its anion 5^- with $CoCl_2$ and di- or tetramethylpyrrolide ion in THF yielded the triple-decker complexes $(\eta^5\text{-}NC_4Me_2R_2)Co(\mu,\eta^5\text{-}Et_2C_2B_3H_3)Co(\eta^5\text{-}C_5Me_5)$ (**6**) as red-brown crystals,[8] accompanied by the tetracarbon metallacarborane[9] side product $(C_5Me_5)_2Co_2Et_4C_4B_6H_6$ (**7**) which evidently forms via metal-promoted oxidative fusion[10] of 5^-. The corresponding reaction of the cymene–ruthenium–carborane complex anion[1b] 8^- with $CoCl_2$ and di- or tetramethylpyrrolide ion afforded the mixed-metal triple-decker complexes $(\eta^5\text{-}NC_4Me_2R_2)Co(\mu,\eta^5\text{-}Et_2C_2B_3H_3)Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)$ (**9**) as Kelly green solids.[11] A bis(pyrrolyl) triple decker **10**, was prepared via treatment of $4a^-$ with $CoCl_2$ and the tetramethylpyrrolide ion.[12]

The new complexes, all air-stable species, were characterized from unit- and high-resolution mass spectra, ^{11}B and ^1H NMR spectra, and infrared spectra, which in all cases are consistent with the assigned structures. In particular, the ^{11}B NMR patterns are similar to those observed for analogous arene- and cyclopentadienyl–metal–carboranyl double- and triple-decker complexes whose structures have been established crystallographically.[1b,6a–c] Thus, **6**, **9**, and **10** all exhibit low-field ^{11}B NMR signals (ca. 44–60 ppm to low field of BF_3 etherate) which are characteristic[1b,6a,c] of triple-decker complexes containing *cyclo*-$R_2C_2B_3H_3^{4-}$ bridging ligands.

These findings further document the extraordinary versatility of the small C_2B_3 and C_2B_4 carborane ligands as building-block units for the construction of highly stable multidecker sandwich compounds of first-, second-, and third-row transition metals.[1b,5,13] In the pyrrolyl species, functionalization at the nitrogen site(s) is anticipated to extend still further the versatility of this chemistry, e.g., via controlled N–X–N intermolecular linkage.

Acknowledgment. We thank Dr. Mike Kinter and Dr. James Davis, Jr., for the mass spectra and Dr. Martin Attwood for the boron NMR spectra. The support of the National Science Foundation (Grant No. CHE 87-21657) is gratefully acknowledged.

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[8] **6a**: a filtered solution of KNC_4Me_4, prepared from 66 mg (0.54 mmol) of HNC_4Me_4 and excess KH in THF, was combined with a THF solution of 5^-, prepared from 0.168 g (0.54 mmol) of $(C_5Me_5)Co(Et_2C_2B_3H_5)$ (**5**) and excess KH in THF, and added to anhydrous $CoCl_2$ (0.070 g, 0.54 mmol) at −196 °C. After the solution was stirred at room temperature for 2 h, the flask was opened in air, the THF removed by evaporation, the residue extracted with diethyl ether and filtered through silica gel, and the volume of the filtrate reduced by evaporation. Purification was achieved via column chromatography on silica, initially with 1:1 dichloromethane/*n*-hexane, which afforded 23 mg (14%) of brown crystalline **7**, identified spectroscopically (closely resembling its known C_5H_5 counterpart[9]), followed by 1:1 CH_2Cl_2/acetone, which gave 67 mg (25%) of red-brown crystalline **6a**: mp 165 °C; ^1H NMR (δ, ppm, $CDCl_3$) 1.55 (s, 15 H, Cp^*CH_3), 1.59 (t, 6 H, ethyl CH_3), 1.80 (s, 6 H, 3,4-CH_3), 1.81 (s, 6 H, 2,5-CH_3), 2.55 (m, 2 H, ethyl CH_2), 2.74 (m, 2 H, ethyl CH_2); ^{11}B NMR (δ, ^1H decoupled) 8.39 (2 B, B[4,6]), 56.53 (1 B, B[5]); IR (neat, cm^{-1}) 2960 s, 2906 s, 2870 s, 2488 s, 1728 m, 1469 s, 1446 s, 1376 s, 1316 m, 1285 m, 1026 s, 906 w, 819 s; MS (70 eV) *m/z* 493 (base), parent; exact mass calcd for $^{59}Co_2{}^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{40}{}^+$ 493.2104, found 493.2113. An analogous procedure using dimethylpyrrolide gave 19 mg (15%) of brown **7** and 34 mg (18%) of red-brown crystalline **6b**, mp 90 °C.

[9] (a) Wong, K.-S.; Bowser, J. R.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 5045. (b) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 1936.

[10] Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55 and references therein.

[11] **9a**: filtered solutions of KNC_4Me_4, prepared from 0.85 g (0.70 mmol) of HNC_4Me_4 and excess KH in THF, and 0.245 g (0.70 mmol) of $K^+(p\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_4H_5)^-$ (ref 1b) were combined with anhydrous $CoCl_2$ (90 mg, 0.70 mmol) at liquid N_2 temperature, then warmed to room temperature, and stirred for 2 h. The reactor was opened in air, and the products were worked up as described for **6a** above to give 50 mg (14%) of **9a**: ^1H NMR (δ, ppm, $CDCl_3$) 1.18 (d, 6 H, isopropyl CH_3), 1.48 (t, 6 H, ethyl CH_3), 1.83 (s, 6 H, 3,4-CH_3), 1.87 (s, 6 H, 2,5-CH_3), 1.97 (s, 3 H, cymene CH_3), 2.46 (m, 3 H, ethyl CH_2 and isopropyl H), 2.88 (m, 2 H, ethyl CH_2), 4.86 (dd, 4 H, cymene H); ^{11}B NMR (δ, ^1H decoupled) 5.94 (2 B, B[4,6]), 45.53 (1 B, B[5]); IR (neat, cm^{-1}) 2960 s, 2925 s, 2870 s, 2474 s, 1731 m, 1465 s, 1447 s, 1379 s, 1276 m, 1032 m, 823 s; MS (70 eV) *m/z* 534 (base), parent; exact mass calcd for $^{104}Ru^{59}Co^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{39}{}^+$ 537.1748, found 537.1758. The procedure employed for **9a**, with the same molar quantities of reagents but with $HNC_4Me_2H_2$ in place of tetramethylpyrrole afforded 67 mg (19%) of **9b**.

[12] **10**: filtered solutions of KNC_4Me_4, prepared from 0.55 g (0.45 mmol) of HNC_4Me_4 and excess KH in THF, and 0.125 g (0.42 mmol) of $K^+(\eta^5\text{-}NC_4Me_4)Co(Et_2C_2B_3H_4{}^-)$ ($4b^-$, prepared from 0.45 mmol of **4b** and excess KH in THF) were combined with anhydrous $CoCl_2$ (57 mg, 0.44 mmol) at liquid N_2 temperature, then warmed to room temperature, and stirred for 2 h. The reactor was opened in air, and the products were worked up as described for **6a** to give 27 mg (14%) of red-brown solid **10** accompanied by the fusion products $(NC_4Me_4)_2Co_2Et_4C_4B_6H_6$ and $(NC_4Me_4)CoEt_4C_4B_7H_7$. **10**: ^1H NMR (δ, ppm $CDCl_3$): 1.65 (t, 6 H, ethyl CH_3), 1.77 (s, 12 H, 3,4-CH_3), 1.80 (s, 12 H, 2,5-CH_3), 2.77 (q, 4 H, ethyl CH_2); ^{11}B NMR (δ, ^1H decoupled) 8.90 (2 B, B[4,6]), 59.10 (1 B, B[5]); IR (neat, cm^{-1}) 2962 s, 2925 s, 2871 s, 2854 m, 2507 s, 1468 m, 1446 m, 1434 m, 1376 s, 1334 m, 1285 m, 1032 m, 962 w, 904 w, 815 s; MS (70 eV) *m/z* 480 (base), parent; exact mass calcd for $^{59}Co_2{}^{14}N_2{}^{12}C_{22}{}^{11}B_3{}^1H_{37}{}^+$ 480.1900, found 480.1879.

[13] Attwood, M. A.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics* **1989**, *8*, 1300.

Clusters Containing Carbene Ligands. A New Route to Alkyl(dialkylamino)carbene Ligands by a Novel 1,1-Hydrogenation of Ynamine Ligands

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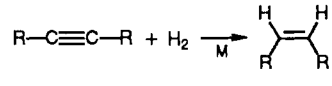
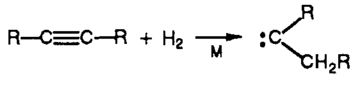
Summary: The cluster complex $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**1**) was synthesized in 87% yield from the reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with MeC_2NMe_2 at 68 °C. The ynamine ligand in **1** was found to resemble an (α,α-dimetallioethyl)(dimethylamino)carbene ligand. When treated with H_2 (10 atm/125 °C), compound **1** was converted to $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**) in 33% yield by a novel 1,1 hydrogenation of the ynamine ligand to yield an ethyl(dimethylamino)carbene ligand. Compounds **1** and **2** were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. For **1**: space group $P\bar{1}$, a = 9.397 (1) Å, b = 13.406 (7) Å, c = 8.914 (3) Å, α = 92.84 (4)°, β = 115.20 (3)°, γ = 97.54 (4)°. For 2814 reflections, R = 0.030 and R_w = 0.035. For **2**: space group $P\bar{1}$, a = 9.955 (1) Å, b = 13.971 (2) Å, c = 8.227 (1) Å, α = 102.91 (1)°, β = 113.134 (9)°, γ = 92.06 (1)°. For 2606 reflections, R = 0.027 and R_w = 0.031.

The hydrogenation of alkynes by metal complexes invariably proceeds to yield olefins, usually with cis stereochemistry, by the 1,2 addition of hydrogen to the alkynyl group (eq 1).[1,2] An alternative, 1,1 dihydrogenation to form carbenes has not yet been reported (eq 2).[3]



(1)



(2)

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[1] James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973; pp 240–242.

[2] (a) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (b) Muetterties, E. L. *Pure Appl. Chem.* **1978**, *50*, 941. (c) Burch, R. R.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 4257.

0276-7333/89/2308-2493$01.50/0

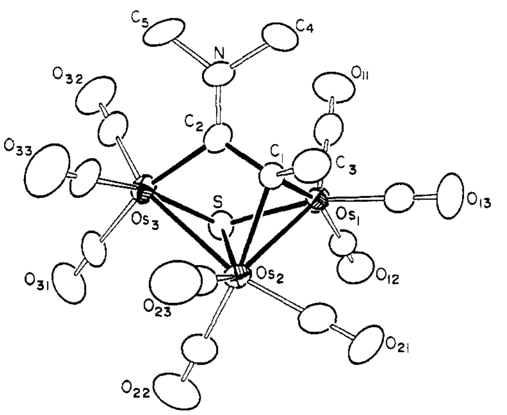

Figure 1. An ORTEP drawing of $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (1) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) and angles (deg): Os(1)–Os(2) = 2.776 (1), Os(2)–Os(3) = 2.820 (2), Os (1)⋯Os(3) = 3.941 (1), Os(3)–C(2) = 2.10 (1), C(1)–C(2) = 1.42 (1), C(2)–N = 1.34 (1), C(1)–C(2)–N = 121 (1), Os(3)–C(2)–N = 127.1 (7).

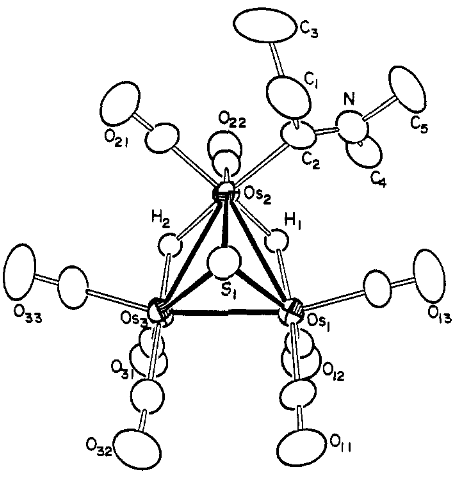

Figure 2. An ORTEP diagram of $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (2) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) and angles (deg) Os(1)–Os(2) = 2.9284 (6), Os(1)–Os(3) = 2.7785 (8), Os(2)–Os(3) = 2.9253 (8), Os(2)–C(2) = 2.10 (1), C(2)–N = 1.30 (1), Os(2)–C(2)–N = 127.1 (9).

Recently, we and others have been investigating the unusual coordination behavior of ynamine ligands $RC{\equiv}CNR_2$, in metal cluster complexes.[4-6] Structural evidence suggests that the amine-substituted carbon atom may have carbene-like character in these complexes. Herein, we wish to report the synthesis of the new ynamine ligand cluster complex $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (1) and its novel reaction with hydrogen to yield the carbene-containing cluster complex $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (2) by the transfer of two hydrogen atoms to the same carbon atom of the alkyne ligand.

The reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$[8] with MeC_2NMe_2 in refluxing hexane solvent yields compound 1, in 87% yield. The molecular structure of 1 was established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of the molecule is shown in Figure 1.[9,10] The molecule consists of an open triangular cluster of three metal atoms supported by a triply bridging sulfido ligand and a triply bridging MeC_2NMe_2 ligand. As found in other ynamine ligand cluster complexes,[4-6] the MeC_2NMe_2 ligand in 1 also exhibits an anomalous coordination. In particular, carbon C(2) is bonded by only one metal atom Os(3); the C–N distance is 1.34 (1) Å and indicative of C–N multiple bonding; the nitrogen atom is planar and the *N*-methyl groups are spectroscopically inequivalent due to hindered rotation about the C(2)–N bond. Carbon C(1) bridges the Os(1)–Os(2) metal–metal bond, and in accord with a similar formulation in the complex $Os_3(CO)_9(\mu_3\text{-}HC_2NEt_2)(\mu\text{-}H)_2$,[5] we propose to describe the ynamine ligand in 1 as a (α,α dimetallioethyl)(dimethylamino)carbene with the carbene center located at C(2).

When treated with hydrogen (10 atm) at 125 °C, compound 1 was converted to compound 2 in 33% yield.[11] The molecular structure of 2 was also established by a single-crystal X-ray diffraction analysis, and an ORTEP drawing of the molecule is shown in Figure 2.[9,12] The molecule consists of closed triangular cluster of three metal atoms with a triply bridging sulfido ligand, eight linear terminal carbonyl ligands, and a terminally coordinated ethyl(dimethylamino)carbene ligand. This complex is similar to the related carbene-cluster complexes $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$[13] and $Os_3(CO)_8[C(Ph)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$[14] that have been prepared by other methods. The carbene ligand in 2 shows no unusual structural features, and the *N*-methyl groups are spectroscopically inequivalent due to hindered rotation about the C–N bond. Compound 2 contains two hydride ligands that bridge the Os(1)–Os(2) and Os(2)–Os(3) bonds, δ = −20.66 and −21.85 ppm.

The formation of 2 requires the loss of one carbonyl ligand from 1 and the addition of 2 equiv of H_2. Both H_2 additions are believed to occur at the metal centers, but two hydrogen atoms have been shifted to the methyl-substituted carbon atom of the ynamine ligand to produce the ethyl group of the carbene ligand. The carbene remains coordinated to the cluster by the NMe_2-substituted

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(3) As written, this reaction is probably thermodynamically unfavorable, but in the presence of suitable substituents R and metal atoms for complexation, it could become favorable.

(4) Adams, R. D.; Tanner, J. T. *Organometallics* **1989**, *8*, 563.

(5) Adams, R. D.; Tanner, J. T. *Organometallics* **1988**, *7*, 2241.

(6) Cabrera, E.; Daran, J. C.; Jeannin, Y.; Kristiansen, O. *J. Organomet. Chem.* **1986**, *310*, 367.

(7) Compound 1 was isolated by TLC on silica gel. IR (ν(CO) in hexane): 2088 w, 2066 vs, 2039 s, 2008 vs, 2004 (m, sh), 1988 m, 1981 m, 1971 m, 1962 vw cm^{-1}; ^{1}H NMR (in $CDCl_3$): δ 3.39 (s, 3 H), 3.10 (s, 3 H), 2.28 (s, 3 H). Satisfactory elemental analyses (C, H, N) have been obtained.

(8) Adams, R. D.; Horváth, I. T.; Kim, H. S. *Organometallics* **1984**, *3*, 548.

(9) Diffraction measurments were made on a Rigaku AFC6 automatic diffractometer by using Mo Kα radiation. Structure solutions and refinements were performed on a Digital Equipment Corp. MICROVAX II computer by using the Molecular Structure Corp. TEXSAN program library. The data were corrected for absorption.

(10) Crystals of 1 were grown by slow evaporation of solvent from hexane solutions at 5 °C. Compound 1 crystallized in the triclinic crystal system: space group $P\bar{1}$, a = 9.397 (4) Å, b = 13.406 (7) Å, c = 8.914 (3) Å, α = 92.84 (4)°, β = 115.20 (3)°, γ = 97.54 (4)°, V = 1000.3 (8) Å^3, Z = 2, ρ_{calc} = 3.11 g/cm^3. The structure was solved by the heavy-atom method and was refined (2814 reflections) to the final values of the residuals R = 0.030 and R_w = 0.035.

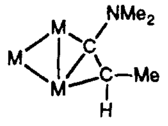
(11) The reaction was performed in a stainless-steel Parr high-pressure reactor (5 h). Compound 2 was separated by TLC on silica gel. The products $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (13%) and 2 (33%) were eluted in this order. For 2: IR(ν(CO) in hexane) 2083 s, 2046 vs, 2030 s, 2002 vs, 1985 s, 1969 m, 1960 w cm^{-1}; ^{1}H NMR (in $CDCl_3$) δ 3.75 (s, 3 H), 3.37 (s, 3 H), 3.44 (q, 1 H, J_{H-H} = 7.7 Hz), 3.43 (q, 1 H, J_{H-H} = 7.6 Hz), 1.12 (t, 3 H, J_{H-H} = 7.7 Hz), −20.66 (s, 1 H), −21.85 (s, 1 H). Satisfactory elemental analyses have been obtained.

(12) Crystals of 2 were grown from hexane/CH_2Cl_2 solutions at −20 °C. Compound 2 crystallized in the triclinic crystal system: space group $P\bar{1}$, a = 9.955 (1) Å, b = 13.971 (2) Å, c = 8.227 (1) Å, α = 102.91 (1)°, β = 113.134 (9)°, γ = 92.06 (1)°, V = 1015.8 (6) Å^3, Z = 2, ρ_{calc} = 2.97 g/cm^3. The structure was solved by direct methods (MITHRIL) and was refined (2606 reflections) to the final values of the residuals R = 0.027 and R_w = 0.031. The hydride ligands were located and refined.

(13) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1985**, *107*, 6107.

(14) Adams, R. D.; Babin, J. E.; Kim, H. S. *J. Am. Chem. Soc.* **1987**, *109*, 1414.

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]



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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.

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy, Grant No. DEFG84ER13296.

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$_3$)$_3$RhCl-Catalyzed Hydrosilylation of Unsaturated Molecules by 1,2-Bis(dimethylsilyl)ethane: Unprecedented Rate Difference between Two Si–H Bonds

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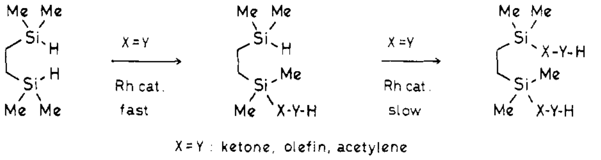
Received May 18, 1989

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.