Oxidative Addition of Silanes to $Ru_5(CO)_{15}(\mu_5\text{-}C)$ under Photolytic Conditions. The Synthesis and Structural Characterizations of $Ru_5(CO)_{14}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$ and $Ru_5(CO)_{15}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$

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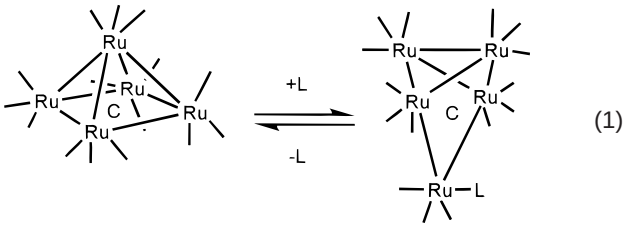
The reaction of $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**, with triethylsilane in the presence of UV−vis irradiation has yielded two new cluster complexes: $Ru_5(CO)_{14}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, **2**, in 11% yield and $Ru_5(CO)_{15}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, **3**, in 4% yield. Compound **2** can be converted to **3** in 89% yield under an atmosphere of CO at 25 °C. Compound **3** is converted back to **2** when heated to 97 °C. Compounds **2** and **3** were both characterized by single-crystal X-ray diffraction analyses. Compound **2** contains a square pyramidal cluster of five ruthenium atoms with a μ_5-carbido ligand. The $SiEt_3$ ligand is coordinated to one of the basal ruthenium atoms. The Ru−Ru bond from this ruthenium atom to the apical ruthenium atom is unusually long at 3.1353(8) Å. Compound **3** contains an open $Ru_5(\mu_5\text{-}C)$ cluster where one ruthenium atom bridges a butterfly arrangement of four ruthenium atoms. The silyl group is bonded to the bridging ruthenium atom, and the hydride ligand bridges the hinge bond of the butterfly.

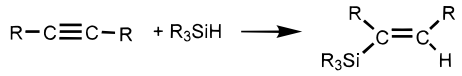
Introduction

The chemistry of the cluster complex $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**, has recently attracted considerable attention.[1] This compound will readily add small molecules such as MeCN under mild conditions by cleaving one of its metal−metal bonds to yield an opened cluster having a bridged butterfly structure, eq 1.[2]



(1)

The activation of silanes by metal complexes is a key step in the catalytic processes known as hydrosilylation, e.g., eq 2.[3]



(2)

Polynuclear metal carbonyl complexes have shown some potential for serving as catalysts for hydrosilylation reactions.[4] In this report the first example of the addition of a silane ($HSiEt_3$) to **1** is described.

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 Nicolet 5DXBO FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.9 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Triethylsilane was purchased from Aldrich and was used without further purification. $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**, was prepared according to the published procedure.[5] Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Reaction of 1 with Et_3SiH. In the absence of a solvent, a 12.4 mg amount of **1** (0.013 mmol) was dissolved in Et_3SiH (1 mL) in a 25 mL three-neck round-bottom flask equipped with

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a reflux condenser and a stir bar. The reaction mixture was irradiated (medium-pressure mercury lamp at 360 W) for 1 h, and the excess Et_3SiH was then removed in vacuo. The products were separated by TLC using pure hexane to yield 1.4 mg of $Ru_5(CO)_{14}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, **2**, in 11% yield and 0.50 mg of $Ru_5(CO)_{15}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, **3**, in 4% yield. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2101 (w), 2069 (s), 2063(vs), 2048(m), 2031(m), 2021(m), 2002 (w), 1960 (vw). ^1H NMR (δ in $CDCl_3$): 1.01 ppm (q, CH_2), 0.99 ppm (t, CH_3), −22.83 ppm (s, RuH). Anal. Calcd: C 24.59, H 1.57. Found: C 24.26, H 1.86. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane): 2105 (vw), 2071 (s), 2058 (s), 2025 (m), 2003 (m), 1991 (vw), 1986 (vw). ^1H NMR (δ in $CDCl_3$): 1.25 ppm (q, CH_2), 1.14 ppm (t, CH_3), −22.35 ppm (s, RuH). Anal. Calcd: C 24.65, H 1.56. Found: C 24.58, H 1.55.

Carbonylation of 2. A 6.6 mg amount of **2** (0.0064 mmol) was dissolved in 10 mL of hexane. Carbon monoxide was then allowed to purge slowly through the solution at 25 °C for 10 min. The reaction solution changed from an orange-yellow to a light yellow color. An IR spectrum of the reaction mixture showed the disappearance of **2** and formation of **3**. The solvent was then removed in vacuo. Separation by TLC using a pure hexane solvent yielded 6.0 mg (89%) of **3**.

Decarbonylation of Compound 3. A 6.0 mg amount of **3** (0.0057 mmol) was dissolved in 10 mL of heptane. The reaction mixture was brought to reflux for 10 min. The solution turned from light yellow to a darker orange-yellow color. The IR spectrum of the reaction mixture showed disappearance of **3** and formation of **2**. The solvent was then removed in vacuo and was separated by TLC by using a hexane solvent to yield 2.0 mg of **2** (34%).

Crystallographic Analysis. Yellow crystals of **2** suitable for X-ray diffraction analysis were grown in a hexane solution by cooling to −25 °C under a nitrogen atmosphere. Orange-yellow crystals of **3** suitable for X-ray diffraction analysis were grown by slow evaporation of a hexane/methylene chloride solvent mixture at −25 °C. The crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation at 20 °C. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a Silicon Graphic Indigo 2 computer by using the TEXSAN motif structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] Lorentz/polarization (*Lp*) and absorption corrections were applied to the data for each structure. Full matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.06)I_{net})^2]^{1/2}/Lp$.

Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was established on the basis of the patterns of systematic absences observed during the collection of the intensity data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. 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 the hydrogen atoms on the silyl ligand were calculated by assuming idealized tetrahedral geometries at the carbon atoms with C−H distances of 0.95 Å. The scattering contributions of the hydrogen atoms were included in the structure factor calculations, but their positions were not refined.

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

Table 1. Crystallographic Data for Compounds 2 and 3

	2	**3**
empirical formula	$Ru_5SiO_{14}C_{21}H_{16}$	$Ru_5SiO_{15}C_{22}H_{16}\cdot 0.5CH_2Cl_2$
fw	1025.78	1096.26
cryst syst	monoclinic	monoclinic
a (Å)	9.602(1)	38.60(1)
b (Å)	17.018(4)	9.671(2)
c (Å)	19.597(4)	18.782(3)
β (deg)	103.15(1)	103.98(2)
V (Å^3)	3118.4(9)	6805(3)
space group	$P2_1/c$ (No.14)	$C2/c$ (No. 15)
Z	4	8
D_{calc} (g/cm^3)	2.18	2.14
μ(Mo, Kα), cm^{-1}	24.6	23.5
no. obs. ($I>3\sigma(I)$); no. variables	3038; 397	3433; 409
residuals:[a] *R*; R_w	0.025; 0.038	0.030; 0.047
goodness of fit (GOF)	1.00	1.05
max shift/error on final cycle	0.03	0.00
largest pk final diff map, e$^-$/Å^3	0.44	0.67
abs corr, coeff max/min	DIFABS, 1.0/0.72	DIFABS, 1.0/0.57

[a] $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl} wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}(w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Compound **3** crystallized in the monoclinic crystal system. The space groups *Cc* and *C*2/*c* were indicated by the patterns of systematic absences observed during the collection of the intensity data. The centrosymmetric space group *C*2/*c* was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydride ligand was located and refined with an isotropic thermal parameter. The positions of the hydrogen atoms on the silyl ligand were calculated by assuming idealized tetrahedral geometries at the carbon atoms and using C−H = 0.95 Å. The scattering contributions of the hydrogen atoms were included in the structure factor calculations, but their positions were not refined. A molecule of CH_2Cl_2 from the crystallization solvent was found cocrystallized with the complex in the final stages of the analysis. It was located on a crystallographic 2-fold rotation axis. It was included in the analysis and was satisfactorily refined.

Results and Discussion

Two new silyl-containing pentaruthenium compounds, $Ru_5(CO)_{14}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, **2**, in 11% yield and $Ru_5(CO)_{15}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, **3**, in 4% yield, were obtained from the reaction of $HSiEt_3$ with $Ru_5(CO)_{15}(\mu_5\text{-}C)$ in the presence of UV−vis irradiation without solvent. In the absence of UV−vis irradiation, these compounds were not obtained in significant amounts. Both compounds were characterized by a combination of IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **2** is shown in Figure 1. Selected bond distances and angles are listed in Table 2. The molecule contains a square pyramidal pentaruthenium cluster with an interstitial carbido ligand that is analogous to that of its parent **1**.[2a] The $SiEt_3$ ligand is coordinated to one of the ruthenium atoms in the basal plane. The Ru−Si distance of 2.454(2) Å is typical of Ru−Si distances found in a number of triruthenium carbonyl containing cluster

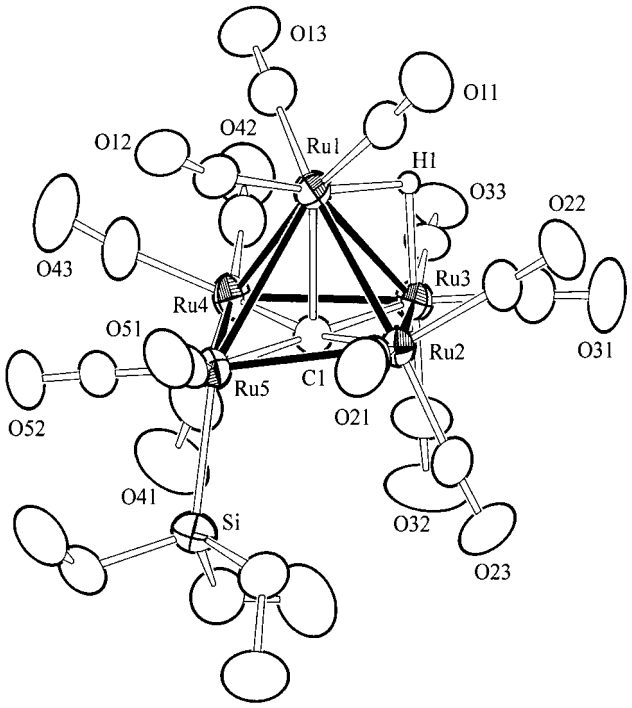

Figure 1. ORTEP diagram of $Ru_5(CO)_{14}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, **2**, showing 40% probability thermal ellipsoids.

complexes containing $SiEt_3$ ligands: $[Ru_3(CO)_{10}(SiEt_3)_2(\mu\text{-}H)]^-$, Ru−Si = 2.441(3) Å, 2.450(2) Å;[7] $Ru_3(CO)_8(SiEt_3)_2(\mu\text{-}C_4H_4N_2)(\mu\text{-}H)_2$, Ru−Si = 2.460(6) Å, 2.455(5) Å;[8] $Ru_3(CO)_6(PPh_3)(SiEt_3)(\mu_3\text{-}HNC_6H_3Me)[\mu\text{-}PhCC(H)Ph)](\mu\text{-}H)$, Ru−Si = 2.432(2) Å;[9] $Ru_3(CO)_8(SiEt_3)(\mu_3\text{-}HNC_6H_3Me)(\mu\text{-}H)_2$, Ru−Si = 2.435(4) Å.[10] Interestingly, the Ru−Ru bond from the silyl-substituted ruthenium atom to the apical ruthenium atom is unusually long, 3.1353(8) Å. This is much longer than the other Ru−Ru bonds in **2** and is also longer than those in **1**, where the longest Ru−Ru bonding distance is 2.882(2) Å. Also, there is no significant elongation of the corresponding Ru−Ru bond at 2.813(1) Å in the phosphine derivative $Ru_5(CO)_{14}(PPh_3)(\mu_5\text{-}C)$, **4**, where the bulky PPh_3 ligand occupies a position analogous to that of the silyl group in **2**,[2a] so it seems unlikely that the bond elongation observed in **2** is due to steric crowding effects. We have no explanation for the unusual length of this Ru−Ru bond at this time. The hydride ligand was located and refined in the structural analysis. This ligand bridges the Ru(1)−Ru(3) bond, which is also slightly elongated, 2.8788(8) Å, as is typically found for bridging hydride ligands.[11] The hydride ligand exhibits the usual high-field resonance shift in the ^{1}H NMR spectrum, δ −22.83 ppm.

The molecular structure of **3** is shown in Figure 2. Selected bond distances and angles are listed in Table 3. This compound contains an open $Ru_5(\mu_5\text{-}C)$ cluster where one ruthenium atom bridges a butterfly arrangement of the four other ruthenium atoms. The silyl group

Table 2. Selected Intramolecular Distances and Angles for $Ru_5(CO)_{14}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, 2[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Si	Ru(5)	2.454(2)	Ru(1)	C(1)	2.187(6)
Ru(1)	Ru(2)	2.8383(8)	Ru(2)	C(1)	1.994(6)
Ru(1)	Ru(3)	2.8788(8)	Ru(3)	C(1)	2.092(6)
Ru(1)	Ru(4)	2.8022(8)	Ru(4)	C(1)	2.010(6)
Ru(1)	Ru(5)	3.1353(8)	Ru(5)	C(1)	2.034(6)
Ru(2)	Ru(3)	2.8389(8)	Ru(1)	H(1)	1.87(7)
Ru(2)	Ru(5)	2.9170(7)	Ru(3)	H(1)	1.86(8)
Ru(3)	Ru(4)	2.8561(8)	O(av)	C(av)	1.14(1)
Ru(4)	Ru(5)	2.8866(8)			

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Ru(2)	Ru(1)	Ru(4)	89.89(2)	Ru(2)	Ru(5)	Ru(4)	86.72(2)
Ru(3)	Ru(1)	Ru(5)	86.53(2)	Si	Ru(5)	Ru(1)	156.08(6)
Ru(3)	Ru(2)	Ru(5)	91.58(2)	Si	Ru(5)	Ru(2)	102.69(6)
Ru(2)	Ru(3)	Ru(4)	88.80(2)	Si	Ru(5)	Ru(4)	119.11(6)
Ru(3)	Ru(4)	Ru(5)	91.86(2)				

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

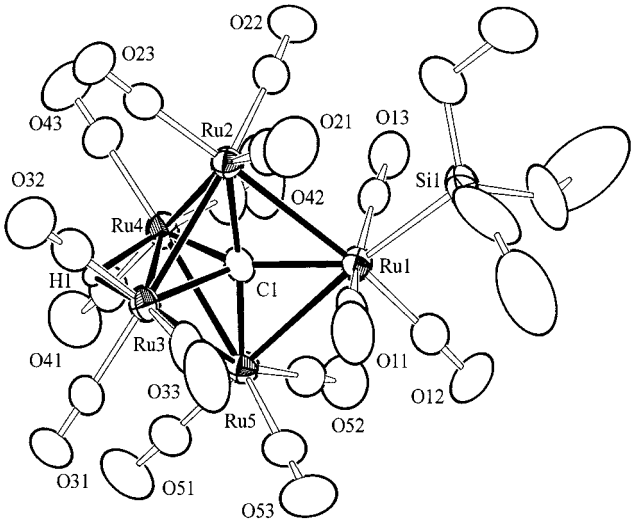

Figure 2. ORTEP diagram of $Ru_5(CO)_{15}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, **3**, showing 40% probability thermal ellipsoids.

is bonded to the bridging ruthenium atom, and the hydride ligand bridges the hinge bond of the Ru_4 butterfly. Its ^{1}H NMR signal shows the usual high-field shift, δ −22.35. Compound **3** is structurally similar to the previously reported compound $Ru_5(CO)_{15}(NCMe)(\mu_5\text{-}C)$, **5**.[2] The Ru−Si distance in **3**, 2.539(2) Å, is slightly longer than that found in other Ru−Si cluster complexes; see above. Unlike that found in compound **2**, the Ru−Ru bond trans to the silyl ligand is very similar in length, Ru(1)−Ru(2) = 2.9920(7) Å, to the one cis to the silyl ligand, Ru(1)−Ru(5) = 2.9842(8) Å, but both distances are significantly longer than the corresponding distances in **5**.

It is proposed that the irradiation of **1** produces the loss of a CO ligand that is followed by the oxidative addition of Et_3SiH to one of the basal positioned ruthenium atoms to yield the major product **2**. Some of the released CO may then readd to the product **2** to form the minor product **3**; see Scheme 1. This is supported by the fact that we have confirmed in an independent test that CO will add to **2** under the conditions of the original synthesis to form **3** in high yield. The increase

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Scheme 1

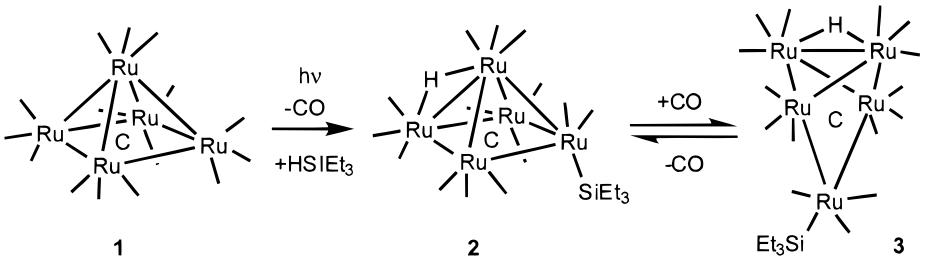

Table 3. Selected Intramolecular Distances and Angles for $Ru_5(CO)_{15}(SiEt_3)(\mu_5\text{-}C)(\mu\text{-}H)$, 3[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Ru(1)	Ru(2)	2.9920(7)	Ru(1)	Si(1)	2.539(2)
Ru(1)	Ru(5)	2.9842(8)	Ru(1)	C(1)	2.163(6)
Ru(2)	Ru(3)	2.8605(8)	Ru(2)	C(1)	1.953(7)
Ru(2)	Ru(4)	2.850(1)	Ru(3)	C(1)	2.134(6)
Ru(3)	Ru(4)	2.8496(9)	Ru(4)	C(1)	2.136(7)
Ru(3)	Ru(5)	2.8479(7)	Ru(5)	C(1)	1.975(7)
Ru(4)	Ru(5)	2.8428(8)	O	C(av)	1.14(2)

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Ru(2)	Ru(1)	Ru(5)	82.07(2)	Ru(2)	Ru(4)	Ru(5)	87.13(3)
Ru(1)	Ru(2)	Ru(3)	86.75(2)	Ru(1)	Ru(5)	Ru(3)	87.12(2)
Ru(1)	Ru(2)	Ru(4)	86.60(2)	Ru(1)	Ru(5)	Ru(4)	86.87(2)
Ru(2)	Ru(3)	Ru(5)	86.83(2)	Ru(2)	Ru(1)	Si(1)	103.02(6)
Ru(5)	Ru(1)	Si(1)	174.69(6)	Ru	C	O(av)	176(1)

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

in the number of electrons to the cluster when the CO is added to **2** causes the cleavage of one of the Ru−Ru bonds to yield the open cluster **3**. This reaction is analogous to the cluster-opening addition of MeCN to **1** to yield **5**, eq 1.[2a] The addition of CO to **2** is partially reversible. When heated to 97 °C, compound **3** is converted back to **2** in 34% yield, but CO will not displace the silane molecule from **2** to reform **1** at 1 atm at 25 °C. It will be of interest to see if unsaturated donors, such as alkenes and alkynes, can be added to **2** and if the silyl ligand can then be transferred to these molecules. It may even be possible to develop catalytic hydrosilylation processes by using a combination of silane and substrate activation processes employing Ru_5C intermediates.

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Supporting Information Available: Tables of final atomic coordinates, bond distances, bond angles, and anisotropic thermal parameters are available for the structural analyses of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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