

Reactivity of an Osmium Silylene Complex toward Chlorocarbons: Promotion of Metal Redox Chemistry by a Silylene Ligand and Relevance to the Mechanism of the Direct Process

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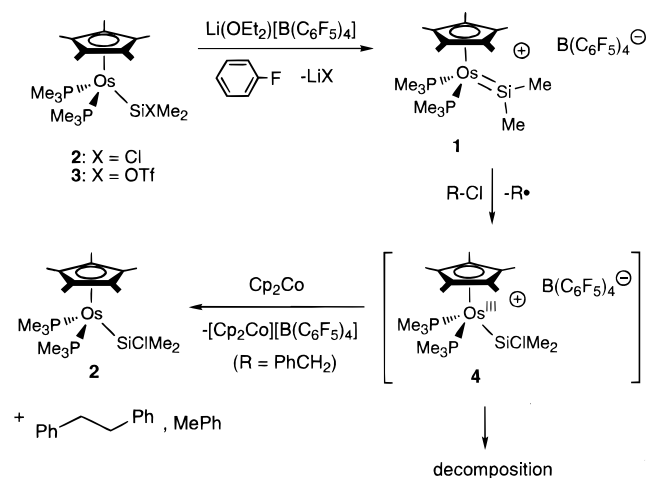
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Base-free transition-metal silylene complexes occupy an unusual position in organometallic chemistry, in that they possess a Lewis acidic center directly bound to the metal.^{1–3} Much of the known chemistry for these recently discovered species is dominated by the acidity of the silicon center, with the transition metal being less involved in documented reactivity modes. Here we report the synthesis and characterization of a base-free osmium silylene complex, $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{Os}=\text{SiMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**; $\text{Cp}^* = \text{C}_5\text{Me}_5$), which demonstrates previously unknown reactivity toward chlorocarbons. This reactivity relates to the possible intermediacy of surface-bound silylene fragments in the Direct Process, which is the primary industrial source of organosilanes.⁴ In the Direct Process, silicon is combined with methyl chloride in the presence of a heterogeneous copper-based catalyst to produce methylchlorosilanes. Although the mechanism of this process is not entirely understood, it is believed that transient silylene species produced on the catalyst surface (e.g., $:\text{SiMeCl}$ and $:\text{SiCl}_2$) combine with MeCl to produce the observed products.⁴

Initial attempts to generate the osmium silylene complex **1** were patterned after the synthesis of the ruthenium analogue.^{1j} However, addition of $\text{Li}(\text{OEt})_2[\text{B}(\text{C}_6\text{F}_5)_4]$ to $\text{Cp}^*(\text{Me}_3\text{P})_2\text{OsSiMe}_2\text{OTf}$ (**2**)⁵ in dichloromethane rapidly afforded a green solution, which turned brown within seconds. Analysis of the reaction mixture by ¹H NMR spectroscopy revealed the presence of a complex mixture of compounds, including paramagnetic species (as judged by broad NMR resonances). However, replacing dichloromethane with fluorobenzene as the reaction solvent facilitated the generation of a bright-yellow solution of **1**, as determined by multinuclear NMR spectroscopy.⁶ The presence of the base-free silylene ligand in **1** was confirmed by a characteristic ²⁹Si NMR shift of δ 350,¹ demonstrated by a ²⁹Si–¹H HMQC experiment. X-ray quality crystals of **1** were obtained by slow diffusion of pentane into a concentrated fluorobenzene solution of **1** at room temperature. Although X-ray crystallography confirmed the connectivity and gross structural features of the complex, including the

Scheme 1



planarity at silicon, refinement of accurate metric parameters was confounded by disorder in the Cp^* ring, which could not be satisfactorily modeled. In contrast to the analogous ruthenium complex, silylene **1** can also be generated from the corresponding silyl chloride complex, $\text{Cp}^*(\text{Me}_3\text{P})_2\text{OsSiMe}_2\text{Cl}$ (**3**),⁵ by reaction with $\text{Li}(\text{OEt})_2[\text{B}(\text{C}_6\text{F}_5)_4]$. Compound **1** is stable for at least 7 days in fluorobenzene solution at room temperature.

Given its thermal stability, it seemed that the complex reaction mixture observed in attempts to generate **1** in dichloromethane might have resulted from reaction with the chlorocarbon solvent. Furthermore, as similar compounds such as **2** and **3** can be recrystallized from dichloromethane with no evidence of decomposition, this reactivity appeared to involve the silylene ligand. Addition of dichloromethane to a solid sample of **1** afforded the same complex mixture of products and color changes observed in attempts to prepare **1** in CH_2Cl_2 . This result was somewhat surprising given the relative stability of $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{Ru}=\text{SiMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ under similar conditions (half-life \approx 7 h at room temperature),^{1j} however, this contrast is consistent with the expected difference in oxidation potentials for ruthenium and osmium.⁷

The first step in the reaction of **1** with dichloromethane was presumed to be abstraction of halide by the silicon center, with accompanying oxidation of the metal center to give a paramagnetic Os(III) silyl complex (**4**; Scheme 1). Low-temperature (1.3 K) EPR spectra of samples prepared by the addition of dichloromethane-*d*₂ or benzyl chloride to **1** taken within seconds of combining the reactants confirmed the presence of an Os(III) species ($g_1 = 1.82$, $g_2 = 2.29$, $g_3 = 2.43$).⁸ We therefore propose the unusual redox process given in Scheme 1, mediated by the presence of a Lewis-acidic center in the coordination sphere of the metal. This mechanism, featuring halogen-atom abstraction

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(6) Synthesis of **1**: To a -35 °C solution of **3** (100 mg, 0.15 mmol) in fluorobenzene (2 mL) was added a -35 °C solution of $\text{Li}(\text{OEt})_2[\text{B}(\text{C}_6\text{F}_5)_4]$ (110 mg, 0.15 mmol) in 1.5 mL of fluorobenzene. A color change to bright yellow and formation of white precipitate (LiOTf) were immediately observed after the addition. The reaction mixture was then filtered to remove the LiOTf . Subsequent removal of the volatile material and trituration with hexane (3×3 mL) left a bright yellow solid of **1** in 48% yield (85 mg). Anal. Calcd for $\text{C}_{42}\text{H}_{30}\text{BF}_{20}\text{OsP}_2\text{Si}$: C, 41.53; H, 3.24. Found: C, 41.34; H, 3.43. ¹H NMR (fluorobenzene, external $\text{C}_6\text{D}_6 = 7.15$ ppm): δ 1.57 (s, 15 H, C_5Me_5), 1.25 (vt, N = 8.8 Hz, 18 H, PMe_3), 0.65 (s, 6H, SiMe_2). ³¹P{¹H} NMR (fluorobenzene, external H_3PO_4) δ -49.9. ¹³C{¹H} NMR δ 94.32 (br s, C_5Me_5), 24.53 (vt, N = 53.4 Hz, PMe_3), 15.12 (s, SiMe_2), 10.43 (s, C_5Me_5).

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(8) These values are consistent with those observed for a related $\text{Cp}^*\text{Os(III)}$ species. See Gross, C. L.; Girolami, G. S. *Organometallics* **1996**, *15*, 5359.

with production of a carbon-based radical, is supported by observed relative reactivities (PhCH_2Cl , $\text{Ph}_3\text{CCl} > \text{CH}_2\text{Cl}_2 \gg \text{MeI}$, PhF), which reflect stabilities for the corresponding carbon-centered radicals. Whereas an equimolar amount of benzyl chloride reacted within seconds with a solution of **1** in fluorobenzene at $-35\text{ }^\circ\text{C}$, an excess of iodomethane did not react with **1** in fluorobenzene even after 2 days at room temperature (as indicated by ^1H NMR spectroscopy).

Additional support for a radical-based mechanism was obtained by trapping experiments in the reaction of **1** with benzyl chloride. Immediate addition of the reductant cobaltocene to a green solution generated by the reaction of **1** with benzyl chloride (in fluorobenzene) resulted in a rapid color change to orange. The ^1H NMR spectrum of the resulting solution revealed the major products to be an equimolar mixture of $\text{Cp}^*(\text{Me}_3\text{P})_2\text{OsSiMe}_2\text{Cl}$ and $[\text{Cp}_2\text{Co}][\text{B}(\text{C}_6\text{F}_5)_4]$. The reaction mixture also contained small amounts of toluene (6%) and bibenzyl (2%), which indicate the intermediacy of benzyl radical.

To further probe details of the mechanism of chlorine atom transfer from carbon to silicon, an equimolar solution of benzyl chloride and 2- α -chloroisodurene [$\text{ClCH}_2(2,6\text{-Me}_2\text{-C}_6\text{H}_3)$] was combined with a fluorobenzene solution of **1**. ^1H NMR spectroscopy

demonstrated that the less sterically encumbered benzyl chloride was preferentially consumed in a ratio of 30:1. We conclude from these data that the reaction proceeds via intimate interaction between the two species (involving coordination of the alkyl chloride to silicon) and not by way of an outer-sphere electron-transfer process.

In conclusion, a new reaction type for transition-metal silylene complexes has been discovered: halogen-atom abstraction, involving a silylene-mediated redox reaction of a metal center. In this process, the synergetic action of a readily oxidized (electron-rich) osmium center with a Lewis-acidic silylene ligand promotes cleavage of the carbon-halogen bond. For the first time, a molecular species has been shown to model a potentially key step in the Direct Process, involving reaction of a metal-bound silylene fragment with a chlorocarbon.

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