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Nucleophilic ring opening of bridging thietane ligands in trirhenium carbonyl cluster complexes

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a solution of bromocyclopropane (freshly distilled, 13.0 g, 0.107 mol) in THF (50 mL) was added to the addition funnel. A few drops of this solution were added to the flask. Once reaction seemed to have begun, the remainder of the solution was added dropwise to the reaction flask, which periodically was cooled with an ice bath to maintain approximately ambient temperature. After addition was complete, more magnesium (0.50 g, 0.021 mol) was added. The mixture was stirred at ambient temperature until most of the magnesium had disappeared, following which it was refluxed for 30 min. The flask was cooled with an ice bath, dioxane (9.52 g, 0.108 mol) was added dropwise, and the mixture was stirred overnight. The reaction contents were transferred to a centrifuge tube under a blanket of nitrogen. After centrifugation, the clear supernatant liquid was removed from the precipitate with a syringe and the concentration determined.[52]

NMR Observations of Solutions of Diethylmagnesium and Dicyclopropylmagnesium. ^{13}C NMR spectra (20 MHz) were taken of two series of solutions prepared using stock THF solutions of diethylmagnesium and of dicyclopropylmagnesium; the combined concentration of the two components was ~0.3 M in one series and ~0.4 M in the other. Only single sets of absorptions were seen for ethyl and cyclopropyl groups. These absorptions were sharp between +30 and -90 °C, although particularly below 0 °C a downfield shift (~0.5 ppm) of absorptions for carbons bound to Mg was noted as the temperature was lowered. As the mole fraction of dicyclopropylmagnesium increased, the absorptions at 25 °C of CMg of both the ethyl and cyclopropyl groups moved linearly to lower frequency.

NMR Observations of Solutions of Me_2Mg and 1. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were taken in THF solutions having 1.0 M concentrations of Me_2Mg, of 1, or of both. The ^1H (^{13}C) absorption of =CH of 1 was δ 7.168 (118.60) when alone and δ 7.170 (118.60) when Me_2Mg was present; the absorption of Me_2Mg was δ -1.855 (-17.04) when alone and δ -1.868 (-16.87) when 1 was present. A shift of similar magnitude to higher frequency of the ^{13}C NMR absorption of Me_2Mg was seen when dilution was with an alkane rather than with 1.

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Nucleophilic Ring Opening of Bridging Thietane Ligands in Trirhenium Carbonyl Cluster Complexes

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The reactions of 3,3-dimethylthietane, $\overline{\mathrm{SCH_2CMe_2CH_2}}$ (3,3-DMT), and thietane, $\overline{\mathrm{SCH_2CH_2CH_2}}$, with $Re_3(CO)_{10}(NCMe)_2(\mu\text{-}H)_3$, **1**, have yielded the new complexes $Re_3(CO)_{10}[\mu\text{-}\overline{\mathrm{SCH_2CMe_2CH_2}}](\mu\text{-}H)_3$, **2a**, and $Re_3(CO)_{10}[\mu\text{-}\overline{\mathrm{SCH_2CH_2CH_2}}](\mu\text{-}H)_3$, **2b**. Compound **2a** was characterized crystallographically and was found to consist of a trirhenium cluster with three bridging hydride ligands and a bridging thietane ligand coordinated through its sulfur atom. **2a** and **2b** react with halide ions by ring-opening additions to the 3,3-DMT ligand to yield the complex anions $[Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2X)(\mu\text{-}H)_3]^-$, **3a–6a**, X = F (71%), Cl (71%), Br (84%), I (87%), and $[Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}H)_3]^-$, **4b** (67%). Similarly, addition of NMe_3 to **2a** and **2b** yielded the ring-opened zwitterions $Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2NMe_3)(\mu\text{-}H)_3$, **7a** (43%), and $Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2NMe_3)(\mu\text{-}H)_3$, **7b** (44%). Compounds **4a** and **7b** were characterized crystallographically. They are zwitterions positively charged at the nitrogen atoms and negatively charged on the trirhenium clusters. Complex **7b** was also obtained in a 48% yield from the reaction of $Re_3(CO)_{12}(\mu\text{-}H)_3$ with Me_3NO in the presence of thietane, but the corresponding reaction using 3,3-DMT yielded only **2a** and $Re_3(CO)_{11}(\overline{\mathrm{SCH_2CMe_2CH_2}})(\mu\text{-}H)_3$, **8**. Attempts to obtain a ring-opening addition to **2a** by reaction with PMe_2Ph yielded only $Re_3(CO)_{10}(PMe_2Ph)_2(\mu\text{-}H)_3$ by ligand substitution. Attempts to obtain ring-opening addition to **8** by reaction with I^- yielded only $[Re_3(CO)_{11}I(\mu\text{-}H)_3]^-$ by ligand substitution. Crystal Data: for **2a**, space group = $C2/c$, a = 15.749 (2) Å, b = 9.082 (2) Å, c = 31.799 (5) Å, β = 99.17 (1)°, Z = 8, 2325 reflections, R = 0.037; for **4a**, space group = $P\bar{1}$, a = 13.140 (2) Å, b = 17.966 (4) Å, c = 12.252 (3) Å, α = 93.27 (2)°, β = 101.31 (2)°, γ = 74.90 (2)°, Z = 2, 4495 reflections, R = 0.034; for **7b**·$0.5Me_2C{=}O$, space group = $P2_1/c$, a = 8.475 (1) Å, b = 11.740 (5) Å, c = 26.085 (3) Å, β = 93.74 (1)°, Z = 4, 2234 reflections, R = 0.032.

Introduction

In recent studies we have shown that the bridging thietane ligands in the osmium carbonyl cluster complexes $Os_3(CO)_{10}[\mu\text{-}\overline{\mathrm{SCH_2CMe_2CH_2}}]$,[1,2] $Os_3(CO)_9[\mu\text{-}\overline{\mathrm{SCH_2CMe_2C}}\text{-}H_2](\mu_3\text{-}S)$,[3] and $Os_4(CO)_{12}(\mu\text{-}CO)[\mu\text{-}\overline{\mathrm{SCH_2CMe_2CH_2}}]$[4] are activated toward ring-opening addition of nucleophiles through the cleavage of one of the carbon–sulfur bonds (e.g. eqs 1 and 2). An important step

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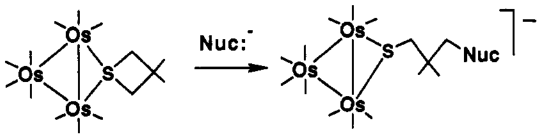
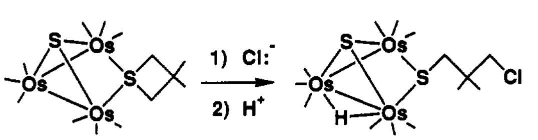


(1)



(2)

in the desulfurization of sulfur-containing heterocycles is the cleavage of the carbon–sulfur bonds.[5-7] Rhenium carbonyl cluster complexes exhibit many structural and reactivity properties similar to osmium cluster complexes but also usually contain several hydride ligands.[8] In an effort to expand the scope of the ring-opening addition reaction of bridging thietanes in metal cluster complexes, we have now prepared the new trirhenium complexes $\mathrm{Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu\text{-}H)_3}$, **2a**, and $\mathrm{Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CH_2CH_2}](\mu\text{-}H)_3}$, **2b**, examined their molecular structures, investigated their reactions toward halides, NMe_3, and PMe_2Ph, and studied crystallographically the molecular structures of two of the ring-opened products that were obtained. The results of these studies are reported here.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were stored over 4-Å molecular sieves. $\mathrm{Re_3(CO)_{12}(\mu\text{-}H)_3}$[9] and 3,3-dimethylthietane[10] (3,3-DMT) were prepared by the published procedures. Trimethylamine *N*-oxide dihydrate (Aldrich) was dehydrated by using a Dean–Stark apparatus with benzene as the solvent prior to use. 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 obtained on a Bruker AM-300 operating at 300 MHz. Separations were performed by TLC in air on Analtech 0.25-mm silica gel 60-Å F_{254} plates. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of $\mathbf{Re_3(CO)_{10}(NCMe)_2(\mu\text{-}H)_3}$, 1. A 46.3-mg amount of $\mathrm{Re_3(CO)_{12}(\mu\text{-}H)_3}$ (0.052 mmol) was dissolved in a mixture of 50 mL of methylene chloride and 5 mL of acetonitrile in a 100 mL rb (round-bottomed) flask. A 9.5-mg amount of Me_3NO (0.13 mmol) was added, and the resulting solution was allowed to react at 25 °C for 1 h. The volatiles were removed in vacuo, and the product was separated by TLC using a hexane/methylene chloride 2/1 solvent mxiture to yield 41.0 mg of $\mathrm{Re_3(CO)_{10}(NCMe)_2(\mu\text{-}H)_3}$ (1, 86% yield). Spectra of 1 were the same as that reported for this compound prepared by a different procedure.[11]

Preparation of $\mathbf{Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu\text{-}H)_3}$, 2a. A 20.1-mg amount of 1 (0.022 mmol) was dissolved in 25 mL of methylene chloride in a 50-mL rb flask. A 2.2-μL amount of 3,3-DMT (0.022 mmol) was added, and the resulting solution was stirred at 25 °C for 1 h. The volatiles were removed in vacuo, and the products were separated by TLC using a hexane/methylene chloride 2/1 solvent mixture as the eluent to yield 8.9 mg of **2a** (0.0094 mmol, 43% yield). IR (ν(CO)) for **2a** (cm^{-1} in hexane): 2104 (m), 2050 (m), 2032 (vs), 2016 (s), 1989 (vs), 1977 (m), 1963 (m), 1948 (m). ^{1}H NMR for **2a** (δ in $CDCl_3$): 3.73 (s, 2H), 3.63 (s, 2H), 1.54 (s, 6H), −13.49 (s, 1H), −16.51 (s, 2H). Anal. Calcd for **2a**: C, 19.07; H, 1.37; N, 0.00. Found: C, 20.36; H, 1.54; N, 0.04. A mass spectrum showed the parent ion $m/z = 944$ and ions due to the loss of 10 CO ligands in combination with the loss of the dimethylthietane ligand.

Preparation of $\mathbf{Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CH_2CH_2}](\mu\text{-}H)_3}$, 2b. A 18.7-mg amount of 1 (0.020 mmol) was dissolved in 25 mL of methylene chloride in a 50 mL rb flask. A 1.5-μL amount of thietane (0.020 mmol) was added, and the resulting solution was allowed to stir at 25 °C for 1 h. The volatiles were removed in vacuo, and the products were separated by TLC using hexane/methylene chloride 2/1 solvent mixture as the eluent to yield 11.6 mg of $\mathrm{Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CH_2CH_2}](\mu\text{-}H)_3}$ (**2b**, 63% yield). IR (ν(CO)) for **2b** (cm^{-1} in CH_2Cl_2): 2103 (w), 2047 (w), 2027 (vs), 2010 (m), 1993 (s), 1956 (s), 1942 (s). ^{1}H NMR for **2** (δ in $CDCl_3$): 3.99 (t, 2H), 3.87 (t, 2H), 3.19 (quintet, 2H), −13.54 (s, 1H), −16.59 (s, 2H).

Reaction of 2a with Halides. (a) $\mathrm{[NBu_4][Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2F)(\mu\text{-}H)_3]}$ (**3a**) was prepared by combining a 6.0-mg amount of **2a** (0.0064 mmol) dissolved in 25 mL of CH_2Cl_2 with 9.5 mL of a solution of 1.0 M $\mathrm{[NBu_4]F}$ in THF (0.0095 mmol). The reaction solution was allowed to stir at 25 °C for 10 min. The volatiles were then removed in vacuo, and the residue was separated by TLC with a hexane/acetone 3/1 solvent mixture to yield 4.9 mg of **3a** (71%). IR (ν(CO)) for **3a** (cm^{-1} in CH_2Cl_2): 2096 (w), 2020 (m), 1999 (vs), 1941 (br, w), 1899 (br, s). ^{1}H NMR for **3a** (δ in $CDCl_3$): 4.26 (d, CH_2F, $^2J_{H-F} = 47.9$ Hz, 2H), 3.10 (t, NCH_2, 8H), 2.39 (s, SCH_2, 2H), 1.62 (m, $NCH_2CH_2CH_2$, 8H), 1.47 (sextet, $NCH_2CH_2CH_2CH_3$, $^3J_{H-H} = 7.3$ Hz, 8H), 1.24 (d, CH_3, $^4J_{H-F} = 3.7$ Hz, 6H), 1.04 (t, $NCH_2CH_2CH_2CH_3$, $^3J_{H-H} = 7.3$ Hz, 12H), −12.45 (s, Re–*H*, 1H), −16.36 (s, Re–*H*, 2H).

(b) $\mathrm{[PPN][Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)_3]}$ (**4a**) was prepared similarly in 71% yield from a 15.4-mg amount of **2a** (0.016 mmol) and a 11.5-mg amount of [PPN]Cl (0.020 mmol) in CH_2Cl_2 solvent. IR (ν(CO)) for **4a** (cm^{-1} in CH_2Cl_2): 2096 (w), 2020 (m), 2000 (vs), 1937 (br, w), 1897 (br, s). ^{1}H NMR for **4a** (δ in $CDCl_3$): 7.67–7.43 (m, 30H), 3.55 (s, CH_2Cl, 2H), 2.41 (s, CH_2S, 2H), 1.08 (s, CH_3, 6H), −12.39 (s, Re–*H*, 1H), −16.36 (s, Re–*H*, 2H). Anal. Calcd for **4a**: C, 40.3; H, 2.86; N, 0.92. Found: C, 40.5; H, 2.79; N, 0.89.

(c) $\mathrm{[NBu_4][HRe_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2Br)(\mu\text{-}H)_3]}$ (**5a**) was prepared similarly in 84% yield from a 9.8-mg amount of **2a** (0.010 mmol) and 5.0 mg of NBu_4Br (0.016 mmol) in CH_2Cl_2 solvent. IR (ν(CO)) for **5a** (cm^{-1} in CH_2Cl_2): 2097 (w), 2021 (m), 2000 (vs), 1943 (br, w), 1900 (br, s). ^{1}H NMR for **5a** (δ in $CDCl_3$): 3.50 (s, SCH_2, 2H), 3.13 (m, 8H, NCH_2), 2.43 (s, CH_2Cl, 2H), 1.65 (m, 8H, NCH_2CH_2), 1.47 (m, 8H, $NCH_2CH_2CH_2$), 1.13 (s, CH_3, 6H), 1.04 (t, 12H, $NCH_2CH_2CH_2CH_3$), −12.46 (s, Re–*H*, 1H), −16.36 (s, Re–*H*, 2H).

(d) $\mathrm{[NBu_4][Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2I)(\mu\text{-}H)_3]}$ (**6a**) was prepared similarly in 87% yield from a 14.5-mg amount of **2a** (0.015 mmol) and a 8.5-mg amount of NBu_4I (0.023 mmol) in CH_2Cl_2 solvent. IR (ν(CO)) for **6a** (cm^{-1} in CH_2Cl_2): 2096 (w), 2020 (m), 2000 (vs), 1942 (br, w), 1903 (br, s). ^{1}H NMR for **6a** (δ in $CDCl_3$): 3.37 (s, SCH_2, 2H), 3.15 (m, 8H, NCH_2), 2.44 (s, CH_2Cl, 2H), 1.65 (m, 8H, NCH_2CH_2), 1.47 (m, 8H, $NCH_2CH_2CH_2$), 1.15 (s, CH_3, 6H), 1.04 (t, 12H, $NCH_2CH_2CH_2CH_3$), −12.46 (s, Re–*H*, 1H), −16.37 (s, Re–*H*, 2H).

Reaction of 2b with [PPN]Cl. A 10.3-mg amount (0.0112 mmol) of **2b** was dissolved 25 mL of CH_2Cl_2 in a 50-mL rb flask. A 6.6-mg amount of [PPN]Cl (0.0112 mmol) was added, and the resulting solution was allowed to react at 25 °C for 1 h. The

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volatiles were removed in vacuo, and the products were separated by TLC using hexane/acetone 2/1 solvent mixture to yield 11.2 mg of $[PPN][Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}H)_3]$ (**4b**, 67%). IR (ν(CO)) for **4b** (cm^{-1} in CH_2Cl_2): 2096 (w), 2032 (w), 2020 (w), 1999 (vs), 1942 (m), 1902 (m). ^1H NMR for **4b** (δ in $CDCl_3$): 3.64 (t, 2H, $J_{H-H} = 6.7$ Hz), 2.45 (t, 2H, $J_{H-H} = 7.3$ Hz), 2.15 (tt, 2H, $J_{H-H} = 7.3$ Hz, $J_{H-H} = 6.7$ Hz), −12.50 (s, 1H), −16.47 (s, 2H).

Reaction of 2a with NMe_3. A 17.2-mg amount of **2a** (0.0182 mmol) was dissolved in 25 mL of methylene chloride in a 50 mL rb flask. The flask was purged with anhydrous NMe_3 gas for 30 min and was then closed and allowed to stir at 25 °C for 18 h. The volatiles were removed in vacuo, and the product was isolated by TLC using a hexane/acetone 2/1 solvent mixture as the eluent to yield 7.2 mg of $Re_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2NMe_3](\mu\text{-}H)_3$ (**7a**, 39% yield). IR (ν(CO)) for **7a** (cm^{-1} in CH_2Cl_2): 2096 (w), 2023 (m), 2002 (vs), 1948 (br), 1912 (br). ^1H NMR (δ in acetone-d_6): 3.77 (s, 2H), 3.54 (s, 9H), 2.59 (s, 2H), 1.43 (s, 6H), −12.35 (s, 1H), −16.39 (s, 2H).

Reaction of 2b with NMe_3. A 20.5-mg amount (0.0224 mmol) of **2b** was dissolved in 25 mL of methylene chloride in a 50 mL rb flask. This solution was then purged for 30 min with NMe_3. The solvent was then removed in vacuo, and the products were separated by TLC with a hexane/acetone 2/1 solvent mixture to yield 9.1 mg of **7b** (42%). IR (ν(CO)) for **7b** (cm^{-1} in acetone): 2097 (w), 2022 (m), 2002 (vs), 1948 (m), 1906 (s). ^1H NMR for **7b** (δ in acetone-d_6): 3.69 (m, 2H,$^2J_{H-H} = -10.0$ Hz, $^3J_{H-H} = 12.3$ Hz, $^3J_{H-H} = 4.7$ Hz), 3.43 (s, 9H), 2.45 (t, 2H, $^3J_{H-H} = 7.1$ Hz), 2.23 (m, 2H, $^2J_{H-H} = -10.0$ Hz, $^3J_{H-H} = 7.1$, $^3J_{H-H} = 12.3$ Hz, $^3J_{H-H} = 4.7$ Hz), −12.47 (s, 1H), −16.54 (s, 2H). Anal. Calcd (found for $\mathbf{7b}\cdot 0.5Me_2C{=}O$: C, 21.10 (21.31); H, 2.09 (2.03); N, 1.43 (1.38).

Reaction of $Re_3(CO)_{12}(\mu\text{-}H)_3$ with Me_3NO and Thietane. A 25.3-mg amount of $Re_3(CO)_{12}(\mu\text{-}H)_3$ (0.028 mmol) was dissolved in 25 mL of methylene chloride in a 50 mL rb flask. A 4.0-mg amount of Me_3NO (0.056 mmol) and 2.0 μL of thietane (0.028 mmol) were added, and the resulting solution was allowed to react at 25 °C for 1 h. A white precipitate formed. The volatiles were removed in vacuo, and the product was separated by TLC using a hexane/acetone 2/1 solvent mixture as the eluent to yield 13.1 mg of $Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2NMe_3)(\mu\text{-}H)_3$ (**7b**; 0.013 mmol, 48%).

Reaction of $Re_3(CO)_{12}(\mu\text{-}H)_3$ with Me_3NO and 3,3-DMT. A 98.0-mg amount (0.109 mmol) of $Re_3(CO)_{12}(\mu\text{-}H)_3$ was dissolved in 50 mL of CH_2Cl_2 in a 100 mL rb flask. A 16.4-mg amount of Me_3NO (0.218 mmol) and 11.5 μL of 3,3-DMT (0.109 mmol) was added, and the resulting solution was allowed to stir at 25 °C for 1 h. The solvent was then removed in vacuo, and the residue was separated by TLC using a hexane/methylene chloride 2/1 solvent mixture to yield in order of elution 46.5 mg of $Re_3(CO)_{11}(\overline{SCH_2CMe_2CH_2})(\mu\text{-}H)_3$ (**8**, 43% yield) and 10.8 mg of $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu\text{-}H)_3$ (**2a**, 10% yield). IR (ν(CO)) for **8** (cm^{-1} in hexane): 2115 (w), 2092 (m), 2035 (s), 2021 (s), 2007 (vs), 1989 (w), 1977 (s), 1945 (m), 1936 (m). ^1H NMR for **8** (δ in $CDCl_3$): 3.45 (s, 4H), 1.35 (s, 6H), −15.14 (s, 2H), −17.40 (s, 1H). Anal. Calcd (found) for **8**: C, 19.8 (20.1); H, 1.33 (1.33).

Transformation of 8 to 2a by Decarbonylation with Me_3NO. A 45.6-mg amount (0.047 mmol) of **8** was dissolved in 25 mL of methylene chloride in a 50-mL rb flask. A 5.3-mg amount of Me_3NO (0.070 mmol) was added, and the resulting solution was allowed to stir at 25 °C for 1 h. The volatiles were then removed in vacuo, and the residue was separated by TLC using a mixture of hexane/methylene chloride 2/1 as the eluent to yield in order of elution 10.6 mg of unreacted **8** and 23.0 mg of **2a** (65% yield based on the amount of **8** consumed).

Reaction of 8 with NBu_4I. A 3.4-mg amount of NBu_4I was added to a solution of 9.7 mg of **8** (0.010 mmol) in approximately 1 mL of acetone-d_6. The solution was then placed in a NMR tube, and spectra were recorded periodically. The compound $[NBu_4][Re_3(CO)_{11}I(\mu\text{-}H)_3]$[12] (**9**) was formed in nearly quantitative yield after 3.5 days as determined by a combination of IR and NMR spectroscopies.

Attempted Protonation of 4a with Acetic Acid. A 5.7-mg amount of **4a** (0.0038 mmol) was dissolved in $CDCl_3$ in a NMR tube, and 5.5 μL (a 20-fold excess) of glacial acetic acid was added. After 10 h, only the unchanged resonances of **4a** were observed in the hydride region of the spectrum. **4a** was recovered unchanged from these reactions.

Reaction of 2a with Dimethylphenylphosphine. A 16.0-mg amount of **2a** (0.017 mmol) was dissolved in 25 mL of methylene chloride in a 50-mL rb flask. A 12.5-μL amount of PMe_2Ph (0.088 mmol) was added, and the resulting solution was allowed to stir for 2 h at 25 °C. The volatiles were removed in vacuo, and the product was separated by TLC using hexane/methylene chloride 2/1 to yield 5.0 mg of $Re_3(CO)_{10}(PMe_2Ph)_2(\mu\text{-}H)_3$ (**10**, 26%). IR (ν(CO)) for **10** (cm^{-1} in CH_2Cl_2): 2097 (w), 2020 (vs), 2001 (s), 1957 (m), 1912 (s). ^1H NMR for **10** (δ in CD_2Cl_2): 7.6–7.2 (m, 10H), 2.06 (d, $^2J_{H-P} = 8.0$ Hz, 6H), 2.02 (d, $^2J_{H-P} = 8.0$ Hz, 6H), −15.63 (d, $^2J_{H-P} = 14.48$ Hz, 2H), −16.35 (t, $^2J_{H-P} = 14.86$ Hz, 1H). The mass spectrum of **10** showed the parent ion $m/e = 1118$ and ions due to the loss of each of 10 CO ligands, one PMe_2Ph ligand, and a combination of PMe_2Ph and CO ligands.

Crystallographic Analyses

Colorless crystals of **2a** were grown from a solution in a methylene chloride/hexane solvent mixture by slow evaporation of solvent at 25 °C. Colorless crystals of **4a** were grown by slow evaporation of solvent from a solution in a diethyl ether/methanol solvent mixture at 25 °C. Colorless crystals of **7b** were grown by slow evaporation of solvent from a solution in an acetone/benzene solvent mixture at 25 °C. All data crystals 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. All unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of these analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[13a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[13b] Lorentz–polarization (Lp) and absorption corrections were applied in each analysis. Full-matrix least-squares refinements minimized the function

$$\sum_{hkl} w(|F_o| - |F_c|)^2$$

where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. For each analysis the positions of all hydrogen atoms on the ligands were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **2a** crystallized in the monoclinic crystal system. Two possible space groups $C2/c$ and Cc were established on the basis of the systematic absences observed during the collection of data. The centrosymmetric space group $C2/c$ was assumed and confirmed by successful solution and refinement of the structure. 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 three hydride ligands were located in a difference Fourier map and were refined on their positional parameters only.

Compound **4a** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms except the phenyl ring carbon atoms of the PPN ion were refined with anisotropic thermal parameters. The hydride ligands were located in chemically reasonable positions in a difference Fourier map but could not be adequately refined. In the end they were added to the structure as fixed contributions only.

Compound **7b** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was established on the basis of the systemic

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[12] Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1981**, *220*, C11.

[13] (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.

Table I. Crystallographic Data for Diffraction Studies

	compd		
	2a	**4a**	**7b**
empirical formula	$Re_3SO_{10}C_{15}H_{13}$	$Re_3ClSP_2O_{10}NC_{51}H_{43}$	$Re_3SO_{10}NC_{16}H_{18}$
M_r	943.94	1517.98	975.00
cryst system	monoclinic	triclinic	monoclinic
lattice params			
a, Å	15.749 (2)	13.140 (2)	8.475 (1)
b, Å	9.082 (2)	17.966 (4)	11.740 (5)
c, Å	31.779 (5)	12.252 (3)	26.085 (3)
α, deg	90.0	93.27 (2)	90.0
β, deg	99.17 (1)	101.31 (2)	93.74 (1)
γ, deg	90.0	74.90 (2)	90.0
V, Å^3	4487 (1)	2738 (1)	2590 (2)
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z value	8	2	4
D_{calc}, g/cm^3	2.79	1.84	2.50
μ(Mo Kα), cm^{-1}	165.0	69.0	143.0
temp, °C	20	20	20
2θ max, deg	45.0	41.5	43.0
no. of observns ($I > 3\sigma(I)$)	2325	4495	2234
no. of variables	271	442	280
residuals: R, R_w	0.037, 0.038	0.034, 0.035	0.032, 0.033
goodness of fit indicator	1.94	1.63	1.64
max shift in final cycle	0.28	0.01	0.05
largest peak in final diff map, e/Å^3	1.80	1.15	1.66
abs corr	empirical	analytical	empirical

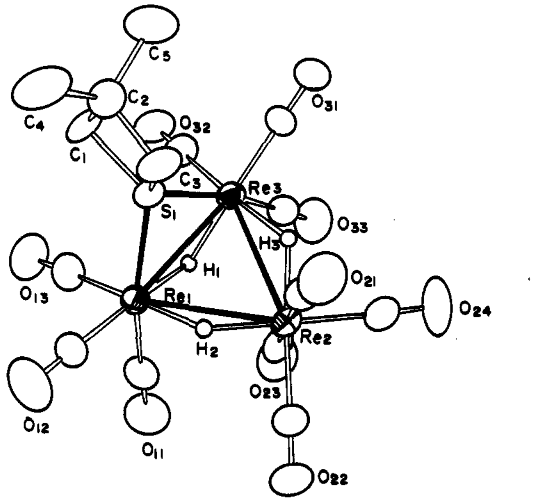


Figure 1. ORTEP diagram of $Re_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2](\mu\text{-}H)_3$, **2a**, showing 50% probability thermal ellipsoids.

absences observed during the collection of 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 ligands were not located and were ignored. In the final stages of the analysis, a collection of four small peaks that had the shape of the molecule acetone (the crystallization solvent) were observed in the difference Fourier analysis. They were disordered about a symmetry center remote from the molecule. This was included in the analysis, partially refined, but included finally as a fixed contribution at half-occupancy since the refinement did not converge well.

Table II. Positional Parameters and B(eq) Values (Å^2) for $Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2)(\mu\text{-}H)_3$, 2a

atom	x	y	z	B(eq)
Re(1)	0.64196 (03)	0.28595 (07)	0.59633 (02)	3.43 (3)
Re(2)	0.43995 (03)	0.31384 (07)	0.56482 (02)	3.33 (3)
Re(3)	0.52051 (03)	0.27048 (07)	0.66234 (2)	3.41 (3)
S(1)	0.6129 (02)	0.4684 (04)	0.64715 (13)	3.6 (2)
O(11)	0.6419 (10)	0.0257 (18)	0.5353 (06)	9 (1)
O(12)	0.7429 (09)	0.4537 (17)	0.5373 (06)	8.2 (9)
O(13)	0.8117 (08)	0.1826 (16)	0.6491 (05)	7.9 (8)
O(21)	0.3943 (08)	0.6479 (15)	0.5595 (05)	6.7 (7)
O(22)	0.4293 (07)	0.3111 (16)	0.4672 (04)	6.2 (7)
O(23)	0.4595 (08)	−0.0343 (15)	0.5667 (05)	7.4 (8)
O(24)	0.2473 (07)	0.2654 (16)	0.5655 (06)	9 (1)
O(31)	0.4108 (07)	0.4449 (15)	0.7168 (04)	5.4 (6)
O(32)	0.6464 (08)	0.1632 (16)	0.7394 (04)	7.1 (7)
O(33)	0.4102 (08)	−0.0081 (16)	0.6663 (05)	8.3 (9)
C(1)	0.6906 (09)	0.5621 (19)	0.6873 (06)	4.9 (8)
C(2)	0.6446 (09)	0.7080 (17)	0.6793 (06)	4.2 (8)
C(3)	0.5819 (10)	0.6629 (17)	0.6392 (05)	4.5 (8)
C(4)	0.6992 (13)	0.834 (02)	0.6712 (06)	8 (1)
C(5)	0.5939 (14)	0.748 (02)	0.7160 (07)	7 (1)
C(11)	0.6436 (10)	0.124 (02)	0.5583 (06)	5 (1)
C(12)	0.7046 (10)	0.397 (02)	0.5594 (06)	4.5 (9)
C(13)	0.7469 (11)	0.2192 (20)	0.6297 (07)	5 (1)
C(21)	0.4162 (09)	0.527 (02)	0.5633 (06)	4.2 (8)
C(22)	0.4321 (10)	0.3067 (19)	0.5031 (06)	4.3 (8)
C(23)	0.4557 (10)	0.092 (03)	0.5675 (06)	6 (1)
C(24)	0.3186 (11)	0.2881 (19)	0.5637 (06)	5.2 (9)
C(31)	0.4526 (09)	0.374 (02)	0.6975 (05)	4.1 (8)
C(32)	0.5997 (10)	0.2065 (19)	0.7103 (06)	4.7 (8)
C(33)	0.4529 (10)	0.095 (02)	0.6660 (06)	5 (1)
H(1)	0.583 (06)	0.167 (12)	0.629 (03)	2.0
H(2)	0.544 (06)	0.346 (12)	0.566 (03)	2.0
H(3)	0.439 (06)	0.356 (12)	0.616 (03)	2.0

Results and Discussion

A summary of the results of the reactions of dimethylthietane with the trirhenium clusters in this study is shown in Scheme I. Most of the corresponding reactions using the unsubstituted thietane ligand were also established. The reactions of 3,3-dimethylthietane, $SCH_2CMe_2CH_2$ (3,3-DMT), and thietane, $SCH_2CH_2CH_2$, with the lightly stabilized trirhenium cluster complex $Re_3(CO)_{10}(NCMe)_2(\mu_3\text{-}H)_3$, **1**, yielded the new complexes $Re_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2](\mu\text{-}H)_3$, **2a** (43%), and $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2](\mu\text{-}H)_3$, **2b** (63%), respectively, by substitution of the two MeCN ligands with one thietane ligand. Both products were characterized by IR, ^1H NMR, and mass spectrometry. To be certain about the nature of the coordination of the thietane ligand, a single-crystal X-ray diffraction analysis of **2a** was also performed. An ORTEP drawing of **2** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The molecule consists of a triangular cluster of three rhenium atoms that are joined by three hydride-bridged rhenium–rhenium bonds. To maintain 18-electron configurations at all of the metal atoms, the 3,3-DMT

Scheme I

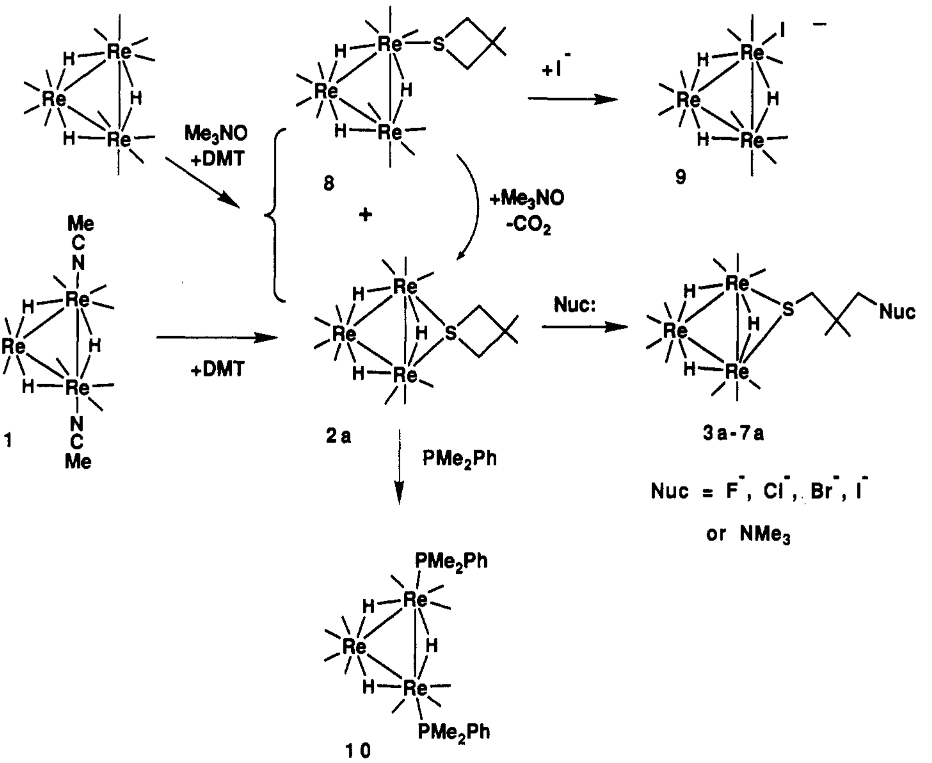


Table III. Intramolecular Distances for 2a[a]

Re(1)-Re(2)	3.1894 (9)	Re(2)-H(2)	1.66 (9)
Re(1)-Re(3)	3.059 (1)	Re(2)-H(3)	1.7 (1)
Re(1)-S(1)	2.408 (4)	Re(3)-S(1)	2.410 (4)
Re(1)-C(11)	1.91 (2)	Re(3)-C(31)	1.91 (2)
Re(1)-C(12)	1.94 (2)	Re(3)-C(32)	1.90 (2)
Re(1)-C(13)	1.91 (2)	Re(3)-C(33)	1.93 (2)
Re(1)-H(1)	1.8 (1)	Re(3)-H(1)	1.8 (1)
Re(1)-H(2)	1.8 (1)	Re(3)-H(3)	1.9 (1)
Re(2)-Re(3)	3.180 (1)	S(1)-C(1)	1.83 (1)
Re(2)-C(21)	1.97 (2)	S(1)-C(3)	1.84 (2)
Re(2)-C(22)	1.95 (2)	O-C(av)	1.15 (2)
Re(2)-C(23)	2.03 (2)	C(1)-C(2)	1.51 (2)
Re(2)-C(24)	1.92 (2)	C(2)-C(3)	1.54 (2)

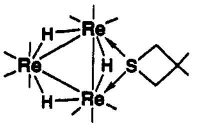
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

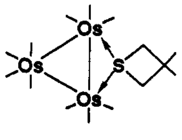
Table IV. Intramolecular Bond Angles for 2a[a]

Re(2)-Re(1)-Re(3)	61.15 (2)	Re(3)-Re(2)-C(24)	104.1 (6)
Re(2)-Re(1)-S(1)	82.50 (8)	Re(1)-Re(3)-Re(2)	61.45 (2)
Re(2)-Re(1)-C(11)	88.6 (5)	Re(1)-Re(3)-S(1)	50.6 (1)
Re(2)-Re(1)-C(12)	110.3 (5)	Re(1)-Re(3)-C(31)	147.8 (5)
Re(2)-Re(1)-C(13)	158.3 (6)	Re(1)-Re(3)-C(32)	99.3 (5)
Re(3)-Re(1)-S(1)	50.6 (1)	Re(1)-Re(3)-C(33)	119.4 (5)
Re(3)-Re(1)-C(11)	118.1 (5)	Re(2)-Re(3)-S(1)	82.7 (1)
Re(3)-Re(1)-C(12)	151.0 (5)	Re(2)-Re(3)-C(31)	109.5 (4)
Re(3)-Re(1)-C(13)	100.6 (6)	Re(2)-Re(3)-C(32)	158.2 (5)
S(1)-Re(1)-C(11)	168.3 (5)	Re(2)-Re(3)-C(33)	91.3 (5)
S(1)-Re(1)-C(12)	102.5 (5)	Re(1)-S(1)-Re(3)	78.8 (1)
S(1)-Re(1)-C(13)	94.9 (6)	Re(1)-S(1)-C(1)	127.6 (5)
Re(1)-Re(2)-Re(3)	57.40 (2)	Re(1)-S(1)-C(3)	130.0 (6)
Re(1)-Re(2)-C(21)	105.2 (4)	Re(3)-S(1)-C(1)	124.4 (6)
Re(1)-Re(2)-C(22)	102.3 (4)	Re(3)-S(1)-C(3)	126.0 (5)
Re(1)-Re(2)-C(23)	78.4 (4)	C(1)-S(1)-C(3)	77.5 (7)
Re(1)-Re(2)-C(24)	159.4 (6)	S(1)-C(1)-C(2)	92 (1)
Re(3)-Re(2)-C(21)	101.0 (5)	C(1)-C(2)-C(3)	98 (1)
Re(3)-Re(2)-C(22)	158.3 (5)	S(1)-C(3)-C(2)	91 (1)
Re(3)-Re(2)-C(23)	79.0 (5)	Re-C-O(av)	175 (2)

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

ligand was adopted as a bridging ligand and serves as a four-electron donor by coordinating both of the lone pairs of electrons on the sulfur atom to the metal atoms. The rhenium–sulfur distances, 2.408 (4) and 2.410 (4) Å, are not unusual.[14] The 3,3-DMT ligand possesses a slightly puckered four-membered ring. The dihedral angle of 12.4° between the C(1)–C(2)–C(3) and C(1)–S–C(3) planes is slightly less than that observed for the bridging 3,3-DMT ligand in the osmium complex $Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$, 11, 20.6°.[2] The observation of a single resonance for the methyl groups in the ^1H NMR spectrum indicates that the puckered ring is rapidly inverting its configuration on the NMR time scale at 25 °C. The hydride ligands were located and refined structurally, and there is one ligand bridging each of the three metal–metal bonds. The Re(1)–Re(2) and Re(2)–Re(3) distances are typical of hydride-bridged Re–Re bonds.[11,15] The Re(1)–Re(3) distance is significantly shorter, 3.059 (1) Å, due to the contraction effect of the bridging thietane ligand across that bond.[16] Only two hydride resonances were observed in the ^1H NMR spectrum, −13.49 (1H) and −16.51 (2H), due to the rapid inversion of configuration of the puckered thietane ligand. The complex also contains 10 linear terminal carbonyl ligands distributed as shown in Figure 1. Except for the presence of the bridging hydride ligands, the structure of 2a is very similar to that of the osmium complex 11.


2a


11

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(14) Bonfichi, R.; Ciani, G.; D'Alfonso, G.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1982**, *231*, C35.

(15) Wei, C. Y.; Garlaschelli, L.; Bau, R.; Koetzle, T. F. *J. Organomet. Chem.* **1981**, *213*, 63.

(16) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.

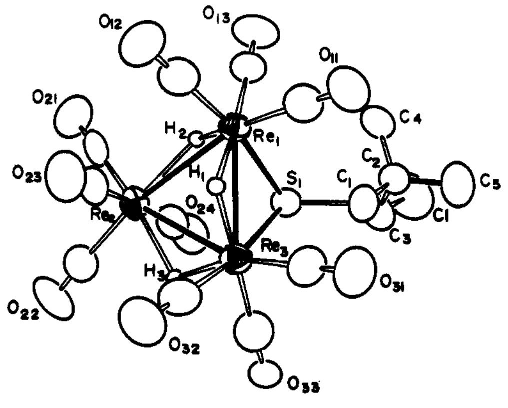

Figure 2. ORTEP diagram of the complex anion of the salt $[PPN][Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)_3]$, **4a**, showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and B(eq) Values (Å^2) for $[PPN][Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)_3]$, 4a

atom	x	y	z	B(eq)
Re(1)	0.92020 (04)	0.29929 (03)	1.00569 (04)	3.50 (3)
Re(2)	0.99616 (04)	0.12903 (03)	1.10745 (04)	3.80 (3)
Re(3)	0.80894 (04)	0.26420 (03)	1.18031 (04)	3.63 (3)
Cl	1.1808 (03)	0.4741 (03)	1.4400 (04)	10.0 (3)
S(1)	0.9621 (02)	0.32412 (18)	1.2085 (02)	3.7 (2)
P(1)	0.4037 (02)	0.20048 (19)	0.6750 (02)	3.6 (2)
P(2)	0.5049 (02)	0.24228 (19)	0.4976 (02)	3.5 (2)
O(11)	0.7719 (07)	0.4604 (06)	0.9469 (08)	6.4 (6)
O(12)	0.8523 (08)	0.2397 (06)	0.7716 (08)	6.8 (6)
O(13)	1.1139 (07)	0.3377 (06)	0.9374 (07)	6.7 (6)
O(21)	1.1740 (07)	0.0519 (06)	0.9762 (08)	7.0 (6)
O(22)	0.9894 (08)	−0.0174 (06)	1.2215 (08)	7.5 (7)
O(23)	0.8083 (07)	0.1112 (06)	0.9141 (08)	6.4 (6)
O(24)	1.1699 (08)	0.1461 (06)	1.3137 (08)	7.0 (7)
O(31)	0.6368 (07)	0.4164 (06)	1.1760 (08)	6.7 (6)
O(32)	0.6360 (08)	0.1756 (06)	1.1081 (08)	6.9 (7)
O(33)	0.8194 (07)	0.2472 (07)	1.4292 (08)	8.4 (8)
N	0.4244 (07)	0.2154 (05)	0.5552 (07)	3.9 (5)
C(1)	0.9153 (08)	0.4259 (07)	1.2449 (09)	4.3 (7)
C(2)	1.0037 (09)	0.4689 (07)	1.2770 (09)	4.3 (7)
C(3)	1.0779 (10)	0.4280 (08)	1.3790 (10)	5.6 (8)
C(4)	1.0637 (10)	0.4662 (08)	1.1835 (11)	5.7 (8)
C(5)	0.9513 (11)	0.5510 (09)	1.3083 (12)	7 (1)
C(11)	0.8290 (10)	0.4002 (09)	0.9675 (10)	4.7 (8)
C(12)	0.8788 (09)	0.2619 (08)	0.8595 (11)	4.9 (8)
C(13)	1.0405 (10)	0.3230 (07)	0.9649 (09)	4.6 (7)
C(21)	1.1035 (10)	0.0822 (07)	1.0242 (10)	4.4 (7)
C(22)	0.9930 (10)	0.0335 (08)	1.1786 (11)	5.0 (8)
C(23)	0.8762 (10)	0.1194 (07)	0.9836 (11)	4.4 (7)
C(24)	1.1049 (10)	0.1427 (08)	1.2361 (11)	4.8 (8)
C(31)	0.7034 (10)	0.3584 (09)	1.1775 (11)	5.0 (8)
C(32)	0.7006 (10)	0.2087 (08)	1.1358 (10)	4.8 (8)
C(33)	0.8145 (09)	0.2534 (08)	1.3334 (12)	5.2 (8)

Table VI. Intramolecular Distances for 4a[a]

Re(1)–Re(2)	3.204 (1)	Re(3)–S(1)	2.478 (3)
Re(1)–Re(3)	2.9955 (8)	Re(3)–C(31)	1.88 (2)
Re(1)–S(1)	2.478 (3)	Re(3)–C(32)	1.92 (1)
Re(1)–C(11)	1.92 (2)	Re(3)–C(33)	1.88 (1)
Re(1)–C(12)	1.90 (1)	Cl–C(3)	1.79 (1)
Re(1)–C(13)	1.90 (1)	S(1)–C(1)	1.83 (1)
Re(2)–Re(3)	3.201 (1)	C(1)–C(2)	1.54 (2)
Re(2)–C(21)	1.89 (1)	C(2)–C(3)	1.52 (2)
Re(2)–C(22)	1.98 (1)	C(2)–C(4)	1.50 (2)
Re(2)–C(23)	2.00 (1)	C(2)–C(5)	1.52 (2)
Re(20–C(24)	1.96 (1)	O–C(av)	1.16 (1)

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

Table VII. Intramolecular Bond Angles for 4a

Re(2)–Re(1)–Re(3)	62.07 (2)	Re(1)–Re(3)–C(31)	98.5 (4)
Re(2)–Re(1)–S(1)	77.33 (8)	Re(1)–Re(3)–C(32)	118.0 (3)
Re(2)–Re(1)–C(11)	158.6 (3)	Re(1)–Re(3)–C(33)	146.3 (3)
Re(2)–Re(1)–C(12)	92.3 (4)	Re(2)–Re(3)–S(1)	77.38 (7)
Re(2)–Re(1)–C(13)	108.2 (4)	Re(2)–Re(3)–C(31)	160.1 (4)
Re(3)–Re(1)–S(1)	52.81 (7)	Re(2)–Re(3)–C(32)	94.2 (4)
Re(3)–Re(1)–C(11)	97.6 (3)	Re(2)–Re(3)–C(33)	107.8 (4)
Re(3)–Re(1)–C(12)	116.4 (4)	S(1)–Re(3)–C(31)	95.0 (4)
Re(3)–Re(1)–C(13)	150.3 (4)	S(1)–Re(3)–C(32)	169.6 (4)
S(1)–Re(1)–C(11)	96.1 (4)	S(1)–Re(3)–C(33)	94.4 (4)
S(1)–Re(1)–C(12)	167.6 (4)	Re(1)–S(1)–Re(3)	74.38 (8)
S(1)–Re(1)–C(13)	98.5 (4)	Re(1)–S(1)–C(1)	112.8 (4)
Re(1)–Re(2)–Re(3)	55.77 (2)	Re(3)–S(1)–C(1)	109.0 (4)
Re(1)–Re(2)–C(21)	100.5 (4)	S(1)–C(1)–C(2)	115.1 (8)
Re(1)–Re(2)–C(22)	160.8 (4)	C(1)–C(2)–C(3)	106 (1)
Re(1)–Re(2)–C(23)	78.3 (4)	C(1)–C(2)–C(4)	111 (1)
Re(1)–Re(2)–C(24)	100.7 (4)	C(1)–C(2)–C(5)	108 (1)
Re(3)–Re(2)–C(21)	156.2 (4)	C(3)–C(2)–C(4)	111 (1)
Re(3)–Re(2)–C(22)	106.7 (4)	C(3)–C(2)–C(5)	109 (1)
Re(3)–Re(2)–C(23)	81.2 (3)	C(4)–C(2)–C(5)	112 (1)
Re(3)–Re(2)–C(24)	94.5 (4)	Cl–C(3)–C(2)	113.7 (9)
Re(1)–Re(3)–Re(2)	62.16 (2)	Re–C(av)–O	178 (1)
Re(1)–Re(3)–S(1)	52.81 (7)		

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

When treated with soluble halide salts, **2a** and **2b** react by a ring-opening addition of the halide ions to the thietane ligand to yield salts of the complex anions $[Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2X)(\mu\text{-}H)_3]^-$, **3a–6a**, X = F (71%), Cl (71%), Br (84%), and I (87%), and $[Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}H)_3]^-$, **4b** (67%). The reactions of **2a** with each halide ion were studied. For **2b** only the reaction with Cl$^-$ was studied. All of the products were characterized by IR and ^{1}H NMR spectroscopy. Compound **4a** was also characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of the complex anion **4a** is shown in Figure 2, and final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. This cluster consists of a triangular arrangement of three rhenium atoms bridged on one edge by the sulfur atom of a 3-chloro-2,2-dimethylpropanethiolato ligand. Both rhenium–sulfur distances are identical, 2.478 (3) Å, and are significantly longer than those in **2a**. The hydride ligands (located but not refined) bridge each metal–metal bond in a fashion similar to that observed in **2a**, δ = −12.39 (s, 1H) and −16.36 (s, 2H). Interestingly, the sulfur-bridged metal–metal bond is significantly shorter, 2.9955 (8) Å, than that in **2a**. The complex contains 10 linear terminal carbonyl ligands arranged similarly to those in **2a**. All of the other halide addition products were believed to have similar structures.

When treated with NMe$_3$, **2a** and **2b** both undergo a ring-opening addition to the thietane ligand to yield the complexes $Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2NMe_3)(\mu\text{-}H)_3$, **7a** (43%), and $Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2NMe_3)(\mu\text{-}H)_3$, **7b** (44%), respectively. The reaction of **2b** proceeds significantly faster (30 min) than that of **2a** (18 h). The slowness of the reaction of **2a** might be due to the steric blockage at the carbon site of addition by the *gem*-methyl groups on the adjacent carbon atom. It was shown that these additions proceed by a backside nucleophilic attack at the site of addition in the osmium complex **10**.[1b] Due to the rapid reaction of **2b** with NMe$_3$, it was found that the reaction of $Re_3(CO)_{12}(\mu\text{-}H)_3$ with Me$_3$NO in the presence of thietane yielded **7b** as the principal product, whereas the reaction of $Re_3(CO)_{12}(\mu\text{-}H)_3$ with Me$_3$NO in the presence of 3,3-DMT yielded only a combination of **2a** and $Re_3(CO)_{11}(\overline{SCH_2CMe_2CH_2})(\mu\text{-}H)_3$, **8**, by replacement of two and one CO ligands with a 3,3-DMT, respectively. Although **8** was not characterized crystallographically, it is believed that the 3,3-DMT ligand is coordinated to only one metal atom as found in the related osmium complex

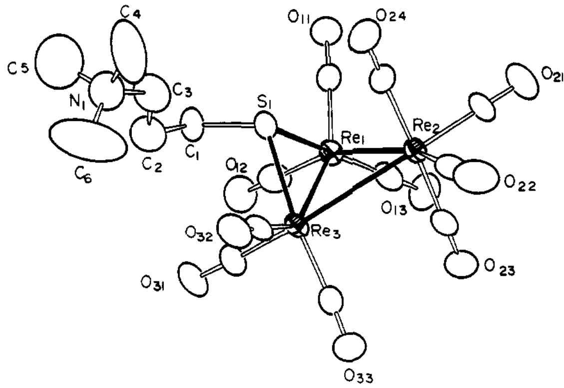

Figure 3. ORTEP diagram of $Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2NMe_3)(\mu\text{-}H)_3$, **7b**, showing 50% probability thermal ellipsoids.

Table VIII. Positional Parameters and *B*(eq) Values (Å²) for 7b

atom	*x*	*y*	*z*	*B*(eq)
Re(1)	0.25447 (07)	0.19910 (06)	0.64744 (02)	3.38 (3)
Re(2)	−0.02984 (07)	0.31218 (06)	0.705292 (19)	3.23 (3)
Re(3)	0.07671 (07)	0.39137 (06)	0.59426 (02)	3.45 (3)
S(1)	0.3249 (04)	0.4034 (04)	0.64920 (13)	3.7 (2)
O(11)	0.5239 (13)	0.1439 (12)	0.7280 (04)	6.1 (7)
O(12)	0.4555 (15)	0.1295 (14)	0.5590 (05)	7.6 (8)
O(13)	0.1084 (17)	−0.0405 (13)	0.6488 (05)	6.8 (8)
O(21)	−0.0761 (18)	0.1716 (13)	0.8015 (04)	8.3 (9)
O(22)	−0.3186 (16)	0.4514 (15)	0.7326 (05)	9 (1)
O(23)	−0.2327 (14)	0.1453 (13)	0.6347 (04)	6.1 (7)
O(24)	0.1879 (15)	0.4696 (12)	0.7720 (05)	6.4 (8)
O(31)	0.2483 (13)	0.3769 (13)	0.4953 (04)	6.3 (7)
O(32)	0.0416 (17)	0.6490 (13)	0.5813 (04)	6.2 (8)
O(33)	−0.2371 (14)	0.3446 (12)	0.5330 (04)	5.9 (7)
N	0.525 (02)	0.7596 (17)	0.6187 (07)	7 (1)
C(1)	0.494 (02)	0.4264 (16)	0.6103 (06)	5 (1)
C(2)	0.494 (03)	0.557 (03)	0.5915 (08)	11 (2)
C(3)	0.502 (04)	0.632 (03)	0.6298 (10)	12 (2)
C(4)	0.489 (04)	0.827 (03)	0.6661 (11)	13 (2)
C(5)	0.691 (04)	0.779 (03)	0.6145 (11)	14 (3)
C(6)	0.446 (06)	0.808 (04)	0.5767 (11)	21 (4)
C(11)	0.4232 (19)	0.1609 (14)	0.6974 (06)	3.8 (8)
C(12)	0.380 (02)	0.1548 (19)	0.5920 (06)	6 (1)
C(13)	0.162 (02)	0.0525 (18)	0.6483 (06)	5 (1)
C(21)	−0.0560 (20)	0.2187 (17)	0.7644 (06)	5 (1)
C(22)	−0.211 (02)	0.4028 (18)	0.7217 (05)	5 (1)
C(23)	−0.1598 (18)	0.2040 (18)	0.6602 (05)	4 (1)
C(24)	0.1085 (20)	0.4145 (16)	0.7469 (06)	4 (1)
C(31)	0.1810 (19)	0.3824 (15)	0.5323 (05)	4.2 (8)
C(32)	0.055 (02)	0.5500 (18)	0.5871 (05)	4 (1)
C(33)	−0.1188 (20)	0.3608 (16)	0.5570 (06)	4.2 (9)

Table IX. Intramolecular Distances for 7b[a]

Re(1)–Re(2)	3.2124 (9)	Re(3)–C(31)	1.89 (1)
Re(1)–Re(3)	3.003 (1)	Re(3)–C(32)	1.88 (2)
Re(1)–S(1)	2.472 (5)	Re(3)–C(33)	1.90 (2)
Re(1)–C(11)	1.92 (2)	S(1)–C(1)	1.83 (2)
Re(1)–C(12)	1.92 (2)	O–C(av)	1.15 (2)
Re(1)–C(13)	1.89 (2)	N–C(3)	1.54 (3)
Re(2)–Re(3)	3.2262 (8)	N–C(4)	1.51 (3)
Re(2)–C(21)	1.92 (2)	N–C(5)	1.44 (3)
Re(2)–C(22)	1.94 (2)	N–C(6)	1.37 (3)
Re(2)–C(23)	2.01 (2)	C(1)–C(2)	1.61 (4)
Re(2)–C(24)	1.96 (2)	C(2)–C(3)	1.33 (3)
Re(3)–S(1)	2.471 (4)		

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

Table X. Intramolecular Bond Angles for 7b[a]

Re(2)–Re(1)–Re(3)	62.44 (2)	Re(3)–Re(2)–C(22)	108.2 (5)
Re(2)–Re(1)–S(1)	77.17 (9)	Re(3)–Re(2)–C(23)	80.3 (4)
Re(2)–Re(1)–C(11)	109.0 (4)	Re(3)–Re(2)–C(24)	97.3 (5)
Re(2)–Re(1)–C(12)	159.0 (5)	Re(1)–Re(3)–Re(2)	61.97 (2)
Re(2)–Re(1)–C(13)	92.7 (5)	Re(1)–Re(3)–S(1)	52.6 (1)
Re(3)–Re(1)–S(1)	52.58 (9)	Re(2)–Re(3)–S(1)	76.91 (8)
Re(3)–Re(1)–C(11)	144.7 (5)	Re(2)–Re(3)–C(31)	157.4 (5)
Re(3)–Re(1)–C(12)	98.1 (6)	Re(2)–Re(3)–C(32)	110.1 (4)
Re(3)–Re(1)–C(13)	119.6 (5)	Re(2)–Re(3)–C(33)	96.8 (4)
S(1)–Re(1)–C(11)	92.6 (5)	S(1)–Re(3)–C(31)	94.1 (5)
S(1)–Re(1)–C(12)	97.6 (6)	S(1)–Re(3)–C(32)	94.3 (5)
S(1)–Re(1)–C(13)	169.3 (5)	S(1)–Re(3)–C(33)	171.4 (5)
Re(1)–Re(2)–Re(3)	55.59 (2)	Re(1)–S(1)–Re(3)	74.8 (1)
Re(1)–Re(2)–C(21)	105.7 (5)	S(1)–C(1)–C(2)	109 (1)
Re(1)–Re(2)–C(22)	163.7 (5)	C(1)–C(2)–C(3)	114 (2)
Re(1)–Re(2)–C(23)	82.1 (4)	N–C(3)–C(2)	120 (3)
Re(1)–Re(2)–C(24)	94.2 (5)	Re–C–O(av)	177 (2)
Re(3)–Re(2)–C(21)	160.2 (5)		

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

$Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2})$, **12**.[17]

The molecular structure of **7b** was established by X-ray diffraction analysis, and an ORTEP drawing of its molecular structure is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected interatomic distances and angles are listed in Tables IX and X. This molecule is very similar to those of the halide addition products. The thietane ring was opened, and the NMe_3 molecule was added to the carbon atom of the cleaved carbon–sulfur bond. It is thus transformed to a quaternary nitrogen that is positively charged. A formal negative charge is presumably delocalized in the trirhenium cluster as in the halide complexes **3**–**6**. Thus, the complexes **7** are zwitterions, and this may explain their low solubility in all but very polar solvents such as acetone. The molecular dimensions about the Re_3 cluster are very similar to those in **4a**. The hydride ligands, $\delta = -12.47$ (1H) and −16.54 (2H), were not located in this structural analysis but are believed to bridge the Re–Re bonds in a manner similar to that found in **2a** and **4a**. In addition to the resonances of the hydride ligands, the ^1H NMR spectrum of **7b** in acetone-d_6 shows a singlet at 3.44 (9H) due to the three equivalent methyl groups on the nitrogen atom, a triplet at 2.45 (2H) due to the sulfur-bound methylene group, and a complex multiplet at 2.22 (2H) due to the methylene group between the two methylene groups. The nitrogen bound methylene group appears as an AA′ multiplet at 3.69 ppm ($^2J_{H-H} = -10.0$ Hz, $^3J_{H-H} = 12.3$ Hz, $^3J_{H-H} = 4.7$ Hz), due to coupling to the magnetically inequivalent hydrogen atoms on the neighboring methylene group.

An attempt was made to induce the bridging 3,3-DMT ligand in **2a** to open by addition of PMe_2Ph, but this reaction led only to the formation of $Re_3(CO)_{10}(PMePh)_2(\mu\text{-}H)_3$ by ligand substitution.[11]

In our studies of the ring-opening additions of halide ions to bridging thietane ligands in osmium complexes, we found that the anionic complexes could be neutralized easily by protonation to yield hydride-containing complexes.[1,3,4] Thus, an attempt to neutralize the anion **4a** by protonation using a 20-fold excess of glacial acetic acid was made, but no evidence for proton addition to the complex was obtained by the NMR spectroscopy, and the anion was recovered unchanged from the reaction.

In previous studies of osmium cluster complexes we were able to induce bridging thietane ligands to open by the addition of selected nucleophiles and the cleavage of one of the carbon–sulfur bonds.[1-4] We have found that the bridging thietane ligands in the complexes **2** can also be opened by the addition of halide ion or NMe_3 under mild conditions to yield the anionic complexes **3a**–**6a** and **4b** and the zwitterions **7a**,**b**, respectively. These complexes

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[17] Adams, R. D.; Pompeo, M. P. *Organometallics* **1992**, *9*, 1718.

Organometallics **1992**, *11*, 3801–3804 3801

contain bridging thiolato ligands serving as three-electron donors. Although edge-bridging thiolato ligands are commonly found in osmium cluster complexes,[1-4,18] these may be the first examples of these ligands in trirhenium complexes.[14] The tertiary phosphine, PMe_2Ph, did not add at the thietane carbon atom but instead displaced the thietane ligand and added two PMe_2Ph ligands to the cluster.

Unlike the previously studied osmium complexes, we were unable to protonate the anionic clusters in this study. In the osmium clusters the protonation reactions led to the formation of complexes with bridging hydride ligands. In these rhenium complexes each rhenium–rhenium interaction already contains one bridging hydride ligand; thus, the addition of another hydrogen atom would require the placement of two hydride ligands across one metal–metal bond or the formation of a terminal hydride ligand. Although complexes with two hydride ligands bridging one Re–Re bond are known,[19] they are not commonly found in electron-saturated complexes such as these.

Complex **8** was not characterized crystallographically but is believed to contain a thietane ligand coordinated in a terminal fashion by using only one of the lone pairs of electrons on the sulfur atom as found in the related osmium complex $Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2})$, **12**. An attempt was also made to induce the terminal 3,3-DMT ligand in **8** to open by reaction with I^-, but this reaction led only to the formation of $[Re_3(CO)_{11}I(\mu\text{-}H)_3]^-$, **9**, by ligand substitution. In this and all previous cases, we have observed nucleophilic ring-opening addition reactions only for bridging thietane ligands.[1]

We have proposed previously that the activation of *bridging* thietane ligands to ring opening by nucleophiles can be explained by the withdrawl of electron density from the sulfur atom via the σ-donation of the *two* lone pairs of electrons to the metal atoms. This will in turn lead to some withdrawl of electron density from the carbon atoms bonded to the sulfur atom, thus making them more susceptible to attack by nucleophiles. Similar mechanisms have been proposed to explain the cleavage of C–S bonds in other sulfur-containing ligands.[20]

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Supplementary Material Available: Tables of hydrogen atom and phenyl ring carbon atom positional parameters and anisotropic thermal parameters for the structural analyses of compounds **2a**, **4a**, and **7b** (12 pages). Ordering information is given on any current masthead page.

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Transition Metal Polyhydride Complexes. 5. Complexes with a Cyclopentadienyl Ligand

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Ab initio calculations with effective core potentials have been used to study the relative stabilities of classical and nonclassical isomers of 18-electron polyhydride transition metal complexes with an η^5-C_5H_5 ligand. Systematic calculations on $MH_nL_{4-n}Cp$ (n = 1–4), where M = Ru, Rh, Os, and Ir and L = PH_3 and CO, indicate that most polyhydrides with a cyclopentadienyl ligand adopt classical isomers. The strong "σ"- and "π"-donating ability of the Cp ligand increases the transfer of metal d electrons to hydrides and stabilizes the classical isomers. Although the nonclassical form is stabilized by replacing phosphine ligand(s) with π-accepting CO ligand(s), the classical form is still preferred for most complexes.

Introduction

Extensive studies of transition metal polyhydride complexes have led to the conclusion that polyhydrides may adopt both classical structures having terminal hydride ligands and nonclassical structures containing η^2-H_2 ligands.[1-25] In a series of papers, we suggested the use of the second-order Møller–Plesset (MP2)[26] perturbation calculations as a mean of obtaining reliable results on deter-

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