*, 4305.

Scheme 1

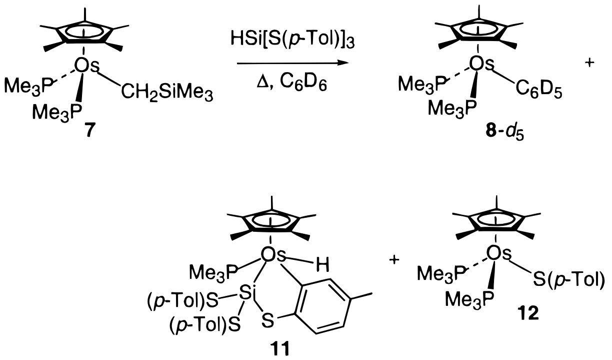


Scheme 2



activation of the solvent. In cyclohexane, these reactions gave multiple uncharacterized products. In the analogous ruthenium system, activation of the solvent was not observed unless a very bulky silane (e.g., HSi(SMes)$_3$ or HSi(SCy)$_3$) was used.[36]

The ruthenium alkyl Cp*(PR$_3$)$_2$RuCH$_2$SiMe$_3$ reacts with HSi[S(*p*-Tol)]$_3$ and HSiMe$_2$[S(*p*-Tol)] in toluene at 100 °C to cleanly give Cp*(PR$_3$)$_2$RuSi[S(*p*-Tol)]$_3$ and Cp*(PR$_3$)$_2$RuSiMe$_2$[S(*p*-Tol)], respectively.[6c] However, reaction of **7** with HSi[S(*p*-Tol)]$_3$ at 115 °C in benzene-d_6 gave three products: **8**-d_5, **11**, and **12**, in a 10:9:1 ratio (eq 7). In cyclohexane, only **11** and **12** were formed, in a 3:2 mixture. Complex **11** was formulated as the metallacycle species Cp*(PMe$_3$)(H)Os{C$_6$H$_3$(3-Me)(6-S)Si[S(*p*-Tol)]$_2$} from its ^{1}H NMR spectrum (vide infra). The other product, Cp*(PMe$_3$)$_2$OsS(*p*-Tol) (**12**), was identified by comparison to an authentic sample (prepared from Cp*(PMe$_3$)$_2$OsBr (**6**) and LiS(*p*-Tol)). Similarly, **7** reacted with HSiMe$_2$[S(*p*-Tol)] in cyclohexane at 115 °C to give the analogous metallacycle Cp*(PMe$_3$)(H)Os{C$_6$H$_3$(3-Me)(6-S)SiMe$_2$} (**13**) and **12** in an 8:1 ratio.



(7)

The ^{1}H NMR spectra of the cyclometalated hydrido silyl complexes **11** and **13** feature OsH resonances as doublets at δ −13.38 ($^2J_{PH}$ = 32.0 Hz) and −15.10 ($^2J_{PH}$ = 32.0 Hz), respectively. The large $^2J_{PH}$ coupling constants are consistent with a *cis* arrangement of the hydride and phosphine ligands. Similar observations have been reported for Cp*Os(PPh$_3$)H$_3$, where the $^2J_{PH}$ coupling is larger for the *cis* hydrides ($^2J_{PH}$ = 33.5 Hz) as compared to the *trans* hydride ($^2J_{PH}$ = 8 Hz).[20a] The ^{1}H and ^{13}C NMR data also showed that the two R groups on silicon in **11** and **13** are diastereotopic, as expected for the structures drawn in Scheme 3.

The formation of metallacycle complexes **11** and **13** can be rationalized by two different mechanisms (pathways a and b in Scheme 3), depending on the relative ordering of the Si−H and C−H bond activations. In the mechanism represented by path a, intermolecular Si−H bond activation by Cp*(PMe$_3$)OsCH$_2$SiMe$_3$ occurs before an intramolecular arene C−H bond activation in the intermediate Cp*(PMe$_3$)OsSiR$_2$S(*p*-Tol). In the alternative mechanism of path b, arene C−H bond activation occurs first and the cyclometalated product results from intramolecular oxidative addition of the Si−H bond. The intermolecular arene C−H activation in the second mechanism would presumably be promoted by the ortho-directing, activating thiolate group. However, pathway b seems somewhat unlikely given the fact that Cp*(PMe$_3$)$_2$OsPh is not an intermediate in the reaction of **7** with silanes in benzene (vide infra). Although the

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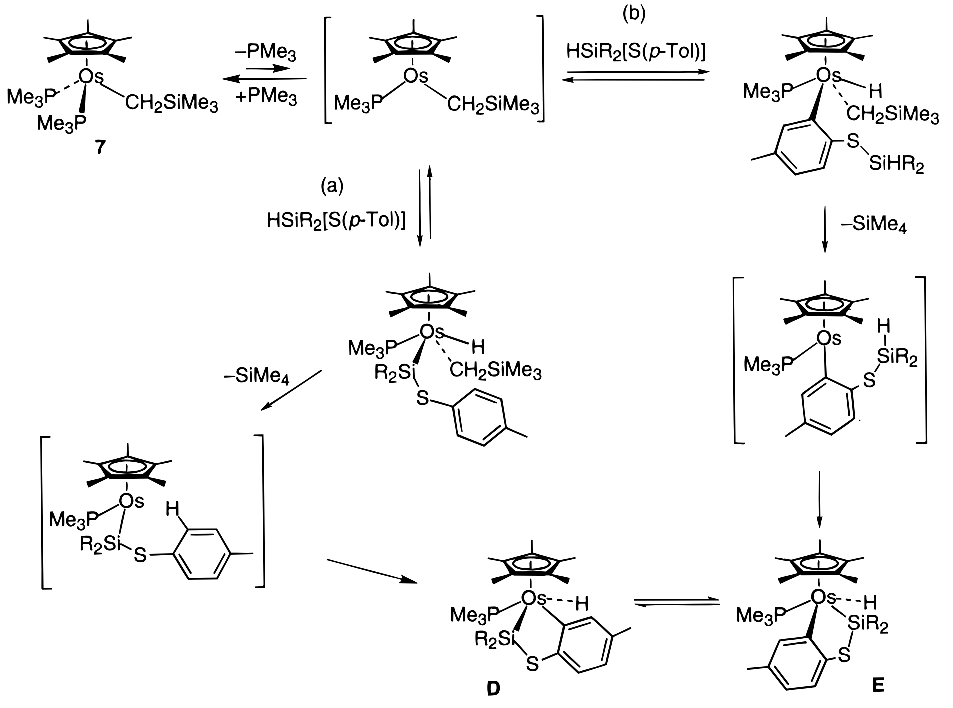
[36] Grumbine, S. K. Ph.D. Thesis, University of California, San Diego, CA, 1993.

Scheme 3



R = S(*p*-Tol) (**11**), Me (**13**)

two mechanisms should give rise to different isomers of the product (**D** and **E**), a Berry-type isomerization would probably allow conversion to the more thermodynamically favored isomer.[37] Thus, the mechanism cannot be identified simply from the regiochemistry of the isolated product, which was confirmed by an X-ray diffraction study (vide infra).

The cyclometalated complex **13** was separated from the reaction mixture by taking advantage of the different solubility properties for **13** and the decomposition product **12**. While **12** is readily soluble in most common organic solvents, **13** is soluble only in dichloromethane and aromatic hydrocarbons. Thus, washing the crude solid mixture with pentane followed by crystallization from a dichloromethane/ether mixture afforded pure **13** as colorless crystals in 77% yield.

To investigate the regiochemistry of the product, the molecular structure of **13** was determined by X-ray crystallography. The structure is shown in Figure 2, and selected bond distances and angles are summarized in Table 1. The structure shows the configuration of the molecule to be that of isomer **E** in Scheme 3. As expected from the large $^2J_{PH}$ coupling constant, the hydride and phosphine ligands are in a *cis* arrangement. The five-membered metallacycle ring has an "open-envelope" conformation; the plane of the Si−Os−C(14) flap is 40.8° out of the approximate plane of the other four atoms (C(14)−C(19)−S−Si; root-mean-square deviation from planarity = 0.086 Å). The hydride ligand was located and refined at a distance of 1.59(5) Å from Os, and the Os−Si bond length of 2.382(2) Å is quite normal.[38] Interestingly, the hydride ligand is quite close to the Si center (2.06(5) Å), and the Si−Os−H bond angle (59(2)°) is rather acute. Although these parameters might suggest η^2-silane character, the Si−H interaction is rather weak, as evidenced by the low $^2J_{SiOsH}$ coupling constant (15 Hz). In complexes exhibiting strong M−H−Si interactions, the Si−H distances are shorter than 2.00 Å and the $^2J_{SiMH}$ coupling constants are usually well above 20 Hz.[39] Thus, the proximity of the hydride ligand to the silicon atom in **13** might simply be due to steric crowding in the molecule.

The reaction of alkyl complex **7** with excess $HSiR_2Cl$ (R = Ph, Me) in toluene at 115 °C gave a mixture of the osmium(IV) bis(silyl)hydride complex $Cp^*(PMe_3)Os(H)(SiR_2Cl)_2$ (R = Ph (**14**) or Me (**16**)) and the osmium(II) mono(silyl) complex $Cp^*(PMe_3)_2OsSiR_2Cl$ (R = Ph (**15**)

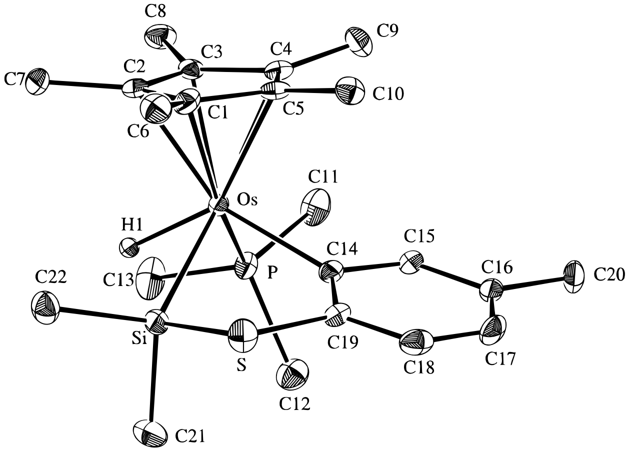


Figure 2. ORTEP drawing of $Cp^*(PMe_3)(H)\overline{Os\{C_6H_3(3-Me)(6-S)Si}Me_2\}$ (**13**) with 40% probability thermal ellipsoids.

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[37] Isomers **D** and **E** can be interconverted by two cycles of a combined Berry-turnstile mechanism, see: Smith, J. M.; Coville, N. J. *Organometallics* **1996**, *15*, 3388.

[38] A search of the Cambridge Structural Database revealed a mean Os−Si single bond length of 2.40(2) Å.

[39] (a) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (b) Colomer, E.; Corriu, R. J. P.; Marzin, C.; Vioux, A. *Inorg. Chem.* **1982**, *21*, 368. (c) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (d) Luo, X.-L.; Kubas, G. J.; Bryan, J. C.; Burns, C. J.; Unkefer, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 10312. (e) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 13

Bond Distances			
Os−Cp*[a]	1.921	Si−C(21)	1.872(6)
Os−Si	2.382(2)	Si−C(22)	1.893(6)
Os−P	2.298(2)	Si−S	2.187(2)
Os−H(1)	1.59(5)	S−C(19)	1.788(6)
Os−C(14)	2.157(6)		
Bond Angles			
P−Os−Si	103.17(5)	Os−Si−C(21)	120.9(2)
P−Os−C(14)	87.8(2)	Os−Si−C(22)	119.1(2)
P−Os−H(1)	75(2)	C(21)−Si−C(22)	102.8(3)
Si−Os−C(14)	77.7(1)	S−Si−C(21)	104.7(2)
Si−Os−H(1)	59(2)	S−Si−C(22)	103.6(2)
C(14)−Os−H(1)	127(2)	Os−C(14)−C(19)	125.4(4)
Si−S−C(19)	93.0(2)	Os−Si−S	103.62(7)
S−C(19)−C(14)	120.6(4)		

[a] Cp* = Cp* ring plane.

or Me (**17**); eq 8). The reaction with $HSiPh_2Cl$ produced

$$\underset{\mathbf{7}}{\mathrm{Cp^*(PMe_3)_2OsCH_2SiMe_3}} + (2x+y)\mathrm{HSiR_2Cl} \xrightarrow[-x\mathrm{PMe_3}]{\Delta,\ -\mathrm{SiMe_4}} \underset{\substack{\mathbf{14},\ \mathrm{R} = \mathrm{Ph} \\ \mathbf{16},\ \mathrm{R} = \mathrm{Me}}}{x\mathrm{Cp^*(PMe_3)Os(H)(SiR_2Cl)_2}} + \underset{\substack{\mathbf{15},\ \mathrm{R} = \mathrm{Ph} \\ \mathbf{17},\ \mathrm{R} = \mathrm{Me}}}{y\mathrm{Cp^*(PMe_3)_2OsSiR_2Cl}} \quad (8)$$

mostly the white, crystalline Os(IV) complex **14**, while the reaction with $HSiMe_2Cl$ yielded primarily the mono(silyl) complex **17**. However, the product distributions for these reactions are strongly influenced by the reaction conditions.

The reaction with $HSiPh_2Cl$ can be driven exclusively to the bis(silyl) hydride complex **14** by periodic exposure of the reaction mixture to a vacuum to remove PMe_3. On the other hand, attempts to obtain pure mono(silyl) complex **15** were unsuccessful. Unlike its ruthenium analog $Cp^*(PMe_3)Ru(H)(SiPh_2Cl)_2$, which can be driven cleanly to $Cp^*(PMe_3)_2RuSiPh_2Cl$ by heating to 100−110 °C for 36 h with excess PMe_3,[6b] **14** did not react with PMe_3 (≥100 equiv), even after heating to 150 °C for 3 days in a closed vessel. This presumably reflects the greater tendency of osmium toward higher oxidation states and/or the more kinetically inert character of osmium vs ruthenium.

In theory, reaction of **7** with 1 equiv of $HSiPh_2Cl$ should give only the osmium(II) silyl **15**. In practice, however, heating an equimolar mixture of $HSiPh_2Cl$ and **7** in cyclohexane resulted in a 2:1 mixture of **14** and **15**, as well as unreacted starting material and a decomposition product, $Cp^*(PMe_3)_2OsCl$. It was also hoped that the addition of free PMe_3 at the beginning of the reaction would favor formation of mono(silyl) **15** over **14**. However, carrying out the reaction under varying concentrations of silane and free phosphine, as well as varying the reaction time, had little effect on the product ratio. For example, heating a 10:5:1 mixture or a 5:10:1 mixture of $HSiPh_2Cl$, PMe_3, and **7** at 115 °C for 18 h or 2 days (in a closed vessel) yielded the same ratio of **14** to **15** (2:1). Increasing the temperature of the reaction to 155 °C (above the boiling point of the silane) changed the product ratio to favor the mono(silyl) **15** (5:1 ratio of **15** to **14**), but at higher temperatures (≥160 °C) many decomposition products were produced (in addition to **14** and **15**). Attempts to separate the solid mixture of **14** and **15** by fractional recrystallization also met with little success. These results imply that the rate of addition of a second silane to the intermediate $[Cp^*(PMe_3)OsSiPh_2Cl]$ (k_{Si} in Scheme 2) is faster than the rate of phosphine coordination (k_P) and that the bis(silyl) hydride complex **14** is quite inert.

The reaction conditions also governed the distribution of products from the reaction of **7** with excess $HSiMe_2Cl$. Highest yields for the mono(silyl) complex **17** were obtained by heating a closed flask containing **7** and a large excess (>100 equiv) of neat silane. The flask was heated by partially submerging it in an oil bath at 115 °C. However, under certain conditions, the bis(silyl) hydride **16** was formed along with **17**. For example, when **7** and $HSiMe_2Cl$ (≤20 equiv) were heated in toluene at 115 °C for 20 h, a 1:3 mixture of **16** and **17** resulted. When the same reaction was carried out in hexane or without solvent, only the bis(silyl) **16** was observed. Like **14**, the Os(IV) complex **16** cannot be converted to the corresponding mono(silyl) derivative **17** by heating (150 °C, 1 week) in the presence of excess PMe_3. However, the two products can be separated from the solid mixture by careful fractional recrystallization from a dichloromethane/ether mixture. Currently, we do not understand the observed concentration effects on the relative yields of **16** and **17**, but these results suggest that a mechanism other than that described in Scheme 2 might be in operation.

Both bis(silyl) hydride complexes **14** and **16** were isolated as the *trans* isomers, as indicated by ^1H and ^{29}Si NMR spectroscopy. The OsH resonances display low $^2J_{PH}$ coupling constants (8 Hz for **14**; 12 Hz for **16**), which indicate a *trans* arrangement for the phosphine ligands. The $^{29}Si\{^1H\}$ NMR spectrum of **16** contained only one resonance for the two silyl ligands (a doublet at δ 28.44), which further supports a *trans* geometry for the complex.

We considered the possibility that formation of the osmium silyl derivatives in arene solvents occurs via initial C−H activation of the solvent to form the aryl complex. However, since $Cp^*(PMe_3)_2OsPh$ (**8**) does not react with silanes ($HSiPh_2Cl$ or $HSiMe_2[S(p\text{-Tol})]$) even at 150 °C over 3 days, this does not seem likely.

Osmium(II) silyl complexes $Cp^*(PMe_3)_2OsSiR_3$ ($SiR_3 = SiMeCl_2$ (**18**), $SiCl_3$ (**19**)) can be obtained cleanly from reaction of the alkyl complex **7** with the corresponding hydrosilanes (neat, excess) at 115 °C (eq 9). In contrast

$$\underset{\mathbf{7}}{\mathrm{Cp^*(PMe_3)_2OsCH_2SiMe_3}} + \mathrm{HSiR_3} \xrightarrow{\Delta} \underset{\substack{\mathbf{18},\ \mathrm{SiR_3} = \mathrm{SiMeCl_2} \\ \mathbf{19},\ \mathrm{SiR_3} = \mathrm{SiCl_3}}}{\mathrm{Cp^*(PMe_3)_2OsSiR_3}} + \mathrm{SiMe_4} \quad (9)$$

to the reactions with $HSiPh_2Cl$ and $HSiMe_2Cl$, no bis(silyl) hydride species were observed.

We, therefore, observe that the electronic properties of the hydrosilanes play a strong role in influencing the rate and course of the osmium silylation reactions. Qualitatively, the presence of more electronegative substituents leads to slower reactions. Thus, while the reaction with $HSiMe_2Cl$ is complete in less than 24 h, the reaction involving $HSiMeCl_2$ requires 2 days and the one with $HSiCl_3$ takes at least 14 days. This trend is opposite to that found for reactions of $Cp(PMe_3)_2$-

$RuCH_2SiMe_3$, which follow the reactivity ordering $HSiCl_3 > HSiMeCl_2 > HSiMe_2Cl$.[33] It seems likely that the rates of these reactions are determined by the series of steps leading to complete oxidative addition of the silane (see Scheme 2), since the subsequent alkane reductive elimination step is expected to be fast.[9] Note also that an intermediate η^2-silane complex of the type $Cp'(PMe_3)M(\eta^2\text{-}HSiX_3)(CH_2SiMe_3)$ (Cp' = Cp or Cp*) may immediately precede the oxidative addition step. For ruthenium, the observed trend may reflect a large contribution by the oxidative addition step. In this case, formation of the M−Si bond may provide a significant thermodynamic driving force for the reaction, with silanes that result in a stronger M−Si bond reacting faster.[33] Silyl groups with greater π-acceptor ability ($SiCl_3 > SiMeCl_2 > SiMe_2Cl$)[40] should provide more stabilization for an electron-rich metal fragment. For the osmium system, the oxidative addition should be highly favored and the ligand substitution kinetics may play a greater role in defining the relative rates. If in this case the rate of silylation is influenced heavily by the ability of the reacting silane to compete with phosphine for the empty site at osmium, then the more electron-rich silanes will react more rapidly and the reactivity ordering observed for the osmium system would be expected. Determination of the true origin of these trends, however, must await further mechanistic studies.

The formation of Os(IV) bis(silyl) hydride complexes is also heavily influenced by the nature of the silane reactant, such that more electropositive substituents on the hydrosilane favor this reaction pathway. This observation may be analyzed in terms of the mechanism in Scheme 2 and the competition between silane and phosphine for trapping of an intermediate **C** which already has one silyl group bound to osmium. Lichtenberger *et al.*, using valence photoelectron spectroscopy, have shown that the $SiCl_3$ ligand has considerable π-acceptor ability, while the $SiMe_3$ ligand has negligible π-acceptor character and binds to the metal primarily as a σ-donor.[40] This is consistent with the observed trend in our system: as the groups on silicon become more electronegative, the silyl ligand becomes a better π-acceptor, thus favoring addition of σ-donating PMe_3 to intermediate **C**. On the other hand, silyl ligands with significant σ-donor properties appear to promote silane addition to form the less electron-rich Os(IV) bis(silyl) hydride complex.

The alkyl complex $Cp(PPh_3)_2OsCH_2SiMe_3$ (**4**) was observed to react with excess $HSiR_2Cl$ (R = Ph, Me; neat or in benzene) to give the corresponding osmium(IV) species $Cp(PPh_3)Os(H)(SiR_2Cl)_2$ (R = Ph (**20**) or Me (**21**)) as the major products in solution (by NMR spectroscopy; eq 10). Consistent with earlier observations, these

$$\underset{\mathbf{4}}{Cp(PPh_3)_2OsCH_2SiMe_3} + 2HSiR_2Cl \xrightarrow[-PPh_3]{\Delta} Cp(PPh_3)Os(H)(SiR_2Cl)_2 + SiMe_4 \quad (10)$$

$$R = Ph\ (\mathbf{20})$$
$$R = Me\ (\mathbf{21})$$

reactions proceeded at much lower temperatures (65−80 °C) than those required for silylation of **7**. The preferred formation of bis(silyl) hydride complexes in these reactions may be attributed to the relatively labile phosphine ligand. Unfortunately, attempts to separate **20** and **21** from free PPh_3 were unsuccessful. Like the Cp* analogs **14** and **16**, both **20** and **21** are formed solely as the *trans* isomers, as indicated by their ^1H NMR spectra. Interestingly, while the OsH resonance for **21** (doublet at δ −11.70, $^2J_{PH}$ = 8.0 Hz) is similar to those found for **14** and **16**, the OsH resonance for **20** appears as a singlet at δ −10.65. The gated ^{31}P NMR spectrum of **20** also confirmed the unusually low *trans* $^2J_{PH}$ coupling constant, in that the phosphorus signal was observed as a singlet.

The Cp analog of **7**, $Cp(PMe_3)_2OsCH_2SiMe_3$ (**5**), reacted with $HSiPh_2Cl$ (2 equiv) in toluene to give the osmium(II) silyl derivative $Cp(PMe_3)_2OsSiPh_2Cl$ (**22**) as the major product (by NMR spectroscopy; eq 11). The

$$\underset{\mathbf{5}}{Cp(PMe_3)_2OsCH_2SiMe_3} + HSiPh_2Cl \xrightarrow{\Delta} \underset{\mathbf{22}}{Cp(PMe_3)_2OsSiPh_2Cl} + SiMe_4 \quad (11)$$

reaction required a higher temperature (150−165 °C) and a longer time (4 days) than the analogous reaction in the Cp* system, as expected. Also, unlike the Cp* derivative, no bis(silyl) hydride complex was observed in the product mixture. This is presumably due to the higher Os−PMe_3 bond strength in the Cp (vs the Cp*) complexes, which favors the addition of phosphine over silane to intermediate **C** (Scheme 2). Unfortunately, complex **22** could not be obtained in analytically pure form either by recrystallization under various conditions or by sublimation at 100 °C under vacuum, which did not separate the complex from small quantities of impurities.

The reaction of **5** with excess $HSiMe_2Cl$ (ca. 20 equiv) in toluene at 150−165 °C did not give the expected silyl complex $Cp(PMe_3)_2OsSiMe_2Cl$. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the resulting residue in dichloromethane-d_2 revealed the presence of two major products in roughly equal amounts. These compounds were readily separated by the addition of toluene, which dissolved one product and left the other as a white solid, which gave a ^1H NMR spectrum that is consistent with a cationic dihydride $[Cp(PMe_3)_2OsH_2]^+X^-$. In particular, a triplet resonance at δ −13.95, which integrated as two hydrogens, was observed in the spectrum. The hydride ligands in this cation are probably *trans*, since the $^2J_{PH}$ coupling constant of 33.1 Hz is very similar to those observed for *trans*-$[Cp(PR_3)_2Os(H)_2]^+$ ($(PR_3)_2 = (PPh_3)_2$, $(Ph_2PMe)_2$, $(PPh_3)(P(OEt)_3)$, dppm, dppe, dppp).[17,24,41] At this point, the identity of the anion X^- remains unclear, as does the mechanism of formation for this complex. However, note that Lemke has shown that $Cp(PMe_3)_2RuH$ reacts with chlorosilanes $ClSiR_3$ to produce $[Cp(PMe_3)_2RuH_2]^+Cl^-$ and $Cp(PMe_3)_2RuSiR_3$, probably via nucleophilic attack of ruthenium onto the chlorosilane.[42] Concentration of the toluene extract gave a white solid, which analyzed by NMR and mass spectroscopy as $Cp(PMe_3)_2OsSiMeCl_2$ (**23**). The redistribution chemistry leading to the formation of **23** is presumably promoted by the high temperature. Redis-

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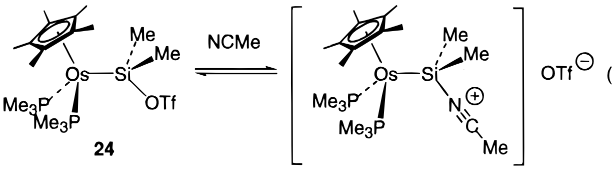
tributions of this sort may proceed via intermolecular exchanges involving silylene intermediates, as observed in the $Cp^*(PMe_3)_2Ru$ system.[6f]

The derivatization of a metal-bound silyl group represents an important synthetic pathway to new metal–silicon species. For example, chloride/triflate exchanges have been used to provide $Cp^*(PMe_3)_2RuSiR_2OTf$ derivatives, which are precursors to silylene complexes.[6] Since the silylation reactions described above proved to be rather limited in scope, we developed alternative routes to osmium(II) silyl complexes based on substitution at silicon.

The chloride in **17** is readily exchanged for the more labile triflate group, via reaction with Me_3SiOTf in dichloromethane at room temperature (eq 12). The light

$$\underset{\textbf{17}}{Cp^*(PMe_3)_2OsSiMe_2Cl} + Me_3SiOTf \xrightarrow[-Me_3SiCl]{CH_2Cl_2} \underset{\textbf{24}}{Cp^*(PMe_3)_2OsSiMe_2OTf} \quad (12)$$

yellow, crystalline complex $Cp^*(PMe_3)_2OsSiMe_2OTf$ (**24**) appeared to possess a covalent Si–O bond, as judged by its solubility in nonpolar aromatic solvents and from infrared data. Compound **24** displays an infrared band close to the typical range for covalent triflates[19] in both the solid state (Nujol mull, $\nu(SO_3) = 1352\ cm^{-1}$) and dichloromethane solution ($\nu(SO_3) = 1352\ cm^{-1}$). However, in acetonitrile, only ionic triflate ($\nu(SO_3) = 1269\ cm^{-1}$) was detected by infrared spectroscopy. Thus, **24** is extensively dissociated in acetonitrile solution and is presumed to exist as the base-stabilized silylene adduct $[Cp^*(PMe_3)_2OsSiMe_2(NCMe)]OTf$, which is probably best represented by the "silyl" resonance form in eq 13.



(13)

Similar observations have been made for analogous ruthenium complexes.[6b,c]

The $^{29}Si\{^1H\}$ NMR spectrum of **24** exhibits a triplet at δ 83.43 ($^2J_{SiP} = 23$ Hz; benzene-d_6 solution). This chemical shift lies downfield from that for the corresponding chloro(silyl) complex **14** (δ 46.76, $^2J_{SiP} = 20$ Hz). For comparison, the ruthenium complex $Cp^*(PMe_3)_2RuSiMe_2OTf$ has a ^{29}Si NMR shift of δ 133.3 ($^2J_{SiP} = 33$ Hz).[6c] Downfield ^{29}Si shifts for compounds containing sp^2-hybridized silicon[43] and arguments based on correlations between ^{13}C and ^{29}Si NMR data[43a] suggest that **24** might possess a slight amount of silylene (M=Si) character. However, since the ^{29}Si NMR resonance for **24** is significantly lower than those found for base-free silylene complexes (251–276 ppm),[6d,e,36] it is best to regard **24** as a tetravalent silicon species.

The solid-state structure of **24** was determined by single-crystal X-ray crystallography. An ORTEP drawing of the molecule is shown in Figure 3, and relevant bond distances and angles are listed in Table 2. Molecules of **24** adopt a three-legged piano-stool coordination geometry, and the silicon atom exists in a distorted tetrahedral environment. The staggered conformation about the Os–Si bond is similar to those observed for $Cp^*(PMe_3)_2RuSiR_2OTf$ (R = Ph,[6b] S(*p*-Tol)[6c]), in that the triflate group is in a position anti to the Cp* ligand.

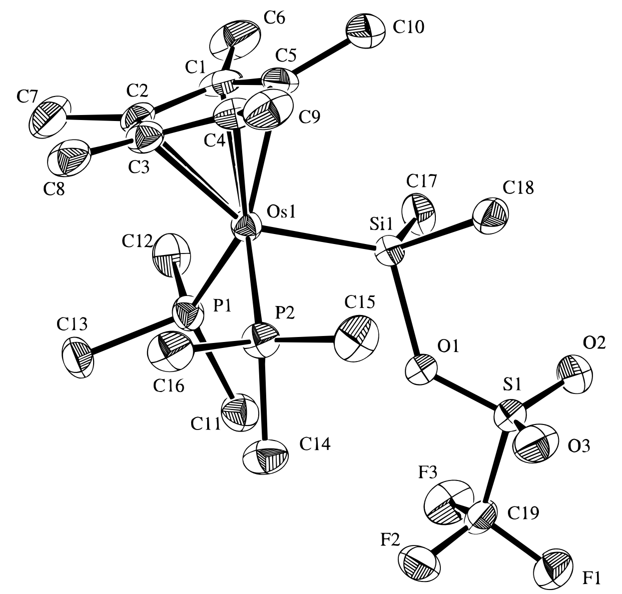


Figure 3. ORTEP drawing of $Cp^*(PMe_3)_2OsSiMe_2OTf$ (**24**) with 40% probability thermal ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 24

Bond Distances			
Os(1)–Cp*[a]	1.950	Si(1)–O(1)	1.866(5)
Os(1)–Si(1)	2.334(2)	Si(1)–C(17)	1.886(8)
Os(1)–P(1)	2.285(2)	Si(1)–C(18)	1.901(8)
Os(1)–P(2)	2.282(2)		
Bond Angles			
P(1)–Os(1)–Si(1)	91.01(7)	Os(1)–Si(1)–O(1)	115.3(2)
P(2)–Os(1)–Si(1)	90.68(7)	Os(1)–Si(1)–C(17)	119.1(3)
P(1)–Os(1)–P(2)	94.17(8)	Os(1)–Si(1)–C(18)	120.8(3)
O(1)–Si(1)–C(17)	96.6(3)	C(17)–Si(1)–C(18)	103.6(4)
O(1)–Si(1)–C(18)	96.9(3)		

[a] Cp* = Cp* ring plane.

Several features of the structure seem to support the presence of some multiple bonding between Os and Si. The Os–Si bond length of 2.334(2) Å is comparable to the corresponding value in the base-stabilized osmium silylene complex $(TTP)OsSiEt_2\cdot 2THF$ (2.325(8) Å; TTP = tetraphenylporphyrin)[44] and is shorter than a typical Os–Si single bond.[38] Silylene character in **24** is also supported by the relatively long Si–O bond length of 1.866(5) Å. Typical Si–O bonds in four-coordinate silicon compounds are in the range 1.63–1.66 Å,[45] whereas metal–silylene complexes stabilized by oxygen bases have Si–O distances between 1.68 and 1.85 Å.[1,5b,6b,c,44,46] In fact, the Si–O bond length in **24** is longer than reported Si–O distances in silylene complexes containing coordinated oxygen donors.[47] The Si–O distance in **24** is significantly longer than the Si–O distances in base-stabilized silylene complexes of the type $(CO)_nM{=}SiX_2(HMPA)$ ($n = 5$, M = Cr; $n = 4$,

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(47) The longest Si–O distance in a "base-stabilized" silylene complex previously reported (1.856(5) Å) is in $Cp^*(PMe_3)_2RuSi[S(p\text{-}Tol)]_2OTf$ (ref 6c).

M = Fe), which vary from 1.68 to 1.78 Å,[5b] and longer than those found in (TTP)Os=SiEt$_2$·2THF (1.82(2) Å)[44] and ruthenium triflato(silyl) complexes of the type Cp*(PMe$_3$)$_2$RuSiR$_2$OTf (R$_2$ = [S(*p*-Tol)]$_2$, (SMes)(Cl), Ph$_2$) (1.82−1.85 Å).[36]

The summation of angles at silicon, ignoring the Si−OTf bond, may also be used to evaluate the hybridization at silicon.[5b,6c] These values range widely (336−353°) in the base-stabilized silylene complexes characterized crystallographically,[1a,b,6a−c,44,48] with the mean value (345°) falling exactly between the ideal values for sp^2 (360°) and sp^3 hybridization (329°). Summation of the angles Os−Si−C(17), Os−Si−C(18), and C(17)−Si−C(18) in **24** gives a value (343.5°) which might be interpreted in terms of partial sp^2 character at silicon. The bond angles around the silicon also reflect considerable distortion from a tetrahedral geometry. The Os−Si−C angles of 119.1(3)° and 120.8(3)° are larger than the Os−Si−O angle of 115.3(2)°, and the C−Si−O angles of 96.6(3)° and 96.9(3)° are rather acute.

Although complex **24** appears to have some silylene character, as evidenced by its solid-state structure and its lability in acetonitrile, the structural and spectroscopic data are much more consistent with an sp^3-hybridized (and silyl-like) silicon center. The short Os−Si bond and the long Si−O(triflate) distance may be alternatively rationalized as resulting from significant $d_\pi-\sigma^*$ π-donation from the metal center to the silyl ligand.[1a,b,40] Such $d_\pi-\sigma^*$ donation should be heavily favored by the high electronegativity of the triflate group, which contributes to greater $d_\pi-\sigma^*$ overlap by concentrating much of the σ^* orbital in the vicinity of the metal atom.

Initial attempts to substitute the chloride groups in Cp*(PMe$_3$)$_2$OsSiMeCl$_2$ (**18**) were unsuccessful. For example, reaction of **18** with equimolar or excess amounts of Me$_3$SiOTf at room temperature gave only a complex mixture of products. Similarly, **18** did not react with nucleophilic reagents such as MesLi, LiSCy, or NaOMe, even after prolonged heating. Clean substitution was finally achieved using LiS(*p*-Tol). Thus, heating a mixture of **18** and LiS(*p*-Tol) (3 equiv) in toluene overnight at 40−50 °C gave Cp*(PMe$_3$)$_2$OsSiMe[S(*p*-Tol)]$_2$ (**25**) in 90% yield (by NMR spectroscopy). Complex **25** can be isolated as colorless crystals in 67% yield after recrystallization from a dichloromethane/diethyl ether mixture.

Like their bromo and alkyl precursors, most of the osmium silyl complexes show low-intensity osmium satellites in the ^{31}P{^{1}H} NMR spectra and $^1J(^{187}$Os,^{31}P) coupling constants ranging from 260 to 280 Hz. It is not entirely clear why the coupling constants for the silyl derivatives are lower than those for the bromo and alkyl complexes (300−313 Hz), since values of ^1J(M,P) coupling are dependent on a number of contributing factors, such as M−P bond strength, metal oxidation state, and structural effects.[27a,49]

Conclusions

The synthesis of new osmium alkyl and silyl complexes have been developed. The preparation of alkyl complexes of the type Cp(PR$_3$)$_2$OsCH$_2$EMe$_3$ (R = Ph, Me; E = C, Si) required the use of dialkylmagnesium reagents. We have also isolated and structurally characterized an osmium(II) triflate complex Cp(PPh$_3$)$_2$OsOTf (**2**), which possesses a chemically labile triflate group and may, therefore, prove useful in synthetic applications, as has the ruthenium analog Cp(PPh$_3$)$_2$RuOTf.[50] Convenient synthetic routes to complexes containing the electron-rich Cp*(PMe$_3$)$_2$Os fragment have been developed, and the alkyl derivatives, like the corresponding ruthenium alkyls, thermally activate arene C−H and Si−H bonds.

Reactions of osmium alkyl complexes toward hydrosilanes were found to differ significantly from those of analogous ruthenium compounds. For example, reactions of Cp*(PMe$_3$)$_2$OsCH$_2$SiMe$_3$ (**7**) with (arylthio)silanes did not give the expected Os(II) silyl complexes; instead, activation of both the Si−H and arene C−H bonds of the silanes took place, giving Os(IV) metallacycles. This reactivity may be attributed to the stronger basicity of Cp*Os(II), compared to Cp*Ru(II), complexes.[26] The rates and product distributions for reactions of osmium alkyl complexes with hydrosilanes were found to be very sensitive to reaction conditions, the electronic nature of the hydrosilanes, and the lability of the Os−P bonds. In general, it appears that Os(II) silyl complexes are favored in reactions involving complexes with strong Os−P bonds and silanes with electronegative substituents. Unlike the Cp*(PMe$_3$)Ru(H)(SiX$_3$)$_2$ complexes, the Os(IV) bis(silyl) hydrides are kinetically stable and are not readily converted to mono(silyl) bis(phosphine) complexes of the type Cp*(PMe$_3$)$_2$OsSiX$_3$. The chloro(silyl) complex Cp*(PMe$_3$)$_2$OsSiMe$_2$Cl (**17**) is easily converted to the triflato(silyl) complex Cp*(PMe$_3$)$_2$OsSiMe$_2$(OTf) (**24**), which is currently being examined as a precursor to the base-free silylene complex Cp*(PMe$_3$)$_2$Os=SiMe$_2$$^+$.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques and/or in a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Diethyl ether (Et$_2$O), pentane, hexane, and toluene were distilled from sodium benzophenone ketyl and stored under N$_2$ prior to use. Dichloromethane was distilled from CaH$_2$. Benzene-d_6 was purified by vacuum distillation from Na/K alloy. Dichloromethane-d_2 was distilled from CaH$_2$ and degassed with two freeze−pump−thaw cycles prior to use. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. The silanes HSiPh$_2$Cl, HSiMe$_2$Cl, HSiMeCl$_2$, and HSiCl$_3$ were distilled under N$_2$ and degassed before use. The compounds

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$(Me_3SiCH_2)_2Mg$,[51] PMe_3,[52] $Cp(PMe_3)_2OsBr$,[24] $Cp^*{}_2Os_2Br_4$,[20a] $HSi[S(p\text{-Tol})]_3$,[53] and $HSiMe_2[S(p\text{-Tol})]$[53] were prepared by literature methods.

NMR spectra were recorded at 400.13 MHz (^1H), 100.62 MHz (^{13}C), 161.98 MHz (^{31}P), and 59.6 MHz (^{29}Si). The spectra were obtained at room temperature in benzene-d_6, unless otherwise noted. The ^1H resonances for the PMe_3 ligands in complexes of the type $Cp'(PMe_3)_2OsX$ ($Cp' = Cp, Cp^*$) appear as a $A_9XX'A'_9$ pattern, the appearance of which is a "filled-in doublet" (fd) with the separation of the outer lines $N = {}^2J_{PH} + {}^4J_{PH}$.[54] In the $^{13}C\{^1H\}$ NMR spectra, the PMe_3 resonances appear as a virtual triplet (vt) with the separation of the outer lines $N = {}^1J_{PC} + {}^3J_{PC}$.[54] Melting points were measured on a Mel-Temp II apparatus in sealed capillaries under nitrogen and are uncorrected. Elemental analyses were performed by the UC Berkeley College of Chemistry Microanalytical Laboratory. IR spectra were obtained on a Mattson Galaxy Series FTIR 3000 spectrometer as Nujol mulls on NaCl plates, unless otherwise specified, and all absorptions are reported in cm^{-1}. Mass spectroscopic (MS) analysis were obtained at the UC Berkeley mass spectrometry facility on AEI MS-12 mass spectrometers. X-ray diffraction studies were performed in the UCB X-ray Diffraction facility (CHEXRAY).

$Cp(PPh_3)_2OsBr$ (1).[15,21b] An ampule of OsO_4 (1.0 g, 3.93 mmol) was broken in a flask containing 48% HBr (37 mL), and the red solution was heated at reflux for 2 h in air. Water and excess HBr were removed from the mixture by distillation at 50 °C under vacuum, leaving a dark red residue. The residue was dissolved in absolute ethanol (20 mL) and added to a stirred, boiling solution of triphenylphosphine (6.30 g, 24.0 mmol) in ethanol (180 mL), followed immediately by a solution of freshly distilled cyclopentadiene (10 mL) in ethanol (20 mL). Water (25 mL)[55] was then added to the mixture via syringe, and the crimson suspension was heated at reflux for 2 h, resulting in a color change to orange. After the reaction mixture was cooled to room temperature, the resulting orange-yellow powder was filtered, washed with ethanol (2 × 10 mL) and hexane (2 × 10 mL), and dried under vacuum to give pure **1**, mp 180−182 °C dec (lit.[21b] 180−181 °C dec). The orange filtrate was concentrated to 40 mL and cooled to −35 °C to obtain the remaining product. Overall yield: 97% (3.25 g) (lit.[21b] 89%). ^1H NMR: δ 7.55 (br m, 12H, Ph), 6.93 (br m, 18H, Ph), 4.35 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR: δ −5.67 ($^1J_{OsP}$ = 312 Hz).

$Cp(PPh_3)_2OsOSO_2CF_3$ (2). To a mixture of **1** (150 mg, 0.17 mmol) and $AgOSO_2CF_3$ (47 mg, 0.18 mmol) was added 5 mL of toluene at room temperature. The resulting mixture was stirred for 30 min and then filtered to remove the AgBr salt. Removal of solvent from the bright red-orange solution gave **2** as a red solid (0.12 g, 72%, mp 118−120 °C) in >95% purity by ^1H NMR. ^1H NMR: δ 7.28 (br m, 12 H, Ph), 6.93 (br m, 18 H, Ph), 4.63 (s, 5 H, Cp). $^{31}P\{^1H\}$ NMR: δ 5.51. $^{19}F\{^1H\}$ NMR (376.48 MHz): δ −14.3. $^{13}C\{^1H\}$ NMR: δ 140.4, 140.0, 134.4, 128.6, 127.3 (Ph). The analytically pure toluene adduct **2**·$C_6H_5CH_3$ was obtained by recrystallization from toluene. Anal. Calcd for $C_{49}H_{43}F_3O_3OsP_2S$: C, 57.64; H, 4.24. Found: C, 57.46; H, 4.14. IR (KBr): 1481 (m), 1434 (m), 1313 (s, $\nu(SO_3)$), 1263 (w), 1228 (m), 1201 (s), 1091 (m), 1001 (s).

Orthometalation of $Cp(PPh_3)_2OsOTf$ (2) to $Cp(PPh_3)(H)Os(2\text{-}C_6H_4PPh_2)$ (2a). Allowing a solution of **2** in CH_2Cl_2 to stand at room temperature for 8 h resulted in a color change from red-orange to yellow. The ^1H and $^{31}P\{^1H\}$ NMR spectra showed that complete conversion of **2** to **2a** had taken place. Crystals of **2** also decomposed to **2a** upon standing at room temperature under N_2 (drybox) over 1 month. Spectral data for **2a**: ^1H NMR (CD_2Cl_2): δ 7.55−6.59 (br m, ArH), 5.29 (s, 5 H, Cp), −11.18 (dd, $^2J_{PH}$ = 34 Hz, 26 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 6.34 (d, $^2J_{PP}$ = 21 Hz), −71.33 (d, $^2J_{PP}$ = 21 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 149.15, 133.85, 133.75, 131.68, 129.62, 129.55, 129.05, 128.94 (Ph), 87.86 (Cp). IR (CH_2Cl_2): 1986 (m, ν(Os−H)), 1484 (m), 1438 (m), 1275 (s, $\nu(SO_3)$), 1220 (m), 1155 (s), 1099 (m), 1030 (s), 881 (w).

X-ray Crystal Structure Determination of 2·C_6H_6. Red blocklike crystals of **2**·C_6H_6 were obtained from slow evaporation of a benzene solution at room temperature. A single crystal was mounted on a glass capillary using Paratone-N hydrocarbon oil, centered in the beam, and cooled to −104 °C by a nitrogen-flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. All measurements were made on a Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo Kα radiation (λ = 0.710 69 Å). Collection of 60 10-s frames, followed by spot integration and least-squares refinement, gave a preliminary orientation matrix and cell constants. A hemisphere of data was collected using ω scans of width 0.3°. The raw data were integrated (XY spot spread = 1.60°; Z spot spread = 0.60°) using SAINT (*SAX Area-Detector Integration Program*, v. 4.024; Siemens Industrial Automation, Inc.: Madison, WI, 1995). Data analysis was performed using Siemens XPREP (part of the *SHELXTK Crystal Structure Determination Package*; Siemens Industrial Automation, Inc.: Madison, WI, 1995). The 8822 reflections measured were averaged, yielding 5876 unique reflections (R_{int} = 2.0%). The data were corrected for Lorentz and polarization effects. No correction for crystal decay was necessary, but a semiempirical absorption correction (T_{max} = 0.264, T_{min} = 0.200) was applied. The space group $P\bar{1}$ was confirmed by the refinement.

The structure was solved using the teXsan software package (Crystal Structure Analysis Package; Molecular Structure Corporation, 1992) by direct methods (SIR92) and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned idealized positions and were included in the structure factor calculations but were not refined. The final residuals for the 523 variables refined against the 5696 accepted data for which $I > 3\sigma(I)$ were R = 1.8%, R_w = 2.9%, and GOF = 1.41. Using all 5877 unique data (including systematic absences), R = 1.9% and R_w = 2.9%. The maximum and minimum peaks in the final difference Fourier map had electron densities of 0.61 and −0.63 $e^-/Å^3$, respectively. The weighting scheme was based on counting statistics and included a factor (p = 0.030) to downweight the intense reflections. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion. The crystal and data collection parameters for this data set are given in Table 3.

Reaction of $Cp(PPh_3)_2OsOTf$ (2) with Me_3SiCH_2MgCl. To a cooled (−35 °C), stirred solution of **2** (51 mg, 0.055 mmol) in toluene (5 mL) was added via syringe 0.04 mL (0.07 mmol) of a 1.7 M solution of Me_3SiCH_2MgCl in Et_2O. An immediate color change to bright yellow was observed. The reaction mixture was allowed to warm to room temperature and was then stirred for 16 h. Removal of solvent from the yellow mixture gave a yellow solid, which was shown by ^1H and $^{31}P\{^1H\}$ NMR to be a 1:1 mixture of $Cp(PPh_3)_2OsCH_2SiMe_3$ (**4**; compared with spectral data of a pure sample synthesized as described below) and $Cp(PPh_3)_2OsCl$.[22a] The two compounds can be separated by extraction with hexane (the yellow alkyl complex **4** is hexane-soluble while the orange chloro complex is not).

Reaction of $Cp(PPh_3)_2OsBr$ (1) with $Mg(CH_2CMe_3)_2$. Mixing an orange solution of **1** (30 mg, 0.035 mmol) in benzene-

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[55] The reaction will not work with complete exclusion of water, and a much longer reaction time is required (with lower yield of product) when less than 25 mL of water is added to the reaction mixture.

Table 3. Crystal and Data Collection Parameters for Complexes $2\cdot C_6H_6$, 13, and 24[a]

	$2\cdot C_6H_6$	13	24
empirical formula	$C_{48}H_{41}F_3O_3OsP_2S$	$C_{22}H_{37}OsPSSi$	$C_{19}H_{39}F_3O_3OsP_2SSi$
fw	1007.05	582.85	684.80
cryst color, habit	red, block	colorless, plate	yellow, block
cryst size, mm	0.30 × 0.31 × 0.27	0.13 × 0.10 × 0.08	0.20 × 0.10 × 0.20
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	12.2274(1)	8.9271(3)	9.4152(1)
b, Å	12.7827(2)	9.5732(3)	16.6655(3)
c, Å	13.6433(2)	16.0925(5)	17.3217(3)
α, deg	93.227(1)	74.883(1)	90.0
β, deg	94.503(1)	86.281(1)	104.329(1)
γ, deg	100.970(1)	63.136(1)	90.0
V, Å^3	2081.47(5)	1182.16(6)	2633.38(7)
Z	2	2	4
D_{calcd}, g cm^{-3}	1.607	1.637	1.727
μ(Mo Kα), cm^{-1}	32.44	56.01	51.24
temp, °C	−104 ± 1	−124 ± 2	−111 ± 1
scan type	ω	ω	ω
2θ range, deg	3−47	3−47	3−52
no. of rflns measd			
total	8822	4997	12608
unique	5876 ($R_{int} = 2.0\%$)	3326 ($R_{int} = 2.7\%$)	5830 ($R_{int} = 5.4\%$)
T_{min}/T_{max}	0.200/0.264	0.477/0.589	0.234/0.365
no. of observations ($I > 3.00\sigma(I)$)	5696	3034	4297
no. of params	523	235	271
residuals R; R_w, %	1.8; 2.9	2.4; 3.2	4.0; 5.0
R_{all} R; R_w, %	1.9; 2.9	2.9; 3.5	5.5; 5.5
goodness of fit	1.41	1.24	1.50
max peak in final diff map, e$^-$/Å^3	0.61	0.52	0.63
min peak in final diff map, e$^-$/Å^3	−0.63	−0.67	−1.83
p factor	0.03	0.03	0.03

[a] General information: diffractometer, Siemens SMART; radiation, Mo Kα radiation ($\lambda = 0.710\ 69$ Å); monochromator, graphite.

d_6 with $(Me_3CCH_2)_2Mg$ (6 mg, 0.04 mmol) at room temperature resulted in an instant color change to yellow and formation of a white precipitate. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed the major product (>90%) in solution to be $Cp(PPh_3)_2OsCH_2CMe_3$ (**3**). ^1H NMR: δ 7.18 (br m, 12 H, Ph), 6.99 (br m, 18 H, Ph), 4.67 (s, 5 H, Cp), 2.21 (t, $^3J_{PH} = 8.9$ Hz, 2 H, $OsCH_2$), 1.15 (s, 9 H, CMe_3). $^{31}P\{^1H\}$ NMR: δ 1.25.

$Cp(PPh_3)_2OsCH_2SiMe_3$ (4). To a mixture of **1** (150 mg, 0.17 mmol) and $(Me_3SiCH_2)_2Mg$ (35 mg, 0.18 mmol) was added 5 mL of cold (−35 °C) toluene. The resulting suspension was allowed to warm to room temperature and was then stirred for 15 h, during which time a color change from orange to bright yellow was observed. After removal of the solvent under vacuum, the yellow residue was extracted with hexane (2 × 10 mL). The combined extracts were concentrated to ca. 3 mL and cooled to −35 °C for 12 h, giving pure **4** (mp 225−226 °C) as bright yellow crystals (120 mg, 79%). ^1H NMR: δ 7.24 (br m, 12 H, Ph), 6.96 (br m, 18 H, Ph), 4.50 (s, 5 H, Cp), 0.61 (t, $^3J_{PH} = 8.0$ Hz, 2 H, $OsCH_2$), 0.35 (s, 9 H, $SiMe_3$). $^{31}P\{^1H\}$ NMR: δ 1.93 ($^1J_{OsP} = 313$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.4, 140.0, 134.4, 128.6, 127.3 (Ph), 77.37 (s, Cp), 4.31 (s, $SiMe_3$), −0.42 (t, $^2J_{PC} = 8.0$ Hz, $OsCH_2$). Anal. Calcd for $C_{45}H_{46}OsP_2Si$: C, 62.33; H, 5.35. Found: C, 62.53; H, 5.38. IR: 2727 (w), 2667 (w), 1583 (w), 1236 (m), 1182 (w), 1155 (w), 1086 (m), 995 (w), 854 (m), 821 (m), 744 (m), 694 s (m).

$Cp(PMe_3)_2OsCH_2SiMe_3$ (5). A mixture of $Cp(PMe_3)_2OsBr$ (100 mg, 0.20 mmol), $(Me_3SiCH_2)_2Mg$ (61 mg, 0.31 mmol), and toluene (3 mL) was stirred for 2 h at room temperature, until the orange mixture turned pale yellow. The solvent was then removed *in vacuo*, and the residue was extracted with hexane (2 × 5 mL). Removal of the hexane left a pale yellow solid, which was crystallized from Et_2O at −35 °C to give 60 mg (60%) of **5** as pale yellow prisms (mp 72−73 °C). The complex can also be sublimed at 50−65 °C under vacuum. ^1H NMR: δ 4.41 (s, 5 H, Cp), 1.22 (fd, $N = 8.4$ Hz, 18 H, PMe_3), 0.29 (s, 9 H, $SiMe_3$), −0.14 (t, $^3J_{PH} = 7.9$ Hz, 2 H, $OsCH_2$). $^{31}P\{^1H\}$ NMR: δ −46.39 ($^1J_{OsP} = 305$ Hz). $^{13}C\{^1H\}$ NMR: δ 73.34 (t, $^2J_{PC} = 2.5$ Hz, Cp), 22.6 (vt, $N = 47.3$ Hz, PMe_3), 4.30 (s, $SiMe_3$), −44.21 (t, $^2J_{PC} = 7.4$ Hz, $OsCH_2$). Anal. Calcd for $C_{15}H_{34}OsP_2Si$: C, 36.42; H, 6.93. Found: C, 36.48; H, 7.07. IR: 2723 (w), 2665 (w), 1277 (m), 1236 (m), 1097 (w), 953 (s), 933 (s), 854 (s), 821 (m), 794 (w), 671 (w).

$Cp^*(PMe_3)_2OsBr$ (6). To a stirred, brown-black solution of $Cp^*_2Os_2Br_4$ (1.20 g, 1.24 mmol) in CH_2Cl_2 (20 mL) was added via syringe 0.84 mL (8.1 mmol) of neat PMe_3. A color change to yellow-brown took place immediately after the addition, and the mixture was stirred in a closed flask at room temperature for 11 h. The volatile materials were then removed under vacuum, and the residue was extracted 3 times with hot (50 °C) hexane to give 100 mL of combined extracts. The resulting orange solution was concentrated to ca. 15 mL and cooled to −80 °C. Dark orange plates of **6** were collected and dried (mp 196−197 °C dec). Yield: 0.82 g (59%). ^1H NMR: δ 1.65 (t, $^4J_{PH} = 1.0$ Hz, 15 H, C_5Me_5), 1.37 (fd, $N = 8.5$ Hz, 18 H, PMe_3). $^{31}P\{^1H\}$ NMR: δ −47.5 ($^1J_{OsP} = 301$ Hz). $^{13}C\{^1H\}$ NMR: δ 83.84 (t, $^2J_{PC} = 2.4$ Hz, C_5Me_5), 21.5 (vt, $N = 45.3$ Hz, PMe_3), 11.31 (s, C_5Me_5). Anal. Calcd for $C_{16}H_{33}BrOsP_2$: C, 34.47; H, 5.97. Found: C, 34.45; H, 6.04. IR: 2723 (m), 2669 (m), 1923 (m), 1911 (m), 1296 (m), 1277 (s), 1261 (s), 1155 (w), 1093 (m), 1024 (s), 937 (s), 848 (w), 798 (s), 665 (s).

$Cp^*(PMe_3)_2OsCH_2SiMe_3$ (7). To a cold (−35 °C), stirred solution of **4** (0.654 g, 1.17 mmol) in toluene (20 mL) was added 0.75 mL (1.3 mmol) of a 1.7 M solution of Me_3SiCH_2MgCl in Et_2O via syringe. The reaction mixture was allowed to warm to room temperature and was then stirred for 13 h. After removal of the volatile components *in vacuo*, the residue was extracted with hexane (2 × 20 mL). The combined extracts were concentrated to dryness, leaving a pale yellow solid of **7** (0.65 g, 98%) in >95% purity by ^1H NMR. Analytically pure **7** (mp 220−222 °C) was obtained by recrystallization from pentane. Anal. Calcd for $C_{20}H_{44}OsP_2Si$: C, 42.53; H, 7.85. Found: C, 42.62; H, 7.76. ^1H NMR: δ 1.72 (s, 15 H, C_5Me_5), 1.26 (fd, $N = 7.6$ Hz, 18 H, PMe_3), 0.37 (s, 9 H, $SiMe_3$), −0.27 (t, 2H, $^3J_{PH} = 6.2$ Hz, $OsCH_2$). $^{31}P\{^1H\}$ NMR: δ −50.5 ($^1J_{OsP} = 303$ Hz). $^{13}C\{^1H\}$ NMR: δ 85.36 (t, $^2J_{PC} = 2.7$ Hz, C_5Me_5), 21.8 (vt, $N = 43.7$ Hz, PMe_3), 11.74 (s, C_5Me_5), 5.33 (s, $SiMe_3$), −0.88 (t, $^2J_{PC} = 6.4$ Hz, $OsCH_2$). IR: 1884 (w), 1292 (w), 1275 (m), 1261 (m), 1234 (w), 1090 (w), 1026 (m), 951 (s), 933 (s), 848 (s), 820 (m), 800 (m), 696 (w), 671 (w).

Thermolysis of Cp*(PMe$_3$)$_2$OsCH$_2$SiMe$_3$ (7) in C$_6$D$_6$. A solution of **7** (10 mg, 0.018 mmol) in benzene-*d*$_6$ (0.5 mL) was sealed in a J. Young Valve NMR tube and heated to 115 °C. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 10 h, all of **7** was consumed to give Cp*(PMe$_3$)$_2$OsC$_6$D$_5$ (**8**-*d*$_5$; identified by comparisons to the spectra of **8**) and Me$_3$SiCH$_2$D in quantitative yield (by NMR).

Cp*(PMe$_3$)$_2$OsPh (8). To a solution of **5** (50 mg, 0.09 mmol) in toluene (2 mL) was added 0.05 mL (0.1 mmol) of a 2.0 M solution of PhMgBr in THF via syringe. The mixture was heated to 70 °C and then stirred for 6 h. After removal of the solvent, the residue was extracted with 10 mL of hexane and the extract was concentrated to dryness. The dark yellow solid was recrystallized from Et$_2$O at −35 °C to give **8** as pale yellow crystals (27 mg, 54%), mp 318−320 °C. ^{1}H NMR: δ 7.57 (d, J = 6.5 Hz, 2 H, *o*-ArH), 7.08 (m, 2 H, *m*-ArH), 7.01 (m, 1 H, *p*-ArH), 1.61 (t, $^4J_{\rm PH}$ = 1.0 Hz, 15 H, C$_5$*Me*$_5$), 1.32 (fd, N = 8.0 Hz, 18 H, PMe$_3$). ^{31}P{^{1}H} NMR: δ −47.7 ($^1J_{\rm OsP}$ = 313 Hz). ^{13}C{^{1}H} NMR: δ 145.65 (t, $^2J_{\rm PC}$ = 5.0 Hz, *ipso*-ArC), 128.53, 126.40, 119.24 (Ph), 87.62 (t, $^2J_{\rm PC}$ = 2.8 Hz, *C*$_5$Me$_5$), 22.1 (vt, N = 35.3 Hz, PMe$_3$), 11.18 (s, C$_5$*Me*$_5$). Anal. Calcd for C$_{22}$H$_{38}$OsP$_2$: C, 47.64; H, 6.90. Found: C, 48.11; H, 6.96. IR: 1562 (m), 1292 (w), 1274 (m), 1057 (w), 1016 (m), 948 sh, 935 (s), 848 (m), 702 (m), 663 (m), 642 (w).

Thermolysis of Cp(PMe$_3$)$_2$OsCH$_2$SiMe$_3$ (5) in C$_6$D$_6$. A sealed NMR tube containing a solution of **5** (10 mg, 0.020 mmol) in benzene-*d*$_6$ was heated to 170 °C. A slow conversion of **5** to Me$_3$SiCH$_2$D and Cp(PMe$_3$)$_2$OsC$_6$D$_5$ (**9**-*d*$_5$) was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The reaction was complete (by NMR) after 10 days of heating at 160−170 °C. **9**-*d*$_5$: ^{1}H NMR δ 4.40 (s, 5 H, Cp), 1.26 (fd, N = 8.4 Hz, 18 H, PMe$_3$). ^{31}P{^{1}H} NMR: δ −43.7.

Thermolysis of Cp(PPh$_3$)$_2$OsCH$_2$SiMe$_3$ (4) in C$_6$D$_6$. A solution of **4** (10 mg, 0.011 mmol) in benzene-*d*$_6$ (0.5 mL) in a sealed J. Young valve NMR tube was heated to 60−67 °C. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 48 h, all of **4** was converted into SiMe$_4$ and a complex formed whose spectral data are consistent with Cp(PPh$_3$)Os(2-C$_6$H$_4$PPh$_2$) (**10**). **10:** ^{1}H NMR δ 7.31 (br m, 9 H, ArH), 6.91 (br m, 20 H, ArH), 4.41 (s, 5 H, Cp). ^{31}P{^{1}H} NMR: δ 2.58 (d, J = 14 Hz), 1.97 (d, J = 14 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 134.43, 134.33, 134.23, 128.72, 127.37, 127.17, 127.07 (Ph), 82.35 (Cp).

Reaction of Cp*(PMe$_3$)$_2$OsCH$_2$SiMe$_3$ (7) with HSi[S(*p*-Tol)]$_3$. A flask containing **7** (10 mg, 0.018 mmol), HSi[S(*p*-Tol)]$_3$ (7.0 mg, 0.018 mmol), and cyclohexane (2 mL) was sealed with a Teflon stopcock and heated to 115 °C for 36 h. Removal of the volatile materials gave a yellow oil, whose spectroscopic characteristics (^{1}H and ^{31}P NMR) are consistent with Cp*(PMe$_3$)(H)$\overline{\text{Os}\{\text{C}_6\text{H}_3\text{(3-Me)(6-S)Si}}$[S(*p*-Tol)]$_2$} (**11**) and Cp*(PMe$_3$)$_2$OsS(*p*-Tol) (**12**) in a 3:2 mixture. **11:** ^{1}H NMR δ 7.79 (d, J = 7.9 Hz, 2 H, SC$_6$*H*$_4$Me), 7.76 (d, J = 8.0 Hz, 2 H, SC$_6$*H*$_4$Me), 7.67 (d, J = 7.8 Hz, 1 H, OsC$_6$*H*$_3$(3-Me)(6-S)Si), 7.00 (s, 1 H, OsC$_6$*H*$_3$(3-Me)(6-S)Si), 6.93 (d, J = 7.9 Hz, 2 H, SC$_6$*H*$_4$Me), 6.89 (d, J = 8.0 Hz, 2 H, SC$_6$*H*$_4$Me), 6.68 (d, J = 7.8 Hz, 1 H, OsC$_6$*H*$_3$(3-Me)(6-S)Si), 2.16 (s, 3 H, OsC$_6$H$_3$(3-*Me*)(6-S)Si), 2.05 (s, 3 H, SC$_6$H$_4$*Me*), 2.03 (s, 3 H, SC$_6$H$_4$*Me*), 1.62 (s, 15 H, C$_5$*Me*$_5$), 1.26 (d, $^2J_{\rm PH}$ = 9.6 Hz, 9 H, PMe$_3$), −13.38 (d, $^2J_{\rm PH}$ = 32.0 Hz, 1 H, OsH). ^{31}P{^{1}H} NMR: δ −49.4.

Independent Synthesis of Cp*(PMe$_3$)$_2$OsS(*p*-Tol) (12). A flask charged with **6** (50 mg, 0.09 mmol), LiS(*p*-Tol) (25 mg, 0.16 mmol), and toluene (3 mL) was heated with stirring to 80 °C for 10 h. Removal of the volatile components under vacuum, extraction with hexane (10 mL), and concentration to dryness gave a yellow solid. Recrystallization from Et$_2$O afforded **12** as bright yellow plates (30 mg, 55%), mp 211−213 °C. ^{1}H NMR: δ 7.56 (d, J = 8.1 Hz, 2 H, SC$_6$*H*$_4$Me), 6.93 (m, J = 8.1 Hz, 2 H, SC$_6$*H*$_4$Me), 2.24 (s, 3 H, SC$_6$H$_4$*Me*), 1.71 (s, 15 H, C$_5$*Me*$_5$), 1.32 (fd, N = 8.2 Hz, 18 H, PMe$_3$). ^{31}P{^{1}H} NMR: δ −49.1 ($^1J_{\rm OsP}$ = 300 Hz). ^{13}C{^{1}H} NMR: δ 131.19, 130.04, 129.02, 128.45 (S*C*$_6$H$_4$Me), 87.13 (t, $^2J_{\rm PC}$ = 2.3 Hz, *C*$_5$Me$_5$), 20.85 (s, SC$_6$H$_4$*Me*), 20.5 (vt, N = 43.3 Hz, PMe$_3$), 11.18 (s, C$_5$*Me*$_5$). Anal. Calcd for C$_{23}$H$_{40}$OsP$_2$S: C, 45.98; H, 6.71. Found: C, 47.04; H, 6.75. IR: 2727 (w), 1591 (w), 1275 (m), 1169 (w), 1076 (m), 1026 (w), 924 (s), 847 (w), 802 (m), 665 (m), 488 (s).

Cp*(PMe$_3$)(H)$\overline{\text{Os}\{\text{C}_6\text{H}_3\text{(3-Me)(6-S)Si}}Me_2$} (13). A flask containing **7** (150 mg, 0.27 mmol), HSiMe$_2$[S(*p*-Tol)] (49 mg, 0.27 mmol), and cyclohexane (2 mL) was closed (Teflon stopcock), and the contents were heated to 115 °C with stirring for 15 h. The volatile materials were then removed, giving a yellow-white solid whose spectral data are consistent with a 1:9 mixture of **12** and **13**. The crude solid was extracted with pentane (2 × 5 mL) to give a yellow solution and an undissolved white solid. The yellow solution was filtered, concentrated, and cooled to −35 °C to give yellow crystals of **12**. The remaining white solid was recrystallized from CH$_2$Cl$_2$/Et$_2$O at −35 °C to give **13** (118 mg, 77%) as white crystals, mp 149−150 °C dec. Anal. Calcd for C$_{22}$H$_{37}$OsPSSi: C, 45.34; H, 6.40. Found: C, 45.10; H, 6.19. ^{1}H NMR: δ 7.79 (d, J = 7.7 Hz, 1 H, OsC$_6$*H*$_3$(3-Me)(6-S)Si), 7.01 (s, 1 H, OsC$_6$*H*$_3$(3-Me)(6-S)Si), 6.67 (d, J = 7.7 Hz, 1 H, OsC$_6$*H*$_3$(3-Me)(6-S)Si), 2.20 (s, 3 H, OsC$_6$H$_3$(3-*Me*)(6-S)Si), 1.57 (s, 15 H, C$_5$*Me*$_5$), 1.15 (d, $^2J_{\rm PH}$ = 9.2 Hz, 9 H, PMe$_3$), 0.94 (s, 3 H, Si*Me*$_2$), 0.82 (s, 3 H, Si*Me*$_2$), −15.10 (d, $^2J_{\rm PH}$ = 32.0 Hz, $^1J_{\rm OsH}$ = 83 Hz, $^2J_{\rm SiOsH}$ = 15 Hz, 1 H, OsH). ^{31}P{^{1}H} NMR: δ −48.5. ^{13}C{^{1}H} NMR: δ 155.86 (s), 146.10 (d, $^2J_{\rm PC}$ = 9.6 Hz, OsC), 130.04 (s), 127.30 (s), 125.43 (s), 124.68 (s, S*C*$_6$H$_4$Me), 93.88 (s, *C*$_5$Me$_5$), 22.17 (d, $^1J_{\rm PC}$ = 36.5 Hz, PMe$_3$), 20.78 (s, SC$_6$H$_4$*Me*), 16.72 (s, Si*Me*), 10.41 (s, C$_5$*Me*$_5$), 8.03 (s, Si*Me*). ^{29}Si{^{1}H} NMR: δ 30.55 (d, $^2J_{\rm SiP}$ = 12.2 Hz). IR (CH$_2$Cl$_2$): 3934 (m), 3053 (s), 2983 (m), 2684 (w), 2303 (m), 1442 (m), 1421 (m), 1041 (w), 897 (m), 702 (s).

X-ray Crystal Structure Determination of 13. Colorless platelike crystals of **13** were obtained from a CH$_2$Cl$_2$/Et$_2$O solution at −35 °C. A single crystal was mounted on a glass capillary using Paratone *N* hydrocarbon oil. The data collection, reduction, and refinement were carried out as described for **2**·C$_6$H$_6$, except that the hydride position was located in the difference Fourier map and was refined isotropically. The crystal and data collection parameters are given in Table 3.

Cp*(PMe$_3$)Os(H)(SiPh$_2$Cl)$_2$ (14) and Cp*(PMe$_3$)$_2$OsSiPh$_2$Cl (15). (a) A flask charged with **7** (81 mg, 0.14 mmol) and neat HSiPh$_2$Cl (0.2 g, 0.9 mmol) was sealed with a Teflon stopcock, and the contents were heated to 115 °C with stirring for 18 h, during which time a white solid precipitated from the yellow solution. The volatile components were removed under vacuum, pentane (5 mL) was added, and the supernatant was filtered. The remaining white microcrystals were washed with cold (−35 °C) pentane (5 mL) and dried *in vacuo* to give pure **14** (mp 283−285 °C) in 48% yield (28 mg). Cooling the yellow supernatant to −35 °C gave a white solid, shown by NMR to be a 2:1 mixture of **14** and **15**. Attempts to separate pure **15** from the mixture were unsuccessful. **15:** ^{1}H NMR δ 7.94 (m, 4 H, Ph), 7.61 (m, 2 H, Ph), 7.25 (t, J = 7.2 Hz, 4 H, Ph), 1.55 (s, 15 H, C$_5$*Me*$_5$), 1.35 (fd, N = 8.0 Hz, 18 H, PMe$_3$). ^{31}P{^{1}H} NMR: δ −52.8.

(b) Alternatively, **14** can be synthesized in pure form by heating **7** and excess HSiPh$_2$Cl to 115 °C in a closed flask for 12 h, with brief, periodic (ca. 3 times) exposure to vacuum to remove PMe$_3$. Removal of the volatile materials, addition of a 1:1 mixture of CH$_2$Cl$_2$ and Et$_2$O to the resulting mixture, and cooling (−35 °C) gave white crystals of **14** in 60−84% yield. Anal. Calcd for C$_{37}$H$_{45}$Cl$_2$OsPSi$_2$: C, 53.03; H, 5.41. Found: C, 52.73; H, 5.69. ^{1}H NMR: δ 8.35 (d, J = 6.96 Hz, 4 H, Ph), 8.00 (d, J = 6.9 Hz, 4 H, Ph), 7.35 (t, J = 7.6 Hz, 4 H, Ph), 7.16 (t, J = 7.4 Hz, 2 H, Ph), 6.96 (t, J = 7.2 Hz, 4 H, Ph), 6.86 (t, J = 7.3 Hz, 2 H, Ph), 1.42 (s, 15 H, C$_5$*Me*$_5$), 1.09 (d, $^2J_{\rm PH}$ = 9.5 Hz, 9 H, PMe$_3$), −13.08 (d, $^2J_{\rm PH}$ = 8.0 Hz, 1 H, OsH). ^{31}P{^{1}H} NMR: δ −57.3 ($^1J_{\rm OsP}$ = 260 Hz). ^{13}C{^{1}H} NMR: δ 146.86 (d, $^3J_{\rm PC}$ = 3.9 Hz, *ipso*-ArC), 135.29, 134.97, 128.47, 128.13, 127.42, 127.34 (Ph), 97.18 (d, $^2J_{\rm PC}$ = 2.0 Hz, *C*$_5$Me$_5$), 22.03 (d, $^1J_{\rm PC}$ = 39.2 Hz, PMe$_3$), 10.41 (s, C$_5$*Me*$_5$). IR: 2725 (w), 2673 (w), 2017 (m, ν(Os−H)), 1306 (m), 1155 (w), 1088 (m), 1028 (w), 953 (s), 933 (m), 852 (w), 735 (s), 700 (m), 685 (w).

Cp*(PMe$_3$)(H)Os(SiMe$_2$Cl)$_2$ (16). A closed flask containing **7** (500 mg, 0.90 mmol) and excess HSiMe$_2$Cl (2.0 mL, 18 mmol) was heated to 120 °C for 15 h. Removal of the volatiles and recrystallization of the residue from CH_2Cl_2/Et_2O gave 350 mg (66%) of **16** as colorless blocks, mp 265 °C dec. Anal. Calcd for $C_{17}H_{36}Cl_2OsP_2Si$: C, 34.51; H, 6.13. Found: C, 34.33; H, 6.12. ^{1}H NMR: δ 1.64 (s, 15 H, C_5Me_5), 1.35 (d, N = 9.2 Hz, 9 H, PMe_3), 0.943 and 0.939 (2 overlapping singlets, 6H, SiMe_2), −15.27 (d, $^2J_{PH}$ = 12.0 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR: δ −53.4. $^{13}C\{^1H\}$ NMR: δ 96.01 (t, $^2J_{PC}$ = 2.2 Hz, C_5Me$_5$), 23.26 (d, $^1J_{PC}$ = 38.1 Hz, PMe_3), 17.55 (s, SiMe), 17.35 (s, SiMe), 10.85 (s, C_5Me_5). $^{29}Si\{^1H\}$ NMR: δ 28.44 (d, $^2J_{SiP}$ = 19.8 Hz). IR: 3839 (m), 3745 (s), 2360 (s), 2318 (m), 2087 (m, ν(Os−H)), 1280 (m), 1234 (m), 1030 (m), 951 (s).

Cp*(PMe$_3$)$_2$OsSiMe$_2$Cl (17). A flask containing **7** (190 mg, 0.34 mmol) and excess $HSiMe_2Cl$ (ca. 3 mL) was sealed with a Teflon stopcock. The flask was partially submerged in a 115 °C oil bath, and the mixture was heated with stirring for 20 h, until the solution turned colorless. All volatile materials were then removed *in vacuo* to give a yellow-white solid, shown by ^{1}H NMR and $^{31}P\{^1H\}$ NMR to be a 10:1 mixture of **17** and **16**. A minimum amount of CH_2Cl_2 was added to dissolve the solid, the solution was filtered, and Et_2O was added dropwise until cloudiness appeared. Cooling the CH_2Cl_2/Et_2O solution to −35 °C afforded pure **17** as white crystals (mp >360 °C dec). Further concentration and cooling resulted in crystallization of more product and an overall yield of 88% (0.17 g). Anal. Calcd for $C_{18}H_{39}ClOsP_2Si$: C, 37.85; H, 6.88. Found: C, 37.81; H, 6.93. ^{1}H NMR: δ 1.66 (t, $^4J_{PH}$ = 1.2 Hz, 15 H, C_5Me_5), 1.35 (fd, N = 8.3 Hz, 18 H, PMe_3), 1.03 (s, 6 H, $SiMe_2$). $^{31}P\{^1H\}$ NMR: δ −48.7 ($^1J_{OsP}$ = 280 Hz). $^{13}C\{^1H\}$ NMR: δ 90.25 (t, $^2J_{PC}$ = 2.5 Hz, C_5Me$_5$), 24.4 (vt, N = 46.2 Hz, PMe_3), 16.37 (s, SiMe_2), 11.73 (s, C_5Me_5). $^{29}Si\{^1H\}$ NMR: δ 46.76 (t, $^2J_{SiP}$ = 20 Hz). IR: 2721 (w), 2669 (w), 1298 (w), 1277 (m), 1223 (w), 1155 (w), 1066 (w), 1030 (m), 955 (s), 935 (s), 850 (m), 827 (m), 791 (m).

Cp*(PMe$_3$)$_2$OsSiMeCl$_2$ (18). A flask charged with **7** (100 mg, 0.18 mmol) and excess $HSiMeCl_2$ (ca. 3 mL) was sealed with a Teflon stopcock and heated with stirring at 115 °C for 36 h, until the solution turned colorless. Removal of the volatiles *in vacuo* and recrystallization of the resulting white solid from CH_2Cl_2/Et_2O at −35 °C gave white crystals of **18** (85 mg, 80%), mp >360 °C. Anal. Calcd for $C_{17}H_{36}Cl_2OsP_2Si$: C, 34.51; H, 6.13. Found: C, 34.33; H, 6.12. ^{1}H NMR: δ 1.64 (s, 15 H, C_5Me_5), 1.39 (s, 3 H, SiMe), 1.35 (fd, N = 8.6 Hz, 18 H, PMe_3). $^{31}P\{^1H\}$ NMR: δ −48.5 ($^1J_{OsP}$ = 272 Hz, $^2J_{SiP}$ = 21 Hz). $^{13}C\{^1H\}$ NMR: δ 91.16 (t, $^2J_{PC}$ = 1.6 Hz, C_5Me$_5$), 23.87 (vt, N = 46.2 Hz, PMe_3), 22.04 (s, SiMe), 11.47 (s, C_5Me_5). $^{29}Si\{^1H\}$ NMR: δ 41.19 (t, $^2J_{SiP}$ = 24.4 Hz). IR: 2731 (m), 2719 (m), 1300 (m), 1280 (s), 1236 (w), 1028 (m), 848 (m), 789 (s), 719 (m), 669 (m).

Cp*(PMe$_3$)$_2$OsSiCl$_3$ (19). To a solution of **7** (48 mg, 0.085 mmol) in benzene (1 mL) was added excess $HSiCl_3$ (0.2 mL, 2.0 mmol). The resulting mixture was heated in a closed system (Teflon stopcock) at 110−115 °C for 16 days. The white solid that precipitated out of the solution was filtered and dried *in vacuo*. Recrystallization by slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution at room temperature gave 20 mg (38%) of pure **19** as white plates, mp >360 °C. Anal. Calcd for $C_{16}H_{33}Cl_3OsP_2Si$: C, 31.40; H, 5.43. Found: C, 31.78; H, 5.36. ^{1}H NMR: δ 1.61 (s, 15 H, C_5Me_5), 1.32 (fd, N = 8.7 Hz, 18 H, PMe_3). $^{31}P\{^1H\}$ NMR: δ −49.3. $^{13}C\{^1H\}$ NMR: δ 91.96 (s, C_5Me$_5$), 23.37 (vt, N = 50.1 Hz, PMe_3), 11.70 (s, C_5Me_5). $^{29}Si\{^1H\}$ NMR: δ −15.92 (t, $^2J_{SiP}$ = 27.5 Hz). IR (CH_2Cl_2): 3801 (m), 2915 (m), 2073 (w), 1479 (w), 1375 (w), 1298 (m), 1030 (m), 958 (s), 944 (s), 858 (m), 673 (m).

Reaction of Cp(PPh$_3$)$_2$OsCH$_2$SiMe$_3$ (4) with HSiR$_2$Cl (R = Ph, Me). A mixture of **4** (20 mg, 0.023 mmol) and excess silane (ca. 0.1 mL) in a Teflon-stoppered flask was heated at 80−85 °C for 12 h. Removal of the volatiles gave a pale-yellow waxy solid. $Cp(PPh_3)Os(H)(SiPh_2Cl)_2$ (**20**): ^{1}H NMR δ 7.91 (m, 4 H, Ph), 7.44 (m, 5 H, Ph), 7.38 (m, 5 H, Ph), 7.23 (m, 6 H, Ph), 4.86 (s, 5 H, Cp), −10.65 (s, OsH). $^{31}P\{^1H\}$ NMR: δ −2.16. $Cp(PPh_3)Os(H)(SiMe_2Cl)_2$ (**21**): ^{1}H NMR δ 4.76 (s, 5 H, Cp), 0.95 (s, 6 H, SiMe_2), 0.60 (s, 6 H, SiMe_2), −11.70 (d, $^2J_{PH}$ = 8.0 Hz, OsH). $^{31}P\{^1H\}$ NMR: δ 9.33.

Reaction of Cp(PMe$_3$)$_2$OsCH$_2$SiMe$_3$ (5) with HSiR$_2$Cl (R = Ph, Me). (a) A mixture of **5** (20 mg, 0.040 mmol) and $HSiPh_2Cl$ (18 mg, 0.082 mmol) in toluene (3 mL) was heated in a Teflon-stoppered flask with stirring at 150−165 °C for 4 days. The volatile materials were removed, leaving a yellow-white residue. The residue was extracted with hexane (2 × 2 mL) to remove the excess silane and leave a white solid, shown by NMR to be mostly $Cp(PMe_3)_2OsSiPh_2Cl$ (**22**). ^{1}H NMR: δ 7.82 (d, J = 7.0 Hz, 4 H, Ph), 7.61 (d, J = 6.0 Hz, 2 H, Ph), 7.28 (t, J = 7.0 Hz, 4 H, Ph), 4.36 (s, 5 H, Cp), 1.27 (fd, N = 8.9 Hz, 18 H, PMe_3). $^{31}P\{^1H\}$ NMR: δ −46.7 ($^1J_{OsP}$ = 280 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 135.00, 134.94, 134.75, 128.87, 127.25, 127.14 (SiPh_2Cl), 77.70 (t, $^2J_{PC}$ = 2.2 Hz, C_5H_5), 25.94 (vt, N = 53.4 Hz, PMe_3). MS (EI): m/z 626 [M$^+$]. Repeated attempts to obtain satisfactory microanalysis data on this material after recrystallization or sublimation at 100 °C *in vacuo* were unsuccessful.

(b) A mixture of **5** (20 mg, 0.040 mmol) and $HSiMe_2Cl$ (0.1 mL, 0.9 mmol) in toluene (3 mL) was heated in a Teflon-stoppered flask at 150−165 °C for 4 days, with stirring. The volatile materials were removed, leaving a white residue. The residue was extracted with toluene (2 × 5 mL). The toluene extract was concentrated to dryness *in vacuo*, giving a white solid whose spectroscopic characteristics are consistent with $Cp(PMe_3)_2OsSiMeCl_2$ (**23**). ^{1}H NMR: δ 4.36 (s, 5 H, Cp), 1.30 (fd, N = 8.8 Hz, 18 H, PMe_3), 0.99 (s, 3 H, SiMe). $^{31}P\{^1H\}$ NMR: δ −45.0. $^{13}C\{^1H\}$ NMR: δ 77.22 (t, $^2J_{PC}$ = 2.2 Hz, C_5H_5), 26.28 (vt, N = 52.3 Hz, PMe_3), 17.01 (s, SiMe). MS (EI): m/z 522 [M$^+$]. The undissolved white solid remaining after the extraction was dissolved in CD_2Cl_2; its spectral data is consistent with *trans*-$Cp(PMe_3)_2Os(H)_2^+$: ^{1}H NMR (CD_2Cl_2) δ 5.48 (s, 5 H, Cp), 1.84 (fd, N = 6.5 Hz, 18 H, PMe_3), −13.95 (t, $^2J_{PH}$ = 33.1 Hz, 2 H, OsH_2).

Cp*(PMe$_3$)$_2$OsSiMe$_2$OTf (24). To a cold (−35 °C), stirred solution of **17** (150 mg, 0.26 mmol) in CH_2Cl_2 (3 mL) was added Me_3SiOTf (120 mg, 0.54 mmol). The mixture was allowed to warm to room temperature and was then stirred for 2 h, during which time the colorless solution turned light yellow. The volatile components were removed, and the resulting residue was recrystallized from a 1:1 mixture of CH_2Cl_2 and Et_2O at −35 °C to afford pure **24** as light yellow crystals (mp 190−192 °C) in 81% yield (145 mg). Anal. Calcd for $C_{19}H_{39}F_3O_3OsP_2SSi$: C, 33.32; H, 5.74. Found: C, 33.32; H, 5.75. ^{1}H NMR: δ 1.52 (s, 15 H, C_5Me_5), 1.22 (fd, N = 8.2 Hz, 18 H, PMe_3), 0.98 (s, 6 H, $SiMe_2$). $^{31}P\{^1H\}$ NMR: δ −49.6 ($^1J_{OsP}$ = 267 Hz). $^{13}C\{^1H\}$ NMR: δ 90.29 (t, $^2J_{PC}$ = 2.2 Hz, C_5Me$_5$), 24.22 (vt, N = 46.5 Hz, PMe_3), 13.12 (s, SiMe_2), 11.36 (s, C_5Me_5). $^{29}Si\{^1H\}$ NMR: δ 83.43 (t, $^2J_{SiP}$ = 23 Hz). $^{19}F\{^1H\}$ NMR (376.48 MHz): δ −14.8. IR: 2725 (w), 2675 (w), 1352 (s, $\nu(SO_3)$), 1300 (w), 1282 (m), 1236 (m), 1194 (s), 1151 (m), 1130 (w), 968 (s), 941 (s), 833 (m), 781 (w), 739 (w), 712 (m), 669 (m), 644 (m), 629 (s), 511 (w). IR (CH_2Cl_2): $\nu(SO_3)$ 1352 (s). IR (CH_3CN): $\nu(SO_3)$ 1269 (s).

X-ray Crystal Structure Determination of 24. Yellow blocklike crystals of **24** were obtained from a CH_2Cl_2/Et_2O solution at −35 °C. A single crystal was mounted on a glass capillary using Paratone-N hydrocarbon oil. The data collection, reduction, and refinement were carried out as described for **2**·C_6H_6. The cell parameters and data collection parameters are given in Table 3.

Cp*(PMe$_3$)$_2$OsSiMe[S(*p*-Tol)]$_2$ (25). A mixture of **18** (58 mg, 0.098 mmol) and LiS(*p*-Tol) (40 mg, 0.31 mmol) in toluene (2 mL) was heated with stirring at 50−55 °C for 8 h. Filtration of the resulting mixture and removal of the volatiles *in vacuo* left a yellow-white solid. Recrystallization of the solid by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution gave colorless crystals of **25** (50 mg, 67%), mp 185 °C dec. Anal. Calcd for $C_{31}H_{50}OsP_2S_2Si$: C, 48.54; H, 6.57. Found: C, 48.13; H, 6.55. ^{1}H NMR: δ 7.38 (d, J = 7.8 Hz, 4 H, ArH), 6.88 (d, J = 7.8 Hz, 4 H, ArH), 2.09 (s, 6 H, SC_6H_4Me), 1.92 (s, 15 H, C_5Me_5), 1.45 (fd, N = 7.7 Hz, 18 H, PMe_3), 0.83 (s, 3 H, SiMe).

$^{31}P\{^1H\}$ NMR: δ −51.0 ($^1J_{OsP}$ = 278 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 135.60, 135.43, 134.90, 128.81 (SC_6H_4Me), 91.75 (s, C_5Me_5), 24.43 (vt, N = 47.9 Hz, PMe_3), 21.07 (s, SC_6H_4Me), 12.20 (s, C_5Me_5), 10.29 (s, $SiMe$). $^{29}Si\{^1H\}$ NMR: δ 18.86 (t, $^2J_{SiP}$ = 18.3 Hz). IR: 1294 (m), 1280 (m), 1234 (w), 1088 (w), 1018 (w), 854 (m), 841 (m), 806 (s), 779 (s), 763 (s), 708 (m), 667 (m).

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Supporting Information Available: Tables of crystal data, collection, and refinement parameters, positional and anisotropic displacement parameters, bond distances and angles, and least-squares planes for **2**·C_6H_6, **13**, and **24** (28 pages). Ordering information is given on any current masthead page.

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