

Synthetic Development and Chemical Reactivity of Transition-Metal Silylene Complexes

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ABSTRACT

A variety of transition-metal complexes with terminal silylene ligands have become available in recent years, because of the discovery of several preparative methods. In particular, three general synthetic routes to these complexes have emerged, on the basis of anionic group abstraction, coordination of a free silylene, and α -hydrogen migration. The direct transformation of organosilanes to silylene ligands at a metal center (silylene extrusion) has also been observed, and this has further spurred the exploration of silylenes as ligands. This Account describes the synthetic development of silylene ligands in our laboratory and resulting investigations of stoichiometric and catalytic chemistry for these species.

Introduction

The close relationship of carbon and silicon in the periodic table has inspired many attempts to observe chemical parallels between these two elements. Thus, some of the earliest research on silicon chemistry sought to develop pathways to diverse arrays of catenated structures similar to those observed for carbon.¹ Whereas this endeavor did not prove fruitful, it established the high reactivity of simple hydrosilanes, such as SiH_4 , and foreshadowed the discovery of polysilanes with σ -conjugated silicon backbones.² Early attempts to prepare multiply bonded compounds of silicon, analogous to those observed for carbon, helped fortify the idea that multiple bonds are inherently

more stable for the lighter, second period elements.³ Further investigation of this concept contributed to the discovery of silicone polymers and eventually to the discovery of the first compounds with double bonds to silicon, silenes and disilenes.⁴ Whereas much of the exploration of silicon has been patterned after the “blueprint” of known carbon chemistry, this research has consistently revealed marked differences between the two elements and has led to an appreciation for the novel and useful properties of silicon-based materials.

Potential carbon–silicon analogies have also motivated the development of transition-metal–silicon chemistry. In particular, one such potential relationship has led to heightened curiosity over metal silylene complexes, $L_n\text{MSiR}_2$, which may possess metal–silicon multiple-bond character and exhibit reactivity patterns analogous to those of the well-known carbene and alkylidene complexes.⁵ Transition-metal silylene complexes are also of interest as postulated intermediates in a number of metal-catalyzed transformations involving organosilicon compounds.^{6–8} Although metal complexes of this type have been synthetic targets since the 1960s, they have been realized as definitively isolated compounds for only a little less than 15 years. Early, unsuccessful attempts to synthesize silylene complexes produced evidence that these compounds are inherently very reactive, and heightened interest in the generation of stable examples. Significant progress finally came in 1987 with reports of two so-called base-stabilized silylene complexes, $(\text{CO})_4\text{FeSi}(\text{O}^t\text{Bu})_2[\text{OP}(\text{NMe}_2)_3]$ (**1**) and $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuSiPh}_2(\text{NCMe})]^+$ (**2**).^{9–11} While such species may reversibly dissociate the base to provide kinetic access to a base-free silylene complex, the ground-state structures appear to involve considerable metal–silicon single-bond character (and sp^3 silicon), with the positive charge localized primarily on the silicon-bound base. Currently, there are several established routes to base-free silylene complexes bearing a variety of substituents at silicon. This synthetic accessibility to silylene complexes has allowed explorations of their structural, spectroscopic, chemical, and catalytic properties. In this Account, we describe the evolution of metal silylene complexes in our laboratories, from a synthetic novelty to accessible species that engage in unusual stoichiometric and catalytic transformations.

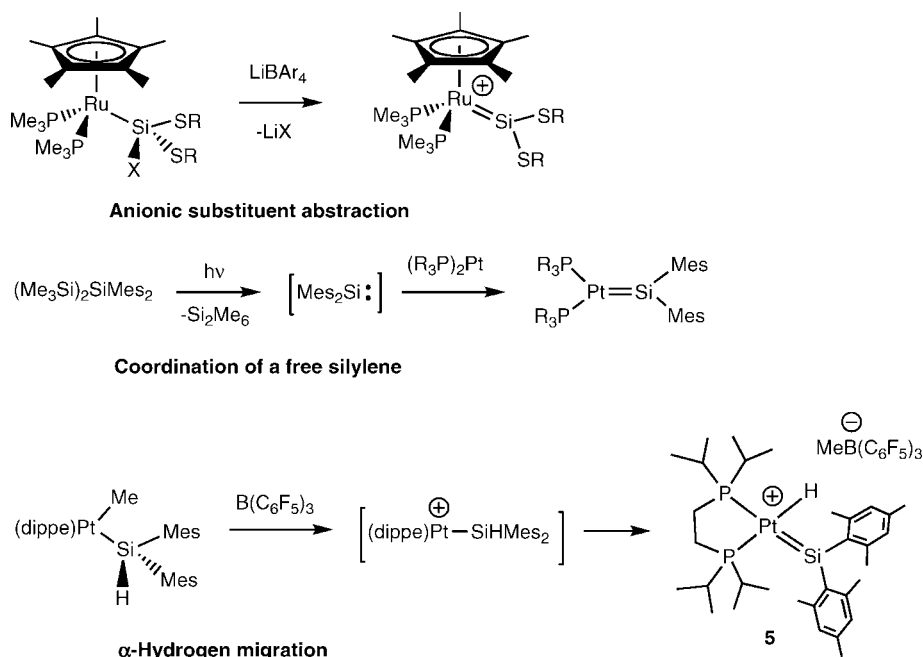
Rory Waterman completed his B.S. degree in chemistry at the University of Rochester in 1999. In 2004, he earned a Ph.D. degree in chemistry at The University of Chicago under Professor Gregory L. Hillhouse, studying the organometallic chemistry of three-coordinate nickel complexes. From 2004 to 2006, he was a Miller Institute for Basic Research in Science Research Fellow in the laboratories of Professor T. Don Tilley, investigating α elimination and E–H bond activation chemistry. He is currently Assistant Professor of Chemistry at the University of Vermont, with interests in synthetic inorganic and organometallic chemistry, catalysis, and metal–ligand multiple bonding.

Paul G. Hayes was awarded a B.Sc. (honors) degree from Mount Allison University in 1999. In 2004, he completed his Ph.D. research on cationic organoscandium complexes under the tutelage of Professor Warren Piers at the University of Calgary. During his time in Calgary, he was awarded NSERC and Sir Izaak Walton Killam Doctoral Fellowships as well as a Ralph Steinhauer Award of Distinction. In 2004, he undertook a NSERC Postdoctoral Fellowship in the laboratories of Professor T. Don Tilley, where he developed new routes to transition-metal silylene and stannylyne complexes. He recently joined the Department of Chemistry and Biochemistry at the University of Lethbridge as an Assistant Professor; his current research interests include synthetic and mechanistic organometallic chemistry, with a particular focus on the development of new chemical transformations and catalysis.

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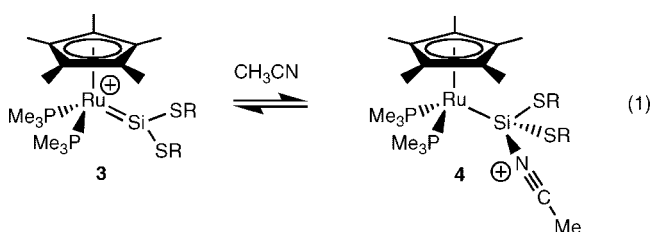
T. Don Tilley received his B.S. degree from the University of Texas, Austin, in 1977. In 1982, he earned his Ph.D. degree at the University of California, Berkeley, with R. A. Andersen, studying organometallic lanthanide chemistry. In 1982–1983, he participated in a NSF-sponsored postdoctoral exchange program, working with Professors Robert Grubbs and John Bercaw at Caltech and with Professors Luigi Venanzi and Piero Pino at the ETH in Zürich, Switzerland. He started his independent career at the University of California, San Diego, in 1983 and rose to the rank of Professor of Chemistry before moving to his current positions as Professor of Chemistry at the University of California, Berkeley, and Senior Scientist at Lawrence Berkeley National Laboratory (1994). His research interests include synthetic, structural, catalytic, and mechanistic investigations in inorganic and organometallic chemistry.

Scheme 1. Synthetic Routes to Silylene Complexes



Synthetic Routes to Silylene Complexes

Transition-metal silylene compounds of the type L_nMSiRR' possess three-coordinate silicon centers and characteristic low-field ^{29}Si nuclear magnetic resonance (NMR) chemical shifts in the range of δ 200–370. A common feature of silylene compounds is the Lewis acidity of the silicon center. This represents an unusual situation, because Lewis acidic centers are rarely found as donor atoms in transition-metal complexes. As will be illustrated, this pairing of an acidic silicon center with a transition metal accounts for much of the observed reaction chemistry. An archetypical reaction type for silylene complexes is the coordination of a Lewis base to the low-valent silicon center. A representative example of such coordination is the reaction of $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{Ru}=\text{Si}(\text{SR})_2][\text{BPh}_4]$ (**3a**, $\text{R} = p\text{-tol}$; **3b**, $\text{R} = \text{Et}$) with acetonitrile to form the base-stabilized silylene complex $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuSiR}_2(\text{NCCH}_3)][\text{BPh}_4]$ (**4a** and **4b**; eq 1).¹² The reverse reaction, whereby a Lewis base is lost from a base-complexed silylene ligand to afford the terminal silylene ligand has not been directly observed, but there is considerable kinetic evidence for this dissociation process.¹³



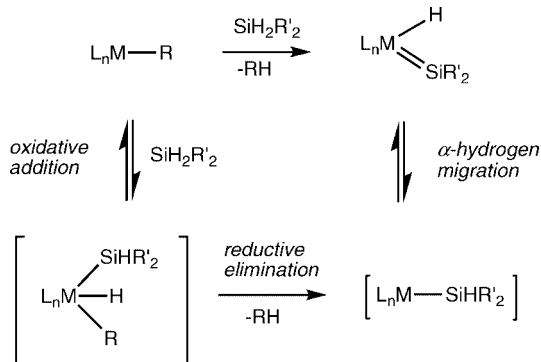
Complexes **3a** and **3b**, the first examples of isolated base-free silylene species, were prepared by abstraction of a triflate group from $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuSi}(\text{SR})_2\text{OTf}$. The abstraction of an anionic group, commonly Cl^- or OTf^- , has provided a reliable procedure for the synthesis of silylene complexes (Scheme 1). This abstraction method

is tolerant of an array of silicon substituents and has been successfully employed with metals from groups 8, 9, and 10.¹⁴ Of course, this approach necessarily produces a cationic (and more electrophilic) silylene complex.

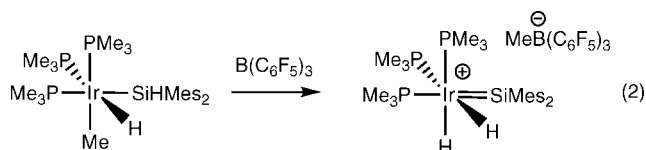
A second type of silylene complex has become available with the discovery of isolable, free silylenes, in which the divalent silicon center is stabilized by π donation from two nitrogen substituents. The coordination complexes of these silylenes appear to be distinct from those mentioned above, as indicated by their significantly higher field ^{29}Si NMR chemical shifts (97.5–146.9 ppm), which are similar to resonances previously observed for base-stabilized silylene complexes of the type $L_nMSiR_2(\text{B})$ ($\text{B} =$ two-electron donor).^{15,16} Also, complexes of stable, free silylenes appear to be weakly Lewis acidic at silicon, whereas the previously described L_nMSiRR' examples usually bind strongly to Lewis bases. These remarkably stable silylenes have been the subject of thorough reviews, and their coordination chemistry will not be discussed here.¹⁵ However, it should be noted that the strategy of capturing a thermally *unstable* silylene fragment with a metal center is also possible. Low-valent platinum species $L_2\text{Pt}$ ($\text{L} = {}^i\text{Pr}_3\text{P}$ and Cy_3P) have been shown to intercept photochemically generated dimesitylsilylene to form the terminal three-coordinate Pt–silylene complexes $L_2\text{Pt}=\text{SiMes}_2$ (Scheme 1; $\text{Mes} =$ mesityl or 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$).¹⁷ Interestingly, these platinum complexes exhibit strongly downfield ^{29}Si NMR resonances of δ 358 and 367 for the ${}^i\text{Pr}_3\text{P}$ and Cy_3P derivatives, respectively.

A third route to silylene complexes takes advantage of the propensity of the α substituent of a silyl ligand, particularly hydrogen, to migrate to a vacant coordination site on a metal (a 1,2 shift). The first example of a silylene complex prepared by this α -migration method is $(\text{dippe})\text{Pt}(\text{H})=\text{SiMes}_2^+$ [**5**, $\text{dippe} = 1,2\text{-bis}(\text{diisopropylphosphino})\text{ethane}$],¹⁸ although considerable indirect

Scheme 2. Direct Activation of Silanes via Silylene Extrusion



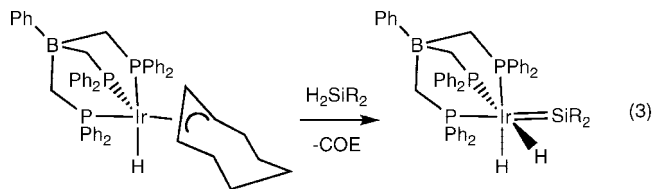
evidence for reversible 1,2 migrations of this type had previously accumulated.^{7,14i,19} In the synthesis of **5**, a vacant coordination site on platinum was generated by the reaction of the platinum precursor (dippe)PtMe(SiHMe₂) with B(C₆F₅)₃ to abstract methide. The putative, three-coordinate platinum silyl intermediate rapidly undergoes α -hydrogen migration to give **5** (Scheme 1). A related example was seen in the B(C₆F₅)₃ abstraction of methide from *fac*-IrH(Me)(SiHMe₂)(PMe₃)₃ to afford the cationic silylene complex [*fac*-(Me₃P)₃H₂Ir=SiMe₂][MeB(C₆F₅)₃] (eq 2).²⁰



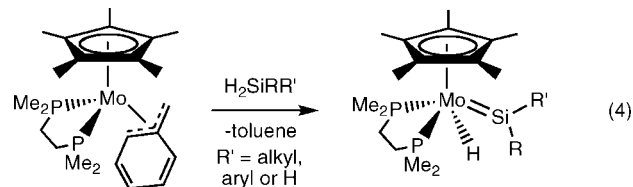
This strategy is not limited to the abstraction of a methide ligand from a metal. A family of cationic osmium complexes with terminal silylene ligands, of the general form [Cp*(Me₃P)(H)₂Os=SiRR'] [B(C₆F₅)₄] (R = H, aryl, or silyl; R' = R or aryl), have been obtained by abstraction of a bromide ligand from the neutral precursors Cp*(Me₃P)(Br)HOsSiHRR'.²¹

Our desire to explore catalytic chemistry involving silylene complexes (*vide infra*) required the discovery of reactions that readily form silylene ligands via the direct addition of a silicon-containing compound to a metal complex (the catalyst precursor). This goal was accomplished with the development of reaction sequences that combine silane Si-H oxidative addition, reductive elimination to open a coordination site, and α -H migration from silicon to the metal center. Thus, primary and secondary silanes are activated at the metal center to produce hydrido silylene complexes (Scheme 2). In initial work, [PhBP₃]IrH(η^3 -C₈H₁₃) (PhBP₃ = Ph(CH₂PPh₂)₃⁻) was found to react with dimethylsilane to rapidly generate the silylene complex [PhBP₃]H₂Ir=SiMe₂ (eq 3).^{20,22} The elimination of cyclooctene drives the reaction by removing a hydrogen atom and producing an open coordination site for α -hydrogen migration.

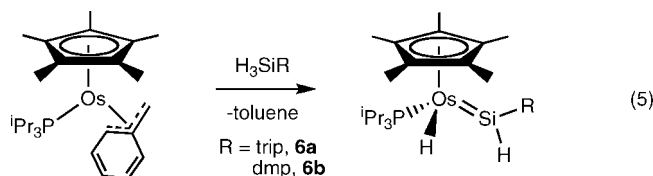
Related activations of organosilanes (silylene extrusion) have proven possible for a variety of silanes and for transition metals from groups 6–9. For example, a family of molybdenum silylene complexes has been prepared by the reaction of the benzyl precursor Cp*(dmpe)Mo(η^3 -



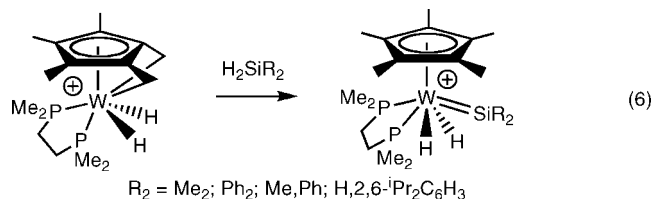
CH₂Ph) with silanes, as depicted in eq 4. This route is noteworthy because it allows for the generation of primary or H-substituted silylene ligands (L_nM=SiHR), which were previously elusive.²³



In reactions analogous to those of eq 4, neutral osmium complexes of the type Cp*(P^{*i*}Pr₃)Os(H)=SiHR (**6a**, R = 2,4,6-^{*i*}Pr₃C₆H₂; **6b**, R = 2,6-dimesitylphenyl) were prepared (eq 5).²⁴ Thus, treatment of the osmium benzyl complex Cp*(P^{*i*}Pr₃)Os(CH₂Ph) with primary silanes results in toluene elimination and formation of the corresponding silylene complex. Benzyl complexes, such as those shown above, are quite useful as precursors to neutral silylene complexes, because they participate in η^3/η^1 equilibria that provide an open coordination site for initial Si-H bond activation. Also, the elimination reaction that precedes the second Si-H bond activation (α migration) affords a relatively unreactive organic product (toluene). In this way, these benzyl derivatives serve as synthons for the 15-electron fragments Cp*(dmpe)Mo and Cp*(^{*i*}Pr₃)Os.

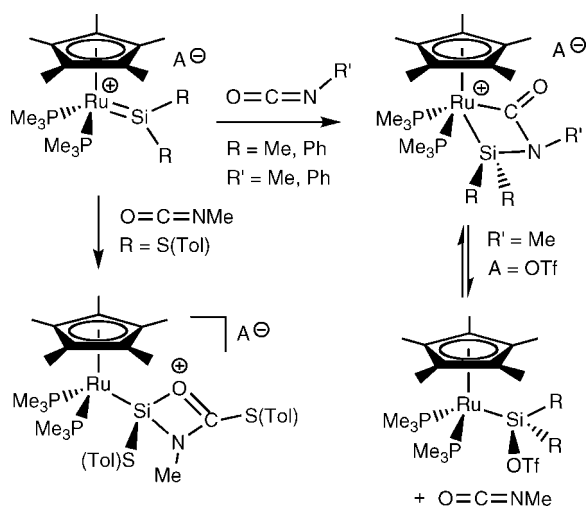


A related system involves a tungsten complex, the doubly metallated [(η^7 -C₅Me₃(CH₂)₂)(dmpe)WH₂][B(C₆F₅)₄], which undergoes an intramolecular elimination process in serving as a synthon for the 14-electron [Cp*(dmpe)W]⁺ cation. The hydride ligands of this complex reversibly migrate back to the η^7 -C₅Me₃(CH₂)₂ ligand, as indicated (for example) by reactions with a range of silanes to give silylene dihydride products of the type [Cp*(dmpe)H₂W=SiRR'] [B(C₆F₅)₄] (eq 6).²⁵



An additional synthetic method, used by Sekiguchi and coworkers to prepare the first group 4 silylene complex, is

Scheme 3. Formal [2 + 2] Cycloaddition with a Silylene Complex

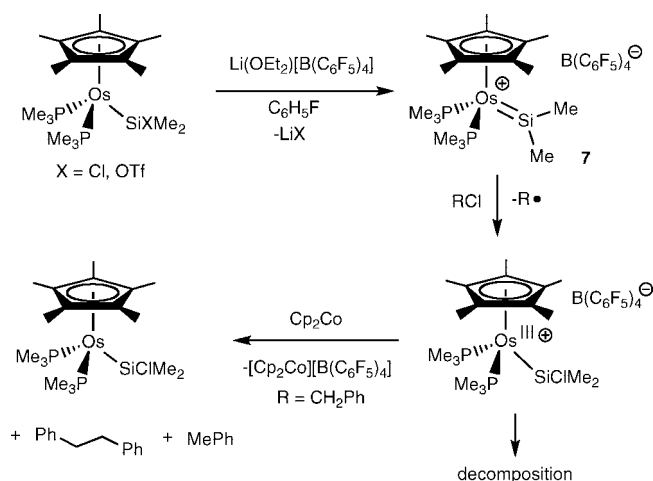


based on the reaction of a metal dihalide with a silyl dianion reagent. The preparation of $\text{Cp}'_2(\text{Me}_3\text{P})\text{Hf}=\text{Si}(\text{Si}'\text{Bu}_2\text{Me})_2$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Et}$) was accomplished by treatment of $\text{Cp}'_2\text{HfCl}_2$ with $\text{Li}_2\text{Si}(\text{Si}'\text{Bu}_2\text{Me})_2$ in the presence of PMe_3 .²⁶

Stoichiometric Reactivity of Silylene Complexes

With the synthesis of stable, isolable silylene complexes, it became possible to explore their reactivity. While some parallels with the chemistry of carbene complexes have been observed, the major chemical themes that have emerged reflect the unique character of silylene complexes. An important type of reaction for carbene complexes involves cycloaddition of the metal-carbon double bond to an unsaturated substrate. However, this reaction type remains virtually unknown for silylene complexes. In the only reported example, cationic ruthenium silylene complexes $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{Ru}=\text{SiR}_2][\text{BPh}_4]$ ($\text{R} = \text{Me}$ or Ph) undergo formal [2 + 2]-cycloaddition reactions with methyl and simple aryl isocyanates according to Scheme 3.²⁷ Mechanistic studies are consistent with a stepwise (rather than concerted) addition involving initial nucleophilic attack of the isocyanate nitrogen at the Lewis acidic silicon center followed by ring closure. This reaction illustrates the strong role that Lewis acidity at the silicon center can play in silylene reactivity. These cycloaddition reactions exhibit reversibility for the triflate derivatives $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuSiR}_2\text{OTf}$. Upon heating for 24 h at 100 °C, $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{Ru}(\text{Si}, \text{C}, \eta^2\text{-SiPh}_2\text{N}(\text{Me})\text{C}=\text{O})][\text{OTf}]$ eliminates methylisocyanate with the concomitant formation of $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuSiR}_2\text{OTf}$. Notably, these silylene complexes have not yet been observed to react with nonpolar unsaturated systems, such as ethylene, acetylene, or 2-butyne. Interestingly, the thiolate derivative $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuSi}(\text{STol})_2][\text{BPh}_4]$ ($\text{Tol} = p\text{-tolyl}$) does not undergo formal [2 + 2] cycloaddition with isocyanates as seen with the aforementioned methyl- and phenyl-substituted silylene species. Rather, a 1,2-dipolar addition of the isocyanate across the Si-S bond occurs to form $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuSi}(\text{STol})\{\text{N}(\text{Me})\text{C}[\text{S}(\text{Tol})\text{O}]\}][\text{BPh}_4]$ (Scheme 3).

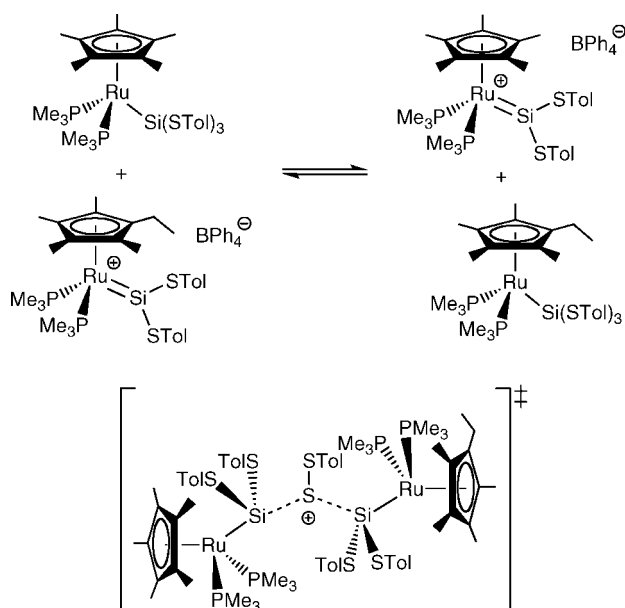
Scheme 4. Silylene Ligand-Mediated Redox Chemistry



Many of the isolated silylene complexes possess an electron-rich metal center, which is postulated to play a role in stabilizing the electron-poor $:\text{SiR}_2$ ligand via $d_{\pi}\text{-}p_{\pi}$ donation. The resulting combination of a reducing metal center and a Lewis acidic donor atom has been observed to give rise to unusual reactivity. In the course of preparing the cationic osmium complex $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{Os}=\text{SiMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**7**) by an abstraction route, a dependence on the solvent was noted.²⁸ Clean formation of **7** required a weakly basic, polar solvent; fluorobenzene was found to be optimal, but chlorocarbons resulted in complex mixtures. Silylene complex **7** stoichiometrically reacted with a range of alkyl chlorides R-Cl via halogen radical abstraction to produce an Os^{III} species $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{OsSiClMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and an alkyl radical $\text{R}\cdot$ (Scheme 4). Mechanistic investigations point to an initial binding of the alkyl halide to silicon. This reaction may therefore be described as a silylene-mediated redox reaction at the metal center. In this process, the synergistic 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, then, a molecular species was shown to model a potentially key step in the direct process, involving the reaction of a metal-bound silylene fragment with a chlorocarbon.⁶

Silylene complexes have often been proposed as catalytic intermediates in the redistribution of substituents at silicon,^{7b} and the exchange of groups at silicon has been attributed to intramolecular migrations in such complexes. Indeed, the observation of α -migration reactions involving silylene complexes is consistent with this hypothesis. However, early investigations into the reactivity of isolated ruthenium silylene complexes revealed the participation of a *bimolecular* process for exchange of groups between silicon centers.²⁹ The reaction of $\text{Cp}^*(\text{Me}_3\text{P})_2\text{Ru}=\text{Si}[\text{S}(\text{Tol})]_2^+$ with $\text{Cp}'(\text{Me}_3\text{P})_2\text{RuSi}[\text{S}(\text{Tol})]_3$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$) gives an equilibrium mixture of starting materials and exchange products $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuSi}[\text{S}(\text{Tol})]_3$ and $\text{Cp}'(\text{Me}_3\text{P})_2\text{Ru}=\text{Si}[\text{S}(\text{Tol})]_2^+$ (Scheme 5). Kinetic analysis of the reaction revealed a bimolecular process likely proceeding through direct transfer of a thiolate group between silicon centers. This bimolecular

Scheme 5. Silylene Ligand Redistribution Chemistry



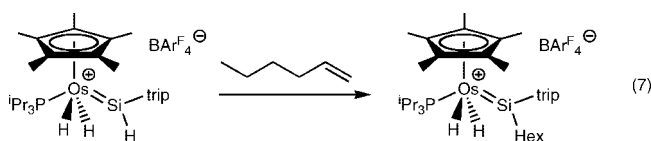
exchange process was also found to be general and facile for alkyl and aryl groups at silicon. In all observed cases, these reactions are thermodynamically driven to form the most stable silylene products. The stability trend with respect to substituents at the silylene silicon atom is consistent with that observed in earlier studies, namely, SR > Me > Ph.¹⁴

Catalytic Chemistry Involving Silylene Ligands

The availability of a range of stable, isolable silylene complexes with various metal centers, ligand sets, and silicon substituents has made it feasible to explore the possible role of such species in catalytic transformations. Much of the speculation regarding silylene complexes as catalytic intermediates has focused on metal-catalyzed silylene-transfer reactions, such as the transfer of :SiMe₂ from Me₃SiSiMe₂H to diphenylacetylene, to produce a disilacyclohexadiene.³⁰ It is also of interest to identify reactivity related to that observed in catalytic reactions of metal carbene and alkylidene complexes. These considerations have motivated us to examine reactions of isolated silylene complexes with unsaturated substrates, and this activity has led to the discovery of a silylene-mediated hydrosilation reaction, as described below.

A clean reaction between an olefin and a silylene complex was first observed for the hydrogen-substituted silylene complex [Cp*(P^{*i*}Pr₃)(H)₂Os=SiH(trip)][B(C₆F₅)₄], which is converted to a new, hexyl-substituted silylene complex upon treatment with 1-hexene (eq 7). This appeared to be an interesting, new type of Si–C bond-forming reaction. However, these osmium silylene complexes were not observed to catalyze hydrosilation reactions (e.g., the hydrosilation of 1-hexene by PhSiH₃ at 100 °C over 18 h). In search of a more reactive system, we turned to analogous complexes involving the second-row transition-metal ruthenium. This led to the preparation of the diethyl ether-stabilized complex [Cp*(P^{*i*}Pr₃)(H)₂Ru=SiH(Ph)·Et₂O][B(C₆F₅)₄] (**8**).³¹ The di-

ethyl ether in complex **8** exhibits high kinetic lability, as evidenced by exchange reactions with a variety of other Lewis bases.



Complex **8** reacts cleanly with 1-hexene to form the new silylene complex [Cp*(P^{*i*}Pr₃)(H)₂Ru=Si(Hex)(Ph)][B(C₆F₅)₄] (**9**). More interestingly, **8** catalyzes the hydrosilation of 1-hexene by phenylsilane, to give PhSi(H)₂Hex as the only silicon-containing product. This hydrosilation catalysis was readily extended to a wide range of alkenes. However, an unusual feature of the catalysis is that only primary silanes are suitable substrates, and in all cases, the hydrosilation is highly selective in giving only the secondary silane as the product. Further unusual features associated with this catalysis include the tolerance of steric hindrance about the C=C double bond (the trisubstituted olefin 1-methylcyclohexene is readily hydrosilated), the complete absence of unsaturated products, such as vinyl silanes, and the exclusive formation of anti-Markovnikov hydrosilation products. Additionally, it seems that the silylene ligand is required for catalytic activity, because control experiments with complexes lacking this group, such as Cp*(P^{*i*}Pr₃)(H)₂RuSi(H)Ph(OTf) and Cp*(P^{*i*}Pr₃)-Ru(H)(Cl)SiH₂Ph, did not afford hydrosilated products, even at elevated temperatures.

The unusual selectivities exhibited by **8** as a hydrosilation catalyst were difficult to explain by known mechanisms. For example, the electrophilic silylene ligand in **8** could participate in a Lewis-acid-catalyzed hydrosilation, as has been proposed for B(C₆F₅)₃, via the abstraction of hydride from silane.³² However, such a mechanism does not seem plausible for **8**, given the exclusive *cis* selectivity observed for the hydrosilation of 1-methylcyclohexene and the high dependence on primary silanes.³¹ A second mechanism to consider is the classic Chalk–Harrod cycle, which would seem possible with hydride migration to the silylene silicon atom, to form a coordinatively unsaturated [Cp*(P^{*i*}Pr₃)(H)RuSiH₂R]⁺ complex.³³ This species could bind olefin, and subsequent steps would form the product via olefin insertion and then reductive elimination. This possibility seems unlikely, because it does not explain the requirement for primary silanes or the insensitivity toward hindered alkenes. Finally, a mechanism involving a [2 + 2] cycloaddition of alkene across the Ru=Si bond can be envisioned, but this is also unlikely given the observed anti-Markovnikov regiochemistry, which would necessitate a sterically demanding and presumably energetically unfavorable, metallacycle intermediate.

The observed features of the catalysis and the considerations mentioned above indicate the operation of a new mechanism for hydrosilation. An intriguing possibility is suggested by the silicenium resonance structure for the ether-free version of **8** (Scheme 6). In this form, the silylene complex possesses an empty p orbital at silicon

Scheme 6. Hydrosilation Mechanism

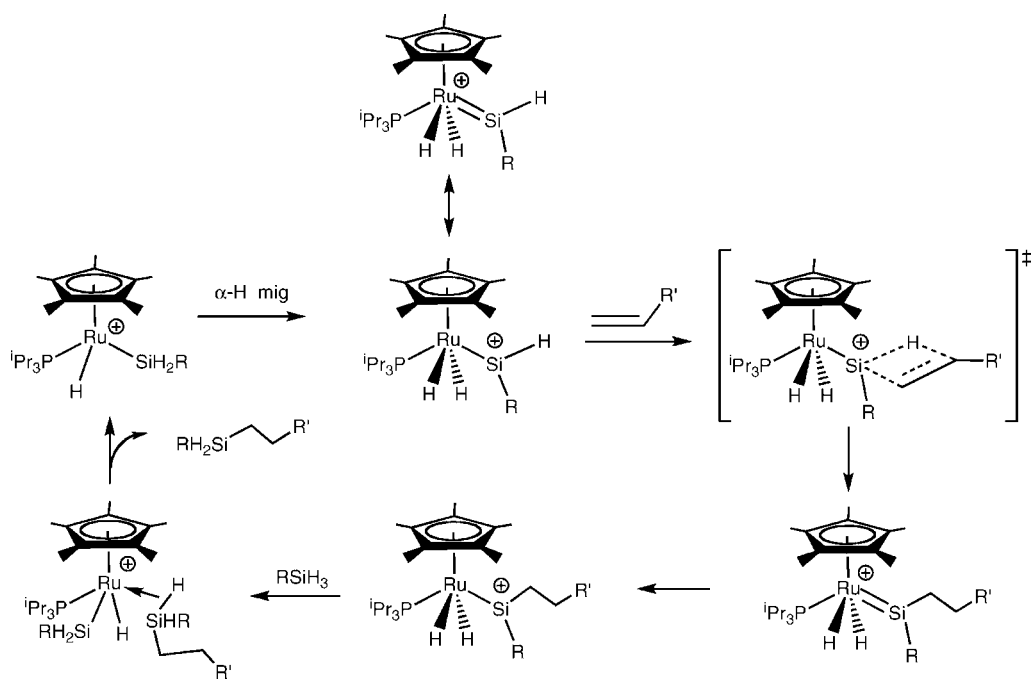
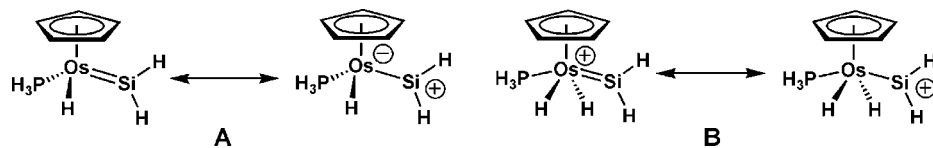


Chart 1



and, in this scheme, is isoelectronic with a borane. Thus, given considerable silicium character for this complex, the direct addition of a Si–H bond to an olefin (as in hydroboration)³⁴ should be possible. This addition produces a new silylene complex, which could undergo a 1,2-hydride shift from the metal to the silylene to give a silyl ligand. A Si–H reductive elimination would then release the product (Scheme 6). The latter elimination is probably associated with the addition of another molecule of silane, but this part of the mechanism is currently not well-understood. This mechanism involving direct Si–H addition is consistent with the observed, stoichiometric transformations of hydrogen-substituted silylene complexes of Ru and Os to the corresponding hexyl-substituted silylene complexes (e.g., eq 7). It is also supported by computational investigations.³⁵ Furthermore, it readily explains a number of observations: the selectivity for primary silanes, the anti-Markovnikov regiochemistry, the requirement of a silylene ligand in the catalyst, and the relative insensitivity to the steric properties of the alkene.

Interestingly, the degree of silicium character of a silylene ligand greatly influences the reactivity toward alkenes. This is illustrated by the fact that neutral osmium silylene derivatives $\text{Cp}^*(\text{P}^i\text{Pr}_3)(\text{H})\text{Os}=\text{SiH}(\text{R})$ (**6a**, R = trip; **6b**, R = dmp; eq 5) fail to react with alkenes, even at elevated temperatures.²⁴ Note that these complexes are simply “deprotonated” analogues of the cationic silylene complexes that add rapidly to alkenes at -80°C . In general, studies of neutral and cationic silylene complexes

of ruthenium and osmium demonstrate that charge localization plays a crucial role in this reactivity. Computational studies on model osmium complexes provide a great deal of insight into this structure–reactivity relationship.²⁴ A significant kinetic barrier was found for the insertion of ethylene into the Si–H bond of the neutral complex, compared to that of the cationic species (18.6 versus 6.3 kcal mol⁻¹). Major contributors to the kinetic barrier to alkene insertion for the neutral silylene complex are the considerable covalent character for the Os=Si double bond and the relatively low positive charge on the silylene ligand (+0.09; structure A in Chart 1). In contrast, the cationic complex possesses a significant positive charge on the silylene silicon atom (+0.52; structure B in Chart 1). Thus, it is postulated that the dramatic difference in reactivity stems from the availability of a strong resonance contributor that places a positive charge upon silicon.²⁴ In this regard, it is interesting to compare this reactivity to hydrocarbations, which involve the addition of cationic methylidyne complexes to alkenes.³⁶

An interesting aspect to the hydrosilation mechanism of Scheme 6 is that it involves the transformation of one substrate (the silane) into a reactive ligand that then reacts directly with the second substrate (the alkene). This allows for the conversion of a reactant without its binding and activation at the metal center of the catalyst. In general, the participation of additional functionalities in the activation and conversion of reactants, in the vicinity of a catalytic metal center, represents a potentially useful

concept for the design of new catalytic systems. Indeed, nature has made extensive use of this principle in the creation of highly effective catalytic enzymes.

Concluding Remarks

Transition-metal silylene complexes have evolved from intriguing synthetic targets and novelties to an accessible class of complexes that exhibit interesting and unusual chemical properties. There are now three major synthetic pathways to silylene complexes, which allow access to a variety of complexes with silylene ligands bonded to a wide range of metal fragments. These methods, anionic group abstraction, coordination of a free silylene moiety, and α -hydrogen migration, are complimentary in that they provide compounds with somewhat different properties.

Notably, much of the chemistry that has thus far been observed for silylene complexes is quite distinct from that of known carbene chemistry. Much of this difference is probably due to the larger size of silicon versus carbon and the greater electrophilicity of the silicon center. For example, this property contributes to the activation of alkyl halides,²⁸ in reactivity analogous to a key step in the direct process. Unlike carbene complexes, silylene complexes appear to be reluctant to participate in [2 + 2] cycloadditions, although reactions of this type have been observed for a highly polarized substrate.²⁷ It should be noted, however, that this generalization must be highly tentative, because most of the silylene complexes that have been investigated are coordinatively saturated and do not possess a vacant coordination site for activation of an unsaturated substrate.

The coupling of two activation steps, Si–H oxidative addition and α -hydrogen migration, allows for the direct conversion of organosilanes to silylene ligands at a metal center. The discovery of this reaction type has led to a number of new silylene complexes, but more importantly, it has allowed access to catalytic reactions that feature the participation of silylene ligands. A new example of this type of catalysis, involving α -hydrogen migration, has been identified for the hydrosilation of alkenes with a ruthenium catalyst. Whereas α migrations are well-known in organometallic chemistry, they have rarely been observed or postulated as key activation steps in a catalytic cycle. The possible participation of this reaction type, involving alkylidene hydride intermediates, has been considered for alkene polymerizations.³⁷ In principle, α migration represents a useful activation step, because it introduces a hydride ligand and a (potentially) reactive metal–ligand multiple bond. Thus, the further development of α -migration chemistry is expected to lead to the discovery of new catalytic processes.

Initial investigations of transition-metal silylene chemistry have produced a number of unexpected chemical properties, and future research in this direction should reveal more reaction types that will prove chemically useful. Hopefully, principles that are established in this area will be more generally applicable to the chemistry of other element–metal-bonded systems.

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