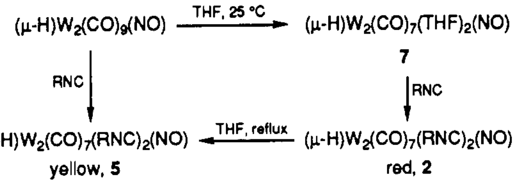
Scheme I



3.4800 (9) Å) are somewhat longer than that in $HW_2(CO)_9(NO)$ (3.329 (1) Å)[5] or in the unsupported complex $Cp_2W_2(CO)_6$ (3.222 (1) Å).[11] To our knowledge, compound 7 is the first structurally characterized tungsten(0) complex that contains THF ligands. The following structural features for 7 are all very similar to those in disubstituted phosphine derivatives[6] of $HW_2(CO)_9(NO)$: (a) the two tungsten atoms with a W-H-W linkage reside in roughly octahedral environments, (b) the overall structure is bent (with the framework bend[12] of 23.9 (2)°) and the equatorial groups are staggered, and (c) the two mutual cis THF ligands are coordinated to the tungsten atom containing the NO ligand and occupy the equatorial exo positions which are less sterically hindered. However, the NO ligand is trans to one of the THF ligands instead of being in the axial position. The overall structure of 2 closely resembles that of 7 except that the NO ligand is in the axial position. It has a framework bend of 24.9 (7)° and an average degree of staggering at 45 (2)°. Complex 5 has an almost perfect eclipsed conformation with an average torsional angle of 2 (1)°. The two MeNC ligands are also mutually cis, and the NO ligand resides in an equatorial site. Unlike the complexes $[Et_4N][HCr_2(CO)_{10}]$,[4b] $[Et_4N][DCr_2(CO)_{10}]$,[4a] and $[Et_4N][HW_2(CO)_{10}]$,[4c] molecule 5 is not subjected to crystallographic symmetry constraints, and its slightly bent structure (8.4 (4)° for the framework bend) is unambiguous. The position of μ-H in 2 was located in the final difference Fourier maps and refined. The observed W-H distances (1.8 (1) Å) are in good agreement with the reported values (1.8–1.9 Å) for the analogous complexes, and the W-H-W angle (143 (7)°) appears to be larger than those frequently observed (115–135°).[2b] The interatomic distances between equatorial ligands on the halves of the dimer are as follows: C(2)-C(11), 3.79 Å; C(1)-C(9), 3.42 Å; C(4)-N(1), 3.32 Å; C(3)-C(7), 3.22 Å. Dahl suggested that interatomic van der Waals forces caused the conformational change in the $HCr_2(CO)_{10}^-$ and $Cr_2(CO)_{10}^{2-}$ anions,[4d] whether the different conformations in the isomeric pair 2, 5 can be accounted for solely by the same factor will be the subject of future study.

The spectroscopic properties[9] for complexes 1–7 are consistent with their formulation. Being trans to CO and NO, respectively, the two RNC or THF ligands in 4–7 are magnetically inequivalent in the ^1H NMR spectra, in contrast to those in 1–3.

In refluxing THF solution, complex 5 is converted to 2 completely within 5 h, whereas there is no interconversion between the two under ambient conditions. Apparently the isomeric complexes form from $HW_2(CO)_{10}(NO)$ via different pathways. Whether cleavage of the W-H-W linkage occurs in any aforementioned reactions is not clear at present. Our successful isolation of $W(CO)_5(py)$ from the reaction of $HW_2(CO)_9(NO)$ with pyridine indicates that cleavage of the dimer might occur in certain circumstances.

The principal reactions in this study are summarized in Scheme I. The synthetic application of these new complexes is currently under investigation. Our preliminary results indicate that complex 7 can initiate the polymerization of norbornadiene and 2,3-dihydrofuran. Treatment of 3 with iodine results in the formation of *cis*-$(^tBuNC)_2W(CO)_2(NO)I$, reported by King.[13]

Acknowledgment. We wish to thank the National Science Council of the Republic of China for support and Professor M. Y. Darensbourg for helpful discussions.

Registry No. 1, 127973-56-2; 2, 127973-57-3; 3, 127973-58-4; 4, 128050-99-7; 5, 128051-00-3; 6, 128051-01-4; 7, 127973-59-5; $HW_2(CO)_9(NO)$, 40270-21-1; $W(CO)_5(py)$, 14586-49-3; *cis*-$(^tBuNC)_2W(CO)_2(NO)I$, 52699-24-8; MeNC, 593-75-9; ^tBuNC, 7188-38-7; $PhCH_2NC$, 10340-91-7; norbornadiene, 121-46-0; 2,3-dihydrofuran, 1191-99-7.

Supplementary Material Available: Tables of atomic coordinates, all bond distances and angles, and anisotropic thermal parameters for 2, 5, and 7 and a table of elemental analyses for 1–7 (12 pages); tables of structure factors for 2, 5, and 7 (45 pages). Ordering information is given on any current masthead page.

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[12] The framework bend is defined as the dihedral angle between the two least-squares planes through the two sets of equatorial ligands. For example, atoms W(1), C(1), C(2), C(3), and C(4) in 2 constitute one of the planes, and atoms W(2), C(6), C(7), C(9), and C(11) constitute the other.

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Nucleophilic Attack of Pentacarbonylrhenate(−I) on Sulfur: Formation of the Doubly Bridged Tetrasulfido Dimer $[(OC)_3Re(\eta^2\text{-}S_4)]_2^{2-}$

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Summary: The title complex is formed by addition of pentacarbonylrhenate(−I) to elemental sulfur and has been characterized by X-ray diffraction.

The nucleophilicity of metalates is well documented in the literature.[2] As part of our continuing effort to examine

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the chemistry of $Re(CO)_5^-$ with various electrophiles,[3] we herein report a ring-opening reaction of sulfur in the presence of the carbonylmetal anion, a phenomenon that mirrors the sulfur-scavenging ability of cyanide, sulfide, sulfite, and phosphines. Known rhenium sulfur complexes include $Re_3S_3(CO)_{13}SnMe_3$,[4a] $Re_6S_3(CO)_{22}$,[4b] $Re_8S_4(CO)_{32}$,[4b] $ReS_2Cp(CO)_2$,[5a] $Re_2SCp_2(CO)_4$,[5b] $Re_2S_5Cp_2(CO)_2$,[5b] $Re_2S_4Cp^*_2$,[6a] $ReCp^*(O)S_4$,[6b] $[Re_4S_4(S_3)_6]^{4-}$,[6c] and ReS_9^-.[6d] The present use of a low-valent rhenium anion is suitable for a convenient entry into sulfur-rich complexes.[7]

$Re(CO)_5^-$ reacts facilely with excess elemental sulfur to give $[Re_2(CO)_6(S_4)_2]^{2-}$, which can be isolated as its orange crystalline n-Bu_4N^+ salt in 75% yield.[8] An X-ray diffraction study[9] reveals a dinuclear structure with two bridging tetrasulfide ligands, each functioning as a six-electron donor (Figure 1). The anionic molecule has a crystallographic center of symmetry midway between the two metal atoms. The two rhenium atoms, in accordance with the 18-electron rule, display a negligible M–M interaction (Re–Re = 4.07 Å). The resultant geometry represents a rare symmetrical unit, with α-S serving as the bridging atoms. A similar fusion among three CuS_4 rings has been reported by Müller et al. in the novel trimeric anion $[Cu_3(S_4)_3)]_3^-$.[10] Our finding is in distinct contrast to the recently reported "unsymmetrical" bridge in $Cp_2Rh_2(\eta^2\text{-}S_4)_2$,[11] in which one of the internal sulfurs of one tetrasulfide group serves as the bridging atom. This latter structure consequently comprises the amalgamation of three five-membered rings instead. The structure of the title compound demonstrates the complexity and diversity of the ligand behavior of the polysulfide ions. The preferred formation of the five-membered chelate complexes MS_4 from polysulfide or sulfur is documented by many examples.[12]

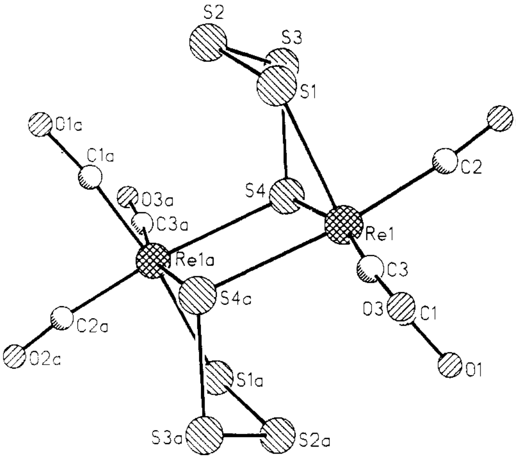

Figure 1. Molecular structure of the anion $[Re_2(CO)_6(S_4)_2]^{2-}$. Selected bond lengths (Å) and angles (deg): Re(1)–S(1) = 2.531 (9), Re(1)–S(4) = 2.488 (9), Re(1)–C(1) = 1.901 (22), Re(1)–C(2) = 1.890 (19), Re(1)–C(3) = 1.635 (47), Re(1)–S(4a) = 2.603 (8), S(1)–S(2) = 2.017 (9), S(2)–S(3) = 2.011 (13), S(3)–S(4) = 2.168 (11), S(4)–Re(1a) = 2.603 (8), C(1)–O(1) = 1.165 (26), C(2)–O(2) = 1.137 (23), C(3)–O(3) = 1.315 (50); S(1)–Re(1)–S(4) = 93.3 (3), S(1)–Re(1)–C(1) = 173.0 (5), S(4)–Re(1)–C(1) = 87.4 (7), S(1)–Re(1)–C(2) = 84.9 (7), S(4)–Re(1)–C(2) = 101.1 (6), C(1)–Re(1)–C(2) = 88.1 (9), S(1)–Re(1)–C(3) = 89.5 (12), S(4)–Re(1)–C(3) = 167.8 (9), C(1)–Re(1)–C(3) = 91.4 (14), C(2)–Re(1)–C(3) = 90.9 (10), S(1)–Re(1)–S(4a) = 90.3 (2), S(4)–Re(1)–S(4a) = 73.7 (3), C(1)–Re(1)–S(4a) = 94.4 (9), Re(1)–S(1)–S(2) = 105.4 (4), S(1)–S(2)–S(3) = 105.2 (4), S(2)–S(3)–S(4) = 102.6 (4), Re(1)–S(4)–S(3) = 99.8 (4), Re(1)–S(4)–Re(1a) = 106.3 (3), S(3)–S(4)–Re(1a) = 110.9 (3), Re(1)–C(1)–O(1) = 168.3 (14), Re(1)–C(2)–O(2) = 173.0 (20), Re(1)–C(3)–O(3) = 171.8 (29).

No unusual feature is found in the cation and the terminal carbonyl groups. The Re–S and S–S bond distances, ranging from 2.531 (9) to 2.488 (9) Å and 2.168 (11) to 2.011 (13) Å, respectively, are in agreement with literature values.[4,5,13] The three metallasulfur rings form a chair

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(8) All manipulations were carried out under dry argon. Solvents were either freshly distilled under argon or used as supplied in Analar grade and deoxygenated. $Re_2(CO)_{10}$ (0.134 g, 0.205 mmol) was dissolved in THF (12 mL) under argon and the solution cooled to 0 °C. Sodium amalgam (1%) (0.30 mL) was added, and the mixture was stirred for 1 h at 0 °C followed by 1 h at room temperature (20 °C). The orange-yellow solution thus obtained was cooled to 0 °C before being transferred to a Schlenk flask containing sulfur (0.079 g, 0.309 mmol) and kept at 0 °C. Most of the sulfur dissolved readily into the solution, which turned orange-red. After it was stirred for 3 h at 0 °C, the mixture was warmed slowly to room temperature and stirring was continued for at least 5 h. The resultant orange solution was filtered and evaporated to dryness. The residue was washed with pentane (2 × 10 mL) and benzene (2 × 10 mL) before being extracted into methanol (20 mL) and filtered to remove any excess sulfur. A filtered methanolic solution (5 mL) of n-Bu_4NBr (1.0 g) was added, and the mixture was concentrated under vacuum to ca. 5 mL. The orange microcrystalline deposits were collected by centrifuge and washed with cold methanol (3 × 5 mL) to give the desired $(n\text{-}Bu_4N)_2[Re_2(CO)_6(S_4)_2]$ (0.197 g, 75% based on $Re_2(CO)_{10}$), which could be further purified by recrystallizing from CH_3CN/CH_3OH; mp 166–168 °C dec. Anal. Calcd for $C_{38}H_{72}N_2O_6Re_2S_8$: C, 35.6; H, 5.7; N, 2.2; S, 20.0. Found: C, 35.8; H, 5.6; N, 2.2; S, 20.2. IR (ν(CO), CH_3CN): 2010 m, 1994 s, 1895 s, br cm^{-1}.

(9) Single crystals that were suitable for X-ray diffraction study were grown at room temperature by slow diffusion of hexane/ethanol in a solution of the sample in acetone. Crystal data: $C_{38}H_{72}N_2O_6Re_2S_8$; M_r = 1281.88; dimensions 0.1 × 0.3 × 0.6 mm^3; triclinic; a = 11.267 (4), b = 11.309 (4), c = 12.232 (4) pm; α = 79.89 (3), β = 81.11 (3), γ = 61.24 (3)°; V = 1340.6 (9) $Å^3$; Z = 1; ρ_{calcd} = 1.588 g cm^{-3}; μ(Mo Kα) = 4.91 mm^{-1}; space group $P1$. Data collection: Nicolet R3 diffractometer, 21 °C, ω scan $4 \leq 2\vartheta \leq 50°$, scan speed 4–30 deg/min. A total of 8401 reflections were collected; of the 4171 independent reflections, 3459 were regarded as observed ($I > 2\sigma(I)$). An empirical absorption correction was used (minimum relative transmission 0.396). Structure solution and refinement: The structure was solved with the SHELXTL PLUS structure solution package.[16] Direct methods and difference Fourier calculations were used; 254 parameters were refined. $R = 0.0754$, $R_w = 0.0660$ ($w = 1/\sigma^2(F)$), and a maximum residual electron density of 2.26×10^{-6} e pm^{-3} was found. Due to the quality of the crystal the standard deviations and thermal parameters are high.

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configuration. The middle four-membered Re_2S_2 ring is planar (nonbonding $S{\cdots}S$ = 3.100 Å; S–Re–S = 73.7 (3)°), but the external five-membered ReS_4 rings adopt an envelope configuration, with the S(3) (and S(3a)) atoms occupying the flap positions. Significant alternation of S–S bond lengths, which has been attributed to M–S π-overlap,[12a,e] is not found (S(internal)–S(internal) = 2.011 (13) Å; average S(external)–S(internal) = 2.093 (11) Å).

The nature of the products is highly sensitive to the stoichiometry of the reactants. With a deficiency of sulfur, viz. 2–8-fold molar excess of Re to S_8, a complex mixture of products is formed, from which the title complex is isolated only in trace quantity. When a 1.5-mol excess of sulfur (S_8) is used, the title dimer is formed as a major product. It is tempting to postulate a reaction intermediate such as $[Re(CO)_4(\eta^2\text{-}S_4)]^-$ that can readily undergo decarbonylation and fusion of the metallasulfur rings to form the isolated dimer. Alternatively, one can suggest the dinuclear doubly sulfide-bridged precursor $[(\eta^2\text{-}S_3)(OC)_3Re(\mu\text{-}S_2)Re(CO)_3(\eta^2\text{-}S_3)]^{2-}$, which may easily release the strain of seven-coordination by coupling between the terminal polysulfide chelates and the sulfide bridges, thus forming an extra S–S bond at the expense of a Re–S bond. Such an intermediate would involve a four-membered ReS_3 ring, which is hitherto unknown. Interestingly, a recent report on $[Au_2(\eta^2\text{-}Se_5)_2(\mu\text{-}Se)_2]^{2-}$[14] has postulated a similar mechanistic pathway, but this mechanism requires a reverse flow of electrons.

The present synthetic route seems to provide the potential for a facile entry into chalcogen-rich complexes.[15] Preliminary results in our laboratory show that $Re(CO)_5^-$ and other carbonylmetalates react readily with selenium and white phosphorus. After this paper had been accepted, we became aware of a report on the selenium compound $[(OC)_3Re(\eta^2\text{-}Se_4)]_2^{2-}$,[17] which has been obtained by another route from Se_4^{2-} and $Re_2(CO)_{10}$ and which shows practically the same structure as the analogous sulfur complex.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles of atoms in the complex (4 pages); a listing of observed and calculated ($10F_o/10F_c$) structure factors (15 pages). Ordering information is given on any current masthead page.

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Stepwise Insertion of Isocyanides and Carbon Dioxide into Vanadium–Aryl Bonds: Chemistry of a Tris(η^2-iminoacyl)vanadium(III) Complex

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Summary: tert-Butyl isocyanide inserts in the three V–C bonds of $[V(Mes)_3(THF)]$ (**1**; Mes ≡ 2,4,6-$Me_3C_6H_2$), leading to the tris(η^2-iminoacyl) complex $[V(\eta^2\text{-}Bu^tNCMes)_3]$ (**2**), the structure of which has been confirmed by X-ray analysis and chemical degradation. Complex **2** inserts carbon dioxide into two V–C bonds, forming $[V(\eta^2\text{-}Bu^tNCMes)\{\eta^2\text{-}Bu^tNC(Mes)C(O)O\}_2]$ (**6**). The two metallacycles in complex **6** contain the deprotonated form of an α-imino carboxylic acid.

The multiple insertion of carbon monoxide or isocyanides into an homoleptic metal–alkyl or metal–aryl bond is quite a rare event, as is the migration of an acyl or an iminoacyl group.[1] The latter reaction is the basis for a significant functionalization of organic residues bonded to metal centers.[1] Studying the chemistry of $[(THF)V(Mes_3]$ (**1**; Mes ≡ 2,4,6-$Me_3C_6H_2$),[2] we observed both a multiple insertion of isocyanides and the migratory capability of an η^2-iminoacyl functionality. Reaction of **1** with Bu^tNC gave at room temperature the insertion of the isocyanide in all three vanadium–aryl bonds, leading to the tris(η^2-iminoacyl) complex **2**.

The analogous reaction with carbon monoxide carried out at −50 °C gave in good yield dimesityl ketone[4] and a, so far, not well characterized vanadium–carbonyl derivative. Dimesityl ketone is derived from a rather rare double

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[3] To a THF (200 mL) solution of **1** (5.62 g, 11.72 mmol) was added dropwise Bu^tNC (2.93 g, 35.30 mmol). The mixture was kept stirring at room temperature for 5 h, and the color changed to dark green. Then the solvent was evaporated to dryness and the residue washed with hexane (40 mL). The solid was recrystallized from hexane (200 mL) (66%). Anal. Calcd for $C_{42}H_{60}N_3V$: C, 76.70; H, 9.12; N, 6.38. Found: C, 76.56; H, 9.02; N, 6.41. μ_{eff} = 2.75 μ_B at 288 K.

[4] Satisfactory NMR, IR, and mass spectra and microanalyses were obtained.