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Coupling of Alkynes on a Cluster Core: Reaction of $Cp'_2Mo_2Co_2(CO)_4S_3$ with Alkynes

Umar Riaz and M. David Curtis*

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

Arnold Rheingold and Brian S. Haggerty

Department of Chemistry, University of Delaware, Newark, Delaware 19716

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Summary: $Cp'_2Mo_2Co_2(CO)_4S_3$ (**1**; $Cp' = C_5H_4CH_3$) reacts with phenylacetylene to yield the cluster $Cp'_2Mo_2Co_2(CO)_2S_3(PhCCH)$ (**2**), which contains a μ_3-η^2-bound alkyne. Cluster **2** adds another 1 mol of alkyne to yield the cluster $Cp'_2Mo_2Co_2(CO)_2S_3(PhCCH)_2$ (**3**), in which the alkynes are coupled to form a molybdacyclopentadiene with each double bond coordinated to a cobalt atom.

The reactions of transition-metal clusters with alkynes result in a number of interesting transformations,[1,2] including oligomerization[3] and C–C bond cleavage.[4] Such reactions are of interest since they might serve as models for similar processes occurring on metal surfaces.[5] We have prepared several mixed-metal sulfido clusters,[6] some of which have been domonstrated to be precursors for HDS catalysts when adsorbed on alumina and to desulfurize thiophene and other organic and inorganic sulfur compounds under mild conditions with the concomitant formation of the cubane cluster $Cp'_2Mo_2Co_2S_4(CO)_2$.[7] Herein we report the reaction of the cluster $Cp'_2Mo_2Co_2(CO)_4(\mu_3\text{-}S)_2(\mu_4\text{-}S)$ (**1**; $Cp' = C_5H_4CH_3$) with alkynes, which results in the sequential addition of 2 equiv of alkyne to the cluster core. These reactions are relevant models for the initial steps of the formation of thiophene from acetylene on sulfided metal surfaces,[8] i.e., the reverse of the desulfurization process.

In refluxing toluene, **1** reacts with phenylacetylene to yield the new cluster **2** in 78% yield[9] after 2 h (Scheme I). Compound **2** has been characterized by IR and ^1H NMR spectroscopies and by elemental analysis. The molecule has been formulated as $Cp'_2Mo_2Co_2(CO)_2S_3(PhCCH)$. The IR spectrum of **2** shows two CO bands at 1977 and 1956 cm^{-1}, and the ^1H NMR spectrum shows inequivalent Cp′ groups, indicating that the Mo atoms are inequivalent. The alkyne C–H proton for **2** resonates at δ 10.17, indicative of a M–C*H* proton. A $^{13}C\{^1H\}$ spectrum of the 4-octyne analogue of **2** (**2a**) (CH_2Cl_2, −50 °C) indicates that the two alkyne carbon atoms are equivalent (δ

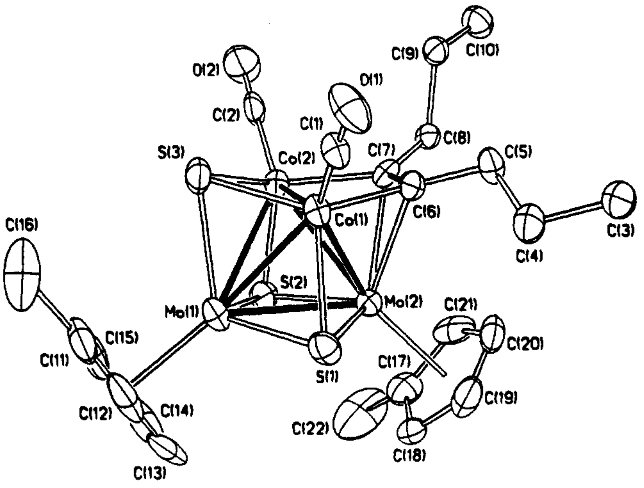
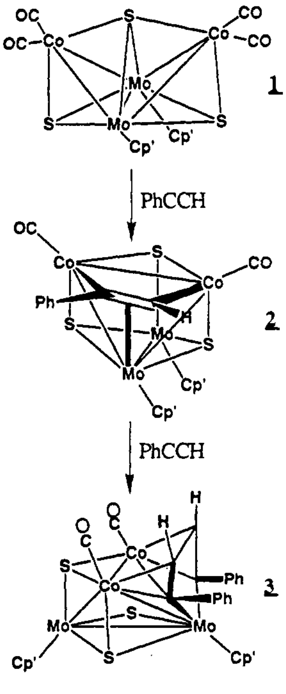


Figure 1. ORTEP drawing of **2a**. Thermal ellipsoids are drawn at the 35% level. Relevant bond distances (Å): Mo1–Mo2, 2.709 (1); Mo1–Co1, 2.645 (2); Mo1–Co2, 2.705 (2); Mo2–Co1, 2.669 (2); Mo2–Co2, 2.602 (2); Co1–Co2, 2.576 (2); Mo2–C6, 2.288 (11); Mo2–C7, 2.235 (10); Co1–C6, 1.922 (9); Co2–C7, 1.910 (8); C6–C7, 1.356 (17). Selected bond angles (deg): Co1–Mo1–Mo2, 59.8 (1); Co1–Mo2–Mo1, 58.9 (1); Mo1–Co1–Mo2, 61.3 (1); C6–Mo2–C7, 34.9 (4).

Scheme I



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[9] The progress of the reaction was monitored via IR spectroscopy. After complete conversion of **1** to **2**, the reaction mixture was cooled to room temperature and the toluene evaporated in vacuo. The resulting solid was dissolved in dichloromethane and the solution filtered through alumina. Evaporation of the dichloromethane yielded **2** as black microcrystals. Spectroscopic and analytical data for **2**: IR (KBr) 1977, 1956 cm^{-1} (ν_{CO}); ^1H NMR (C_6D_6) δ 10.17 (s, 1 H), 7.75–6.9 (5 H), 5.31 (m, 2 H), 5.07 (m, 2 H), 4.26 (m, 2 H), 4.11 (m, 2 H), 1.81 (s, 3 H), 1.55 (s, 3 H). Anal. Calcd for $C_{22}H_{20}Mo_2Co_2S_3O_2$: C, 36.58; H, 2.79. Found: C, 36.48; H, 2.74.

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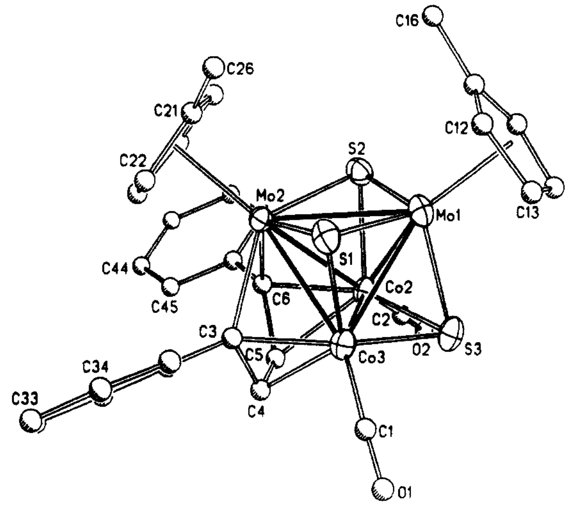

Figure 2. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 35% level. Relevant bond distances (Å): Mol-Mo2, 2.9179 (1); Mol-Co2, 2.716 (1); Mol-Co3, 2.695 (1), Mo2-Co2, 2.781 (2); Mo2-Co3, 2.780 (1); Co2-Co3, 2.616 (1); Mo2-C3, 2.219 (8); Mo2-C6, 2.224 (7); Co2-C5, 2.109 (9); Co2-C6, 1.993 (9); Co3-C4, 2.116 (7); Co3-C3, 1.983 (9); C3-C4, 1.420 (12); C4-C5, 1.452 (11); C5-C6, 1.424 (11). Selected bond angles (deg): Co3-Mol-Mo2, 59.2 (1); Co3-Mo2-Mol, 56.4 (1); Mol-Co3-Mo2, 64.4 (1); C6-Mo2-C3, 74.6 (3); Mo2-C3-C4, 112.7 (6); Co3-C3-C4, 74.9 (6). Distances and angles are for one of the two crystallographically independent molecules.

199). The carbonyl carbon atoms appear at δ 212. An X-ray diffraction analysis of **2a**[10] has also been carried out, and an ORTEP drawing of the structure is shown in Figure 1. The structure consists of a tetrahedral core with sulfur atoms bridging three faces of the tetrahedron and the alkyne bridging the fourth face. The M-M, M-S, and M-C distances are all within the expected ranges. The C-C bond distance 1.356 (17) Å is in the range of a double bond and is similar to distances found in alkynes bound in the μ_3-η^2 mode.[1] The μ_3-η^2 mode of binding is common for trinuclear clusters, but there is only one other example of a tetranuclear cluster containing an alkyne bound in this fashion.[4] Cluster **2** is electron precise (60 VSE) for an all metal-metal-bonded tetrahedron if the alkyne is considered to be a four-electron donor.

When the solution of **1** and phenylacetylene is refluxed for 7 h, a new cluster, **3**, is isolated in 48% yield.[11] Alternatively, **3** can be synthesized by refluxing solutions of **2** with excess phenylacetylene. Compound **3** has also been characterized by IR and ^{1}H NMR spectroscopies and by elemental and X-ray diffraction analyses.[12] It has been formulated as $Cp'_2Mo_2Co_2(CO)_2S_3(PhCCH)_2$. The IR spectrum of **3** shows two CO bands at 1958 and 1970 cm^{-1}, and the ^{1}H NMR spectrum indicates the presence of inequivalent Mo atoms. An ORTEP drawing of the structure is shown in Figure 2. The structure of **3** consists of a tetrahedral metal core containing three triply bridging sulfur atoms, and the fourth face of the tetrahedron contains a metallacyclopentadiene moiety, formed by the head to head coupling of the two alkyne molecules, that is π-bound to the Co atoms and σ-bound to the Mo atom. The M-M and M-S bond distances are all within the expected ranges for the single bonds, although the Mo-Mo bond is longer than the Mo-Mo bond in **2** and in similar clusters. The C-C bond distances within the metallacyclic ring fall in the range 1.420 (12)-1.452 (11) Å—longer than a typical C-C double bond and shorter than a single bond. Hence, there is significant electron delocalization within the metallacycle. Reactions of trinuclear clusters with alkynes have been shown to form metallacyclopentadiene containing clusters,[13] but **3** is the first example of such a transformation occurring on a tetranuclear cluster. If the metallacyclopentadiene moiety is assumed to be a six-electron donor, the electron count for **3** is 62, which is in excess of the 60 electrons required for a tetrahedral cluster with 6 metal-metal bonds. The long Mo-Mo bond in **3** may be a consequence of this excess electron density.

Intermediates in the oligomerization of alkynes on dimetal centers have been characterized,[14] but the conversion of **2** to **3** is the first example of the sequential addition of two alkyne molecules to a cluster core. The alkyne adducts reported here may be relevant intermediates in HDS reactions of thiophene by **1** since C_2-C_4 hydrocarbons are detected in the reaction mixture.[7a] Further work is aimed at elucidating the mechanism of desulfurization reactions of organic sulfides with **1** and at the development of a homogeneous catalytic HDS cycle.

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Supplementary Material Available: Listings of crystal and data collection statistics, atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, and H atom coordinates for **2a** and **3** (Tables 1S-6S and 8S-13S) (20 pages); lists of F_o vs F_c (Tables 7S and 14S) for **2a** and **3** (54 pages). Ordering information is given on any current masthead page.

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(10) Crystals of **2a** were obtained by cooling a dichloromethane/hexane solution to -20°C: space group $C2/c$; a = 33.503 (10) Å, b = 9.818 (3) Å, c = 16.691 (5) Å; β = 14.46 (2)°; Z = 8. Diffraction data were collected on a Nicolet R3m diffractometer. The structure was refined (3563 reflections) to the final values of the residuals R_F = 0.050, R_{wF} = 0.052; SHELXTL software was used for all calculations.

(11) The synthesis of **3** is analogous to the synthesis of **2**. Spectroscopic and analytical data for **3**: IR (KBr) 1970, 1958 cm^{-1} (ν_{CO}); ^{1}H NMR (C_6D_6) δ 7.68-6.99 (10 H), 4.97 (m, 2 H), 4.77 (m, 2 H), 4.51 (m, 2 H), 4.31 (m, 2 H), 4.30 (2 H), 1.80 (s, 3 H), 1.40 (s, 3 H). Anal. Calcd for $C_{30}H_{26}Mo_2Co_2S_3O_2$: C, 43.709; H, 3.18. Found: C, 43.88; H, 3.03.

(12) Crystals of **3** were obtained by cooling a dichloromethane/hexane solution to -20 °C: Space group $P\bar{1}$; a = 10.514 (3) Å, b = 16.669 (5) Å, c = 18.739 (6) Å; α = 63.52 (2)°, β = 88.69 (2)°, γ = 18.739 (6)°; Z = 4. Diffraction data were collected on a Nicolet R3m diffractometer. The structure was refined (9398 reflections) to the final values of the residuals R_F = 0.047, R_{wF} = 0.51; SHELXTL software was used for all calculations.

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