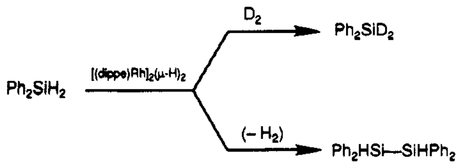
Organometallics **1991**, *10*, 2539–2541

Scheme III



On the basis of the interconvertibility of the silylhydride **2** and the bis(silylene) **3** by either addition of diphenylsilane or addition of H_2, it seemed reasonable that a catalytic cycle could be developed which would allow for the conversion of Ph_2SiH_2 to Ph_2SiD_2 with D_2 (cf. middle of Scheme I). The key to this reaction is that, even in the presence of excess silane, the bis(silylene) **3** reacts with D_2 to generate free Ph_2SiD_2 and the silyl–deuteride $[(dippe)Rh]_2(\mu\text{-}D)(\mu\text{-}\eta^2\text{-}DSiPh_2)$ (**2**-d_2). In the presence of more Ph_2SiH_2, **2**-d_2 is converted to the bis(silylene) **3** and the cycle is complete. This has only been reported previously to occur in the presence of heterogeneous catalysts.[17] Monitoring the reaction under catalytic conditions by ^1H NMR spectroscopy shows the decrease in the intensity of the Si–H resonance with time. If long reaction times are employed, the presence of a new material can be observed; this material has been characterized as 1,1,2,2-tetraphenylsilane, the product of dehydrogenative silicon–silicon coupling of Ph_2SiH_2. The dimerization reaction can be suppressed by dilution and an increase in the pressure of D_2; by the same token, the absence of D_2 (or H_2) favors the formation of $Ph_2HSi\text{-}SiHPh_2$.[18] Further studies on these reactions are in progress.

Acknowledgment. Financial support for this work was provided by the NSERC (operating grants to M.D.F. and a postgraduate scholarship to L.R.). We also thank Johnson Matthey for the generous loan of $RhCl_3$.

Supplementary Material Available: Full details of the crystal structure analysis and tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes (30 pages); a table of measured and calculated structure factor amplitudes (71 pages). Ordering information is given on any current masthead page.

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[17] (17) Sommer, L. H.; Lyons, J. E.; Fujimoto, H.; Michael, K. W. *J. Am. Chem. Soc.* 1967, *89*, 5483.

[18] (18) Typical unoptimized reaction conditions for the production of the disilane are as follows: 254 mg (1.38 mmol) of diphenylsilane was dissolved in 1.25 mL of toluene and placed in a 50-mL round-bottom flask equipped with a stirbar and condenser. The catalyst (1, 1.38 × 10^{-2} mmol, 250 μL of a 0.055 M solution in toluene) was added to the substrate solution by syringe under a strong flow of nitrogen. The solution was degassed and heated to 60 °C under nitrogen open to a Nujol bubbler. After 18–24 h the mixture was taken into a glovebox, where the catalyst was removed on a Florisil column to give 71–77% conversion, as determined by ^1H NMR spectroscopy.

Evidence for the Activation of Thietanes to Ring Opening by Nucleophiles through Bridging Coordination

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Summary: **The reaction of $Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2CH_2})$ (1) with $[Et_4N]^+Cl^-$ in CH_2Cl_2 yielded after acidification the complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2Cl](\mu\text{-}H)$ (3; 55%), which contains a chloroneopentanethiolato ligand that is believed to have been formed by the nucleophilic ring opening of the thietane ligand in 1. In contrast, the reaction of the ring-opened complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (4) with $[Et_4N]^+Cl^-$ yielded only the cluster-opened product $[Et_4N]^+[Os_3(CO)_9(\mu\text{-}SCH_2CMe_2CH_2)(\mu\text{-}Cl)]^-$ (5; 87%). Compounds 3 and 5 were characterized crystallographically.**

In recent reports we have described the first examples of the ring-opening reaction of thietane ligands in metal cluster complexes.[1-3] Both thermal[1,2] and photochemical[3] processes have been observed. In some cases these reactions were accompanied by C–H bond cleavage processes.[1,3] We have now discovered an example of facile nucleophilic ring opening of a bridging 3,3-dimethylthietane ligand (DMT) that appears to be promoted by its bridging coordination.

The reaction of 45 mg of $Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2CH_2})$ (**1**)[1] with 9.0 mg of $[Et_4N]^+Cl^-$ in CH_2Cl_2 proceeds at 25 °C/1.5 h to produce the intermediate species **2** that yields upon protonation (50 μL of acetic acid) the complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2Cl](\mu\text{-}H)$ (**3**) in 55% yield.[4]

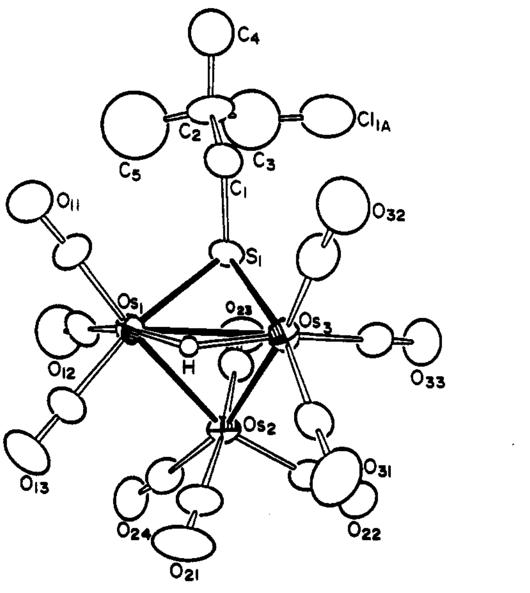

Figure 1. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2Cl](\mu\text{-}H)$ (3). Selected interatomic distances (Å) are as follows: Os(1)–Os(3) = 2.851 (1), Os(1)–S(1) = 2.418 (4), Os(3)–S(1) = 2.404 (4), S(1)–C(1) = 1.81 (2), C(3)–Cl(1A) = 1.54 (4), C(1)–C(2) = 1.56 (2).

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[1] (1) Adams, R. D.; Pompeo, M. P. *Organometallics* 1990, *9*, 2651.

[2] (2) Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* 1991, *113*, 1619.

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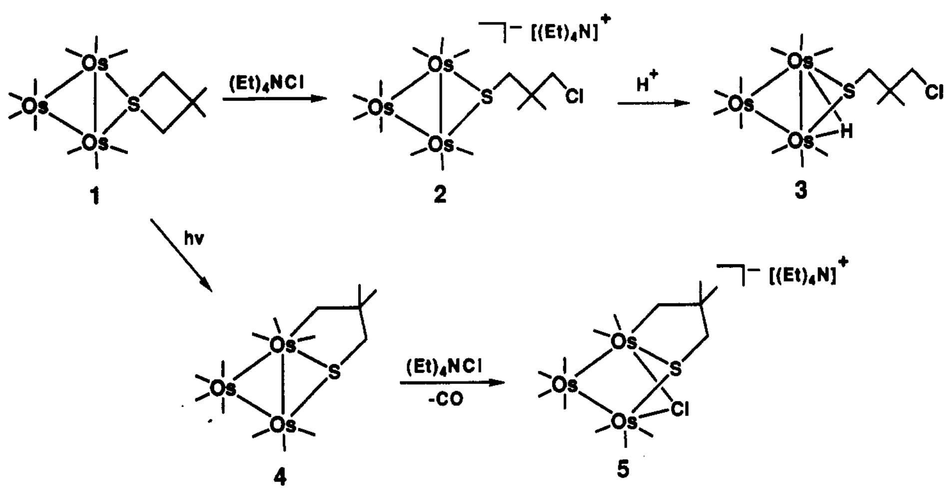
Scheme I



Complex **3** was analyzed crystallographically and was found to contain a chloroneopentanethiolato ligand bridging an edge of a triangular cluster of three osmium atoms (see Figure 1).[5,6] The intermediate **2** is believed to be simply the deprotonated form of **3** (i.e. minus the hydride ligand). This was indicated by its IR and ^{1}H NMR spectra, which were obtained by following the reaction spectroscopically.[7] It is believed that the formation of **2** occurs by a direct nucleophilic attack of chloride ion upon one of the sulfur-bonded methylene groups of the bridging DMT ligand of **1**.

To demonstrate that the reaction does not involve addition to an unobserved ring-opened species, the ring-opened complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (**4**) was prepared by UV irradiation of **1**.[8] When **4** was treated with $[Et_4N]^+Cl^-$ for 11 h at 25 °C, the product $[Et_4N]^+[Os_3(CO)_9(\mu\text{-}SCH_2CMe_2CH_2)(\mu\text{-}Cl)]^-$ (**5**) was obtained in 87% yield by fractional crystallization.[5,9] A structural analysis of **5** revealed a molecule consisting of an open triosmium cluster with a bridging chloride ligand across the open edge of the cluster (see Figure 2).[10] The molecule also contains a 3,3-dimethylthiametallacyclopentane ring with the sulfur atom bridging the open edge of the cluster. This is simply the unmodified ring system that is believed to exist in **4**. In contrast to the reaction of **1** with Cl^-, this reaction occurred by a cluster-opening addition of chloride to one of the metal atoms that was followed by a decarbonylation that led to the formation of the bridging chloride ligand (see Scheme I).

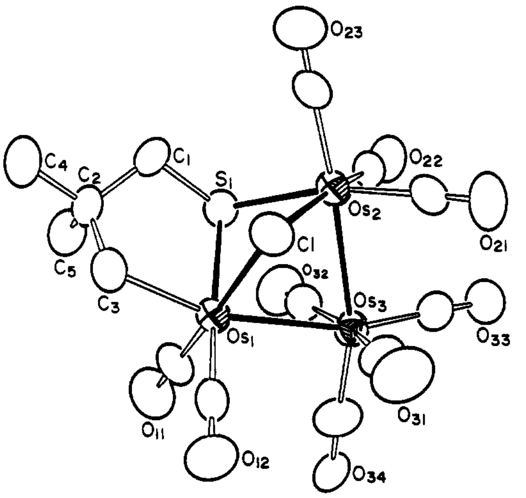


Figure 2. ORTEP diagram of the anion of $[Os_3(CO)_9(\mu\text{-}SCH_2CMe_2CH_2)(\mu\text{-}Cl)]^-$ (**5**). Selected interatomic distances (Å) are as follows: Os(1)···Os(2) = 3.303 (1), Os(1)–S(1) = 2.426 (2), Os(2)–S(1) = 2.427 (3), S(1)–C(1) = 1.83 (1), Os(1)–C(3) = 2.17 (1), Os(1)–Cl = 2.533 (3), Os(2)–Cl = 2.495 (3).

A mixture of DMT and $[Et_4N]^+Cl^-$ in CD_2Cl_2 solution showed no observable reaction by ^{1}H NMR spectroscopy after 48 h at 25 °C.[11] The enhancement of the opening of the DMT ring in **1** is believed to be produced by the removal of electron density from the sulfur atom through its coordination, which in turn makes the adjacent carbon atoms more susceptible to nucleophilic attack.

The opening of sulfur-containing heterocycles is believed to be an integral step in the process of desulfurizing these molecules.[12,13] Angelici has shown that nucleophiles can

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(4) Compound **3** was isolated by TLC on silica gel: IR ν(CO) (cm^{-1}; in hexane) 2110 m, 2069 vs, 2060 s, 2036 vs, 2019 s, 2007 w, 2001 s, 1991 s, 1981 m; ^{1}H NMR (δ; in $CDCl_3$) 3.48 (s, 2 H), 2.38 (s, 2 H), 1.14 (s, 6 H), −17.40 (s, 1 H); mass spectral analysis (*m*/*e*; 70 eV, 100 °C) for ^{192}Os 990 − 28x, x = 0–10 {$[M]^+ - x(CO)$}.

(5) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation (λ = 0.710 69 Å). The structure solution and refinement was made by using the TEXSAN structure solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX. An empirical absorption correction was applied.

(6) Crystal data for **3**: space group $P2_1/c$, a = 11.841 (2) Å, b = 14.310 (3) Å, c = 14.642 (3) Å, β = 100.91 (1)°, Z = 4, 2263 reflections, R = 0.036. The chloromethyl group was disordered unequally in the three sites of the methyl groups on atom C(2). The hydride ligand was located (difference Fourier) but was not refined.

(7) Evidence for the character of **2** was established by IR and ^{1}H NMR spectroscopy of the reaction mixtures prior to the addition of acetic acid: IR ν(CO) (cm^{-1}; in CH_2Cl_2) 2069 w, 2009 s, 1995 vs, 1982 s, 1927 m; ^{1}H NMR (δ; in CD_2Cl_2) 3.57 (s, 2 H), 3.14 (m, 8 H), 2.37 (s, 2 H), 1.26 (m, 12 H), 1.14 (s, 6 H). Efforts to isolate **2** are in progress.

(8) A solution of **1** (40 mg, 0.042 mmol) in 40 mL of hexane was irradiated for 30 min at 25 °C. The red product $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (**4**) was isolated by TLC with use of a 4/1 hexane/CH_2Cl_2 solvent mixture: yield 47%; IR ν(CO) (cm^{-1}; in hexane) 2106 s, 2070 w, 2058 vs, 2045 s, 2037 w, 2021 vs, 2000 s, 1990 s, 1987 s, 1962 vw, 1943 w; ^{1}H NMR (δ; in $CDCl_3$) 3.08 (dd, 1 H, $^2J_{H-H}$ = 11 Hz, $^4J_{H-H}$ = 2.1 Hz), 2.41 (dd, 1 H, $^2J_{H-H}$ = 12 Hz, $^4J_{H-H}$ = 2.1 Hz), 2.10 (d, 1 H, $^2J_{H-H}$ = 12 Hz), 1.89 (d, 1 H, $^2J_{H-H}$ = 11.0 Hz), 1.24 (s, 3 H), 1.12 (s 3 H); mass spectral analysis (*m*/*e*; 70 eV, 120 °C) for ^{192}Os 953 − 28x, x = 0–10 {$[M]^+ - x(CO)$}.

(9) A 4.0-mg (0.022-mmol) amount of $(Et)_4NCl\cdot H_2O$ dissolved in 1 mL of CH_3CN was added to a solution of **4** (20 mg, 0.021 mmol) in 15 mL of CH_2Cl_2 at 25 °C and stirred for 11 h. The solvent volume was reduced, and hexane (10 mL) was added to precipitate yellow $[Et_4N]^+[Os_3(CO)_9(\mu\text{-}Cl)[\mu\text{-}SCH_2CMe_2CH_2]^-$ (**5**): yield 18 mg, 87%; IR ν(CO) (cm^{-1}; in CH_2Cl_2) 2073 m, 2029 vs, 1983 s, 1975 s, 1965 m, 1957 m, 1883 w; ^{1}H NMR (δ; in CD_2Cl_2) 3.17 (q, 8 H, $^3J_{H-H}$ = 7.3 Hz), 2.52 (dd, 2 H, $^2J_{H-H}$ = 11 Hz, $^4J_{H-H}$ = 1 Hz), 1.65 (dd, 2 H, $^2J_{H-H}$ = 11 Hz, $^4J_{H-H}$ = 1 Hz), 1.42 (s, 3 H), 1.32 (t, 12 H, $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-H}$ = 1.8 Hz), 1.26 (s, 3 H).

(10) Crystal data for **5**: space group $P2_1/n$, a = 9.320 (2) Å, b = 18.484 (5) Å, c = 17.943 (3) Å, β = 95.04 (2)°, Z = 4, 2886 reflections, R = 0.024.

(11) $[Et_4N]^+Cl^-$ was predissolved in a minimal quantity of CD_3CN to improve its solubility in CD_2Cl_2.

promote the ring opening of coordinated thiophenes.[13] We have recently reported an unusual example of the ring-opening oligomerization of DMT by 1, which appears to be initiated by nucleophilic attack of a free molecule of DMT upon the bridging DMT ligand.[2] Studies of the ring opening of the bridging DMT ligand by other nucleophiles are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for both of the structural analyses (19 pages); tables of structure factors (36 pages). Ordering information is given on any current masthead page.

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Transformation of Heteroatom-Substituted Alkynes into Substituted Vinylidene Ligands Accompanied by CO Insertion

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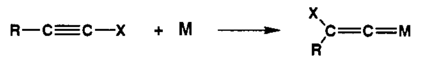
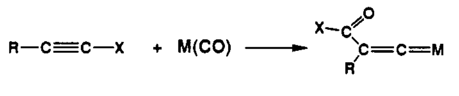
Summary: The reactions of $Mn_2(CO)_9NCMe$ (**1**) with the alkynes $MeC{\equiv}CX$ ($X = OEt, NMe_2$) have yielded the substituted bridging vinylidene complexes $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)C{=}O(X)]$ (**2a**, X = OEt; **2b**, $X = NMe_2$) in 39% and 10% yields, respectively, by a rearrangement of the alkyne accompanied by a CO insertion. Compound **2b** also adds 1 equiv of $MeC{\equiv}CNMe_2$ to form the complex $Mn_2(CO)_7[\mu\text{-}CC(Me)C(NMe_2)C(Me)C{=}O(NMe_2)]$ (**3**) in 50% yield, which contains a four-membered carbocyclic ring.

While there are many examples of the metal-assisted transformation of terminal alkynes into vinylidene ligands,[1] there are relatively few that involve the shift of a non-hydrogen heteroatomic grouping (eq 1).[2-5] We now wish to report the first examples of this transformation involving the substituents OEt and NMe_2 with R = Me in which the shift is also accompanied by a CO insertion (eq 2).



$$R{-}C{\equiv}C{-}X + M \longrightarrow (X)(R)C{=}C{=}M \quad (1)$$

$X = PPh_2$, SMe, Cl, Br, I



$$R{-}C{\equiv}C{-}X + M(CO) \longrightarrow (X{-}C{=}O)(R)C{=}C{=}M \quad (2)$$

$X = OEt, NMe_2$

From the reaction of $Mn_2(CO)_9NCMe$[6] (**1**; 300 mg, 0.744 mmol) with $MeC{\equiv}COEt$ (0.177 mL, 1.86 mmol) at 25 °C in 150 mL of hexane solvent for 24 h, we have isolated by TLC the new yellow compound $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)\text{-}$

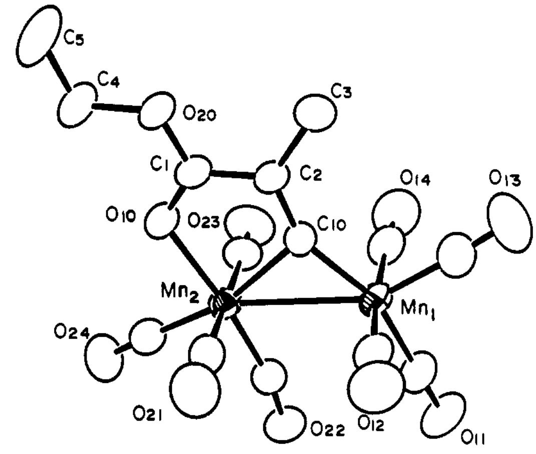
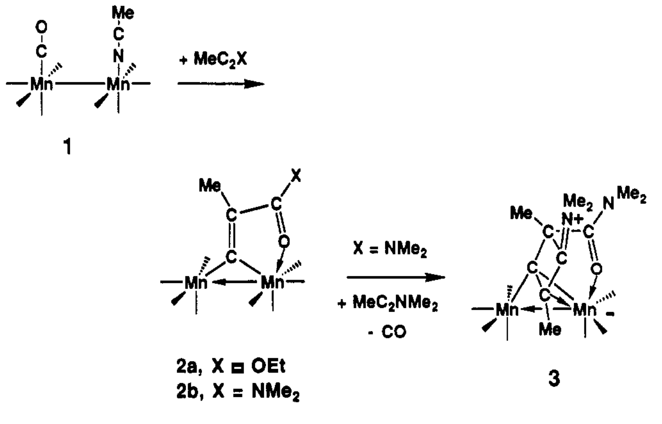


Figure 1. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)C{=}O(OEt)]$ (**2a**). Selected interatomic distances (Å) are Mn(1)-Mn(2) = 2.9147 (6), Mn(1)-C(10) = 1.874 (2), Mn(2)-C(10) = 2.125 (2), Mn(2)-O(10) = 2.068 (2), C(10)-C(2) = 1.339 (3), C(1)-C(2) = 1.440 (3), and C(1)-O(10) = 1.249 (3).

Scheme I



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