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Synthesis and Properties of Bridging Siloxyl Ligands in Dirhenium Carbonyl Complexes

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Reaction of the complex $Re_2(CO)_8[\mu\text{-}C(H)C(H)Bu^n](\mu\text{-}H)$ with $HSi(OMe)_3$ in a refluxing heptane solution yielded the new compound $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (1) in 51% yield. Compound 1 was converted to a PMe_2Ph derivative $Re_2(CO)_7(PMe_2Ph)[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (2) in 25% yield by treatment with Me_3NO in the presence of PMe_2Ph. Compounds 1 and 2 were characterized crystallographically, and each was found to contain an $\eta^2\text{-}Si(OMe)_3$ ligand bridging the two rhenium atoms. In compound 2 the phosphine ligand is coordinated to the rhenium atom that contains the coordinated oxygen atom. Both compounds exhibit a dynamical activity at elevated temperatures in which the OMe groups of the $Si(OMe)_3$ ligand are averaged. The activation barrier in 2 is slightly higher than that in 1. Compound 2 reacts with H_2O at 25 °C to yield the adduct $Re_2(CO)_7(PMe_2Ph)[Si(OMe)_3](H_2O)(\mu\text{-}H)$ (3) in 76%. A structural analysis of 3 showed that the Si–OMe bridge was opened by a cleavage of the Re–O bond and the addition of H_2O to that site. One of the hydrogen atoms of the H_2O ligand is hydrogen bonded to one of the OMe groups of the $Si(OMe)_3$ ligand. Compound 3 readily loses H_2O and is converted back to 2. Crystal data: for 1, space group = $P\bar{1}$, a = 9.766(2)Å, b = 12.344(4)Å, c = 8.741(2)Å, α = 109.52(2)°, β = 110.97(2)°, γ = 79.54(2)°, Z = 2, 2103 reflections, R = 0.039; for 2, space group = $P2_1/c$, a = 14.579(1)Å, b = 7.832(2)Å, c = 22.357(3)Å, β = 101.88(1)°, Z = 4, 2327 reflections, R = 0.035; for 3, space group = $P2_1$, a = 10.347(2)Å, b = 12.482(3)Å, c = 11.026(2)Å, β = 109.53(1)°, Z = 2, 1822 reflections, R = 0.021.

Introduction

Recent studies of the coordination properties of siloxyl ligands, $Si(OR)_3$, have revealed an unexpected basicity of the oxygen atoms for metal atoms.[1,2] A variety of complexes have now been described that contain bridging siloxyl ligands formed by the coordination of one or more of the alkoxy oxygen atoms, (A^1 or B^2).
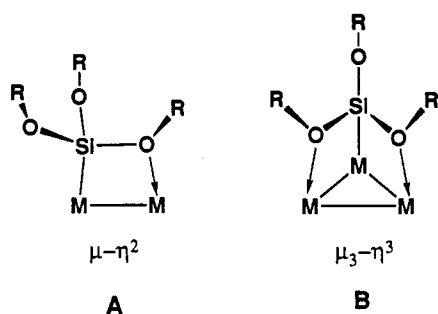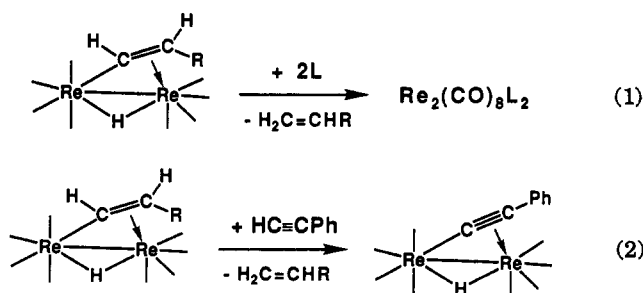

The hydrido(alkenyl)dirhenium carbonyl compounds $Re_2(CO)_8[\mu\text{-}C(H)C(H)R](\mu\text{-}H)$ are known to react with a variety of donors by the elimination of alkene to yield complexes of the type $Re_2(CO)_8L_2$, L = pyridine, PR_3, etc. (eq 1).[3] Reaction of $Re_2(CO)_8[\mu\text{-}C(H)C(H)Me](\mu\text{-}H)$ with phenylacetylene leads to addition with a CH activation that yields the acetylide complex $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C\equiv CPh](\mu\text{-}H)$ (eq 2).[4]

We have now investigated the reaction of $Re_2(CO)_8[\mu\text{-}C(H)C(H)Bu^n](\mu\text{-}H)$ with $(MeO)_3SiH$. We have found that the reaction produces an SiH activation and yields the complex $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}Si(OR)_3](\mu\text{-}H)$ 1, which contains the first example of a $\mu\text{-}\eta^2$-siloxyl ligand in a dirhenium complex. We have also prepared the PMe_2Ph derivative $Re_2(CO)_7(PMe_2Ph)[\mu\text{-}\eta^2\text{-}Si(OR)_3](\mu\text{-}H)$ (2) by reaction of 1 with PMe_2Ph in the presence of Me_3NO. We have found also that complex 2 readily and reversibly adds H_2O in a process that breaks the Si–O bridge to form the complex $Re_2(CO)_8(PMe_2Ph)(H_2O)[Si(OR)_3](\mu\text{-}H)$ (3). Interestingly, one of the hydrogen atoms of the H_2O ligand is hydrogen bonded to one of the methoxyl groupings,

(1) (a) Braunstein, P.; Knorr, M.; Tiripicchio, A.; Tiripicchio Camellini, M.; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1361. (b) Braunstein, P.; Knorr, M. *New J. Chem.* **1990**, *14*, 583. (c) Braunstein, P.; Knorr, M.; Piana, H.; Schubert, U. *Organometallics* **1991**, *10*, 828. (d) Braunstein, P.; Knorr, M.; Villarroya, E.; DeCian, A.; Fischer, J. *Organometallics* **1991**, *10*, 3714. (e) Braunstein, P.; Knorr, M.; Schubert, U.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1507. (f) Braunstein, P.; Douce, L.; Knorr, M.; Strampfer, M.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1992**, 331. (g) Braunstein, P.; Colomer, E.; Knorr, M.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1992**, 903. (h) Aigbirhio, F. I.; Al-Juaid, S. S.; Eaborn, C.; Habtemariam, A.; Hitchcock, P. B.; Smith, J. D. *J. Organomet. Chem.* **1991**, *405*, 149. (i) Balegroune, F.; Braunstein, P.; Douce, L.; Dusausoy, Y.; Grandjean, D.; Knorr, M.; Strampfer, M. *J. Cluster Sci.* **1992**, *3*, 275. (j) Knorr, M.; Braunstein, P. *Bull. Soc. Chim. Fr.* **1992**, *129*, 663.

(2) Adams, R. D.; Cortopassi, J. E.; M. P. Pompeo, M. P. *Inorg. Chem.* **1992**, *31*, 2563.

(3) (a) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644. (b) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4955.

(4) Nubel, P. O.; Brown, T. L. *Organometallics* **1984**, *3*, 29.

providing the first evidence for a substantial proton basicity of the oxygen atoms of a $Si(OR)_3$ ligand.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were stored over 4-Å molecular sieves. The compound $Re_2(CO)_8[\mu\text{-}C(H)C(H)Bu^n](\mu\text{-}H)$ was prepared by the published procedure.[3] Trimethylamine *N*-oxide dihydrate was dehydrated by using a Dean-Stark apparatus with benzene solvent prior to use. All other reagents were purchased from Aldrich and were used as received. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^{1}H NMR spectra were run on a either a Bruker AM-300 or a Bruker AM-500 spectrometer operating at 300 or 500 MHz, respectively. The temperatures for the variable-temperature measurements were calibrated with a standard sample of 80% ethylene glycol in DMSO-d_6. Chromatographic separations were performed in air on Analtech 0.25-mm silica gel 60-Å F_{254} plates. Elemental analyses were performed by either Oneida Research Services, Whitesboro, NY, or Desert Analytics, Tuscon, AZ.

Synthesis of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (1). A 27.6-mg amount of $Re_2(CO)_8[\mu\text{-}C(H)CBu^n](\mu\text{-}H)$ (0.041 mmol) was dissolved in 25 mL of heptane. The solution was heated to reflux, and a 50-μL amount of trimethoxysilane was then added. The reflux was continued for 45 min. The volatiles were removed in vacuo, and the residue was isolated by TLC using a hexane/methylene chloride 6/1 solvent mixture as the eluent. This yielded 15.0 mg of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (1) (0.021 mmol, 51% yield). Spectral data for 1: IR (ν_{CO} (cm^{-1}) in hexane): 2119 (w), 2082 (m), 2024 (vs), 2009 (s), 1999 (s), 1975 (s), 1968 (s), 1963 (s). ^{1}H NMR (δ in CDCl$_3$): 3.82 (s, OCH_3, 3H), 3.54 (s, OCH_3, 6H), −15.26 (s, *Re–H*). Anal. Calcd (found): C, 18.4 (18.7); H, 1.40 (1.40).

Preparation of $Re_2(CO)_7(PMe_2Ph)[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (2). A 39.0-mg amount (0.054 mmol) of 1 was dissolved in 25 mL of methylene chloride. A 4.9-mg sample of Me$_3$NO (0.065 mmol) in 5 mL of methylene chloride was added, and the solution was allowed to stir for 10 min at 25 °C. Next, a 7.7-μL amount of PMe$_2$Ph (0.054 mmol) was added, and the solution was allowed to stir for 1 h at 25 °C. The volatiles were then removed in vacuo, and the residue was isolated by TLC using a hexane/methylene chloride 2/1 solvent mixture as the eluent. This yielded 11.3 mg of 2 (0.013 mmol, 25% yield) as a colorless solid. Spectral data for 2 are as follows. IR (ν_{CO} (cm^{-1}) in hexane): 2084 (m), 2036 (s), 1998 (m), 1973 (s), 1959 (vs), 1946 (m), 1919 (s). ^{1}H NMR (δ in CDCl$_3$): 7.65–7.42 (m, C_6H_5, 5H), 3.64 (s, OCH_3, 3H), 3.58 (s, OCH_3, 3H), 3.41 (s, OCH_3, 3H), 1.92 (d, PCH_3, $^2J_{P-H}$ = 8.3 Hz, 3H), 1.91 (d, PCH_3, $^2J_{P-H}$ = 8.3 Hz, 3H), −14.10 (d, *Re–H*, $^2J_{P-H}$ = 14.5 Hz, 1H). Anal. Calcd (found) for 2·$^1/_2$C$_6$H$_{14}$: C, 28.3 (28.9); H, 3.24 (2.89).

Preparation of $Re_2(CO)_7(PMe_2Ph)(H_2O)[Si(OMe)_3](\mu\text{-}H)$ (3). A 20.7-mg amount of 2 (0.025 mmol) was dissolved in 1 mL of acetone-d_6, and the solution was placed in a 5-mm NMR tube. A 22.5-μL amount of water (1.25 mmol) was added, and after 10 min a NMR spectrum was taken. This showed a complete conversion to 3, as indicated by the presence a new hydride resonance at δ = −12.14 (d, $^2J_{P-H}$ = 19.1 Hz) and the disappearance of the hydride resonance of 2 at δ = −14.10. Compound 3 was then isolated by TLC using a 9/1 hexane/acetone solvent mixture. This yielded 7.4 mg of 2 in the first UV band and 10.3 mg of $Re_2(CO)_7(PMe_2Ph)[Si(OMe)_3](H_2O)(\mu\text{-}H)$ (3) (0.012 mmol, 76% yield based on consumed 2) in the second UV band. The regeneration of 2 is believed to have occurred during the workup. Spectral data for 3 are as follows. IR (ν_{CO} (cm^{-1}) in hexane) 2077 (m), 2027 (s), 1987 (m), 1971 (vs), 1958 (s), 1937 (m), 1915 (m). ^{1}H NMR (δ in wet acetone-d_6): 7.67–7.47 (m, C_6H_5, 5H), 6.52 (br s, H_2O, 2H), 3.47 (s, OCH_3, 9H), 2.11 (d, $^2J_{P-H}$ = 9.2 Hz, PCH_3, 3H), 2.01 (d, $^2J_{P-H}$ = 9.5 Hz, PCH_3, 3H), −12.14 (d, $^2J_{P-H}$ = 19.1 Hz, 1H). Anal. Calcd (found) for 3·$^1/_2$(acetone): C, 26.2 (26.7); H, 2.99 (2.68).

Attempted Hydration of 1. A 12.4-mg sample of 1 (0.017 mmol) and 6.2 μL of H$_2$O (0.35 mmol) were added to approxi-

mately 1 mL of acetone-d_6 in a 5-mm NMR tube. The NMR spectrum showed only 1 after 72 h.

Interconversion of 2 and 3. A 17.7-mg sample of 2 (0.021 mmol) in approximately 1 mL of acetone-d_6 was placed in a 5-mm NMR tube, followed by the addition of 7.7 μL of H$_2$O (0.43 mmol). The NMR spectrum after 5 h showed >95% conversion of 2 to 3. The solution was transferred to a vial containing approximately 20 mg of freshly pulverized CaSO$_4$. The solution was allowed to stand for 24 h and was then filtered into another NMR tube. The NMR spectrum of this sample showed complete conversion of 3 back to 2.

Crystallographic Analysis. Colorless crystals of 1 were grown from a concentrated methylene chloride/heptane solvent mixture at −15 °C. Colorless crystals of 2 were grown from a hexane/methylene chloride solvent mixture at 25 °C. Colorless crystals of 3 were grown by the slow evaporation of solvent from an acetone/heptane solution containing small amounts of H$_2$O at −15 °C. All crystals used in diffraction intensity measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Digital Equipment Corp. VAX station 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[5a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[5b] Lorentz/polarization (*Lp*) and absorption corrections were applied to the data in each analysis. Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. Each structure was solved by a combination of direct methods (MITHRIL) and difference Fourier analyses. Crystal data and results of the analyses are listed in Table I.

Compound 1 crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydride ligand was located and refined with an isotropic thermal parameter. The positions of all hydrogen atoms on the methyl groups were calculated by assuming idealized geometries with C–H = 0.95 Å and using located positions whenever possible. These hydrogen atoms were included in the structure factor calculations without refinement.

Compounds 2 and 3 crystallized in a monoclinic crystal system. The space groups $P2_1/c$ and $P2_1$, respectively, were identified on the basis of the systematic absences in the data. For both analyses all non-hydrogen atoms were refined with anisotropic thermal parameters. For compound 2 the positions of all hydrogen atoms were calculated by using idealized geometries. The position of the hydride ligand was calculated by using the energy minimization procedure in the program HYDEX.[6] For compound 3 the position of the hydride ligand was obtained from a difference Fourier map and it was refined using an isotropic thermal parameter. The positions of the hydrogen atoms on the H$_2$O ligand were obtained from a difference Fourier synthesis, but these could not be refined to a convergence and were included as fixed contributions after a partial refinement. The positions of all other hydrogen atoms were calculated using idealized geometries and were included as fixed contributions. Since compound 3 belongs to a chiral space group, the enantiomeric configuration of the crystal was tested at the end of the analysis by inverting the molecular configuration and refining again. This yielded substantially higher *R* factors (0.026 and 0.028), indicating

(5) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

(6) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

Table I. Crystal Data for Compounds 1–3

	1	2	3
formula	$Re_2SiO_{11}C_{11}H_{10}$	$Re_2PSiO_{10}C_{18}H_{21}$	$Re_2PSiO_{11}C_{18}H_{23}$
fw	718.69	828.83	846.85
crystal system	triclinic	monoclinic	monoclinic
lattice params			
a (Å)	9.766(2)	14.579(1)	10.347(2)
b (Å)	12.344(4)	7.832(2)	12.482(3)
c (Å)	8.741(2)	22.357(3)	11.026(2)
α (deg)	109.52(2)	90.0	90.0
β (deg)	110.97(2)	101.88(1)	109.52(1)
γ (deg)	79.54(2)	90.0	90.0
V (Å^3)	925(1)	2498(1)	1342.1(8)
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)
Z value	2	4	2
ρ_{calc} (g/cm^3)	2.58	2.20	2.10
μ(Mo Kα) (cm^{-1})	133.6	99.7	92.9
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	45.0	42.0	46.0
no. of observns ($I > 3\sigma$)	2103	2327	1822
abs cor	analytical	DIFABS	empirical
residuals: R, R_w	0.039, 0.049	0.035, 0.048	0.021, 0.022
goodness-of-fit indicator	2.50	2.24	1.11
max shift in final cycle	0.07	0.00	0.18
largest peak in final diff map (e/Å^3)	1.39	0.99	0.43
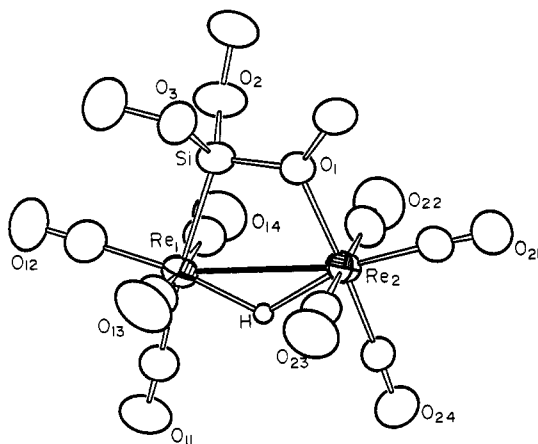
Figure 1. ORTEP diagram of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (1) showing 50% probability thermal ellipsoids.

that the first configuration was the correct one. The values published herein were derived from the first configuration.

Results and Discussion

From the reaction of $Re_2(CO)_8[\mu\text{-}C(H)C(H)Bu^n](\mu\text{-}H)$ with $HSi(OMe)_3$ in a heptane solution at 97 °C, we have obtained the new compound $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (1) in 51% yield. Compound 1 was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of 1 is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected intramolecular bond distances and angles are listed in Tables III and IV, respectively. The molecule contains two $Re(CO)_4$ groups joined by a Re–Re single bond that is bridged by a hydride ligand (located and refined in the analysis) and a η^2-$Si(OMe)_3$ grouping. The silicon atom is coordinated solely to Re(1); Re(1)–Si = 2.477(3) Å. The oxygen atom of one of the OMe groups is coordinated to Re(2); Re(2)–O(1) = 2.202(7) Å. The Re–Re bond is very long, 3.253(1) Å, due to the presence of the bridging hydride ligand; δ = –15.26 ppm.[7] The Re–Re distance in $Re_2(CO)_{10}$ is 3.041(1) Å.[8] As

(7) (a) Teller, R. G.; Bau, R. *Struct. Bonding* 1981, *44*, 1. (b) Churchill, M. R. In *Transition Metal Hydrides*; Bau, R., Ed.; Advances in Chemistry Series 167; American Chemical Society: Washington, DC, 1978.

Table II. Positional Parameters and B(eq) for $HRe_2(CO)_8[Si(\mu\text{-}OMe)(OMe)_2]$ (1)

atom	x	y	z	B(eq) (Å^2)
Re(1)	0.25905(05)	0.29584(05)	0.83194(06)	3.33(2)
Re(2)	0.13523(05)	0.20282(05)	0.41565(06)	3.31(2)
Si	0.4562(03)	0.2532(03)	0.6998(05)	3.4(1)
O(1)	0.3768(08)	0.1864(09)	0.4892(10)	4.2(4)
O(2)	0.5266(10)	0.3672(09)	0.7146(14)	5.3(4)
O(3)	0.5919(09)	0.1564(08)	0.7434(11)	4.4(4)
O(11)	–0.0028(11)	0.3556(11)	0.9763(15)	6.6(6)
O(12)	0.4823(12)	0.3570(12)	1.1953(14)	7.1(6)
O(13)	0.3160(14)	0.0395(10)	0.8285(17)	6.6(6)
O(14)	0.2422(14)	0.5470(10)	0.8154(17)	6.8(6)
O(21)	0.0874(11)	0.1079(10)	0.0305(14)	5.6(5)
O(22)	0.1350(15)	0.4541(11)	0.4001(17)	7.1(6)
O(23)	0.1307(13)	–0.0525(10)	0.4182(17)	6.2(6)
O(24)	–0.1974(10)	0.2291(10)	0.3376(13)	6.1(5)
C(1)	0.4555(15)	0.1314(15)	0.3680(19)	5.1(6)
C(2)	0.6459(17)	0.3770(16)	0.668(02)	6.0(8)
C(3)	0.6951(17)	0.1708(15)	0.911(02)	6.1(7)
C(11)	0.0904(14)	0.3313(13)	0.9201(17)	4.2(6)
C(12)	0.3998(16)	0.3347(13)	1.059(02)	4.9(6)
C(13)	0.2917(15)	0.1331(15)	0.8288(19)	4.5(7)
C(14)	0.2490(15)	0.4550(15)	0.8231(20)	4.8(7)
C(21)	0.1082(13)	0.1453(13)	0.1771(18)	4.0(6)
C(22)	0.1357(17)	0.3631(17)	0.4079(20)	5.2(7)
C(23)	0.1339(14)	0.0410(16)	0.4219(19)	4.8(7)
C(24)	–0.0737(13)	0.2203(14)	0.3637(16)	4.3(6)
H	0.108(14)	0.255(13)	0.633(17)	6(3)

Table III. Intramolecular Distances for 1[a]

Re(1)–Re(2)	3.253(1)	Re(2)–C(23)	2.02(2)
Re(1)–Si	2.477(3)	Re(2)–C(24)	1.91(1)
Re(1)–C(11)	1.98(1)	Re(2)–H	1.9(1)
Re(1)–C(12)	1.92(2)	Si–O(1)	1.692(9)
Re(1)–C(13)	1.97(2)	Si–O(2)	1.62(1)
Re(1)–C(14)	1.98(2)	Si–O(3)	1.64(1)
Re(1)–H	1.8(1)	O(1)–C(1)	1.44(2)
Re(2)–O(1)	2.202(7)	O(2)–C(2)	1.40(2)
Re(2)–C(21)	1.90(1)	O(3)–C(3)	1.42(2)
Re(2)–C(22)	2.00(2)	O–C(av)	1.14(2)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

observed for other bridging $Si(OMe)_3$ groups, the Si–O bond involving the coordinated oxygen atom, Si–O(1) = 1.692(9) Å, is slightly longer than those to the uncoordi-

(8) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* 1981, *20*, 1609.

Table IV. Intramolecular Bond Angles for 1[a]

Re(2)-Re(1)-Si	67.24(9)	O(1)-Re(2)-C(22)	89.5(5)
Re(2)-Re(1)-C(11)	108.6(4)	O(1)-Re(2)-C(23)	90.7(4)
Re(2)-Re(1)-C(12)	158.5(4)	O(1)-Re(2)-C(24)	177.1(4)
Re(2)-Re(1)-C(13)	86.9(4)	Re(1)-Si-O(1)	106.0(3)
Re(2)-Re(1)-C(14)	90.6(4)	Re(1)-Si-O(2)	113.8(4)
Si-Re(1)-C(11)	175.5(4)	Re(1)-Si-O(3)	120.9(4)
Si-Re(1Si-Re(1)-C(12)	91.5(4)	O(1)-Si-O(2)	107.9(5)
Si-Re(1)-C(13)	86.0(4)	O(1)-Si-O(3)	98.8(5)
Si-Re(1)-C(14)	86.3(4)	O(2)-Si-O(3)	107.8(5)
Re(1)-Re(2)-O(1)	73.3(2)	Re(2)-O(1)-Si	111.8(4)
Re(1)-Re(2)-C(21)	167.2(4)	Re(2)-O(1)-C(1)	123.2(7)
Re(1)-Re(2)-C(22)	89.0(4)	Si-O(1)-C(1)	124.8(7)
Re(1)-Re(2)-C(23)	91.3(4)	Si-O(2)-C(2)	130(1)
Re(1)-Re(2)-C(24)	103.8(4)	Si-O(3)-C(3)	122(1)
O(1)-Re(2)-C(21)	93.9(4)	Re-C-O(av)	178(1)

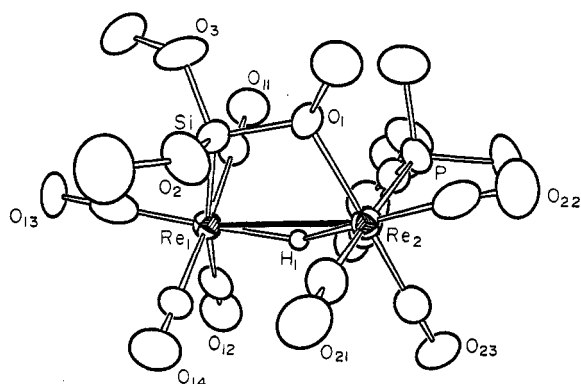[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Figure 2. ORTEP diagram of $Re_2(CO)_7(PMe_2Ph)[\mu-\eta^2-Si(OMe)_3](\mu$-H) (2) showing 50% probability thermal ellipsoids.

nated oxygen atoms, Si-O(2) = 1.62(1) Å and Si-O(3) = 1.64(1) Å.[1,2] The Si-Re(1)-Re(2)-O(1) ring is not exactly planar, but the dihedral angle between the Si-Re(1)-Re(2) and Re(1)-Re(2)-O(1) planes is only 6.9°. As expected, the resonances of the methyl groups appear as two singlets at 3.82 and 3.54 ppm in a 1 to 2 ratio at 27 °C; however at higher temperatures these resonances broaden and coalesce, T_c = 52 °C, as a result of a dynamical averaging process, ΔG^*_{325} = 15.5 kcal/mol. Similar averaging of the OR groups of bridging Si(OR)$_3$ ligands has been observed previously.[1,2]

When compound 1 was treated with Me$_3$NO in the presence of PMe$_2$Ph, the phosphine derivative of 1, $Re_2(CO)_7(PMe_2Ph)(\mu-\eta^2$-Si(OMe)$_3](\mu$-H) (2), was obtained in 25% yield. Compound 2 was also characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of 2 is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected intramolecular bond distances and angles are listed in Tables VI and VII, respectively. This complex is structurally similar to 1, except that it contains a phosphine ligand coordinated *cis* to the Re-Re bond to the rhenium atom that contains the oxygen atom of the bridging η^2-Si(OMe)$_3$ group. The Re-Re bond is also slightly longer than that in 1, 3.2984(8) Å. The bridging hydride ligand was not located in this analysis. Its position was calculated using the energy minimization program HYDEX. The ^{1}H NMR shift of the hydride ligand is similar to that found in 1 with the addition of coupling to the phosphorus atom, δ = -14.10 (d, $^2J_{P-H}$ = 14.5 Hz). The rhenium-silicon bond is identical in length to that in 1, Re(1)-Si = 2.477(4) Å. The rhenium-oxygen bond distance to the coordinated OMe group is

Table V. Positional Parameters and B(eq) for 2

atom	x	y	z	B(eq) (Å²)
Re(1)	0.62759(4)	0.00946(7)	0.36162(3)	2.28(3)
Re(2)	0.84956(4)	0.12009(8)	0.40559(3)	2.52(3)
P	0.8723(3)	0.2254(5)	0.3056(2)	3.3(2)
Si	0.6532(2)	0.2832(5)	0.4181(2)	2.6(2)
O(1)	0.7619(6)	0.349(1)	0.4125(4)	2.8(4)
O(2)	0.6634(8)	0.284(2)	0.4922(5)	4.7(5)
O(3)	0.5902(8)	0.451(1)	0.3943(6)	5.3(6)
O(11)	0.6100(8)	0.247(2)	0.2489(5)	5.1(6)
O(12)	0.6198(8)	-0.315(2)	0.2802(6)	5.3(6)
O(13)	0.4138(6)	0.021(2)	0.3546(5)	4.5(6)
O(14)	0.6463(8)	-0.179(2)	0.4857(6)	5.7(6)
O(21)	0.8380(9)	0.006(2)	0.5353(6)	6.1(7)
O(22)	1.0318(8)	0.303(2)	0.4626(6)	6.3(7)
O(23)	0.9631(8)	-0.197(2)	0.3888(6)	5.5(6)
C(1)	0.799(1)	0.505(2)	0.4423(9)	5.1(9)
C(2)	0.590(2)	0.259(4)	0.521(1)	8(1)
C(3)	0.499(1)	0.461(2)	0.3658(9)	5(1)
C(11)	0.616(1)	0.159(2)	0.2895(6)	2.8(6)
C(12)	0.624(1)	-0.196(2)	0.3128(7)	3.3(7)
C(13)	0.499(1)	0.018(2)	0.3595(6)	3.9(8)
C(14)	0.640(1)	-0.113(2)	0.4406(8)	3.2(7)
C(21)	0.839(1)	0.050(2)	0.4869(7)	3.6(7)
C(22)	0.960(1)	0.238(2)	0.4404(8)	4.6(9)
C(23)	0.921(1)	-0.079(2)	0.3956(7)	3.7(8)
C(51)	0.994(1)	0.240(3)	0.3032(9)	6(1)
C(52)	0.832(1)	0.443(2)	0.2890(8)	5.5(9)
C(53)	0.826(1)	0.106(2)	0.2352(7)	3.6(7)
C(54)	0.797(1)	-0.063(2)	0.2376(7)	3.4(7)
C(55)	0.765(1)	-0.152(2)	0.1845(8)	4.7(8)
C(56)	0.763(1)	-0.076(3)	0.1291(9)	6(1)
C(57)	0.797(2)	0.078(4)	0.1265(9)	8(1)
C(58)	0.826(2)	0.177(3)	0.178(1)	7(1)

Table VI. Intramolecular Distances for 2[a]

Re(1)-Re(2)	3.2984(8)	P-C(51)	1.79(2)
Re(1)-Si	2.477(4)	P-C(52)	1.81(2)
Re(1)-C(11)	1.97(2)	P-C(53)	1.84(2)
Re(1)-C(12)	1.94(2)	Si-O(1)	1.70(1)
Re(1)-C(13)	1.86(2)	Si-O(2)	1.63(1)
Re(1)-C(14)	1.99(2)	Si-O(3)	1.63(1)
Re(2)-P	2.469(4)	O(1)-C(1)	1.44(2)
Re(2)-O(1)	2.225(9)	O(2)-C(2)	1.37(2)
Re(2)-C(21)	1.94(2)	O(3)-C(3)	1.36(2)
Re(2)-C(22)	1.89(2)	O-C(av)	1.16(2)
Re(2)-C(23)	1.91(2)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table VII. Intramolecular Bond Angles for 2[a]

Re(2)-Re(1)-Si	65.50(8)	P-Re(2)-C(23)	89.3(5)
Re(2)-Re(1)-C(11)	90.2(4)	O(1)-Re(2)-C(21)	90.4(6)
Re(2)-Re(1)-C(12)	107.4(4)	O(1)-Re(2)-C(22)	91.9(5)
Re(2)-Re(1)-C(13)	156.4(4)	O(1)-Re(2)-C(23)	177.1(5)
Re(2)-Re(1)-C(14)	87.5(4)	Re(1)-Si-O(1)	105.6(4)
Si-Re(1)-C(11)	83.2(4)	Re(1)-Si-O(2)	119.5(5)
Si-Re(1)-C(12)	171.6(4)	Re(1)-Si-O(3)	121.0(4)
Si-Re(1)-C(13)	91.5(5)	O(1)-Si-O(2)	100.5(5)
Si-Re(1)-C(14)	89.4(5)	O(1)-Si-O(3)	101.8(6)
Re(1)-Re(2)-P	97.16(9)	O(2)-Si-O(3)	105.0(7)
Re(1)-Re(2)-O(1)	71.9(2)	Re(2)-O(1)-Si	108.7(5)
Re(1)-Re(2)-C(21)	86.8(4)	Re(2)-O(1)-C(1)	123.0(8)
Re(1)-Re(2)-C(22)	163.1(5)	Si-O(1)-C(1)	120(1)
Re(1)-Re(2)-C(23)	106.1(5)	Si-O(2)-C(2)	124(1)
P-Re(2)-O(1)	88.9(3)	Si-O(3)-C(3)	129(1)
P-Re(2)-C(21)	175.5(5)	Re-C-O(av)	177(1)
P-Re(2)-C(22)	86.9(5)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

not significantly longer that that in 1, Re(2)-O(1) = 2.225(9) Å. As in 1, the Si-O bond distance involving the coordinated oxygen atom, Si-O(1) = 1.696(9) Å, is again significantly longer than those to the uncoordinated oxygen atoms, Si-O(2) = 1.63(1) Å and Si-O(3) = 1.63(1) Å.[1,2]
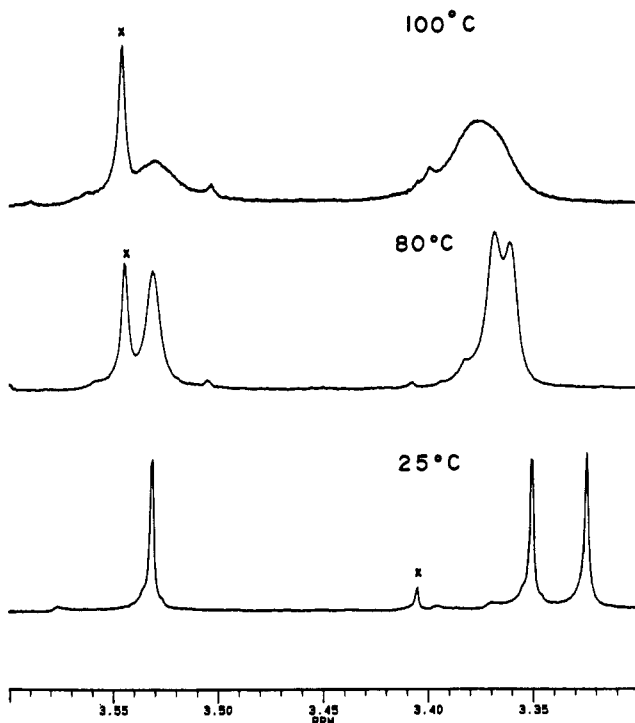
Figure 3. ^{1}H NMR spectra of the three OMe resonances of compound **2** recorded at three different temperatures in toluene-d_8 solvent. The resonance labeled X at approximately 3.55 ppm is for an unidentified decomposition product that was formed when the sample was heated.

The resonances of the methyl groups appear as three singlets at 3.64, 3.58, and 3.41 ppm in a 1:1:1 ratio at 27 °C, and the phosphine methyl groups are inequivalent, 1.92 and 1.91 ppm as expected. As in **1**, the OMe resonances broaden at higher temperatures due to dynamical averaging process, but the coalesence temperature was not yet reached at 110 °C, the highest temperature that could be measured (see Figure 3), and at 100 °C compound **2** was decomposing at a significant rate. We can estimate that the free energy of activation for the OMe averaging in **2** is greater than 18.0 kcal/mol, which would make it at least 2.5 kcal/mol higher than that in **1**. This could be due to a slightly stronger Re–O bond to the OMe group, but this was not confirmed by the structural analysis since the Re–O bond in **2** is not significantly longer than that in **1**. The resonances of the methyl groups on the phosphine ligand were transformed to a single resonance (a doublet), but the transformation was not a process of broadening and coalescence. Instead, the two doublets shifted toward one another and superimposed at 100 °C. These changes are not indicative of a dynamical averaging process, but they also do not rule out that one is occurring.

Compound **2** was found to add 1 equiv of H_2O at 25 °C to yield the adduct $Re_2(CO)_7(PMe_2Ph)[Si(OMe)_3](H_2O)(\mu$-H) (**3**). Although the yield appeared to be quantitative when the reaction was followed by ^{1}H NMR spectroscopy, significant amounts of **2** were recovered after treatment by TLC. It was subsequently found that the addition is reversible and **2** can be regenerated quantitatively if all H_2O is removed from the environment. This was proven by adding the drying agent $CaSO_4$ to a sample of **3** in an NMR tube and observing the regeneration of **2** by ^{1}H NMR spectroscopy over a period of approximately 24 h. Compound **3** was characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram
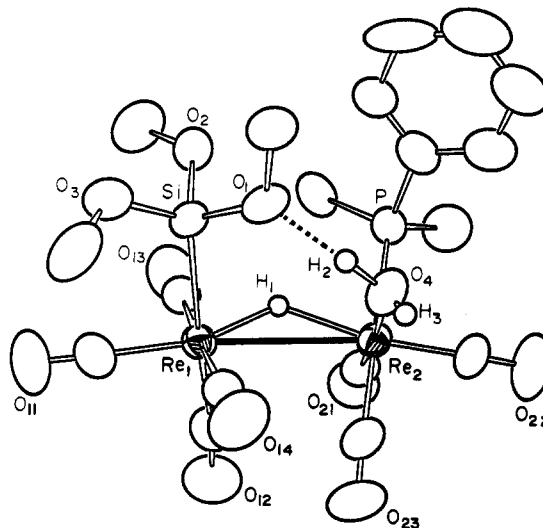

Figure 4. ORTEP diagram of $Re_2(CO)_7(PMe_2Ph)[Si(OMe)_3](H_2O)(\mu$-H) (**3**) showing 50% probability thermal ellipsoids.

Table VIII. Positional Parameters and B(eq) for 3

atom	x	y	z	B(eq) ($Å^2$)
Re(1)	0.02067(5)	0.0947	0.33410(5)	3.22(2)
Re(2)	0.25323(5)	0.27224(5)	0.32029(4)	3.22(2)
P	0.4323(4)	0.1557(3)	0.2900(3)	3.9(1)
Si	0.0168(4)	−0.0032(3)	0.1351(3)	3.5(1)
O(1)	0.0414(8)	0.0827(7)	0.0283(7)	4.3(4)
O(2)	0.1332(8)	−0.0928(7)	0.1431(8)	4.4(4)
O(3)	−0.1254(8)	−0.0682(8)	0.0539(8)	4.8(4)
O(4)	0.1480(9)	0.2690(8)	0.1118(7)	4.4(3)
O(11)	−0.222(1)	−0.043(1)	0.339(1)	7.3(6)
O(12)	0.026(1)	0.221(1)	0.580(1)	9.3(7)
O(13)	0.220(1)	−0.074(1)	0.508(1)	7.5(5)
O(14)	−0.171(1)	0.2602(9)	0.148(1)	6.6(5)
O(21)	0.403(1)	0.257(1)	0.6084(8)	7.0(5)
O(22)	0.430(1)	0.468(1)	0.315(1)	7.8(6)
O(23)	0.040(1)	0.4224(9)	0.371(1)	6.6(6)
C(1)	0.031(2)	0.047(1)	−0.101(1)	5.3(6)
C(2)	0.139(2)	−0.198(1)	0.194(1)	6.6(8)
C(3)	−0.256(2)	−0.021(1)	0.020(2)	7.7(9)
C(11)	−0.132(1)	0.010(1)	0.338(1)	5.0(7)
C(12)	0.031(2)	0.177(1)	0.489(1)	5.4(7)
C(13)	0.150(1)	−0.014(1)	0.443(1)	4.3(6)
C(14)	−0.100(1)	0.200(1)	0.218(1)	4.5(6)
C(21)	0.346(1)	0.261(1)	0.500(1)	4.3(6)
C(22)	0.363(1)	0.393(1)	0.317(1)	4.3(6)
C(23)	0.117(1)	0.365(1)	0.350(1)	4.4(6)
C(51)	0.442(1)	0.020(1)	0.355(1)	5.0(6)
C(52)	0.605(2)	0.205(1)	0.374(2)	8(1)
C(53)	0.430(1)	0.135(1)	0.128(1)	4.7(6)
C(54)	0.387(2)	0.043(1)	0.058(2)	5.7(8)
C(55)	0.385(2)	0.033(2)	−0.067(2)	8(1)
C(56)	0.417(2)	0.120(2)	−0.130(2)	9(1)
C(57)	0.459(3)	0.210(2)	−0.065(2)	10(1)
C(58)	0.465(2)	0.220(1)	0.062(2)	7(1)
H(1)	0.17(1)	0.154(9)	0.31(1)	4.0(5)

of the molecular structure of **3** is shown in Figure 4. Final atomic positional parameters are listed in Table VIII. Selected intramolecular bond distances and angles are listed in Tables IX and X, respectively. This molecule contains two rhenium atoms joined by a hydride-bridged Re–Re single bond, Re(1)–Re(2) = 3.3123(8) Å. The hydride ligand was located and refined; δ = −12.14 ppm ($^2J_{P-H}$ = 19.1 Hz). The Si(OMe)$_3$ ligand is not a bridge as in **1** and **2**, because none of the oxygen atoms of the OMe groups are coordinated. The Si(OMe)$_3$ ligand is coordinated solely to atom Re(1); Re(1)–Si = 2.499(3) Å. The H_2O ligand is coordinated *cis* to the Re–Re bond and *cis* to the phosphine on Re(2). The Re(2)–O(4) distance at

Table IX. Intramolecular Distances for 3[a]

Re(1)–Re(2)	3.3123(8)	Re(2)–H(1)	1.7(1)
Re(1)–Si	2.499(3)	P–C(51)	1.82(1)
Re(1)–C(11)	1.91(2)	P–C(52)	1.82(2)
Re(1)–C(12)	1.96(2)	P–C(53)	1.80(1)
Re(1)–C(13)	2.00(1)	Si–O(1)	1.674(9)
Re(1)–C(14)	1.96(1)	Si–O(2)	1.625(9)
Re(1)–H(1)	1.8(1)	Si–O(3)	1.657(9)
Re(2)–P	2.464(4)	O(1)–C(1)	1.46(1)
Re(2)–O(4)	2.191(7)	O(2)–C(2)	1.42(2)
Re(2)–C(21)	1.89(1)	O(3)–C(3)	1.41(2)
Re(2)–C(22)	1.89(1)	O–C(av)	1.15(2)
Re(2)–C(23)	1.94(2)	O(1)–O(4)	2.61(1)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table X. Intramolecular Bond Angles for 3[a]

Re(2)–Re(1)–Si	94.90(8)	P–Re(2)–O(4)	88.8(3)
Re(2)–Re(1)–C(11)	171.6(5)	O(4)–Re(2)–C(21)	174.8(6)
Re(2)–Re(1)–C(12)	82.1(4)	O(4)–Re(2)–C(22)	94.8(5)
Re(2)–Re(1)–C(13)	97.7(4)	O(4)–Re(2)–C(23)	93.0(5)
Re(2)–Re(1)–C(14)	80.6(4)	Re(1)–Si–O(1)	110.1(3)
Si–Re(1)–C(11)	88.6(5)	Re(1)–Si–O(2)	119.7(4)
Si–Re(1)–C(12)	177.0(4)	Re(1)–Si–O(3)	117.7(3)
Si–Re(1)–C(13)	90.5(4)	O(1)–Si–O(2)	101.2(4)
Si–Re(1)–C(14)	86.3(4)	O(1)–Si–O(3)	104.5(5)
Re(1)–Re(2)–P	101.65(9)	O(2)–Si–O(3)	101.5(5)
Re(1)–Re(2)–O(4)	85.5(2)	Si–O(1)–C(1)	120.5(8)
Re(1)–Re(2)–C(21)	91.6(4)	Si–O(2)–C(2)	126(1)
Re(1)–Re(2)–C(22)	169.4(4)	Si–O(3)–C(3)	122.5(9)
Re(1)–Re(2)–C(23)	79.1(4)	Re–C–O(av)	178(1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

2.191(7) Å is very similar to the Re–O distances found to the bridging oxygen atoms in compounds 1 and 2 and is much shorter than Re–O distances to water ligands in multiply bonded dirhenium complexes where the water ligand is coordinated *trans* to the metal–metal bond (e.g.: $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$, 2.411(4) Å;[9] $Cs_2Re_2Cl_8(H_2O)_2$, 2.66(3) Å;[10] $Re_2(O_2CMe)_2Cl_4(H_2O)_2$, 2.50(2) Å;[11] Na_2-$Re_2(SO_4)_4(H_2O)_2 \cdot 6H_2O$, 2.28(1) Å[12]). A slightly broadened resonance at 6.52 ppm is believed to be due to the hydrogen atoms of the H_2O ligand. NMR samples of 3 contained small amounts of free H_2O, and separate resonances were observed for both the free and coordinated H_2O, indicating that there was no rapid exchange between free and coordinated H_2O on the NMR time scale at 25 °C. Interestingly, one of the OMe groups is positioned close to the H_2O ligand, O(1)···O(4) = 2.61(1) Å. This distance is short enough to suggest the existence of a significant hydrogen-bonding interaction between these atoms.[13] The two hydrogen atoms on the H_2O ligand were located in a difference Fourier synthesis but could not be refined. They are shown in the figure where they were found. Indeed, one of the hydrogen atoms is positioned between the two
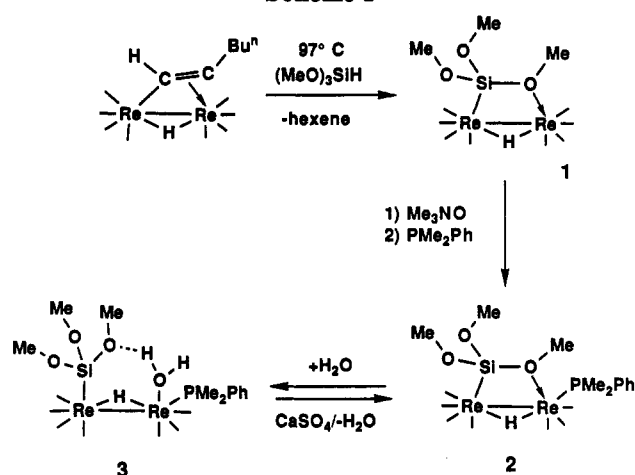
oxygen atoms in a manner consistent with the existence of a hydrogen-bonding interaction, O(1)···H(2) = 1.66 Å. The OMe groups, however, appear as a single resonance at 25 °C at 3.47 ppm due to a rapid exchange of the three groups with the site of hydrogen bonding. An effort was made to observe a slow exchange by recording the spectrum at low temperature, but even at –90 °C in acetone solvent there was no evidence for slow exchange on the NMR time scale. Efforts to prepare an H_2O adduct of 1 by the addition of H_2O were not successful.

A summary of the results of this study are shown in Scheme I. The complex $Re_2(CO)_8[\mu$-C(H)C(H)Bu^n]$(\mu$-H) eliminated its butenyl group and hydride ligand, presumably as hexene, upon reaction with $(MeO)_3SiH$ to yield complex 1 by the activation of the Si–H bond. The loss of the butenyl group and hydride ligand resulted in the loss of four valence electrons from the complex, but the addition of the Si–H bond provided only two. Thus, the oxygen atom of one of OMe groups became coordinated. This resulted in the formation of the bridging η^2-Si(OMe)_3 ligand which serves as a three-electron donor and both rhenium atoms achieve 18-electron configurations. Compound 2 was prepared by treatment of 1 with Me_3NO in the presence of PMe_2Ph. It is structurally similar to 1 and contains a bridging η^2-Si(OMe)_3 ligand. Interestingly, compound 2 added H_2O, reversibly, under very mild conditions to break the bridge of the η^2-Si(OMe)_3 ligand by cleavage of the Re–O bond to yield compound 3. It was found that one of the hydrogen atoms of the H_2O ligand in compound 3 was hydrogen bonded to the oxygen atom of one of the OMe groups.

Scheme I

Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for all of the structural analyses (9 pages). Ordering information is given on any current masthead page.

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(9) Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1991**, *30*, 3971.

(10) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1977**, *16*, 1867.

(11) Koz'min, P. A.; Surazhskaya, M. D.; Kuznetsov, V. G. *Zh. Strukt. Khim.* **1970**, *11*, 313.

(12) Cotton, F. A.; Frenz, B. A.; Shive, L. *Inorg. Chem.* **1975**, *14*, 649.

(13) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 90–96.