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Preliminary Communication

Cluster-assisted cyclooligomerization of thietane. A new route to polythioether macrocycles

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Abstract

The trirhenium complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**1**) was found to produce an oligomerization of thietane at 25° C over 18 h to yield the new complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**2**), in 47% yield. Details of the structure of compound **2** were obtained from a single crystal X-ray diffraction analysis of its PMe_2Ph derivative **3**. It was found to contain a bridging thiolate group $SCH_2CH_2CH_2$ that is terminated with a $SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2$ macrocycle. The macrocycle was cleaved from the cluster by treatment with NaOEt and the free molecule trithiacyclodecane was isolated in 32% yield. Crystal data for **3**: space group = $P2_1/n$, $a = 8.637(2)$ Å, $b = 41.80(1)$ Å, $c = 15.418(2)$ Å, $\beta = 111.79(2)°$, $Z = 4$, 2836 reflections, $R = 0.036$.

In previous studies we have shown that bridging thietane ligands in metal cluster complexes are activated toward ring opening addition by nucleophiles [1]. Recently, we have found a triosmium cluster complex that produces a trimerization of 3,3-dimethylthietane by a series of ring opening additions that was initiated at a bridging thietane ligand and was terminated by an oxidative addition of a C–S bond to the cluster [2]. We have now found that the bridging thietane ligand in the trirhenium complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**1**) also produces an oligomerization of thietane, but this is terminated by a cyclization that yields a cyclotrithiadodecane grouping that remains linked to the cluster through a trimethylenethiolato grouping.

Compound **1** reacts with three equivalents of thietane, $SCH_2CH_2CH_2$, at 25°C over 18 h to yield the new complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**2**), in 47% yield [3]. Compound **2** has been characterized by IR, and ^1H NMR spectroscopy and by a single crystal x-ray diffraction analysis of its PMe_2Ph derivative $Re_3(CO)_9(PMe_2Ph)[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**3**) [4]. The ^1H NMR spectrum of **2** exhibited a complex series of multiplets for the methylene groups: $\delta = 3.91$ (m, 2H), 3.46 (t, 2H, $J_{H-H} = 7.4$ Hz), 3.36 (m, 2H), 2.91 (q, 2H, $J_{H-H} = 5.8$ Hz), 2.78 (q, 2H, $J_{H-H} = 5.8$ Hz), 2.74 (t, 4H, $J_{H-H} = 5.1$ Hz), 2.59 (t, 2H, $J_{H-H} = 7.2$ Hz), 2.19 (m, 6H), 1.87 (q, 2H, $J_{H-H} = 6.2$ Hz) that integrate to 24 H which is consistent with the presence of four equivalents of thietane and two hydride resonances $\delta = -12.46$ (s, 1H, -16.49 (s, 2H). An ORTEP diagram of the molecular structure of **3** shows the manner in which the four molecules of thietane were combined,

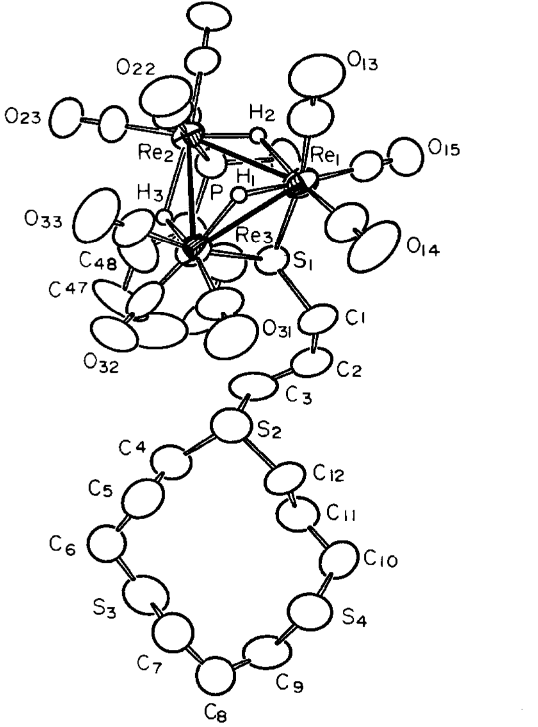

Fig. 1. An ORTEP diagram of $Re_3(CO)_9(PMe_2Ph)[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**3**), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Re(1)–Re(2) = 3.220(1), Re(1)–Re(3) = 3.031(1), Re(2)–Re(3) = 3.211(1), Re(2)–P = 2.458(4), Re(1)–S(1) = 2.466(4), Re(3)–S(1) = 2.461(4), S(2)–C(3) = 1.80(2), S(1)–C(1) = 1.84(2), S(2)–C(4) = 1.80(2), S(2)–C(12) = 1.82(2).

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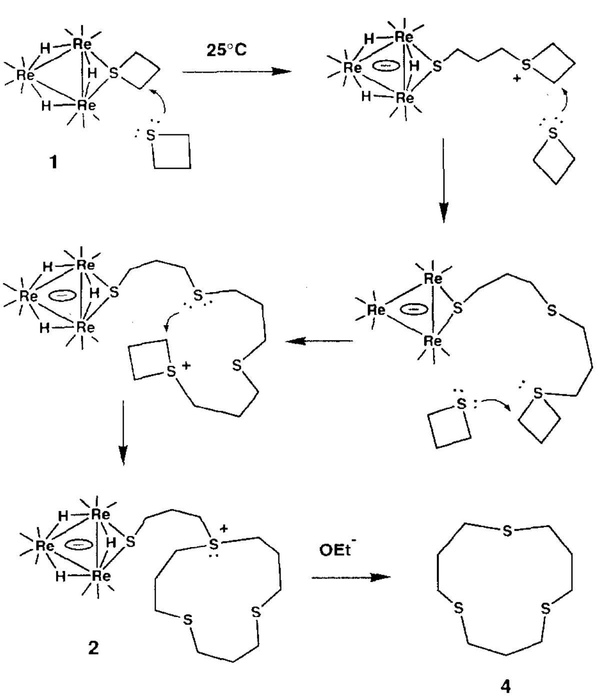

Scheme 1.

see Fig. 1. The molecule contains a triangular trirhenium cluster with nine linear terminal carbonyl ligands and a bridging hydride ligand across each metal–metal bond. There is a μ-$SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2$ grouping which bridges the Re(1)–Re(3) edge of the cluster through the thiolate sulfur atom S(1). This atom is connected by three methylene groups to a 12 atom heterocycle $SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2$ that contains three sulfur atoms uniformly distributed between the nine methylene groups. Sulfur S(2) is a sulfonium center. Since the complex is uncharged overall, the metal cluster grouping must contain a delocalized negative charge. The PMe_2Ph ligand is coordinated in an axial site on the unique metal atom Re(2).

It is proposed that the complex is formed by a series of ring opening oligomerizations that is initiated by the activation of the bridging coordination of the thietane ligand in **1**, see Scheme 1 [1b].

When compound **2** was treated with OEt^- at 25°C for 18 h, the heterocycle grouping was cleaved from the cluster and the free molecule trithiacyclodecane **4** [5] was isolated in 32% yield [6]. The metal containing product has not yet been fully characterized, but it appears to be a trirhenium cluster complex with three bridging hydride ligands, ^1H NMR $\delta = -12.45$ (1H) and -16.52 (2H) ppm [7]. Polythioether macrocycles have recently attracted considerable interest as ligands [8]. Although there are some good procedures for the synthesis of polythioether macrocycles [9], the polymerization of thietanes could provide a new route to these molecules.

Supplementary material available

Tables of crystal data, positional parameters, bond distances and angles, anisotropic thermal parameters for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgments

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References and notes

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3 A 28.1 mg amount of **1** was allowed to react with 7 μl of thietane in 30 ml of methylene chloride at 25°C for 36 h. The product was separated by TLC using a hexane/acetone 2/1 solvent mixture to yield 16.5 mg of $Re_3(CO)_{10}[\mu$-$SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu$-$H)_3$ (**2**), 47%. IR ν_{CO} for **2** (cm^{-1} in CH_2Cl_2): 2097 (w), 2022 (s), 1996 (vs), 1948 (s), 1906 (s). ^1H NMR for **2** (@ 500 MHz, δ in CD_2Cl_2): 3.91 (m, 2H), 3.46 (t, 2H, $J_{H-H} = 7.4$ Hz), 3.36 (m, 2H), 2.91 (q, 2H, $J_{H-H} = 5.8$ Hz), 2.78 (q, 2H, $J_{H-H} = 5.8$ Hz), 2.74 (t, 2H, $J_{H-H} = 5.1$ Hz), 2.59 (t, 4H, $J_{H-H} = 7.2$ Hz), 2.19 (m, 6H), 1.87 (q, 2H, $J_{H-H} = 6.2$ Hz), -12.46 (s, 1H), -16.49 (s, 2H). A 41.2 mg amount of **2** was treated with 5.5. μl of PMe_2Ph in 40 ml of methylene chloride at reflux for 18 h. The product was separated by TLC using a hexane/acetone 2/1 solvent mixture to yield 31.2 mg of $Re_3(CO)_9(PMe_2Ph)[\mu$-$SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu$-$H)_3$ (**3**), 69%. IR νCO for **3** (cm^{-1} in CH_2Cl_2): 2032 (s), 1996 (vs), 1926 (m), 1904 (s). ^1H NMR for **3** (δ in CD_2Cl_2): 7.68 (m, 2H), 7.44 (m, 2H), 7.37 (m, 1H), 3.51 (m, 3H), 3.27 (m, 3H), 3.16 (t, 2H, $J_{H-H} = 6.1$ Hz), 2.91 (q, 2H, $J_{H-H} = 6.5$ Hz), 2.78 (q, 3H, $J_{H-H} = 5.5$ Hz), 2.73 (q, 3H, $J_{H-H} = 6.5$ Hz), 2.61 (d, 2H, $J_{H-H} = 4.1$ Hz), 2.47 (d, 2H, $J_{H-H} = 6.5$ Hz), 2.15 (m, 2H), 1.97 (d, 6H, $J_{P-H} = 16.5$ Hz), 1.87 (t, 2H, $J_{H-H} = 6.1$ Hz), -12.41 (d, 1H, $J_{P-H} = 4.2$ Hz), -15.40 (d, 2H, $J_{P-H} = 16.5$ Hz). Anal. Calcd. for **3**: C, 27.90; H, 3.04. Found C, 27.88; H, 2.31.

4 Crystals of **3** were grown by slow diffusion of hexane into a solution in acetone at 25°C. Crystal data: space group = $P2_1/n$, $a = 8.637(2)$ Å, $b = 41.80(1)$ Å, $c = 15.418(2)$ Å, $\beta = 111.79(2)°$, $Z = 4$, 2836 reflections, $R = 0.036$. Diffraction measurements at 20°C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. 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 to the data.

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6 NaOEt, prepared by dissolving 10 mg of sodium metal in 2 ml of ethanol, was allowed to react with a solution containing 20 mg of **2** in 5 ml of ethanol at 25°C for 18 h. The product trithiacyclodecane [3] **4** was isolated in 32% yield as a colorless band by TLC using an acetone/hexane 3/2 elution solvent mixture.

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