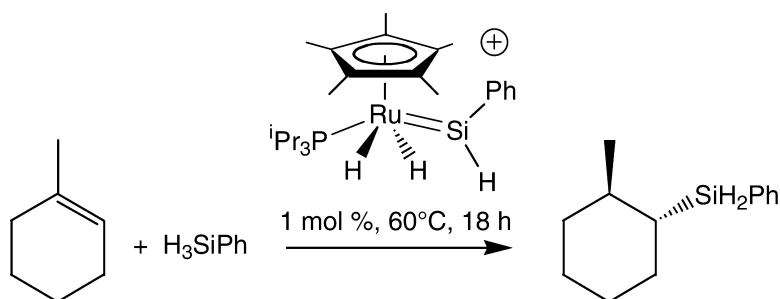Communication

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Catalytic Hydrosilylation of Alkenes by a Ruthenium Silylene Complex. Evidence for a New Hydrosilylation Mechanism

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Hydrosilylation, the addition of silicon and hydrogen across a multiple bond, is an important reaction type in organic synthesis and polymer chemistry, and for the production of organosilicon compounds.[1] The wide variety of catalysts available for these reactions permits synthetic control over the stereo-, regio-, and enantioselectivities of product formation. The largest group of catalysts for the hydrosilylation of alkenes features electron-rich transition metals such as platinum and rhodium, which typically operate by Chalk–Harrod type mechanisms that result in cis addition of the Si−H bond to an alkene.[2] Catalysts based on d^0 metal centers mediate Si−C bond formation via a σ-bond metathesis process and give fewer side products due to alkene isomerization.[3] Finally, strong Lewis acids have been employed as hydrosilylation catalysts that affect trans additions of silanes to alkenes.[4]

Transition metal silylene complexes, in which a three-coordinate silicon center is bound to a metal center, are reactive species that appear to play roles in a number of catalytic and stoichiometric processes.[5] However, no currently accepted hydrosilylation mechanism includes a silylene intermediate. Nevertheless, it seems that silylene complexes may be potentially useful intermediates in new hydrosilylation reactions. This is suggested, for example, by the strong Lewis acidic character of such complexes. In addition, silylene complexes may participate in cycloaddition reactions, as indicated by the observation of metal-catalyzed transfers of silylene fragments to unsaturated carbon−carbon bonds.[5d−g] Here, we report an unusual type of hydrosilylation that appears to proceed by the direct addition of an Si−H bond in a silylene complex to an alkene.

Initial attempts to observe silylene-mediated hydrosilylation chemistry involved derivatives of the electron-rich Cp*(^{i}Pr$_3$P)Os fragment (Cp* = η^5-C$_5$Me$_5$). As previously communicated, Cp*-(^{i}Pr$_3$P)OsBr readily adds PhSiH$_3$ to afford Cp*(^{i}Pr$_3$P)Os(Br)(H)(SiH$_2$-Ph).[6] This reaction type was found to be general for a series of primary silanes ArSiH$_3$, where Ar = Mes (2,4,6-Me$_3$), trip (2,4,6-^{i}Pr$_3$C$_6$H$_2$), dipp (2,6-^{i}Pr$_2$C$_6$H$_3$), and C$_6$F$_5$.[7] Reactions of the resulting Cp*(^{i}Pr$_3$P)Os(Br)(H)(SiH$_2$Ar) with Li[B(C$_6$F$_5$)$_4$] afford unusual, hydrogen-substituted silylene complexes of the type [Cp*(^{i}Pr$_3$P)(H)$_2$-Os=Si(H)Ar][B(C$_6$F$_5$)$_4$].[8] These species are distinguished by a silicon-bound proton resonance shifted to remarkably low field (e.g., +11.5 ppm for Ar = trip, **2**), and by a characteristically downfield ^{29}Si NMR resonance (315 ppm for **2**). Reaction of **2** with 1 equiv of 1-hexene in CD$_2$Cl$_2$ rapidly generated a new silylene complex formulated as [Cp*(^{i}Pr$_3$P)(H)$_2$Os=Si(Hex)trip][B(C$_6$F$_5$)$_4$] (**3**). However, attempts to incorporate this Si−C bond-forming reaction into an osmium-mediated catalytic cycle (e.g., PhSiH$_3$ + 1-hexene + 5% **2**, 100 °C in C$_6$H$_5$F, 18 h) were not successful.

As compared to analogous osmium complexes, ruthenium complexes are generally more labile and therefore more useful in catalysis.[9] Ruthenium silylene complexes were therefore targeted as part of a more reactive system for the hydrosilylation of alkenes. Reaction of Cp*(^{i}Pr$_3$P)Ru(H)(Cl)(SiH$_2$Ph)[10] (**4**) with Li[B(C$_6$F$_5$)$_4$]·

**Table 1.** Results from a Series of Catalytic Runs

silane	alkene	product	yield %[a]
PhSiH$_3$	1-hexene	PhSi(H)$_2$Hex (**7**)	77
PhSiH$_3$	ethene	PhSi(H)$_2$CH$_2$CH$_3$ (**8**)	54
PhSiH$_3$	ethene-d_4	PhSi(H)$_2$CD$_2$CD$_2$H (**9**)	N/A
PhSiH$_3$	cyclohexene	PhSi(H)$_2$Cy (**10**)	72
PhSiH$_3$	styrene	PhSi(H)$_2$CH$_2$CH$_2$Ph (**11**)	94
PhSiH$_3$	1-methylcyclohexene	(±) *trans*-1-PhSiH$_2$-2-Me-*cyclo*-C$_6$H$_{10}$ (**12**)	70
HexSiH$_3$	1-hexene	Hex$_2$SiH$_2$ (**14**)	57

[a] Isolated yields. Catalyst loadings were 0.5−5 mol % of **5**, reaction times were 3−18 h. NMR yields were ≥98% in each case. See Supporting Information for experimental details.

3Et$_2$O afforded the base-stabilized silylene complex [Cp*(^{i}Pr$_3$P)(H)$_2$-Ru=Si(H)Ph·Et$_2$O][B(C$_6$F$_5$)$_4$] (**5**). The Et$_2$O in **5** is loosely bound to the silicon center in solution, as demonstrated by its rapid displacement in CD$_2$Cl$_2$ solution by 1 equiv of either THF or Ph$_2$-CO. The reaction of **5** with 1 equiv of 1-hexene afforded [Cp*-(^{i}Pr$_3$P)(H)$_2$Ru=SiPhHex] [B(C$_6$F$_5$)$_4$] (**6**), as determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Interestingly, **6** does not bind Et$_2$O in CD$_2$Cl$_2$ solution (by NMR spectroscopy). Treatment of a solution of **5** with a 50-fold excess of both 1-hexene and PhSiH$_3$ cleanly generated PhSi(H)$_2$Hex as the only silicon-containing product. This catalytic reaction was found to be general for a variety of alkenes, but was restricted to monosubstituted silanes (Table 1). For example, no catalysis was observed with substrates such as Et$_2$SiH$_2$ and Ph$_2$-SiH$_2$. No further reaction of the products to tertiary or quaternary silanes was observed, even in the presence of excess alkene at long reaction times. Vinyl silanes were not detected by NMR spectroscopy or GC/MS. The clean hydrosilylation of difficult substrates such as 1-methylcyclohexene,[11] the observed selectivity for monosubstituted silanes, the absence of unsaturated products, and the exclusive anti-Markovnikov regiochemistry of addition are unusual.

In considering possible mechanisms for this reaction, it is worth noting that the silylene ligand seems to be necessary for the observed catalysis. Catalytic behavior was observed neither for Cp*-(^{i}Pr$_3$P)(H)$_2$RuSi(H)Ph(OTf) nor for the silyl chloride **4**. The Lewis acidity of the silylene center suggested a mechanism in which **5** behaves similarly to B(C$_6$F$_5$)$_3$ as proposed by Gevorgyan.[4a] However, the exclusive cis-hydrosilylation of 1-methylcyclohexene by **5** and the lack of reactivity of a range of secondary and tertiary silanes appears to exclude this type of mechanism. A second mechanistic possibility involves a [2π+2π] cycloaddition of the metal silicon bond with an alkene. Such processes have been suggested, but they have never been directly observed.[5c] A mechanism including such a cycloaddition as the key Si−C bond-forming step seems unlikely in this case, as the resulting ruthenium-(VI) metallasilacyclobutane intermediate would have to adopt a highly crowded conformation to give the observed anti-Markovnikov regiochemistry. Chalk−Harrod type mechanisms[2] can also be

Scheme 1. Proposed Catalytic Cycle

$[Ru] = Cp^*(P^iPr_3)Ru$
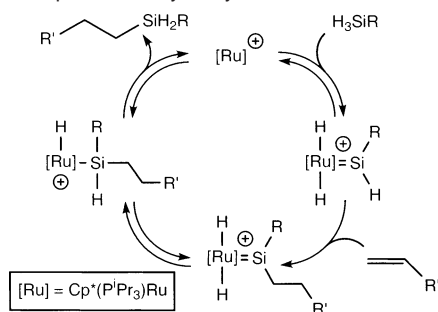
postulated if the silylene complex merely represents a resting state for the catalyst. In such a mechanism, hydride migration to silicon would produce the coordinatively unsaturated intermediate [Cp*-($^iPr_3P$)(H)RuSiH$_2$Ph]$^+$, which could then bind an alkene. Although it is difficult to entirely discount this mechanism, it would not explain the observed selectivity toward primary silanes, especially because the catalysis is insensitive to the steric properties of the alkene. Furthermore, reaction of PhSiH$_3$ with an excess of C$_2$D$_4$ in the presence of 5 mol % **5** afforded PhSi(H)$_2$CD$_2$CD$_2$H as the only observed isotopomer. When deuterated substrates are employed, catalytic hydrosilylation reactions have previously been found to afford mixtures of isotopomers via reversible olefin insertion steps.[2c,11b,12]

In light of these considerations, we propose that the key Si−C bond-forming step in the hydrosilylation reaction catalyzed by **5** proceeds by the concerted addition of the Si−H bond of the silylene across the C=C bond of the substrate in a manner analogous to the B−C bond-forming step in the hydroboration of alkenes[13] (eq 1). Three-coordinate cationic silicon centers are formally isoelectronic with monomeric boranes and can therefore be expected to participate in similar reactions. Direct addition of alkenes to the Si−H bond of a metal−silylene complex also finds precedent in hydrocarbation,[14] in which a cationic diiron-supported C−H ligand adds directly[15] to an alkene without the intermediacy of metal−alkene complexes.

(1)
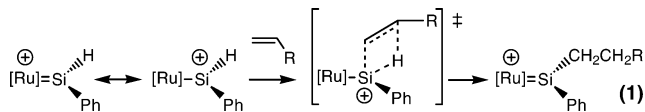
A proposed mechanism for this catalysis (Scheme 1) features activation of two Si−H bonds of the silane substrate, direct addition of an (sp^2)Si−H bond to the alkene, and finally 1,2-H migration and reductive elimination steps.[16] This mechanism accounts for all of the salient features of catalytic hydrosilylation by **5** including the selectivity for primary silanes (required for formation of a hydrogen-substituted silylene ligand), catalytic competence toward cyclic and trisubstituted alkenes, the observed anti-Markovnikov regiochemistry, and the cis-stereochemistry of addition. Further details of the reaction pathway are currently being investigated.

Note Added after ASAP. In the Supporting Information file published 10/18/03, the SiH coupling constants for compounds **1** and **2** were incorrect. The current Supporting Information file published 10/21/03 is correct.

Supporting Information Available: Experimental details for the synthesis of new compounds, procedures for catalytic runs, and schemes illustrating alternate mechanisms (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Hydrocarbation appears in some cases to operate through a stepwise mechanism including carbocation intermediates.[14b] Equation 1 represents the limiting case of [2σ+2π] cycloaddition in which Si−C bond formation is synchronous with Si−H bond breaking. The other limiting mechanism involves formation of a Si−C bond in a four-coordinate, silyl-substituted carbocation followed by intramolecular hydride migration to carbon. The addition of alkenes to R$_3$Si$^+$ species to afford silyl-substituted carbocations may be coupled to intermolecular hydride transfer.[4c] For a stepwise addition, exclusive cis-stereochemistry of addition would not necessarily be expected.

(16) The fragment resulting from reductive elimination of the product in Scheme 1 is drawn as a 14-electron species for simplicity. This intermediate would more likely exist as a labile adduct with coordinated solvent or substrate, or with a metalated ligand.

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