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Alkene Hydrosilation by a Cationic Hydrogen-Substituted Iridium Silylene Complex

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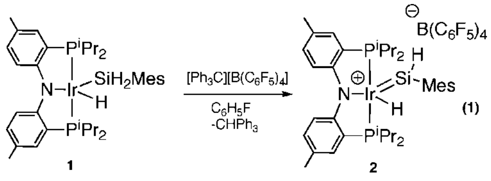
The hydrosilation of olefins is the most versatile and technologically important reaction for formation of silicon−carbon bonds and is used to produce fine chemicals, chemical intermediates, and monomers, and to cross-link organosiloxane polymers.[1] Despite these widespread applications, there is considerable interest in the development of improved hydrosilation catalysts which feature (for example) less expensive metals and/or more regioselective transformations. We recently identified a new type of hydrosilation mechanism that exhibits an unusually high degree of anti-Markovnikov regioselectivity for olefin substrates. This reaction, which is currently associated only with the ruthenium silylene catalyst $[Cp^*(^iPr_3P)H_2Ru{=}SiH(Ph)][B(C_6F_5)_4]$, operates via direct insertion of the olefin into the Si−H bond of the silylene ligand.[2] This mechanism represents a new approach to hydrosilation that might allow extension to a wide range of substrates and conditions. Further development of this catalysis will require more information regarding the factors that control key transformations in the catalytic cycle, such as the conversion of a silane to a silylene ligand at the metal center, and Si−H addition to an olefin. Preliminary results indicate that the nature of the catalytic metal center has a strong influence on the observed reactivity, in that the cationic nature of the metal center is required.[3] Here we report a second type of silylene complex that catalyzes the highly anti-Markovnikov hydrosilation of olefins, apparently by the same type of direct Si−H addition mechanism.

The rigid anionic tridentate pincer ligand $[N(2\text{-}P^iPr_2\text{-}4\text{-}Me\text{-}C_6H_3)_2]^-$ (PNP)[4] has gained popularity as an ancillary ligand for supporting reactive transition metal complexes in both late[5] and early[6] transition metal chemistry. Thus, it was of interest to investigate the ability of this PNP ligand to support silylene complexes and to explore the chemical reactivity of such species. Addition of H_3SiMes to a solution of $(PNP)IrH_2$[7] in hexanes resulted in formation of iridium silyl complex $(PNP)IrH(SiH_2Mes)$ (**1**, Mes = 2,4,6-$C_6H_2Me_3$) as an orange solid isolated in 73% yield. The ^{29}Si NMR spectrum of **1** exhibits an upfield resonance at −70.5 ppm that is consistent with the presence of a silyl ligand.[8]



(1)

The synthesis of cationic silylene complex $[(PNP)(H)Ir{=}SiH(Mes)][B(C_6F_5)_4]$ (**2**) was achieved via a hydride abstraction affected by treatment of **1** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in fluorobenzene (eq 1). Purification of **2** from the triphenylmethane byproduct was achieved by adding the reaction solution to pentane. After 1 h, the pentane/fluorobenzene supernatant was decanted to leave a blue oil, which was dried under vacuum to give **2** as a blue solid.

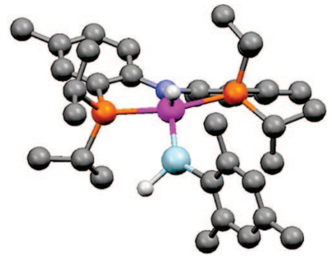


Figure 1. Optimized geometry for rotamer **2b**, $[(PNP)(H)Ir{=}Si(Mes)H]^+$.

Multinuclear NMR spectroscopy confirms the identity of complex **2** as a hydrogen-substituted iridium silylene complex.[9] The Si−H proton of **2** exhibits a downfield ^1H NMR resonance at 10.7 ppm, characteristic of a H-substituted silylene complex.[10] Also, a downfield ^{29}Si NMR resonance for complex **2** at 247 ppm supports the presence of a silylene ligand. No silicon satellites were detected for the iridium hydride resonance via a ^{29}Si-filtered ^1H NMR experiment optimized for a variety of J_{SiH} values, suggesting the absence of a significant interaction between the iridium hydride ligand and the silicon center.

Complex **2** can be stored as a solid at −35 °C for 1 month without significant decomposition. However, a solution of **2** in bromobenzene-d_5 or fluorobenzene decomposed to a mixture of **2** and two unidentified species after 4 days at ambient temperature (by ^1H NMR and ^{31}P NMR spectroscopy). Multiple attempts to obtain X-ray quality crystals of **2** produced viscous oils rather than crystalline material.

A DFT analysis at the B3LYP/LANL2DZ[11] level of theory provided further insight into the geometric and electronic structures of **2**. The geometries of three different rotamers[12] **2a**, **2b**, and **2c** were optimized to a local minimum; the geometries differ primarily in the H−Ir−Si−H dihedral angle (**2a**: 32.3°, **2b**: 121.9°, **2c**: 160.6°) (Figure 1 and Supporting Information). A comparison of the zero-point corrected energies demonstrated that rotamer **2b** is the lowest in energy. The NBO analysis does not support a strong interaction between the iridium hydride and the silicon atom in any of the rotamers, although for **2b** the geometry at silicon would permit such an interaction. The optimized geometry for each rotamer includes a trigonal planar environment for silicon and a summation of angles about silicon of 360°. The computed Ir−Si bond lengths vary between 2.27 and 2.29 Å and are slightly longer than the bond lengths for structurally characterized iridium silylene complexes of the type $[PhB(CH_2PPh_2)_3](H)_2Ir{=}SiRR'$ (2.25, 2.26 Å).[9b]

An orbital analysis of **2** revealed that the LUMO is localized predominantly on the silylene ligand, with considerable character derived from a silicon p-orbital. The HOMO is dominated by

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contributions from the PNP ligand backbone. The natural charges obtained from an NBO analysis suggest localization of the cationic charge on Si. Past experimental and computational studies suggest that this cationic charge localization at silicon promotes alkene binding directly to the silicon center and lowers the activation energy for subsequent alkene insertion into the Si−H bond.[3a] These aspects of the electronic structure of **2** have been correlated with an unusual reaction type—the direct addition of the Si−H bond of the silylene ligand to an olefin.

Compound **2** rapidly reacts with 1-hexene at ambient temperature to afford $[(PNP)(H)Ir{=}SiHex(Mes)][B(C_6F_5)_4]$ (**3**) as a dark blue solid in quantitative yield. Analogously, addition of styrene or *cis*-cyclooctene to **2** rapidly formed $[(PNP)(H)Ir{=}SiCH_2CH_2Ph(Mes)][B(C_6F_5)_4]$ (**4**) and $[(PNP)(H)Ir{=}SiC_8H_{15}(Mes)][B(C_6F_5)_4]$ (**5**), respectively. The ^{29}Si NMR resonances for these silylene complexes (**3**: 296 ppm; **4**: 295 ppm; **5**: 306 ppm) are slightly downfield-shifted with respect to that of **2**. The $^2J_{SiH}$ coupling constants for **3**, **4**, and **5** were found to be smaller than 10 Hz, which is consistent with little to no significant Ir−H−Si interaction. The ^1H, ^{13}C NMR, and 2D NMR spectra of these products reveal that the olefin addition proceeds with ≥95% anti-Markovnikov regioselectivity. Thus, the cationic iridium silylene complex **2** behaves similarly to $[Cp^*(P^iPr_3)H_2Os{=}SiH(Trip)][B(C_6F_5)_4]$ and $[Cp^*(P^iPr_3)H_2Ru{=}SiH(Ph)][B(C_6F_5)_4]$ in its reactions toward olefins.[2,3a,9b]

The silylene complex **2** catalyzes the hydrosilation of both aryl- and alkyl-substituted primary silanes ($RSiH_3$) with a variety of unhindered alkenes (Table 1). Hydrosilation runs were conducted using primary silane substrates with an equimolar amount of alkene with a 5 mol % loading of **2** in bromobenzene-d_5 at 60 °C, and gave a mixture of silane products. The disubstituted silane products ($RR'SiH_2$) are inactive toward further hydrosilation. The hydrosilation catalysis proceeds regioselectively with exclusive formation of anti-Markovnikov products, as in the analogous stoichiometric reactions.

In addition to hydrosilation catalysis, complex **2** was found to be a good catalyst for the redistribution of silanes. For example, phenylsilane in the absence of alkene was added to a 5 mol % solution of **2** in bromobenzene-d_5 in a J. Young NMR tube at ambient temperature. The ^1H NMR spectroscopy indicated the formation of Ph_2SiH_2, $PhSiH_3$ (1:0.3), and SiH_4 gas, as identified by comparisons with authentic samples. Addition of $MesSiH_3$ to a 5 mol % solution of **2** in bromobenzene-d_5 also produced Mes_2SiH_2 (approximately 6 mol %) after heating to 60 °C for 4 h. Therefore, the variability of product yields and mixture of silane products observed for hydrosilation depends on the ease of redistribution of the silane substrate (e.g., $PhSiH_3 > MesSiH_3$) in a concurrent catalytic process.[13] Furthermore, silane redistribution catalysis was not observed for the ruthenium catalyst, which therefore exhibits higher yields for hydrosilation (<98%).

Previous studies on the mechanism of hydrosilation by $[Cp^*(P^iPr_3)H_2)Ru{=}Si(H)Ph][B(C_6F_5)_4]$ indicate that hydrosilation proceeds via direct insertion into the Si−H bond, in a process that is analogous to hydroboration.[14] This work represents the second report of olefin hydrosilation catalyzed by a cationic transition metal silylene complex. The two catalytic systems share two features in common: only primary silanes serve as substrates and hydrosilation proceeds with a very high degree of anti-Markovnikov selectivity. However, complex **2** differs from the ruthenium catalyst in exhibiting a greater sensitivity to the steric properties of the alkene. Thus, no hydrosilation of 1-methylcyclohexene was observed after heating to 60 °C for 2 days in bromobenzene-d_5, and instead only redistribution catalysis occurred as determined by ^1H NMR spectroscopy. Although several mechanisms for hydrosilation can be envisioned for this system, the specificity for primary silane substrates suggests a "direct Si−H addition" process as reported for $[Cp^*(P^iPr_3)H_2)Ru{=}Si(H)Ph][B(C_6F_5)_4]$.

Table 1. Summary of Catalytic Hydrosilation Results

silane	alkene	product	yield (%)[a]
$MesSiH_3$	1-hexene	$H_2SiMes(Hex)$	70
	styrene	$H_2SiMes(CH_2CH_2Ph)$	77
	cis-cyclooctene	$H_2SiMes(C_8H_{15})$	68
$PhSiH_3$	1-hexene	$H_2SiPh(Hex)$	15
	styrene	$H_2SiPh(CH_2CH_2Ph)$	34
$HexSiH_3$	1-hexene	H_2SiHex_2	56
	styrene	$H_2SiHex(CH_2CH_2Ph)$	59
$CySiH_3$	1-hexene	$H_2SiCy(Hex)$	47
	styrene	$H_2SiCy(CH_2CH_2Ph)$	51

[a] Yields determined by integration against an internal standard by ^1H NMR spectroscopy and/or GC−MS.

These results are consistent with a general structure−activity relationship for the reactivity of cationic H-substituted silylene complexes with alkenes. Furthermore, this work suggests that the transition metal fragment supporting the silylene ligand can exhibit strong steric influences over the reactivity toward the olefin substrate; this was not observed in the previous ruthenium system. Further investigations of mechanisms for the iridium catalyst system are still needed to elucidate how to optimize olefin hydrosilation over silane redistribution catalysis via catalyst design.

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Supporting Information Available: Experimental details for synthetic procedures, characterization of new compounds, procedures for catalytic runs, computational details, and complete list of authors for ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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