the well-studied $Cp_2Mo_2(CO)_4$ system.[13] Although there is no evidence at this stage for a multiply bonded intermediate in the $Ru_{10}C_2$ chemistry, we are actively pursuing the implications of this analogy.

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Supplementary Material Available: Tables of the details of crystallographic data collection, atomic coordinates, hydrogen atom parameters, thermal parameters, and selected bond distances and angles for $[Ph_3PCH_2CH_2PPh_3][Ru_{10}C_2(CO)_{22}(C_2Ph_2)]\cdot CH_3OH\cdot 2(CH_3)_2CO$ (15 pages); a table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

Linqing Ma
Damian P. S. Rodgers
Scott R. Wilson
John R. Shapley*

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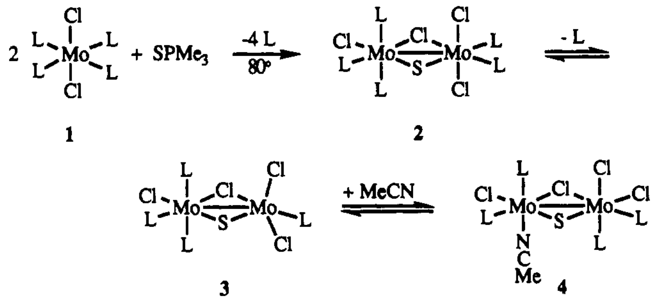
Labile and Coordinatively Unsaturated Molybdenum(III)-μ-Sulfido Dimers, $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4(L)$ (L = PMe_3, MeCN, or Vacant), Formed by Sulfur Atom Abstraction from $SPMe_3$

Three novel molybdenum(III) dimers are reported here, two with edge-shared bioctahedral structures and one with an unprecedented coordinatively unsaturated structure. Facile ligand exchange reactions interconvert the three molecules. While complexes with two metal atoms have been widely studied[1-3] (for instance, there are 93 examples of edge-shared bioctahedral dimers, according to a recent paper[4]), molecules with an open coordination site and/or labile ligands are rare. The synthesis of these compounds, by sulfur atom transfer from $SPMe_3$ to Mo, is also remarkable because phosphines typically remove sulfur from metal complexes, due to the strength of the P-S bond ($\cong$92 kcal/mol[5]).

Reaction of toluene solutions of $MoCl_2(PMe_3)_4$ (**1**)[6] with $^1/_2$ equiv of $SPMe_3$ for 1 day at 80 °C results in the formation of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**2**) along with 4 equiv of free PMe_3 (Scheme I). The reaction is slowed by the buildup of free PMe_3 and requires removal of the phosphine to proceed to completion. When the isolated dark blue-green solid is repeatedly triturated with solvent and stripped of volatiles in vacuo, 1 equiv of bound PMe_3 is lost, resulting in the formation of brown $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4$ (**3**) in high yield (>95% by NMR). Because **2** loses PMe_3 so easily, pure samples are best prepared by recrystallization of **3** in the presence of PMe_3. Thus **2** and **3** + PMe_3 readily interconvert, as confirmed by NMR studies (see below) and by visible spectroscopy: addition of PMe_3 to brownish amber **3** forms blue-green **2**, which is converted back to **3** by the phosphine scavenger $ZnCl_2$. Dissolution of **3** in acetonitrile yields a navy blue adduct, $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4(CH_3CN)$ (**4**; Scheme I). Addition of benzene or toluene to **4** causes loss of the coordinated CH_3CN and forms **3**, indicating a similar **3** $\rightleftarrows$ **4** equilibrium.

Scheme I. Syntheses and Interconversion of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4L'$ Compounds (L' = PMe_3 (**2**), Nothing (**3**), MeCN (**4**) [L = PMe_3])



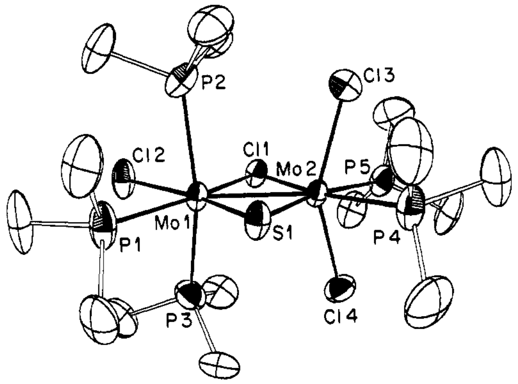


Figure 1. ORTEP drawing of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**2**) with 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Mo(1)-S(1) = 2.2740 (13), Mo(2)-S(1) = 2.2852 (13), Mo(1)-Cl(1) = 2.4360 (12), Mo(2)-Cl(1) = 2.4427 (12); Mo(1)-S(1)-Mo(2) = 72.49 (4), Mo(1)-Cl(1)-Mo(2) = 67.08 (3), P(2)-Mo(1)-P(3) = 164.08 (6), Cl(3)-Mo(2)-Cl(4) = 150.42 (6).

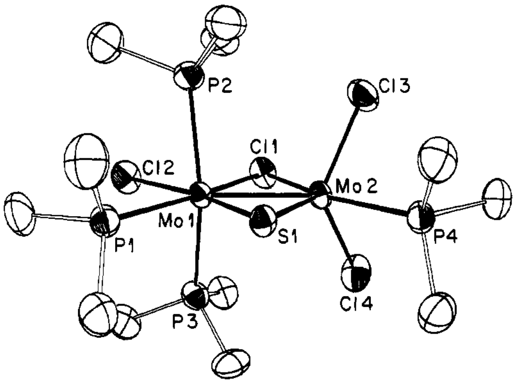


Figure 2. ORTEP drawing of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4$ (**3**) with 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Mo(1)-S(1) = 2.288 (2), Mo(2)-S(1) = 2.222 (2), Mo(1)-Cl(1) = 2.492 (2), Mo(2)-Cl(1) = 2.438 (2); P(2)-Mo(1)-P(3) = 165.87 (7), Cl(3)-Mo(2)-Cl(4) = 124.13 (8), Cl(1)-Mo(2)-P(4) = 166.26 (8).

All three dimers have been characterized by single-crystal X-ray diffraction (Figures 1-3).[7] Complexes **2** and **4** have the edge-shared bioctahedral structure (Scheme I) that is typical of M_2L_{10} compounds,[2,3a-c] but **3** has a unique structure in which one molybdenum is only five-coordinate and coordinatively unsaturated.

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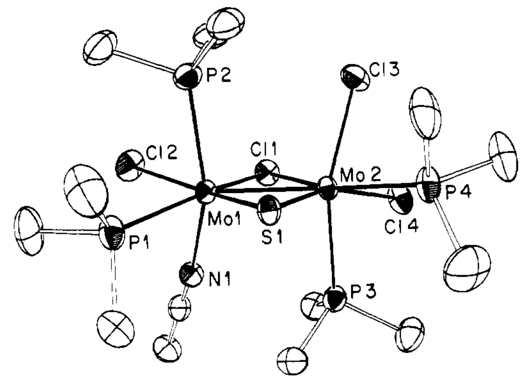


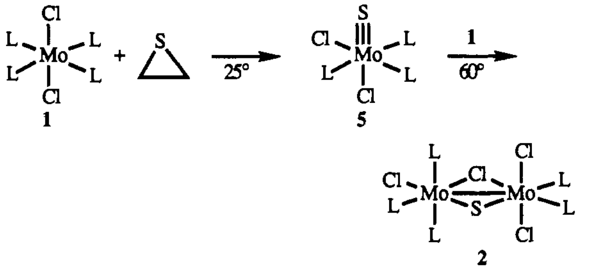
Figure 3. ORTEP drawing of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4(CH_3CN)$ (4) with 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Mo(1)–S(1) = 2.2843 (13), Mo(2)–S(1) = 2.2529 (16), Mo(1)–Cl(1) = 2.4532 (18), Mo(2)–Cl(1) = 2.4477 (13), Mo(1)–N(1) = 2.188 (5), P(2)–Mo(1)–N(1) = 158.48 (13), Cl(3)–Mo(2)–P(3) = 159.80 (6).

Complex **2** has three phosphines on Mo(1) and two on Mo(2). Of the two on Mo(2), the phosphine trans to sulfur, P(5), has a bond length, 2.6866 (15) Å, considerably longer than the other Mo–P distances in **2**–**4** (2.494 (2)–2.5414 (18) Å). The structure of **3** is similar to that of **2** except that this phosphine is absent. While M_2L_9 species such as **3** typically have a confacial bioctahedral geometry (i.e. $L_3M(\mu\text{-}L)_3ML_3$)[3c–e] so that both metals can have octahedral coordination, the structure of **3** has only two bridging ligands. It is best described as the fusion, along a common edge, of an octahedron around Mo(1) and a trigonal bipyramid about Mo(2), with Cl(1) and P(4) as the axial ligands. The conversion of **3** to **4** involves addition of a molecule of acetonitrile, but, surprisingly, the added ligand does not fill the open site on Mo(2)—rather a quite different arrangement of ligands is found: the acetonitrile occupies an apical site on Mo(1), each molybdenum has two phosphines, and the chloride ligands on Mo(2) are cis.

The three structures contain very similar Mo(1)–S(1)–Mo(2)–Cl(1) cores, which are planar and quite symmetrical, suggesting equivalent Mo(III) oxidation states for the two metals. The Mo–S distances (average 2.268 ± 0.046 Å) are indicative of some degree of multiple bonding.[8] The Mo–Mo distances (2.6956 (6), 2.6293 (8), and 2.6779 (6) Å for **2**–**4**) fall in the range typical for Mo(III) dimers and constitute at least a single bond.[1–3,8,9] There is a large twist about the Mo(1)–Mo(2) bond in **4**, with a 29° angle between the P(1)–Cl(2)–Mo(1) and P(4)–Cl(4)–Mo(2) planes. The analogous twist angle in **2** is about 7°, more typical of M_2L_{10} structures.[2,3a–c] The structures of **2**–**4** appear to be influenced by steric interactions across the bridge, as two phosphines are never found in adjacent apical positions and the Mo–Mo–apical ligand angles are all >90° (in **2**, 95–105°).

Solution ^1H and ^{31}P NMR spectra are consistent with the solid-state structures of **2** and **3**.[10] **2** shows a virtual triplet and three doublets in the proton NMR (intensity 2:1:1:1). One of these doublets exchanges on the NMR time scale with the signal for free PMe_3. Mixtures of **2** and **3** also exhibit exchange phenomena, with a triplet and two doublets having chemical shifts in between those for **2** and **3** and a third doublet whose intensity increases with concentration of **2**. Clearly one phosphine in **2** is very labile, presumably P(5), the phosphine with the long Mo–P bond length. The trans effect of the bridging sulfur is likely a cause of this unusual lability, since a structural trans influence is observed (e.g., in **2**, Mo(1)–Cl(2) = 2.5139 (14) Å vs Mo(2)–Cl(3,4) = 2.4096 (15), 2.4286 (15) Å).

The synthesis of **2** likely proceeds by sulfur atom transfer from $SPMe_3$ to **1** to give a Mo(IV) terminal sulfido complex $Mo(S)Cl_2(PMe_3)_3$ (**5**), which subsequently conproportionates with **1**. This reaction sequence has been observed using <1 equiv of ethylene sulfide, a more reactive sulfur atom donor: formation of the previously unknown **5**[11] occurs at 25 °C and conproportionation to form **2** is observed on heating (eq 1; L = PMe_3). This



(1)

pathway is further supported by our report[12] that a tungsten analogue of **1**, $WCl_2(PMePh_2)_4$, reacts with $SPMePh_2$ to form $W(S)Cl_2(PMePh_2)_3$, analogous to **5**. Further work is in progress to explore the synthesis of dimers by conproportionation[13] and to exploit the reactivity and coordinative unsaturation of **3**.

Acknowledgment. We thank the National Science Foundation and the Exxon Education Foundation for financial support.

Supplementary Material Available: Synthetic procedures and tables of spectral data for **2**–**5** and crystallographic procedures and tables of crystal data, positional and isotropic thermal parameters, anisotropic thermal parameters, hydrogen atom parameters, bond distances, nonbonding distances, bond angles, torsional angles, and least-squares planes for **2**–**4** (36 pages); tables of calculated and observed structure factors (28 pages). Ordering information is given on any current masthead page.

Department of Chemistry, BG-10
University of Washington
Seattle, Washington 98195

Keith A. Hall[14]
Susan C. Critchlow
James M. Mayer*,[15]

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(10) Selected NMR data (C_6D_6): δ (multiplicity, *J* (Hz), no. of H's). For **2**: ^1H 1.86 (d, 9, 9 H), 1.74 (d, 8, 9 H), 1.58 (d, 7, 9 H), 0.65 (t, 4, 18 H, trans P*Me*$_3$'s); $^{31}P\{^1H\}$ (in the presence of PMe_3) 9.2 (d of t, 4, 17), −5.1 (d of t, 4, 36.7), −22.0 (d of d, 17, 37, trans *P*Me$_3$'s). For **3**: ^1H 1.71 (d, 10, 9 H), 1.65 (d, 8, 9 H), 0.55 (t, 4, 18 H, trans P*Me*$_3$'s); $^{31}P\{^1H\}$ 18.6 (broad m), 1.5 (t, 30), −19.7 (d of d, 15, 31, trans *P*Me$_3$'s); $^{31}P\{^1H\}$ (at −30 °C (CD_2Cl_2)) 25.4 (t, 14), 6.9 (t, 31), −18.5 (d of d, 14, 31). The spectra of **4** are temperature dependent and are not first order, at 25 °C in CD_3CN: δ 1.8–2.0 (m), 0.7 (very broad).

(11) (a) **5** has been identified by the similarity of its ^1H and ^{31}P NMR spectra to those of $W(S)Cl_2(PMePh_2)_3$[12] and $Mo(O)Cl_2(PMe_3)_3$.[11b] (b) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347.

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