Organometallics **2005,** *24,* 4489−4493

Rhenium Carbonyl Complexes Containing Bridging SiPh$_3$ and SiPh$_2$ Ligands

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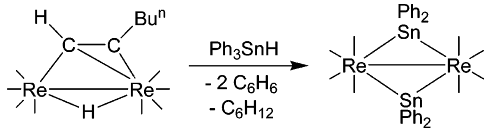
Received May 30, 2005

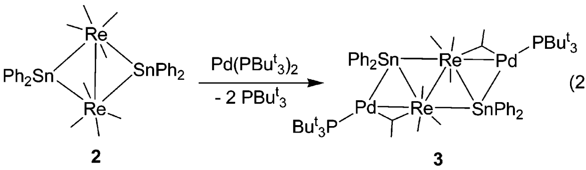
The reaction of Re$_2$(CO)$_8$[μ-C(H)C(H)Bu^n](μ-H) (**1**) with Ph$_3$SiH at 97 °C has yielded the three new compounds Re(CO)$_5$(SiPh$_3$) (**5**), Re$_2$(CO)$_6$(μ-η^7-SiPh$_3$)(μ-H) (**6**), and Re$_2$(CO)$_8$(μ-SiPh$_2$)(SiPh$_3$)(μ-H) (**7**) in 13, 10, and 30% yields, respectively. Compound **5** consists of a single rhenium atom with five carbonyl ligands and a terminal SiPh$_3$ ligand. Compound **6** contains two rhenium atoms with a bridging SiPh$_3$ ligand in which the silicon atom is bonded to one rhenium atom and one phenyl ring is η^6-coordinated to the other rhenium atom. A hydrido ligand bridges the Re−Re bond. Compound **7** contains a Re$_2$(CO)$_8$ group with one bridging SiPh$_2$ ligand and one terminal SiPh$_3$ ligand. A hydrido ligand bridges one of the Re−Si bonds of the bridging SiPh$_2$ ligand. The reaction of **1** with Ph$_3$SiH at 125 °C yielded **5** and **6** and a new product, Re$_2$(CO)$_8$(μ-SiPh$_2$)$_2$ (**8**), which contains two bridging SiPh$_2$ ligands, one on each side of the Re−Re single bond. Compound **7** is a precursor to **8**. Compound **7** was converted into **8** at 125 °C via the elimination of benzene. All four new compounds were characterized by IR and ^{1}H NMR spectroscopy and by single-crystal X-ray diffraction analysis.

Introduction

In recent studies we have found that the complex Re$_2$(CO)$_8$[μ-C(H)C(H)Bu^n](μ-H) (**1**) reacts with Ph$_3$SnH to yield the complex Re$_2$(CO)$_8$(μ-SnPh$_2$)$_2$ (**2**), which contains two Re(CO)$_4$ groups linked by two bridging SnPh$_2$ ligands and an unusually long Re−Re bond; see eq 1.[1] Palladium tri-*tert*-butylphosphine groups can be added to two of the four Re−Sn bonds in **2** to yield the bis-Pd(PBu$^t_3$) adduct, Re$_2$(CO)$_8$(μ-SnPh$_2$)$_2$[Pd(PBu$^t_3$)]$_2$ (**3**), see eq 2.

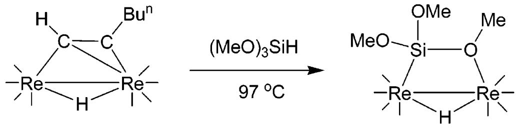


1 **2** (1)



2 **3** (2)

A few years ago, we reported that **1** reacts with HSi(OMe)$_3$ at 97 °C to give the compound Re$_2$(CO)$_8$[μ-η^3-Si(OMe)$_3$](μ-H) (**4**), containing a bridging trimethoxysilyl ligand; see eq 3.[2] As a result, we decided to investigate the reaction of **1** with Ph$_3$SiH.



1 **4** (3)

The activation of Si−H bonds by metal atoms is central to the catalytic processes known as hydrosilylation.[3] Polynuclear metal complexes themselves have shown potential for serving as hydrosilylation catalysts.[4] Consequently, the synthesis and characterization of metal complexes containing silicon is key to understanding the mechanism of these catalytic processes. Metal-silyl and -siloxyl complexes have been reported for almost every transition metal.[5]

We have obtained four new complexes containing rhenium−silicon bonds—Re(CO)$_5$(SiPh$_3$) (**5**), Re$_2$(CO)$_6$-

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10.1021/om0504304 CCC: $30.25

(μ-η^7-$SiPh_3$)(μ-H) (**6**), $Re_2(CO)_8$(μ-$SiPh_2$)($SiPh_3$)(μ-H) (**7**), and $Re_2(CO)_8$(μ-$SiPh_2$)$_2$ (**8**)—from the reaction of **1** with Ph_3SiH. Each of the products was characterized structurally by a single-crystal X-ray diffraction analysis. These results are reported herein.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo-Nicolet Avatar 360 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded at room temperature on a Varian Mercury spectrometer operating at 300.1 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates. $Re_2(CO)_{10}$ was obtained from Strem Chemicals, Inc. Ph_3SiH was purchased from Aldrich and used as received. $Re_2(CO)_8$[μ-C(H)C(H)Bu^n](μ-H) (**1**) was prepared by a previously reported procedure.[6]

Reaction of 1 with Ph_3SiH at 97 °C. Ph_3SiH (144 mg, 0.55 mmol) was added to a solution of **1** (75 mg, 0.11 mmol) in 30 mL of heptane. The reaction mixture was heated to reflux for 5 h. After cooling, the solvent was removed in vacuo. The products were separated by TLC using a 3:1 hexane/CH_2Cl_2 solvent mixture to yield, in order of elution, 8.6 mg (13% yield) of colorless $Re(CO)_5(SiPh_3)$ (**5**), 33.9 mg (30% yield) of colorless $Re_2(CO)_8$(μ-$SiPh_2$)($SiPh_3$)(μ-H) (**7**), and 8.4 mg (10% yield) of $Re_2(CO)_6$(μ-η^7-$SiPh_3$)(μ-H) (**6**). Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane): 2118 (w), 2012 (s), 2002 (m). ^{1}H NMR (CD_2Cl_2 in ppm): δ 7.51 (m, 6 H, Ph), 7.32 (m, 9 H, Ph). Anal. Calc: 47.17 C, 2.58 H. Found: 47.08 C, 2.83 H. Spectral data for **6**: IR ν_{CO} (cm^{-1} in hexane): 2078 (m), 1999 (s), 1990 (m), 1979 (s), 1947 (m). ^{1}H NMR (CD_2Cl_2 in ppm): δ 7.78 (m, 4 H, Ph), 7.38 (m, 6 H, Ph), 6.01 (t, 2 H, Ph), 5.71 (t, 1 H, Ph), 5.28 (d, 2 H, Ph), −18.45 (s, 1 H, μ-H). MS (*e/z*): 800 (M^+), 772 (M − CO), 744 (M − 2CO), 716 (M − 3CO), 688 (M − 4CO), 660 (M − 5CO), 632 (M − 6CO), 554 (M − 6CO − Ph). Anal. Calc: 35.99 C, 2.01 H. Found: 36.39 C, 2.30 H. Spectral data for **7**: IR ν_{CO} (cm^{-1} in hexane): 2106 (m), 2062 (w), 2024 (m), 2012 (vs), 2005 (w), 1991 (m), 1973 (m). ^{1}H NMR (CD_2Cl_2 in ppm): δ 7.60 (m, 6 H, Ph), 7.47 (m, 4 H, Ph), 7.36 (m, 15 H, Ph), −9.43 (s, 1 H, μ-H, $^1J_{Si-H}$ = 44 Hz). Anal. Calc: 43.92 C, 2.52 H. Found: 43.75 C, 2.71 H.

Reaction of 1 with Ph_3SiH at 125 °C. Ph_3SiH (144 mg, 0.55 mmol) was added to a solution of **1** (75 mg, 0.11 mmol) in 30 mL of octane. The reaction mixture was heated to reflux for 12 h. Upon cooling to room temperature, a yellow precipitate formed, which was collected by filtration and recrystallized from hexane/CH_2Cl_2 to give 46.5 mg (44% yield) of $Re_2(CO)_8$(μ-$SiPh_2$)$_2$ (**8**). The mother liquor was dried in vacuo and separated by TLC using a 3:1 hexane/CH_2Cl_2 solvent mixture to yield, in order of elution, 15.8 mg (25% yield) of **5** and 4.9 mg (6% yield) of **6**. No **7** was obtained. Spectral data for **8**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2068 (m), 2010 (s), 1985 (m). ^{1}H NMR (CD_2Cl_2 in ppm): δ 7.67 (m, 8 H, Ph), 7.40 (m, 12 H, Ph). Anal. Calc: 39.99 C, 2.10 H. Found: 39.60 C, 2.02 H.

Conversion of 7 to 8. A solution of **7** (6.1 mg, 0.0059 mmol) in 10 mL of octane was heated to reflux for 8 h. Workup as described above provided 4.7 mg (84% yield) of **8**.

Crystallographic Analyses. Colorless crystals of **5** and **7** suitable for X-ray diffraction analyses were grown by slow evaporation of a hexane/CH_2Cl_2 solvent mixture at 5 °C. Yellow crystals of **6** and **8** were grown from benzene/octane at 5 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program[7] by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[8] All non-hydrogen atoms in the main residue were refined with anisotropic thermal parameters. All phenyl hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. The hydrido ligands were located and structurally refined. Crystal data, data collection parameters, and results of the analyses are listed in Tables 1 and 2.

Table 1. Crystallographic Data for Compounds 5 and 6

	5	**6**
empirical formula	$ReSiO_5C_{23}H_{15}$	$Re_2SiO_6C_{24}H_{16}\cdot C_6H_6$
fw	585.64	878.97
cryst syst	triclinic	orthorhombic
lattice params		
a (Å)	11.0932(12)	9.7639(4)
b (Å)	12.4543(13)	16.9418(7)
c (Å)	16.1824(17)	17.9854(8)
α (deg)	86.041(2)	90
β (deg)	80.139(2)	90
γ (deg)	89.981(2)	90
V (Å^3)	2197.3(4)	2975.1(2)
space group	$P\bar{1}$	$P2_12_12_1$
Z-value	4	4
ρ_{calc} (g cm^{-3})	1.770	1.962
μ(Mo Kα) (mm^{-1})	5.615	8.210
temperature (K)	296(2)	296(2)
$2\theta_{max}$ (deg)	50.06	50.04
no. of observations	6817	5100
no. of params	541	356
goodness of fit	1.082	1.054
max. shift in cycle	0.006	0.003
residuals:[a] R_1; wR_2 ($I > 2\sigma(I)$)	0.0625; 0.1795	0.0179; 0.0445
abs corr	SADABS	SADABS
max./min.	1.000/0.533	0.194/0.076
largest peak (e Å^{-3})	5.228	0.784

[a] $R_1 = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $wR_2 = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF^2_{obs}]^{1/2}$; $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Compound **5** 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. Compound **6** crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was identified uniquely on the basis of the systematic absences in the intensity data. One molecule of benzene cocrystallized with the complex and was successfully located and refined with anisotropic thermal parameters with 8 geometric restraints. Compounds **7** and **8** crystallized in the monoclinic crystal system. For **7** the space group $P2_1/c$ was identified uniquely on the basis of the systematic absences in the intensity data. For **8** the space groups *C*2, *Cm*, and *C*2/*m* were indicated by the systematic absences in the data. The last space group was selected initially and confirmed by the successful solution and refinement of the structure.

Results and Discussion

The reaction of **1** with Ph_3SiH at 97 °C yielded three new Re−Si complexes, $Re(CO)_5(SiPh_3)$ (**5**), $Re_2(CO)_6$(μ-

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Table 2. Crystallographic Data for Compounds 7 and 8

	7	**8**
empirical formula	$Re_2Si_2O_8C_{38}H_{26}$	$Re_2Si_2O_8C_{32}H_{20}$
fw	1039.17	961.06
cryst syst	monoclinic	monoclinic
lattice parameters		
a (Å)	13.6837(6)	14.0667(11)
b (Å)	10.6083(5)	10.6056(8)
c (Å)	24.8274(11)	12.0970(10)
α (deg)	90	90
β (deg)	93.638(1)	117.384(1)
γ (deg)	90	90
V (Å^3)	3596.7(3)	1602.5(2)
space group	$P2_1/c$	$C2/m$
Z-value	4	2
ρ_{calc} (g cm^{-3})	1.919	1.992
μ(Mo Kα) (mm^{-1})	6.843	7.671
temperature (K)	296(2)	296(2)
$2\theta_{max}$ (deg)	50.06	50.04
no. of observations	5674	1464
no. of params	455	124
goodness of fit	1.04	1.078
max. shift in cycle	0.002	0.001
residuals:[a] R_1; wR_2 ($I > 2\sigma(I)$)	0.0207; 0.0478	0.0132; 0.0328
abs corr	SADABS	SADABS
max./min.	0.710/0.452	0.541/0.434
largest peak (e Å^{-3})	0.861	0.356

[a] $R_1 = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $wR_2 = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF^2_{obs}]^{1/2}$; $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

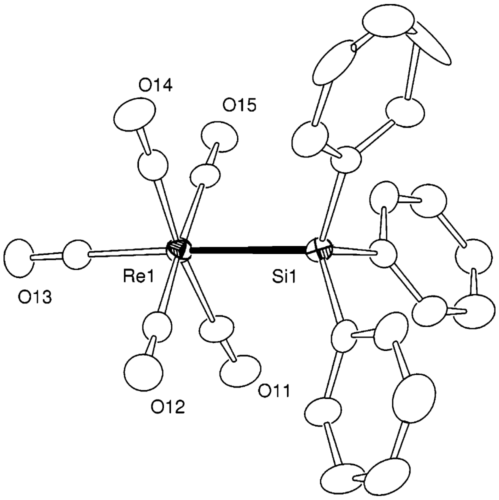


Figure 1. ORTEP diagram of the molecular structure of $Re(CO)_5(SiPh_3)$ (**5**) showing 40% thermal ellipsoid probability. Re(1)−Si(1) = 2.617(4) Å.

η^7-$SiPh_3$)(μ-H) (**6**), and $Re_2(CO)_8(\mu\text{-}SiPh_2)(SiPh_3)(\mu\text{-}H)$ (**7**), in 13, 10, and 30% yields, respectively. All compounds were characterized by IR, ^{1}H NMR, elemental, and single-crystal X-ray diffraction analyses. Compound **5** contains a single rhenium atom with five carbonyl ligands and one terminally coordinated $SiPh_3$ ligand. An ORTEP diagram of the molecular structure of **5** is shown in Figure 1. The molecule has no unusual or unexpected bond distances or angles. The Re−Si distance [2.617(4) Å] is similar to that found in the related compound $Re(CO)_5SiMe_3$ [Re−Si = 2.600(1) Å].[9]

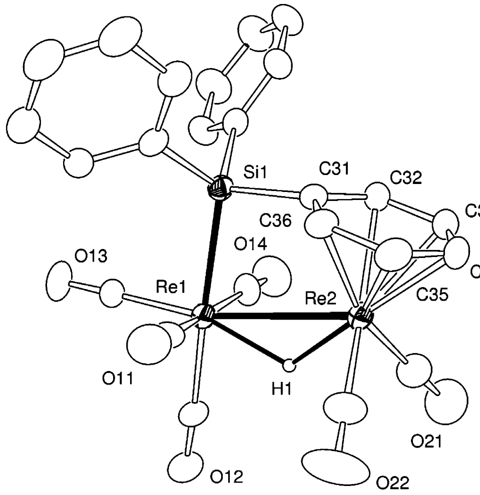
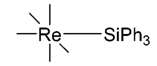


Figure 2. ORTEP diagram of the molecular structure of $Re_2(CO)_6(\mu\text{-}\eta^7\text{-}SiPh_3)(\mu\text{-}H)$ (**6**) showing 40% thermal ellipsoid probability. Selected intramolecular distances (Å) and angles (deg): Re(1)−Re(2) = 3.2192(2), Re(1)−Si(1) = 2.5175(11), Si(1)−C(31) = 1.905(4), Re(1)−H(1) = 1.894(10), Re(2)−H(1) = 1.897(10), Re(2)−Re(1)−Si(1) = 74.91(2).

An ORTEP diagram of the molecular structure of **6** is given in Figure 2. This compound contains a bridging η^7-$SiPh_3$ ligand where the silicon atom is η^1-coordinated to one rhenium atom and one of the phenyl groups is η^6-coordinated to the other rhenium atom. This type of coordination is very rare, but one example was observed previously in the compound $Cp^*FeCr(CO)_3(\mu\text{-}SiMe_2)(\mu\text{-}\eta^7\text{-}SiPhMe_2)$.[10] The two rhenium atoms are linked by a long Re−Re single bond [3.2712(2) Å]. The unusual length of the Re−Re bond may be due to the presence of a bridging hydride ligand that was located and refined [Re(1)−H(1) = 1.894(10) Å, Re(2)−H(1) = 1.897(10) Å, $\delta = -18.45$]. The Re−Re distance in $Re_2(CO)_{10}$ is 3.042(1) Å.[11] The Re−Si distance [2.5175(11) Å] in **6** is quite short in comparison to that observed for **5** and may be related to the coordination of one of the phenyl rings to the neighboring rhenium atom.



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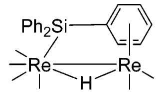

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An ORTEP diagram of the molecular structure of compound **7** is shown in Figure 3. Selected intramolecular bond distances and angles are listed in Table 3. The structure of **7** consists of a central $Re_2(CO)_8$ group containing a $SiPh_2$ ligand that bridges the Re−Re bond and a terminal $SiPh_3$ ligand that is bonded solely to Re(2). As in **6**, the Re−Re bond in **7** is also quite long [3.1486(2) Å]. The hydrido ligand H(1) was located crystallographically and was actually found to bridge the Re(1)−Si(1) bond, although it seems to be more strongly bonded to the rhenium atom than to the silicon atom [Re(1)−H(1) = 1.67(4) Å; Si(1)−H(1) = 1.73(4) Å]. The resonance for this ligand was observed in the ^{1}H NMR spectrum of **7** at −9.43 ppm. The existence of a significant Si−H interaction was confirmed by large coupling between the silicon atom, ^{29}Si, and hydrogen

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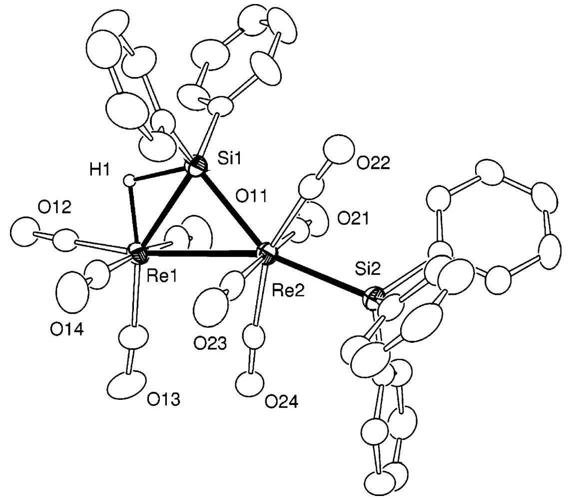


Figure 3. ORTEP diagram of the molecular structure of $Re_2(CO)_8(SiPh_3)(\mu\text{-}SiPh_2)(\mu\text{-}H)$ (**7**) showing 40% thermal ellipsoid probability.

Table 3. Selected Intramolecular Distances and Angles for Compounds 7 and 8[a]

compound **7**		compound **8**	
	Bond Distances (Å)		
Re(1)−Re(2)	3.1486(2)	Re(1)−Si(1)	2.5633(8)
Re(1)−Si(1)	2.5792(9)	Re(1)−Re(1)*[b]	3.0180(3)
Re(2)−Si(1)	2.5041(10)	C−O (av)	1.137(5)
Re(2)−Si(2)	2.5901(9)		
Re(1)−H(1)	1.67(4)		
Si(1)−H(1)	1.73(4)		
C−O (av)	1.13(1)		
	Bond Angles (deg)		
Si(1)−Re(1)−Re(2)	50.66(2)	Re(1)−Si(1)−Re(1)*	72.13(3)
Si(1)−Re(2)−Si(2)	150.56(3)	Si(1)−Re(1)−Si(1)*	107.87(3)
Si(1)−Re(2)−Re(1)	52.81(2)	Si(1)−Re(1)−Re(1)*	53.935(14)
Si(2)−Re(2)−Re(1)	156.34(2)	Re−C−O (av)	177.4(3)
Re(2)−Si(1)−Re(1)	76.53(3)		
Re−C−O (av)	176(1)		

[a] Estimated standard deviations in the least significant figure are given in parentheses. [b] *Indicates an atom related by inversion symmetry.

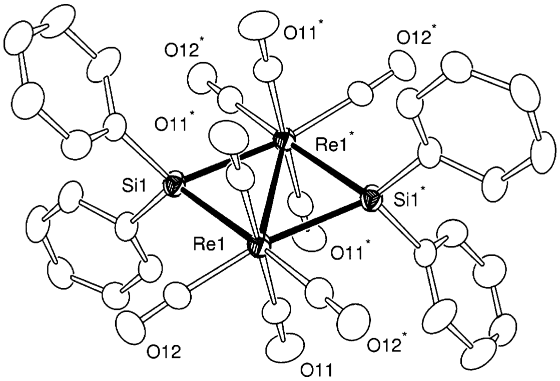
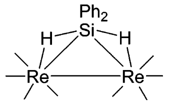


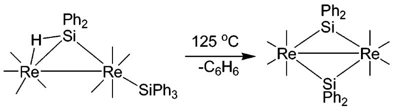
Figure 4. ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}SiPh_2)_2$ (**8**) showing 40% thermal ellipsoid probability.

atom, ${}^{1}J_{^{29}Si-H} = 44$ Hz. This value is slightly smaller than the Si−H coupling observed for the hydrogen atom bridging the Mn−Si bond in the compounds $(C_5H_4Me)Mn(CO)_2(H)SiR_3$, $SiR_3 = SiPh_3$, SiHPhNp (${}^{1}J_{^{29}Si-H} = 65$ and 69 Hz, respectively).[12] Schubert has concluded that no strong Si−H interaction is to be expected if *J*(SiMH) drops below 10−20 Hz.[13] The Si−H distance is slightly longer than that found for Si−H bonds engaged in agostic interactions with transition metal atoms,[5] but is much shorter than the 2.00 Å designated by Schubert as the upper limit for significant Si−H bonding interactions.[13] The Si−H distance in **7** is very similar to the Si−H bond distance of 1.70(3) Å found for the hydrogen atom bridging the Ru−Si bond in the compound $(C_5Me_5)Ru[P(C_6H_{11})_3](CPh_2SiH)$.[14] The bond lengthening effect usually found associated with bridging hydrido ligands is observed in **7** as well, as the Re(1)−Si(1) bond distance [2.5792(9) Å] is significantly longer than the unbridged Re(2)−Si(1) bond distance [2.5041(10) Å]. The compound $Re_2(CO)_8(\mu\text{-}SiPh_2)(\mu\text{-}H)_2$ (**9**) was proposed to have two hydride ligands, one bridging each of the two Re−Si bonds in the molecule. The Re−Si distances in **9** are 2.544(9) Å in length.[15] Curiously, Cowie et al. concluded that the hydride ligands in **9** and in the related compounds $Re_2(CO)_7(\mu\text{-}SiEt_2)_2(\mu\text{-}H)_2$ and $Re_2(CO)_6(\mu\text{-}SiEt_2)_2(\mu\text{-}H)_4$ were "bonded terminally to the rhenium atoms with no attractive interactions to the silicon atoms", even though the hydride ligands were *not* located crystallographically.[16] On the basis of the high-quality structural analysis and the observation of large NMR coupling between the ${}^{29}Si$ and H, we are quite confident that there are significant interactions between the silicon atom and the hydrido ligand in **7**. Similar Si−H interactions probably exist in **9** also.



9

Compound **7** was converted to $Re_2(CO)_8(\mu\text{-}SiPh_2)_2$ (**8**) in 84% yield via the thermal elimination of benzene (confirmed by ${}^{1}H$ NMR spectroscopy) at 125 °C, see eq 4.



7 **8** (4)

Compound **8** can also be obtained in 44% yield directly from the reaction of **1** with Ph_3SiH at 125 °C. An ORTEP diagram of the molecular structure of **8** is given in Figure 4. Selected intramolecular distances and angles are listed in Table 3. Compound **8** contains 2/*m* symmetry in the solid state. The molecule has two $SiPh_2$ ligands that bridge the two $Re(CO)_4$ groups, and it is isostructural with our previously reported dirheniumditin compound, **2**.[1] In earlier studies,[1,17] we have observed that the addition of bridging $SnPh_2$ and $GePh_2$ ligands can result in the elongation of the M−M bond to which they were associated. However, this trend was not observed for **8**, and, in fact, the Re−Re bond distance

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in **8** [3.0180(3) Å] is much shorter than that in **2** [3.1902(4) Å],[1] and even shorter than in $Re_2(CO)_{10}$ [3.042(1) Å].[11] The manganese homologue of **7** was reported by Dahl a number of years ago, and it too has a relatively short Mn−Mn distance [2.871(2) Å].[18]

Concluding Remarks

These new compounds further expand and clarify the nature of the additions and bonding of silyl and silylene groups to dirhenium carbonyl complexes. The reaction of **1** with Ph_3SiH at 97 °C yielded a monorhenium complex **5** and two dirhenium complexes **6** and **7**. At 125 °C, this same reaction yielded **5** and **6** as well as the new dirhenium compound **8**. Compound **7** was shown to be a precursor to **8** (see eq 4), which helps to provide an explanation for the formation of **8** from **1**. This may be relevant to the formation of **2** as well. Compounds **5** and **6** seem to be unrelated to the formation of **7** and **8**. In previous work we showed that **1** reacts with $HSi(OMe)_3$ to yield compound **4**, which contains a bridging trimethoxysilyl ligand, eq 3.[6] The formation of the unusual η^7-bridging $SiPh_3$ ligand in **6** shows that this reaction can be extended to silyl groups bearing phenyl rings.

Acknowledgment. This research was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy under Grant No. DE-FG02-00ER14980.

Supporting Information Available: CIF files are available for each of the structural analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0504304

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