Synthesis of a Tetrametallic Acetylene. X-ray Structures of $[\{(CO)_3Mo(\mu\text{-}S_2CPCy_3)Mn(CO)_3\}_2\text{-}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^{1'}{:}\eta^{1'}\text{-}C_2)]$ and $[[(CO)_3Mo(\mu\text{-}CCPh)(\mu\text{-}S_2CPCy_3)Mn(CO)_3]$

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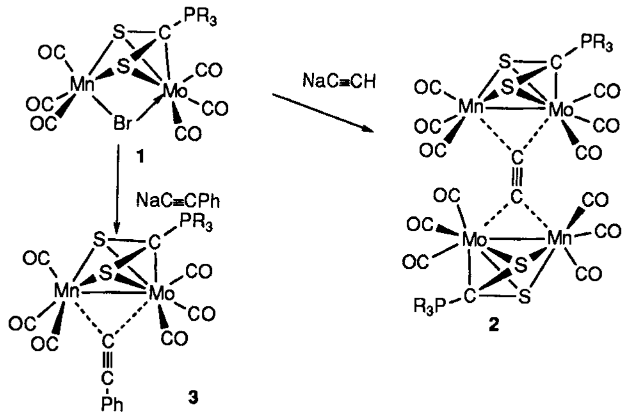
Compounds with C_n bridges between metals have been proposed as models for species present in important metal catalyzed reactions.[1] Many compounds of this class, despite their structural simplicity, have only recently been prepared. Ethynediyls,[2] M−C≡C−M′, compounds in which an acetylenic chain uses one electron in the σ bond to each metal, are a good example: conceptually simple synthetic approaches are rarely successful and the actual preparations involve sophisticated, multistep procedures.

Although many examples of acetylides, RC_2, bridging two metals in a μ_2-$\eta{:}^1\eta^1$ mode have been reported,[3] nearly all the known ethynediyls have a single metal at each end of the C_2 unit.[4] Here we report a straighforward synthesis of the first ethynediyl with a bimetallic unit at each end of the C_2 fragment.

The reaction of $[(CO)_3Mo(\mu\text{-Br})(\mu\text{-}S_2CPCy_3)Mn(CO)_3]$(**1**)[5] with sodium acetylide affords emerald green, air stable $[\{(CO)_3Mo\text{-}(\mu\text{-}S_2CPCy_3)Mn(CO)_3\}_2(\mu_4\text{-}\eta{:}^1\eta{:}^1\eta^{1'}{:}\eta^{1'}\text{-}C_2)]$ (**2**).[6] An X-ray analysis[7] showed a C_2 chain bridging two $(CO)_3Mn(\mu\text{-}S_2CPCy_3)Mo\text{-}(CO)_3$ fragments,[8] each similar to that found in **1**, with the S_2CPCy_3 ligand bonded η^3(S,C,S′) to Mo and η^2(S,S′) to Mn.[9] The Mn−Mo distances [2.961(4) and 2.974(4) Å], significantly shorter than 3.235(1) Å, found in **1**,[13] are consistent with direct Mn−Mo bonds.[14] The C_2 bridge is extremely symmetric [Mn(1)−C(7A)−C(7B) = 139.5 (18)°, Mo(1)−C(7A)−C(7B) = 139.5 (18)°, Mn(2)−C(7B)−C(7A) = 139.2 (17)°, Mo(2)−C(7B)−C(7A) = 139.2 (17)°], and each MnMo pair is within bonding distance of only one of the C_2 atoms. The C(7A)−C(7B) distance, 1.174(30) Å, falls within the range found in ethynediyls.[15] Since each atom of the C_2 chain is tricoordinated, complex **2** might seem a tetrametallic ethene.[2d] However, the four metals are not coplanar: the two MnMo units are staggered, with an angle of 49.2° between the Mo(1)−Mn(1)−C(7A) and Mo(2)−Mn(2)−C(7B) planes.

Scheme 1



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(1) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923−949 (review). Woodworth, B. E.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 7418−7419 and references therein.

(2) Leading references: (a) Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316−2317. (b) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am.Chem. Soc.* **1991**, *113*, 8466−8477. (c) Ramsden, J. A.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5890−5891. (d) Akita, M.; Moro-oka, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 420−432.

(3) Berenguer, J. R.; Falvello, L. R.; Forniés, J.; Lalinde, E.; Tomás, M. *Organometallics* **1993**, *12*, 6−7 and references therein.

(4) In a recent exception, one of the carbon atoms of a C_2 unit binds Re, and the other bridges two Os atoms of an Os_3 triangle: Fallon, S. B.; Arif, A. M.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1997**, 629−630.

(5) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1993**, *12*, 1394−1400.

(6) Sodium acetylide (1 mL of a 18 wt % slurry in xylene/mineral oil, excess) is added under nitrogen to a stirred solution of **1** (0.189 g, 0.25 mmol) in THF (20 mL). After 10 min, the green solution is filtered through a short column of Celite. The solvent is removed in vacuo, and the solid is extracted with CH_2Cl_2 and filtered through a short column of alumina (activation grade IV). (Filtration using alumina was found to be a satisfactory way to remove traces of pyrophoric sodium acetylide. The solid, spectroscopically pure material obtained without filtration through alumina, spontaneously ignited in air.) The volume of the resulting solution is reduced to 5 mL, and hexane (20 mL) is added to cause precipitation of a microcrystalline solid that was washed with hexane (3 × 10 mL) and dried in vacuo. Yield: 0.12 g, 70%. Anal. Calcd for $C_{52}H_{66}Mn_2Mo_2O_{12}P_2S_4$: C, 45.42; H, 4.84. Found: C, 45.54; H, 4.80. IR$_{\nu(CO)}$(CH_2Cl_2): 2032w, 2008s, 1949m, 1924w, 1901m, 1856m. ^{1}H NMR ($CDCl_3$) 2.51 (m, 6H, CH of Cy), 1.94 to 1.26 (m, br, 60 H, CH_2 of Cy). ^{31}P NMR ($CDCl_3$) 34.88 (s). ^{13}C NMR: too insoluble. Crystals for X-ray analysis were grown by vapor diffusion of Et_2O into a concentrated solution of **2** in CH_2Cl_2.

(7) Crystal data: $C_{52}H_{66}Mn_2Mo_2O_{12}P_2S_4$, MW = 1375.0, black plate, monoclinic, $P2_1/c$, $a = 15.930(6)$ Å, $b = 17.036(5)$ Å, $c = 23.615(6)$ Å, $\beta = 94.40(3)°$, $V = 6390(3)$ Å,^{3} $Z = 4$, $D_{calc} = 1.429$ g/cm^3, μ(Mo Kα) = 9.71 cm^{-1}. Siemens R3m/V diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å), 6477 reflections, 3038 with $F > 4\sigma(F)$ used for refinement: $R = 0.0691$, $R_w = 0.0787$.

(8) Two compounds with a μ_4−C_2 ligand have been reported: a tetrametallic ethene was one of the products in the reaction of the ethynediyl Fp′-CC−Fp′ (Fp′= η^5-$C_5Me_5Fe(CO)_2$) with $Ru_3(CO)_{12}$:, see ref 2d. Carbonylation of a pentanuclear cluster containing the $CCPPh_2$ ligand lead to P−C bond cleavage and formation of $Ru_4(\mu_4\text{-}\eta^1,\eta^2\text{-}C_2)(CO)_{12}$: Bruce, M. I.; Snow, M. R.; Tiekink, E. R. T.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1986**, 701−702.

(9) Mononuclear complexes containing S_2CPR_3 ligands in η^2(S, S′) and in η^3(S, C, S′) coordination modes are known. See ref 10, where the first example of a η^3,η^2-μ-S_2CPR_3 ligand is reported. For a discussion of the η^3 and η^2 modes, see ref 11. For other examples of compounds with a η^3,η^2-μ-S_2CPR_3 ligand bridging Mn and Mo, see ref 12.

(10) Miguel, D.; Riera, V.; Miguel, J. A.; Gómez, M.; Soláns, X. *Organometallics* **1991**, *10*, 1683−1692.

(11) Galindo, A.; Mealli, C.; Cuyás, J.; Miguel, D.; Riera, V.; Pérez-Martínez, J. A.; Bois, C.; Jeannin, Y. *Organometallics* **1996**, *15*, 2735−2744.

(12) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1993**, *12*, 2888−2890 and **1994**, *13*, 4667−4669.

(13) A Mn−Mo distance of 3.235(1) Å was found for $[(CO)_3Mo(\mu\text{-Br})\text{-}(\mu\text{-}S_2CPPr^i_3)Mn(CO)_3]$, i.e., the isopropylphosphine analogue of **1**. Given the remote position of the phosphine, we assume that intermetallic distances are essentially the same for both compounds.

(14) For Mn−Mo bond distances see ref 12 and Horton, A. D.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 247−250. Barre, C.; Kubicki, M. M.; Leblanc, J. C.; Moise, C. *Inorg Chem.* **1990**, *29*, 5244−5246.

(15) For a discussion of C−C distances in ethynediyls, see: Heidrich, J.; Steimann, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C. *Organometallics* **1990**, *9*, 1296−1300.

S0002-7863(97)02515-8 CCC: $15.00

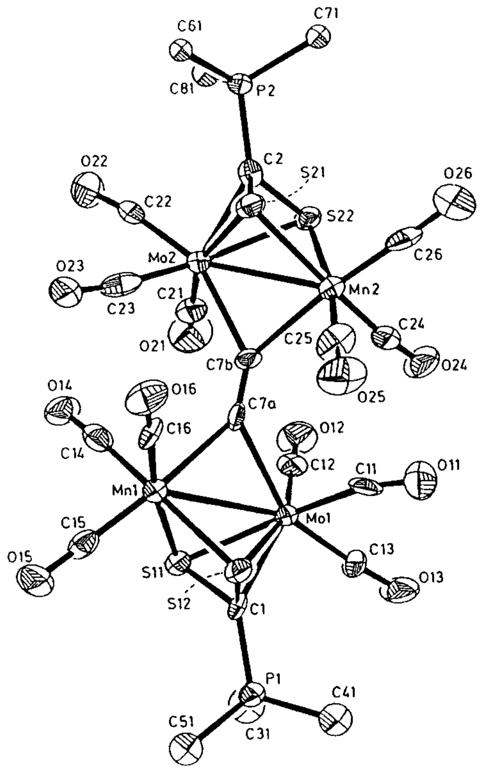


Figure 1. ORTEP drawing of **2**. Cyclohexyl groups are omitted for clarity.

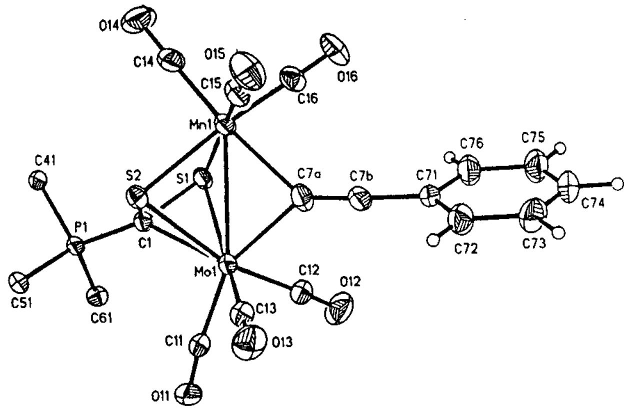
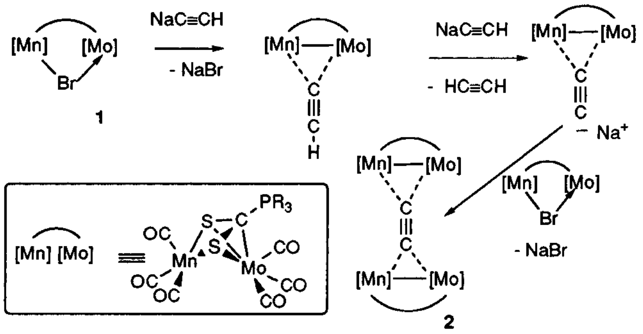


Figure 2. ORTEP drawing of **3**. Cyclohexyl groups are omitted for clarity.

Scheme 2



A useful comparison can be drawn with the phenylacetylide complex $[(CO)_3Mo(\mu\text{-}CCPh)(\mu\text{-}S_2CPCy_3)Mn(CO)_3]$ (**3**, in Scheme 1), synthesized by reaction of **1**[5] with NaCCPh.[16]

The similarity between the IR spectra of **1** and **3** suggested the simple substitution of Br by the CCPh group, so we anticipated a σ, π acetylide donor of one electron to Mn and two to Mo.[17] However, the structural data, determined by X-ray diffraction[18] disagreed with that picture:the Mo−C(7A)−C(7B) and Mn−C(7A)−C(7B) angles are virtually the same (138.7(3) and 137.7(3)°, respectively), so only C(7A) is within metal−C bonding distance, indicating that the CCPh ligand does not employ its π density for the bond with the metals. Therefore, the CCPh ligand must be a single electron donor. The distances Mo−C(7A) = 2.261(4) Å and Mn−C(7A) = 2.218(4) Å, longer than M−C distances in terminal Mo and Mn acetylides,[19] support the idea of a deficient, two electron−three center bond. Furthermore, the linearity of the CCPh ligand [C(7A)−C(7B)−C(71) = 175.5(3)°] and the short C(7A)−C(7B) distance (1.217(6) Å)[14] are in accord with acetylenic character. Since CCPh replaced Br, a three electron donor in **1**, and no other significant differences in the $(CO)_3Mn(\mu\text{-}S_2CPCy_3)Mo(CO)_3$ core exist between **1** and **3**, a metal−metal bond must have been formed. Indeed, the Mo−Mn distance changes from 3.235(1) Å in **1**[12] to 2.975(1) Å in **2**.

The structure of **3** is an unambiguous model to which the unprecedented structure of **2** can be referred. Thus, **2** can be viewed as a dimer of the same "$(CO)_3Mo(\mu\text{-}S_2CPCy_3)(\mu\text{-}C)Mn(CO)_3$" fragment that is bonded to the "*C*Ph" group to form **3**, in which the acetylenic nature of the C≡CPh ligand is obvious. From an alternative point of view, since CCPh is a single electron donor toward the $(CO)_3Mo(\mu\text{-}S_2CPCy_3)Mn(CO)_3$ unit in **3**, each carbon of the C_2 bridge must be a single electron donor toward one of such units in **2**. Hence, **2** can be viewed as a tetrametallic acetylene.

The formation of **2** is likely to take place via initial nucleophilic attack of sodium acetylide to the bromocomplex **1** to afford a terminal acetylide (**A**) which would be deprotonated by excess NaC_2H to give the anionic complex **B**. Reaction of **B** with another molecule of the starting bromo-complex **1** would yield the final tetrametallic **2**.[20]

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Supporting Information Available: X-ray data for **2** and **3** (24 pages). See any current masthead page for ordering and Internet access instructions.

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[16] Freshly cut sodium (0.029 g, 1.25 mmol) is added to a solution of phenylacetylene (145 μL, 1.130 mmol) in toluene (20 mL). The mixture is refluxed until all the sodium is reacted, and the solvent is removed in vacuo. THF (20 mL) and then **1** (0.189 g, 0.25 mmol) are added. After stirring for 15 min, the color changes to a darker red. Workup is as described for **2**. Yield: 0.16 g, 80%. Anal. Calcd for $C_{33}H_{38}MnMoO_6PS_2$: C 51.04, H 4.93. Found C 51.01, H 4.98. $IR_{\nu(CO)}(CH_2Cl_2)$: 2025w, 2006s, 1944m, 1913m, 1862w. ^1H NMR ($CDCl_3$) 7.51 and 7.26 (m, 5H, Ph) 2.54 (m, 3H, CH of Cy), 1.92 to 1.27 (m, br, 30 H, CH_2 of Cy). ^{31}P NMR ($CDCl_3$) 35.27 (s). ^{13}C NMR: too insoluble. Crystals for X-ray analysis were grown by slow diffusion of hexanes into a concentrated solution of **3** in CH_2Cl_2 at −20°.

[17] The $\eta^3,\eta^2\text{-}\mu\text{-}S_2CPCy_3$ ligand is a four electron donor to each metal.[9] Hence, since the Mn−Mo distance is longer than that expected for a bond, electron counting requires Br to be considered as a donor of one electron to Mn and two to Mo in **1**.[5]

[18] Crystal data: $C_{34}H_{40}Cl_2MnMoO_6PS_2$, MW = 861.5, dark red parallelepiped, triclinic, $P\bar{1}$, $a = 12.3978(16)$ Å, $b = 12.4774(15)$ Å, $c = 14.0831(15)$ Å, $\alpha = 72.002(9)°$, $\beta = 86.793(9)°$, $\gamma = 65.120(9)°$, $V = 1872.4(4)$ Å,^{3} $Z = 2$, $D_{calc} = 1.528$ g/cm^3, μ(Mo Kα) = 9.84 cm^{-1}. Siemens R3m/V diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å), for 3930 reflections $F > 6\sigma(F)$ used for refinement: $R = 0.0252$, $R_w = 0.0267$.

[19] Structure of an octahedral phenylacetylide Mn complex: Grigsby, W. J., Nicholson, B. K. *Organometallics* **1993**, *12*, 397−407. For the longest Mo−C(alkynyl) bond length reported, see: Gamasa, M. P.; Gimeno, J.; Zhang, L.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1996**, *514*, 289−297.

[20] A similar sequence was used by Gladysz to synthesize heterobimetallic ethynediyls, see ref 2c.