Communications

The Nature of Alkyne Oligomerization on the Face of a Mixed-Metal Trinuclear Cluster

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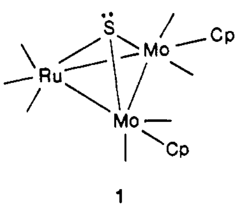
Summary: $RuMo_2(CO)_7(\mu_3\text{-}S)(C_5H_5)_2$ (**1**) reacts with $PhC{\equiv}CH$ by the addition and coupling of 3 equiv to yield $RuMo_2(CO)_2(\mu_3\text{-}S)(C_5H_5)_2[\mu_3\text{-}\eta^6\text{-}HCC(Ph)CHC(Ph)CHC(Ph)]$ (**2**) in 15% yield and $RuMo_2(CO)_2(C_5H_5)_2(\mu_3\text{-}S)[\mu\text{-}\eta^3\text{-}(Ph)CC(H)C(Ph)][\mu_3\text{-}\eta^3\text{-}(H)CC(Ph)CH]$ (**3**) in 11% yield. Compound **2** contains a μ_3-HCC(Ph)CHC(Ph)CHC(Ph) ligand that was formed by the addition and head-to-tail coupling of three $PhC{\equiv}CH$ molecules. This ligand was split by the cleavage of a carbon–carbon bond to yield two dimetallaallyl ligands that are coordinated to a face and the Mo–Mo edge of the cluster in **3**.

The discovery that metal complexes can catalyze the cyclooligomerization of alkynes has been one of the major achievements of the study of organometallic compounds.[1] Recent studies have shown that these reactions are also produced by di- and polynuclear metal complexes, and intermediates that show the details of the coupling processes have been isolated and characterized.[2] The ability of metal atoms to cooperate in the transformation of small molecules is believed to be an important and distinguishing feature of the chemistry of polynuclear metal complexes.[3] We have recently prepared the mixed-metal trinuclear cluster compound $RuMo_2(CO)_7(\mu_3\text{-}S)(C_5H_5)_2$ (1) which has been shown to consist of a triangular cluster of two molybdenum and one ruthenium atom with a triply bridging sulfido ligand.[4-6]



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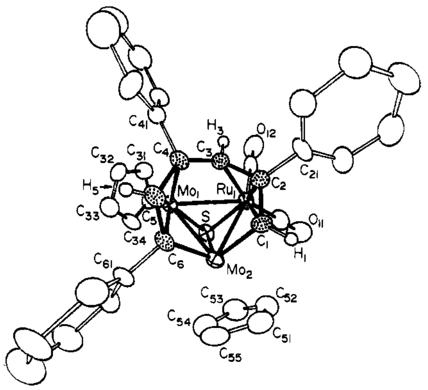

Figure 1. An ORTEP diagram of $RuMo_2(CO)_2(C_5H_5)_2(\mu_3\text{-}S)[\mu_3\text{-}\eta^6\text{-}HCC(Ph)CHC(Ph)CHC(Ph)]$ (2) showing 50% probability thermal ellipsoids.

When 1 was allowed to react with an excess of HC_2Ph in refluxing heptane for 80 min, the products $RuMo_2(CO)_2(C_5H_5)_2(\mu_3\text{-}S)[\mu_3\text{-}\eta^6\text{-}HCC(Ph)CHC(Ph)CHC(Ph)]$ (2) and $RuMo_2(CO)_2(C_5H_5)_2(\mu_3\text{-}S)[\mu\text{-}\eta^3\text{-}PhCC(H)C(Ph)][\mu_3\text{-}\eta^3\text{-}(H)CC(Ph)CH]$ (3) were formed in 15% and 11% yields, respectively.[7] Both compounds were characterized by IR and ^{1}H NMR spectroscopy and by a single-crystal X-ray diffraction analysis.[8,9] An ORTEP diagram of 2 is shown in Figure 1.[9] The molecule consists of a triangular cluster of two molybdenum and one ruthenium atom with a triply bridging sulfido ligand. The Mo(1)–Mo(2) distance at 2.663 (1) Å is much shorter than the corresponding dis-

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(1) (a) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York, 1975; Vol. 2, Chapter 2. (b) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapters 52, 56.3. (c) Cadiot, P.; Chodkiewicz, W. In *Chemistry of Acetylenes*, Viehe, H. G., Eds.; Marcel Dekker: New York, 1969. (d) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapter 8.5. (e) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

(2) (a) Knox, S. A. R., Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, *173*. (b) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, 1982; Vol. 5, Chapter 34, Section 34.4.2.3. (c) Ferrari, R. P.; Vaglio, G. A.; Gambino, O.; Valle, M.; Cetini, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1998.

(3) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127.

(4) Adams, R. D.; Babin, J. E.; Tasi, M. *Angew. Chem., Int. Ed. Engl.* in press.

(5) Compound 1 has also been prepared by another route.[6]

(6) Richter, F.; Roland, E.; Vahrenkamp, H. *Chem. Ber.* **1984**, *117*, 2429.

(7) Compound 1 (30 mg, 0.046 mmol) was refluxed in heptane solvent under N_2 in presence of 50 μL (0.46 mmol) of phenylacetylene for 80 min. The solvent was removed in vacuo. The residue was dissolved in minimum amount of CH_2Cl_2 and was chromatographed by TLC on silica gel with hexane/CH_2Cl_2 (v/v, 7/3) solvent. This yielded 5.6 mg of compound **2** (15%) as a green band, and 4.0 mg of **3** (11%) as an orange band. For **2**: IR (ν(CO)) 1982 (vs), 1923 (s) cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 7.70–7.01 (m, 17 H), 4.91 (s, 5 H), 4.80 (s, 1 H), 4.47 (s, 5 H). Anal. Calcd: C, 57.82; H, 3.85. Found: C, 57.30; H, 3.98 (includes $1.5C_6H_6$). For **3**: IR (hexane): ν(CO) 1994 (vs), 1940 (s) cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 9.58 (s, 2 H), 8.11–6.58 (m, 15 H), 6.46 (s, 1 H), 5.25 (s, 10 H).

(8) Crystals of **2** were grown from solutions in benzene solvent by slow evaporation at 25 °C: space group $P2_1/c$; a = 10.899 (2) Å, b = 23.563 (5) Å, c = 14.562 (3) Å; β = 91.97 (2)°; Z = 4. The crystal lattice contains 1.5 units of benzene in the asymmetric unit. Diffraction data were collected on a Rigaku AFC6 automatic diffractometer. The structure was solved by direct methods (MITHRIL), and was refined (3060 reflections) to the final values of the residuals, R = 0.045 and R_{wF} = 0.045. All calculations were performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., College Station, TX.

(9) Selected interatomic distances (Å) and angles (deg) Mo(1)–Mo(2) = 2.663 (1), Mo(1)–Ru(1) = 3.031 (1), Mo(2)–Ru(1) = 2.775 (1), Ru(1)–C(1) = 2.206(9), Ru(1)–C(2) = 2.18 (1), Ru(1)–C(3) = 2.39 (1), Mo(1)–C(4) = 2.26 (1), Mo(1)–C(5) = 2.27 (1), Mo(1)–C(6) = 2.22 (1), Mo(2)–C(1) = 2.09 (1), Mo(2)–C(6) = 2.08 (1), C(1)–C(2) = 1.42 (1), C(2)–C(3) = 1.46 (1), C(3)–C(4) = 1.44 (1), C(4)–C(5) = 1.44 (1), C(5)–C(6) = 1.42 (1); C(1)–C(2)–C(3) = 119 (1), C(2)–C(3)–C(4) = 128.4 (9), C(3)–C(4)–C(5) = 128 (1), C(4)–C(5)–C(6) = 127 (1).

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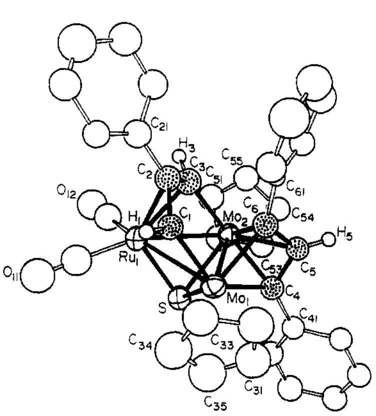


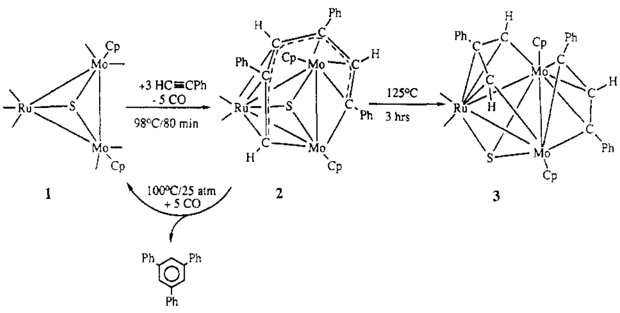
Figure 2. An ORTEP diagram of $RuMo_2(CO)_2(C_5H_5)_2(\mu_3\text{-}S)[\mu\text{-}\eta^3\text{-}PhCC(H)C(Ph)][\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH]$ (**3**) showing 50% probability thermal ellipsoids.

tance in **1** (3.0282 (8) Å) and is similar in length to that of a Mo–Mo double bond (e.g., 2.618 (1) Å, as found in $Mo_2(C_5H_5)_2[(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2]$.[10] The Mo(1)–Ru(1) and Mo(2)–Ru(1) distances are significantly different, 3.031 (1) and 2.775 (1) Å, respectively. The Mo–Ru distances in **1** are 2.8989 (9) and 2.9129 (8) Å. The most important ligand in **2** is the C(H)C(Ph)C(H)C(Ph)C(H)C(Ph) group that contains a C_6 chain that bridges the Mo_2Ru face of the cluster. The three carbon atoms C(1)–C(2)–C(3) are bonded to Ru(1) in a π-allylic fashion. The three carbon atoms C(4)–C(5)–C(6) are similarly bonded to Mo(1). The C–C bond lengths all lie in the range 1.42–1.46 Å and indicate that electron delocalization extends uniformly from C(1) to C(6). The termini of the chain are σ-bonded to Mo(2), Mo(2)–C(1 = 2.09 (1) Å and Mo(2)–C(6) = 2.08 (1) Å. This group was formed evidently by the addition and head-to-tail coupling of 3 equiv of HC_2Ph to **1**. With the assumption that it serves as an eight-electron donor, the metal atoms contain a total of only 46 electrons. This is two less than that required by the EAN rule. The shortness of the Mo–Mo bond may be a consequence of this electronic unsaturation.

It is apparent that the formation of a C–C bond between C(1) and C(6) would complete the cyclization and lead to 1,3,5-$C_6H_3Ph_3$. This transformation was achieved in 80% yield by treatment of **2** with CO at 100 °C/25 atm for 3 h.[11] The principal metal-containing product was **1**, 78% yield.

An ORTEP diagram of **3** is shown in Figure 2.[12] The

Scheme I



structure of **3** consists of a triangular Mo_2Ru cluster that is supported by a triply bridging sulfido ligand. As in **2**, the Mo–Mo distance is unusually short, 2.679 (2) Å. The Ru–Mo distances are normal and equal in length, 2.830 (2) and 2.823 (3) Å. The most interesting ligands are two dimetallaallyl groups. A μ_3-2-phenyldimetallaallyl group bridges the face of the cluster. It is η^3-π-bonded to the ruthenium atom while the ends are σ-bonded to the molybdenum atoms. A μ-1,3-diphenyldimetallaallyl ligand bridges the Mo–Mo edge of the cluster. It is η^3-π-bonded to Mo(2) while both ends are σ-bonded to Mo(1).[14,15] These two ligands were obviously formed by the cleavage of the C(3)–C(4) bond of the C_6 chain in **2**; see Scheme I. Curiously, this bond was originally a C–C triple bond of one of the HC_2Ph monomers. Compound **3** was also obtained (57% yield) directly from **2** by heating to 125 °C in octane solvent.[16]

Cleavage of carbon–carbon bonds in hydrocarbon ligands by the metal atoms alone is an extremely unusual transformation in metal complexes. However, it is well-known and plays a key role in many important reactions that are catalyzed by metal surfaces (e.g., as in petroleum re-forming catalysis).[17] Recent studies have shown that alkyne triple bonds can be cleaved by polynuclear metal complexes.[18]

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Registry No. 1, 92067-61-3; 2, 110096-38-3; 3, 110096-39-4; HC_2Ph, 536-74-3; Mo, 7439-98-7; Ru, 7440-18-8.

Supplementary Material Available: Tables of crystal data, fractional atomic coordinates and thermal parameters, and selected interatomic distances and angles for both structural analyses (28 pages); listings of structure factor amplitudes for both structural analyses (34 pages). Ordering information is given on any current masthead page.

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[10] Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221.

[11] 1,3,5-$C_6H_3Ph_3$ was identified by its characteristic mass spectrum, parent ion *m/e* 306, and by comparison of its ^1H NMR spectrum to that of the reported spectrum, Aldrich Library of NMR Spectra, Aldrich Chemical Co., 1974.

[12] Orange crystals of **3** were grown from hexane/benzene (7/3 v/v) solutions by slow evaporation at 10 °C: space group *C*2/*c*; $a = 35.86$ (1) Å, $b = 12.454$ (6) Å, $c = 14.622$ (3) Å; $\beta = 98.60$ (2)°; $Z = 8$. Diffraction data were collected on a Rigaku AFC6 automatic diffractometer. The structure was solved by direct methods (MITHRIL) and was refined (1867 reflections) to the final values of the residuals, $R = 0.054$ and $R_{wF} = 0.051$. All calculations were performed on a MICROVAX II computer by using the TEXSAN structure solving program library.

[13] Selected interatomic distances (Å) and angles (deg) Mo(1)–Mo(2) = 2.679 (2), Ru(1)–Mo(1) = 2.830 (2), Ru(1)–Mo(2) = 2.823 (3), Mo(1)–C(1) = 2.07 (2), Mo(2)–C(3) = 2.15 (2), Ru(1)–C(1) = 2.18 (2), Ru(1)–C(2) = 2.28 (2), Ru(1)–C(3) = 2.18, Mo(1)–C(4) = 2.16 (2), Mo(1)–C(6) = 2.18 (2), Mo(2)–C(4) = 2.15 (2), Mo(2)–C(5) = 2.35 (2), Mo(2)–C(6) = 2.32 (2), C(1)–C(2) = 1.45 (2), C(2)–C(3) = 1.41 (2), C(4)–C(5) = 1.40 (2), C(5)–C(6) = 1.37 (2); C(1)–C(2)–C(3) = 111 (2), C(4)–C(5)–C(6) = 104 (2). The phenyl ring C(21)–C(26) was found to possess a twofold rotational disorder. This was adequately resolved and refined in the analysis.

[14] Dimetallallyl ligands have been observed previously in polynuclear metal complexes.[15]

[15] a) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 1151. b) Shapley, J. R.; McAteer, C. H.; Churchill, M. R.; Biondi, L. V. *Organometallics* **1984**, *3*, 1595. (c) Beanan, L. R.; Keister, J. B. *Organometallics* **1985**, *4*, 1713 and references therein.

[16] Under these conditions, a small amount of a second orange compound that is believed to be an isomer of **3** was also formed: ν(CO) 1993 (vs), 1938 s cm^{-1}. This compound is currently under study.

[17] Ponec, V. *Adv. Catal.* **1983**, *32*, 149.

[18] (a) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182. (b) Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffman, R. *Organometallics* **1984**, *3*, 619. (c) Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3086.