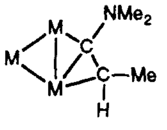
carbon atom. The hydrogen transfers probably occur sequentially, and we anticipate the formation of an intermediate containing σ-π coordinated bridging (dimethylamino)alkenyl ligands such as A.[15,16] The proposed intermediate A has two distinguishing features that facilitate the transfer of the second hydrogen atom to the same carbon that received the first hydrogen atom. The first is the presence of the NMe_2 group that stabilizes the resultant carbene structure by interaction of the nitrogen lone pair of electrons with the carbene–carbon center. The second is the σ-π coordination of the alkenyl ligand. Since the carbon atom that received the first hydrogen atom should remain coordinated, the transfer of the second hydrogen atom is possible. The hydrogenation of acetylide ligands to alkylidyne ligands in certain cluster complexes may possess mechanistic features similar to those reported here.[17]



A

This study provides still further evidence that the multicenter coordination site may, indeed, facilitate novel reactions of small molecules. We believe that the hydrogenation of ynamine ligands to yield carbene ligands may prove to be a general and effective route to the synthesis of aminocarbene ligands in cluster complexes.[18] Efforts to isolate intermediates en route to 2 are in progress.

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Registry No. 1, 122172-03-6; 2, 122172-04-7; $Os(CO)_{10}(\mu\text{-}S)$, 88746-45-6; MeC_2NMe_2, 19006-23-6; $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$, 38979-82-7.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, and bond distances and angles for both crystal structure analyses (16 pages); listings of structure factor amplitudes (37 pages). Ordering information is given on any current masthead page.

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(15) A number of examples of related ligands have been characterized. See a recent review by Deeming for a list of these.[16]

(16) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

(17) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

(18) Adams, R. D. *Chem. Rev.*, in press.

$(PPh_3)_3RhCl$-Catalyzed Hydrosilylation of Unsaturated Molecules by 1,2-Bis(dimethylsilyl)ethane: Unprecedented Rate Difference between Two Si–H Bonds

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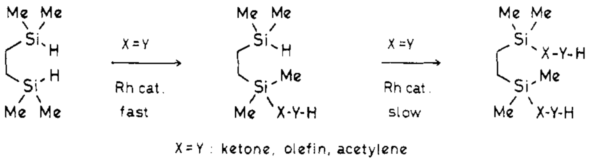
Summary: $(PPh_3)_3RhCl$ catalyzed rapid hydrosilylation of ketones, olefins, and acetylenes with 1,2-bis(dimethylsilyl)ethane (1) to form monohydrosilylation products $Me_2HSi(CH_2)_2SiMe_2Z$ (Z = alkoxy, alkyl, vinyl), selectively.

Although a bidentate organosilane 1,2-bis(dimethylsilyl)ethane (1), is a well-known precursor for stable disilametallacyclopentanes of transition metals,[1] little has been explored on their reactivity in the hydrosilylation of unsaturated molecules.[2] We report here unusual rate features in the $(PPh_3)_3RhCl$-catalyzed hydrosilylation of ketones, olefins, and acetylenes with 1. As shown in eq 1, the reactions involve substantial rate differences between the two Si–H bonds in 1, resulting in selective monofunctionalization of this symmetrical organosilane.



(1)

A benzene solution of 1 and acetone (1:1) was stirred at ambient temperature in the presence of a catalytic amount of $RhCl(PPh_3)_3$ (1 mol %).[3] Only one Si–H bond reacted within 1 h to give $Me_2SiHCH_2CH_2SiMe_2(O^iPr)$ (2) as the sole product. Even with an excess of acetone, the generation of the double hydrosilylation product $[(^iPrO)Me_2SiCH_2]_2$ was never competitive with the selective formation of 2. It is noteworthy that the hydrosilylation of acetone with 1 was 60 times faster than that of other common trialkylsilanes such as Me_2EtSiH and Et_3SiH.[4] The relative rates of the reaction of 1 approached substantially that of Ph_2SiH_2, which is a powerful hydrosilylation reagent in organic synthesis.[5,6]

Ketones generally underwent rapid hydrosilylation at only one Si–H terminus of 1 to form an unsymmetrical compound, $HMe_2SiCH_2CH_2SiMe_2(OR)$. In Table I are summarized representative results. Two important stereo- and regiochemical features are involved in the reactions; the reaction of 4-*tert*-butylcyclohexanone with 1 and subsequent hydrolysis of the silyl ethers provided a mixture of diastereomeric alcohols in which the trans isomer formed by the axial hydride attack was the major product. The hydrosilylation of mesityl oxide with 1 gave only silyl enol ethers by way of 1,4-hydrosilylation. It is known that Ph_2SiH_2 reacts with ketones much faster than do trialkylsilanes, providing distinct stereo- and regiochemical results from trialkylsilanes in the reaction of 4-*tert*-butylcyclohexanone and α,β-unsaturated ketones, respectively;[5,6] hydrosilylation of 4-*tert*-butylcyclohexanone proceeds through axial attack by trialkylsilanes and through rather preferable equatorial attack by Ph_2SiH_2.[6] The hydrosilylation of α,β-unsaturated ketones by trialkylsilanes proceeded via 1,4-addition similar to 1, while Ph_2SiH_2 gave the 1,2-adduct, namely, silyl ethers of the corresponding allylic alcohol.[5] Despite the high reactivity

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(1) (a) Fink, W. *Helv. Chim. Acta* **1974**, *57*, 1010. (b) *Ibid.* **1976**, *59*, 606. (c) Corriu, R. J. P.; Moreau, J.; Pataud-Sat, M. *Organometallics* **1985**, *4*, 623. (d) Varcea, L.; Graham, W. A. G. *Inorg. Chem.* **1974**, *13*, 511.

(2) Corriu, R. J. P.; Moreau, J.; Pataud-Sat, M. *J. Organomet. Chem.* **1982**, *228*, 301.

(3) In a typical example, a mixture of 1 (4 mmol, 586 mg), acetone (4 mmol, 232 mg), and $RhCl(PPh_3)_3$ (0.04 mmol, 38 mg) was stirred in anhydrous benzene for 1–3 at room temperature. All volatiles were distilled away from the catalyst under high vacuum. Pure 3 was obtained by redistillation of the volatiles. Detailed manipulations are described in supplementary material.

(4) The rates were measured for $EtMe_2SiH$, 1, and Ph_2SiH_2 at 30 °C in C_6D_6. Calculated relative rate constants (k_{rel}) for these three hydrosilanes were 1:60:790. The hydrosilylation of other monodentate monohydrosilanes such as 2, Et_3SiH, and $PhMe_2SiH$ were as slow as that of $EtMe_2SiH$.

(5) Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390 and references cited therein.

(6) Misra, R. N.; Semmelhack, M. F. *J. Org. Chem.* **1982**, *47*, 2469.

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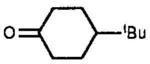
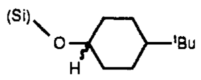
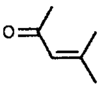
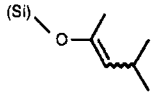
Table I. Hydrosilylation of 1 with Ketones, Olefins, and Acetylenes[a]

X=Y	time, h	products[b]	yield,[c] %
acetone	3	[Si]-O^{i}Pr (2)	75 (>99)
acetophenone	3	[Si]-OCHMePh (3)	67 (>99)
	1		77[d] (>99)
	1		... (>99)
tert-butylethylene	10	[Si]-CH$_2$CH$_2$^{t}Bu (6)	70 (>99)
styrene	48	[Si]-CH$_2$CH$_2$Ph (7)	... (>99)
diphenylacetylene	0.5	[Si]-(Ph)C=CHPh (8)	79 (>99)
dimethylacetylene	1	[Si]-(Me)C=CHMe (9)	68 (>99)

[a] All reactions were carried out by the procedure described in the text. [b] [Si] = -SiMe$_2$CH$_2$CH$_2$SiMe$_2$H. [c] Isolated yields are listed. [d] Determined after hydrolysis.

of 1 in the hydrosilylation, comparable to that of Ph$_2$SiH$_2$, these stereo- and regiochemical features are apparently similar to the results observed with trialkylsilanes. In other words, *the reactivity of one Si-H terminus of 1 is somehow greatly enhanced relative to trialkylsilanes in the (PPh$_3$)$_3$RhCl-catalyzed hydrosilylation of ketones.*

The rate differences between the two Si-H groups in 1 were also observed in the (PPh$_3$)$_3$RhCl-catalyzed hydrosilylation of olefins and acetylenes, giving rise to selective reaction by only one Si-H terminus (Table I). The reactions of acetylenes with 1 were much faster than those with Et$_3$SiH, affording the selective conversion of one Si-H bond to vinylsilyl moieties.[7] In contrast, the reaction of 1 with olefins afforded the corresponding monosilylation products; however, the rate differences between the reactions of 1 and Et$_3$SiH were not very large.[8]

In summary, the rate differences between the two Si-H bonds in 1 in the (PPh$_3$)$_3$RhCl-catalyzed hydrosilylation of unsaturated molecules can be interpreted as enhancement of the reactivity of one Si-H terminus of 1. This enhancement, which was typical in the reactions with ketones and acetylenes, was diminished after one Si-H bond was converted. Thus, it is likely that the bidentate structure of 1 having two Si-H bonds that may undergo oxidative addition to the rhodium center plays an essential role in the rate enhancement.[9] Interestingly, the (PPh$_3$)$_3$RhCl-catalyzed hydrosilylation of acetone by 1,4-bis(dimethylsilyl)butane, Me$_2$HSi(CH$_2$)$_4$SiHMe$_2$, was as slow as that with EtMe$_2$SiH, suggesting that the number of methylene units between the two Si-H groups affects the substantial rate enhancement. We also found that 1,2-bis(dimethylsilyl)benzene rapidly reacts with ketones and olefins to give the corresponding monosilylation products. This suggests that bidentate organosilanes bearing two Si-H groups within appropriate distances may generally provide the rate enhancement described above, resulting in the selective monohydrosilylation. Systematic studies on the reactions of various bidentate organosilanes are actively in progress.

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Supplementary Material Available: Preparative procedures for 2, 3, 6, 8 and their spectral data (4 pages). Ordering information is given on any current masthead page.

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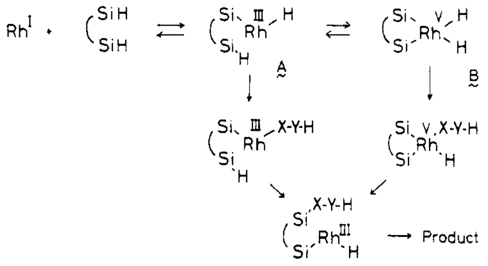
[7] For example, the hydrosilylation of diphenylacetylene with 1 was completed within 0.5 h at 0 °C, whereas no reaction took place with Et$_3$SiH at this temperature.

[8] Relative rate constants measured in benzene at 25 °C; 1:Et$_3$SiH = 3:1.

[9] Recently, Maitlis reported double oxidative addition of organosilanes to a Rh(I) precursor to form Cp*Rh^V(H)$_2$(SiR$_3$)$_2$, which was an active catalyst for the dehydrogenative hydrosilylation of olefins.[10] Since the bidentate organosilane 1 is structurally favorable for the double oxidative addition of Si-H groups to give a five-membered disilarhodacyclic skeleton, the present reactions may involve particularly active Rh(V) dihydride intermediates (B) as shown below. Alternatively, insertion of unsaturated molecules between the Rh-H bond may take place in Rh(III) intermediates (A) and the oxidative addition of the remaining Si-H terminus to the Rh center facilitate the reductive elimination to form the monoadduct.



[10] Ruiz, J.; Bentz, P.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* 1987, 2709.