A 48-Electron Oxo-Capped Dimolybdenum-Iron Cluster, $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-}O)$: Its Synthesis via the Photolytic Reaction of $Fe_2(CO)_9$ with the Mo-Mo Triple-Bonded $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ Dimer and Its Stereochemical Analysis

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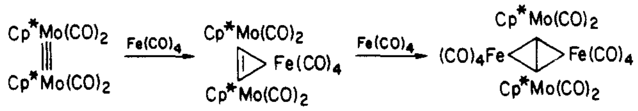
After pretreatment with O_2, photolysis of a toluene suspension of $Fe_2(CO)_9$ and $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ followed by separation of the products via column chromatography resulted in the isolation of the new oxo-capped dimolydenum-iron cluster $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-}O)$ (1). An X-ray diffraction analysis revealed that this mixed-metal cluster contains one $Fe(CO)_3$ and two $(\eta^5\text{-}C_5Me_5)Mo(CO)_2$ fragments linked together in a triangular array by electron-pair metal-metal bonds and a capping oxide atom. The resulting $Mo_2Fe(\mu_3\text{-}O)$ core closely conforms to a mirror-plane geometry with a Mo-Mo distance of 2.914 (1) Å, two Mo-Fe distances of 2.705 (1) and 2.715 (1) Å, two Mo-O distances of 2.015 (3) and 2.019 (3) Å, and an Fe-O distance of 1.902 (3) Å; these molecular parameters are completely consistent with an assignment of formal metal oxidation states of zero to the Fe atom and II to each Mo atom. The single sharp methyl proton resonance displayed by 1 in $CDCl_3$ at room temperature is within the normal range for C_5Me_5 ligands and hence in accord with the expected diamagnetism for this 48-electron trimetal cluster. Compound 1 crystallizes from a hexane-toluene mixture in a monoclinic unit cell of symmetry $I2/a$ and dimensions a = 17.137 (6) Å, b = 14.566 (5) Å, c = 22.869 (8) Å, β = 93.53 (3)°, V = 5697 Å^3; d_{calcd} is 1.70 g/cm^3 for Z = 8. Anisotropic least-squares refinement (RAELS) converged at $R_1(F)$ = 3.71% and $R_2(F)$ = 5.53% for 4463 independent diffractometry data [$I > 3\sigma(I)$] with a data-to-parameter ratio of 21.1:1.

Introduction

Investigations of the chemical and physical properties of organometallic mixed-metal clusters have in the past been hampered by the general lack of rational synthetic procedures for preparing new mixed-metal compounds of a predetermined stoichiometry.[2] Recently, however, synthetic innovations have been reported which have the potential for producing a wide variety of such clusters.[2-5] One notable example of these new synthetic strategies involves the production of 48-electron triangular mixed-metal clusters by the cycloaddition of photochemically or thermally generated, coordinatively unsaturated 16-electron organometallic fragments to 32-electron organometallic dimers which possess metal-metal double bonds. In a specific example which was part of a systematic investigation reported from our laboratories,[4,5] the 48-electron $(\eta^5\text{-}C_5Me_5)_2Co_2Fe(CO)_3(\mu_2\text{-}CO)_2(\mu_3\text{-}CO)$ was synthesized via the cycloaddition of a photolytically generated $Fe(CO)_4$ fragment[6] across the Co-Co double bond of the ethylene-like $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$. Hoffmann[7] and Stone[8] pointed out that these reactions are analogous to the well-known organic reaction by which cyclopropanyl compounds are synthesized by generating methylene moieties in the presence of alkenes.

Scheme I



As an extension of our earlier work[4,5] in this area, we attempted to add photolytically generated, coordinatively unsaturated organometallic species across the formal Mo-Mo triple bond of the inorganic acetylene analogue, $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ (2).[9,10] Our initial attempt to obtain a molybdenum-based mixed-metal cluster involved the photolysis of a solution containing $Fe_2(CO)_9$ and 2. We assumed that either one photogenerated methylene-like $Fe(CO)_4$ fragment would add across the Mo-Mo triple bond of 2 to give a cyclopropene-like cluster, or that two

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[5] Cirjak, L. M. Ph.D. Thesis, University of Wisconsin—Madison, 1980.

[6] For an excellent summary of the photochemistry of $Fe_2(CO)_9$ see: Geoffroy, G. L.; Wrighton, M. D. *Organometallic Photochemistry*; Academic: New York, 1979.

[7] (a) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148-1155. (b) Hoffmann, R. *Science (Washington, D.C.)* **1981**, *211*, 995-1102. (c) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711-724.

[8] Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89-99.

[9] Huang, J.-S.; Dahl, L. F. *J. Organomet. Chem.* **1983**, *243*, 57-68.

[10] Previous investigations of the chemistry of $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ (3) (the cyclopentadienyl analogue of 2) by Curtis and co-workers had indicated that the thermal addition of organometallic species across the Mo-Mo triple bond of 3 does not generally give characterizable new mixed-metal clusters. See, for example: (a) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23-37. (b) Curtis, M. D.; Messerle, L.; Fotinos, N. A.; Gerlach, R. F. In *Reactivity of Metal-Metal Bonds*; Chisholm, M. H., Ed.; ACS Symposium Series 155; American Chemical Society: Washington, DC, 1981; pp 221-257 and references cited therein.

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$Fe(CO)_4$ fragments would add to give a saturated tetrametallic bicyclobutane-like cluster (Scheme I). This initial reaction unexpectedly produced a dimolybdenum–iron cluster which was characterized from spectroscopic and crystallographic measurements as $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\eta_3\text{-O})$ (1).

We concluded that the capping oxide atom was derived either from the cleavage of an iron-bound carbonyl ligand by π-acceptor Mo atom(s) (with iron carbide clusters as possible additional products) or from O_2 and/or H_2O that had been inadvertently admitted into the reaction vessel. Although we have subsequently shown that the capping oxygen atom in 1 is derived from O_2, the possibility of a Mo-promoted C–O bond-cleavage reaction provided the impetus for an extensive investigation of photolytic reactions of a large number of metal carbonyl and metal nitrosyl species with 2. This research has resulted in the isolation of a variety of unusual products whose formation, in several cases, involves the Mo-promoted activation of a bound carbonyl or nitrosyl ligand.[11-13]

Herein are described the preparation, properties, and structure-bonding analysis of the oxo-capped dimolybdenum–iron cluster 1, which was the only mixed-metal organometallic product isolated from the photolytic reaction of an oxygen-pretreated suspension of $Fe_2(CO)_9$ and 2.

Experimental Section

General Procedures. Unless otherwise stated, all manipulations were carried out under an atmosphere of prepurified nitrogen either with standard Schlenk and needle-stock techniques or within a Vacuum Atmospheres glovebox. The following solvents were freshly distilled from the indicated drying agent and saturated with N_2 immediately prior to use: hexane (CaH_2) and dichloromethane (P_2O_5). Toluene was freshly distilled from sodium benzophenone ketyl and saturated either with O_2 or air (for the photolytic reaction) or N_2 (for all other purposes) immediately prior to use. Chloroform-d_1 was dried over molecular sieves and vacuum distilled prior to use. $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ and $Fe_2(CO)_9$ were prepared according to modified published procedures.[14,15]

Infrared spectra were recorded on a Beckman Model 4240 spectrometer with 0.1-mm path-length KBr solution cells. Proton NMR spectra were recorded on either a Bruker WP-200 or WP-270 spectrometer and were referenced indirectly to Me_4Si by the use of residual solvent protons.

Chromatographic separations were performed with Ace Glass medium-pressure chromatographic accessories which were adapted to handle air-sensitive materials. Columns packed with 80–200 mesh Brockman activity I neutral alumina were prepared in hexane. While the title compound was routinely purified via column chromatography, this material could also be separated (with somewhat more difficulty) by solvent extractions.

Preparation of $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-O})$ (1). A 1.00-g (1.74-mmol) sample of 2 and 1.00 g (2.74 mmol) of $Fe_2(CO)_9$ were placed in a water-cooled quartz immersion well photolysis unit equipped with a stir bar. After the addition of toluene, the stirred suspension was saturated either with dry, chemically pure oxygen or with air and then irradiated with a Hanovia 450-W, medium-pressure Hg vapor lamp. Throughout the course of the reaction, a slow stream of N_2 was bubbled through the solution in order to assist in mixing the solution and to facilitate the removal of evolved CO.[16]

Table I. Crystal Data and Details of Data Collection and Analysis of $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-O})$

fw	730.26
cyst syst	monoclinic
cell constants	
a, Å	17.137 (6)
b, Å	14.566 (5)
c, Å	22.869 (8)
β, deg	93.53 (3)
V, Å^3	5697
sys absences	*hkl*, *h* + *k* + *l* = 2n + 1; *h*0*l*, *h* = 2*n* + 1
space group	I2/a (non std cell of C2/*c*)
Z	8
d_{calcd}, g/cm^3	1.70
radiation (λ, Å)	Mo Kα (0.71073)
μ, cm^{-1}	12.99
scan mode	θ–2θ
2θ limits, deg	3.0–50.0
scan speed (deg/min.)	variable; 2.0–24.0
scan width, deg	1.0 below 2θ(Kα_1) to 1.0 above 2θ(Kα_2)
bkd analysis	profile
check ref/freq	0,5,9; 0,7,–5/every 100 ref.
no. of data collected	6629 data in two octants
cutoff criterion	$I_o > 3\ \sigma(I_o)$
no. of independent obsd data	4463
no. of parameters refined	211
GOF	2.605
$R_1(F)$, $R_2(F)$	3.71%, 5.53%

After the solution had been photolyzed for ca. 4 h, the contents of the reaction vessel were transferred to a 300-mL flask where the solvent was evaporated. Small quantities of alumina and dichloromethane were then added to the remaining brown tar, and the resulting suspension was mixed thoroughly. The solvent was then evaporated, and the resulting dry powder carefully loaded onto the top of a chromatography column containing alumina. Elution of the column with a solution of toluene in hexane (40/60 v/v) resulted in the isolation of a red-orange band that contained primarily 2 and $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6$, which were identified by their characteristic infrared spectra. Subsequent elution with toluene alone resulted in the isolation of a brown band consisting primarily of 1. After removal of the solvent from this band, the brown residue was dried in vacuo; recrystallization of the compound from a toluene-hexane mixture gave 1 (200–300 mg, 0.27–0.41 mmol, 16–24% yield) as black microcrystals. Calcd for $C_{27}H_{30}O_8Mo_2Fe$: C, 44.40; H, 4.14. Found: C, 44.68; H, 4.31. A proton NMR spectrum of 1 in $CDCl_3$ consisted of a single sharp resonance at δ 1.89. An infrared spectrum of 1 in toluene exhibited bands in the carbonyl stretching region at 2020 (s), 1978 (vs), 1960 (sh), and 1817 (m) cm^{-1}.

X-ray Crystallographic Determination of the Structure of $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-O})$ (1). Black single crystals of 1 were grown from a hexane-toluene solution. A block-shaped single crystal of dimensions 0.4 × 0.2 × 0.1 mm was epoxied inside an argon-filled Lindemann glass capillary which was then hermetically sealed.

A Syntex (Nicolet) P$\bar{1}$ diffractometer with graphite-monochromated Mo Kα radiation was used to obtain intensity data. Axial photographs were used to verify the approximate dimensions and symmetry of the chosen monoclinic unit cell. Refined lattice constants were determined from least-squares analysis of setting angles for 15 centered, high-angle reflections. The procedures involved in crystal alignment and data collection are described elsewhere.[17] Specific details of this X-ray structural determination are listed in Table I.

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[11] Gibson, C. P.; Mahood, J. A.; Huang, J.-S.; Dahl, L. F. *Abstracts of Papers*, 187th National Meeting of the American Chemical Society, St. Louis, MO; American Chemical Society: Washington, DC, 1984; INORG 202.

[12] (a) Gibson, C. P.; Schugart, K. A.; Fenske, R. F.; Dahl, L. F. submitted for publication. (b) Gibson, C. P.; Dahl, L. F., submitted for publication. (c) Gibson, C. P.; Rae, A. D.; Dahl, L. F., submitted for publication.

[13] Gibson, C. P.; Adams, B. R.; Dahl, L. F. *Abstracts of Papers* 190th National Meeting of the American Chemical Society, Chicago, IL; American Chemical Society; Washington DC, 1985; INORG 73.

[14] King, R. B.; Iqbal, M. Z.; King, A. D., Jr. *J. Organomet. Chem.* **1979**, *171*, 53–63.

[15] King, R. B. *Organometallic Synthesis*; Academic: New York, 1965; Vol. 1.

[16] Pretreatment with either air or dry O_2 gave identical results. Photolysis of the reaction mixture with a continuous purge of air did not result in the isolation of significant quantities of 1.

[17] Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277–284.

Table II. Fractional Coordinates for $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-}O)$

atom	x	y	z
Mo(1)	0.4541 (0)	0.2164 (0)	0.4180 (0)
Mo(2)	0.5334 (0)	0.3113 (0)	0.3264 (0)
Fe	0.5984 (1)	0.2901 (1)	0.4369 (1)
O	0.5018 (2)	0.3417 (2)	0.4076 (1)
C(1)	0.4915 (3)	0.0978 (3)	0.3869 (2)
O(1)	0.5106 (3)	0.0282 (3)	0.3704 (2)
C(2)	0.5183 (3)	0.1760 (3)	0.4869 (2)
O(2)	0.5410 (2)	0.1389 (3)	0.5297 (2)
C(3)	0.4633 (3)	0.2160 (3)	0.2973 (2)
O(3)	0.4245 (2)	0.1631 (3)	0.2692 (2)
C(4)	0.6162 (3)	0.2200 (4)	0.3203 (2)
O(4)	0.6645 (3)	0.1675 (4)	0.3100 (2)
C(5)	0.5974 (4)	0.3265 (5)	0.5126 (3)
O(5)	0.5979 (4)	0.3537 (4)	0.5599 (2)
C(6)	0.6652 (3)	0.1943 (4)	0.4408 (3)
O(6)	0.7078 (3)	0.1335 (4)	0.4412 (2)
C(7)	0.6751 (3)	0.3657 (4)	0.4211 (3)
O(7)	0.7275 (3)	0.4124 (4)	0.4170 (3)
Cp(1)	0.3607 (2)	0.2375 (1)	0.4867 (1)
Cp(2)	0.3398 (2)	0.2984 (2)	0.4399 (1)
Cp(3)	0.3201 (2)	0.2450 (2)	0.3894 (1)
Cp(4)	0.3287 (2)	0.1511 (2)	0.4049 (1)
Cp(5)	0.3538 (2)	0.1465 (2)	0.4650 (1)
Me(1)	0.3767 (3)	0.2642 (2)	0.5495 (1)
Me(2)	0.3362 (3)	0.4003 (2)	0.4439 (2)
Me(3)	0.2857 (3)	0.2808 (2)	0.3321 (1)
Me(4)	0.3045 (3)	0.0712 (2)	0.3668 (1)
Me(5)	0.3606 (3)	0.0609 (2)	0.5012 (1)
Cp(6)	0.5623 (2)	0.3624 (2)	0.2329 (1)
Cp(7)	0.4838 (2)	0.3868 (2)	0.2403 (1)
Cp(8)	0.4831 (2)	0.4522 (2)	0.2858 (1)
Cp(9)	0.5613 (1)	0.4682 (2)	0.3066 (1)
Cp(10)	0.6102 (2)	0.4127 (2)	0.2739 (1)
Me(6)	0.5903 (2)	0.3033 (3)	0.1851 (2)
Me(7)	0.4149 (2)	0.3601 (3)	0.2004 (2)
Me(8)	0.4133 (2)	0.5047 (3)	0.3032 (2)
Me(9)	0.5879 (2)	0.5380 (3)	0.3511 (2)
Me(10)	0.6978 (2)	0.4198 (3)	0.2744 (2)

Systematic absences indicated that the probable space group for the chosen unit cell is either *Ia* (related to an alternative cell of *Cc* symmetry) or *I*2/*a* (related to an alternative cell of *C*2/*c* symmetry).[18] Our selection of the latter centrosymmetric space group was based upon the close correlation of the intensity data from a Wilson plot of the normalized structure factors with a centrosymmetric distribution; this selection was subsequently verified by the successful solution and refinement of the structure under *I*2/*a* symmetry. The intensities of two standard reflections did not show significant variations during data collection.

The positions of the three metal atoms were determined by the application of MULTAN.[19] The remaining 35 non-hydrogen atoms were located by successive difference maps coupled with several cycles of isotropic least-squares refinement with RAELS.[20] At this point, each of the two independent pentamethylcyclopentadienyl ligands was constrained as a rigid group with local C_{5v} symmetry; the methyl hydrogen atoms were included in their idealized positions. Both the positional parameters and the thermal motion of these two groups were refined by use of subsidiary axial systems as described by Rae.[21,22] The thermal librational-like motion of each $(\eta^5\text{-}C_5Me_5)$ ring was treated with a TLX model.[22,23] All other non-hydrogen atoms were refined with individual anisotropic thermal parameters. During a later stage of refinement, the methyl groups of each pentamethylcyclopentadienyl ligand were individually allowed to move away from the plane containing the ring carbon atoms. An empirical absorption correction was applied to the intensity data.[24-27]

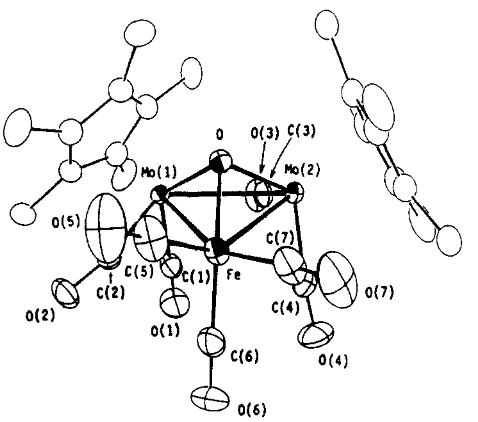

Figure 1. Molecular configuration of $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-}O)$, a 48-electron cluster with a completely bonding $Mo_2Fe(\mu_3\text{-}O)$ core.

The refinement converged with a $R_1(F)$ of 3.71% and a $R_2(F)$ of 5.53% with a data-to-parameter ratio of 21.1/1.[28] The largest parameter change-to-esd ratio for the final cycle was 0.37. A final difference map revealed no unusual features; the largest residual densities corresponded to several small peaks (of electron density less than 10% of that of a typical carbon atom) located at nonmeaningful atomic sites near the molybdenum atoms. Atomic scattering factors and anomalous dispersion corrections were taken from ref 29.

Positional parameters for the non-hydrogen atoms from the last full-matrix least-squares cycle are presented in Table II. Interatomic distances and bond angles are given in Table III. Tables of coordinates and isotropic temperature factors for all hydrogen atoms, anisotropic thermal parameters for all non-hydrogen atoms, and a listing of observed and calculated structure factor amplitudes are available as supplementary material.

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[18] For *I*2/*a*, each of the 38 non-hydrogen and 30 hydrogen atoms in the crystallographically independent molecule of 1 occupies the general eightfold set of positions: $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2) \pm (x, y, z; {}^1/_2 + x, -y, z)$.

[19] (a) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J.-P. *MULTAN-76*; (b) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368–376.

[20] Rae, A. D. RAELS, A Comprehensive Least-Squares Program; University of New South Wales: Kensington, 1976; adapted for a Harris/7 computer by A. D. Rae, University of Wisconsin, Madison, 1983.

[21] Rae, A. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1975**, *A31*, 560–569.

[22] Although the hydrogen atoms are placed in idealized positions, the program RAELS reports esd's for these atoms. These estimates reflect the errors associated with the orientations of the local axial systems (which are calculated from the crystallographic coordinates of the ring carbon atoms) but do not reflect actual esd's of the fractional coordinates of these atoms. Likewise, the thermal factors and associated esd's reported for the hydrogen atoms are not meant to imply that these parameters have been determined accurately for this structure. These values arise from the calculation of the librational-like thermal motion of the rigid $\eta^5\text{-}C_5Me_5$ group. Hydrogen atoms in their idealized positions are included in this calculation.

[23] Rae, A. D. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1975**, *A31*, 570–574.

[24] An absorption tensor is computed from ΔF values by use of an option of the program RAELS.[20,25] This correction is similar to that used by Hope[26] and is similar to the procedure described by Walker and Stuart.[27]

[25] Rae, A. D. *The Refinability of Absorption Corrections*, submitted for publication.

[26] Hope, H., Personal communication (Feb 1984) to L. F. Dahl. The Hope program ABSORPTION (Hope, H.; Moezzi, B., unpublished results) utilizes an empirical absorption tensor from an expression relating $|F_o|$ and $|F_c|$.

[27] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158–166.

[28] The unweighted and weighted discrepancy factors used are $R_1(F) = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ and $R_2(F) = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with individual weights of $w_i = 1/\sigma^2(F_o)$ assigned on the basis of the estimated standard deviation of the observed structure factors. The standard deviation of an observation of unit weight (goodness-of-fit) is defined by $[\sum w_i(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

[29] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 149, 155–158.

Table III. Selected Interatomic Distances and Bond Angles for $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_4(\mu_3\text{-}O)$

A. Interatomic Distances (Å)

Mo(1)–Mo(2)	2.914 (1)	Mo(1)–Fe	2.705 (1)	C(2)–O(2)	1.165 (5)	C(3)–O(3)	1.182 (6)
Mo(1)–O	2.019 (3)	Mo(1)–C(1)	1.989 (5)	C(4)–O(4)	1.161 (6)	C(5)–O(5)	1.151 (7)
Mo(1)–C(2)	1.955 (5)	Mo(1)–C(3)	2.773 (4)	C(6)–O(6)	1.148 (7)	C(7)–O(7)	1.136 (6)
Mo(1)–Cp(1)	2.332 (3)	Mo(1)–Cp(2)	2.374 (3)	Cp(1)–Cp(2)	1.417 (2)	Cp(1)–Cp(5)	1.417 (2)
Mo(1)–Cp(3)	2.385 (3)	Mo(1)–Cp(4)	2.352 (3)	Cp(1)–Me(1)	1.496 (3)	Cp(2)–Cp(3)	1.417 (2)
Mo(1)–Cp(5)	2.319 (3)	Mo(2)–Fe	2.715 (1)	Cp(2)–Me(2)	1.488 (3)	Cp(3)–Cp(4)	1.417 (2)
Mo(2)–O	2.015 (3)	Mo(2)–C(3)	1.926 (5)	Cp(3)–Me(3)	1.497 (3)	Cp(4)–Cp(5)	1.417 (2)
Mo(2)–C(4)	1.956 (5)	Mo(2)–Cp(6)	2.346 (3)	Cp(4)–Me(4)	1.497 (3)	Cp(5)–Me(5)	1.497 (3)
Mo(2)–Cp(7)	2.368 (3)	Mo(2)–Cp(8)	2.392 (3)	Cp(6)–Cp(7)	1.413 (2)	Cp(6)–Cp(10)	1.413 (2)
Mo(2)–Cp(9)	2.385 (3)	Mo(2)–Cp(10)	2.357 (3)	Cp(6)–Me(6)	1.493 (3)	Cp(7)–Cp(8)	1.413 (2)
Fe–O	1.902 (3)	Fe–C(2)	2.479 (5)	Cp(7)–Me(7)	1.498 (3)	Cp(8)–Cp(9)	1.413 (2)
Fe–C(5)	1.812 (6)	Fe–C(6)	1.803 (6)	Cp(8)–Me(8)	1.494 (3)	Cp(9)–Cp(10)	1.413 (2)
Fe–C(7)	1.768 (6)	C(1)–O(1)	1.137 (6)	Cp(9)–Me(9)	1.489 (3)	Cp(10)–Me(10)	1.503 (3)

B. Bond Angles (deg)

Mo(2)–Mo(1)–Fe	57.6 (0)	Mo(1)–Mo(2)–Fe	5.3 (0)	Mo(2)–Fe–C(5)	146.0 (2)	Mo(2)–Fe–C(6)	110.9 (2)
Mo(1)–Fe–Mo(2)	65.0 (0)	Mo(2)–Mo(1)–C(1)	88.9 (1)	Mo(2)–Fe–C(7)	90.4 (2)	O–Fe–C(5)	99.3 (2)
Mo(2)–Mo(1)–C(2)	117.2 (1)	Fe–Mo(1)–C(1)	95.2 (2)	O–Fe–C(6)	149.2 (2)	O–Fe–C(7)	108.9 (2)
Fe–Mo(1)–C(2)	61.8 (1)	O–Mo(1)–C(1)	127.0 (2)	C(5)–Fe–C(6)	102.8 (3)	C(5)–Fe–C(7)	93.6 (3)
O–Mo(1)–C(2)	98.9 (2)	C(1)–Mo(1)–C(2)	81.3 (2)	C(6)–Fe–C(7)	90.8 (3)	Mo(1)–O–Mo(2)	92.5 (1)
Mo(1)–Mo(2)–C(3)	66.3 (1)	Mo(1)–Mo(2)–C(4)	95.8 (2)	Mo(1)–O–Fe	87.2 (1)	Mo(2)–O–Fe	87.7 (1)
Fe–Mo(2)–C(3)	116.8 (1)	Fe–Mo(2)–C(4)	74.4 (2)	Mo(1)–C(1)–O(1)	177.2 (5)	Mo(1)–C(2)–O(2)	163.6 (4)
O–Mo(2)–C(3)	106.2 (2)	O–Mo(2)–C(4)	116.9 (2)	Mo(2)–C(3)–O(3)	167.2 (4)	Mo(2)–C(4)–O(4)	172.4 (5)
C(3)–Mo(2)–C(4)	85.7 (2)	Mo(1)–Fe–C(5)	101.9 (2)	Fe–C(5)–O(5)	176.7 (6)	Fe–C(6)–O(6)	177.7 (6)
Mo(1)–Fe–C(6)	105.8 (2)	Mo(1)–Fe–C(7)	153.9 (2)	Fe–C(7)–O(7)	172.7 (5)		

Results and Discussion

Structural Features of $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-}O)$ and Resulting Bonding Implications. The dimolybdenum-iron cluster $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-}O)$ (1) exists as discrete molecules in the solid state with no unusual intermolecular contacts. The independent molecule (Figure 1) consists of one $Fe(CO)_3$ and two $Mo(\eta^5\text{-}C_5Me_5)(CO)_2$ fragments positioned at the vertices of an isosceles triangle and coordinated to one another by electron-pair metal–metal bonds and by a capping oxide ligand. The resulting $Mo_2Fe(\mu_3\text{-}O)$ core possesses an approximate C_s—*m* geometry with a mirror-bisected Mo–Mo bond of 2.914 (1) Å, two mirror-related Mo–Fe bonds of 2.705 (1) and 2.715 (1) Å, two mirror-related Mo–O bonds of 2.015 (3) and 2.019 (3) Å, and an Fe–O bond of 1.902 (3) Å. These molecular parameters are compatible with a designation of formal oxidation states of zero for the Fe atom and II for each of the two Mo atoms. The observance of a sharp singlet within the normal range for C_5Me_5 ligands in the room-temperature ^1H NMR spectrum of 1 in $CDCl_3$ provides definitive evidence that this 48-electron triangular metal cluster is diamagnetic.

Our initial assignment of the trimetal capping ligand as an oxygen atom was based upon structural-electronic considerations. Several attempts to establish the composition of 1 from mass spectroscopic measurements were unsuccessful. However, convincing evidence for the stoichiometry of 1 was provided from the X-ray crystallographic study. Specifically, three separate least-squares refinements were performed in which the capping ligand was assumed to be one of three isoelectronic species—viz., CH_2, NH, or O.[30] When the scattering power of the capping atom was designated as either a carbon or a nitrogen atom, the resulting isotropic thermal parameters obtained from the refinements were nonpositive definite (i.e., negative *B* values) because of insufficient electron-density for the triply bridging atom. Only when the capping atom was designated as an oxygen atom did the isotropic temperature factor acquired from the refinement conform to a physically meaningful positive value; in this case its value was slightly larger than those for the metal atoms, as expected for a strongly coordinated core atom. These results are also consistent with the thermal ellipsoids (shown in Figure 1) obtained from the anisotropic refinement of this capping ligand as an oxygen atom; the appropriate size, shape, and orientation of the thermal ellipsoid for the oxygen atom relative to those for the other atomic thermal ellipsoids leave no doubt in our minds concerning its identity. This structural feature that the atomic thermal ellipsoids for the $Mo_2Fe(\mu_3\text{-}O)$ core have similar sizes is also observed in other cores of a wide variety of oxide, carbide, and nitride metal clusters.[11-13,31-38] Our subsequent work in this area has produced a variety of other oxo-bridged molybdenum clusters which are presumed to be a consequence of the unusual oxophilicity of a molybdenum atom.[11-13,31,32]

Compound 1 is a typical example of a 48-electron metal cluster which, according to simple electron-counting rules,[39] should possess three metal–metal single bonds. While the use of bond lengths in the assignment of bond orders for organometallic clusters is common, the bond-length/bond-order relationship may be complicated by such factors as the coordination numbers and oxidation states of

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[30] The absence of a proton resonance assignable to a CH_2 group or an infrared band assignable to an NH stretch mitigates against these possibilities.

[31] A structurally analogous 47-electron $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(\eta^5\text{-}C_5H_5)(CO)_4(\mu_3\text{-}O)$ cluster which contains an iron-bound cyclopentadienyl ligand (in place of the three iron-bound terminal carbonyl ligands observed in 1) was recently isolated from the photolytic addition of a 13-electron $Fe(\eta^5\text{-}C_5H_5)$ fragment to the Mo–Mo triple-bonded $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$.[32] Qualitative experiments indicate water to be the main source of the triply bridging oxygen atom in this paramagnetic, redox-active mixed-metal cluster.

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the metal atoms, as well as the nature and geometry of the ligands contained in the molecule. For example, Mo–Mo single-bond lengths in low-valent dimetal and trimetal clusters vary from ca. 2.82 to 3.32 Å,[11-13,32,40] while high-valent dimetal and trimetal clusters may have Mo–Mo single-bond lengths of 2.47–2.79 Å.[41,42] Clearly, the validity of any bond-length/bond-order argument depends on the similarities of the compounds being compared. The Mo–Mo bond length of 2.914 (1) Å in 1 is within the range observed for a number of other compounds containing Mo(II) atoms (range 2.821–3.310 Å; average of 18 mean values 2.95 Å).[11-13,32,40b,d-j,n-p,u,43] More importantly, it is within the range of 2.94 ± 0.05 Å which has been observed for a variety of similar Mo(II) cluster compounds which contain the Mo(η^5-C_5Me_5) moiety.[11-13,32] The two nearly identical Mo–Fe bonds average 2.710 Å, a value which is similar to the Mo–Fe bonds found for other organometallic clusters which contain low-valent Mo and Fe atoms (range 2.734–2.862 Å; average of 9 values 2.81 Å).[11,12b,40b,o,p,41,42]

The two nearly identical Mo(1)–O(μ_3) and Mo(2)–O(μ_3) distances of 2.019 (3) and 2.015 (3) Å, respectively, are similar to Mo–O bond lengths that are observed in other Mo-containing cluster compounds containing the capping oxide ligand.[11-13,32,44] Similarly, the Fe–O(μ_3) bond length, which measures 1.903 (3) Å, is nearly identical to the analogous bond in other iron-containing clusters.[11-13,32,41,42] Bond angles about the capping oxide ligand are all rather close to 90° (87.2 (1)–92.5 (1)°). While these angles are somewhat less than might be expected for an ligand which may reasonably be considered to be an sp^3-hybridized atom, they are similar to values observed in other low-valent oxo-capped molybdenum-containing clusters.[11,31,32]

The three iron-bonded carbonyl ligands are nearly linear (172.7 (5)° to 177.7 (6)°) with normal Fe–CO and C–O bond lengths. Each of the molybdenum atoms is bonded to two carbonyl ligands. The Mo–CO and C–O bond lengths average 1.957 and 1.16 Å, respectively; the Mo–C–O angles range from 163.6 (4)° to 177.2 (5)°. The abnormally bent Mo(1)–C(2)–O(2) and Mo(2)–C(3)–O(3) bond angles of 163.6 (4)° and 167.2 (4)°, respectively, are ascribed to weak interactions of these carbonyl ligands with a second metal atom, as evidenced by the Fe–C(2) and Mo(1)–C(3) distances of 2.479 (6) and 2.773 (4) Å, respectively.

The Mo–C(ring) distances, which range from 2.319 (3) to 2.392 (3) Å, compare well with the Mo–C(ring) bond lengths found in $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ (2).[9] The five C(ring)–C(ring) bond lengths, which were constrained to be identical within each of the C_5Me_5 ligands, were found to be 1.417 (2) and 1.413 (2) Å for the C_5Me_5 ligands attached to Mo(1) and Mo(2), respectively. All methyl substituents in each of the two C_5Me_5 ligands were displaced out of the ring carbon plane away from the attached Mo atoms; the angular variations of the displacements ranged from 1.9° to 8.9°.

Synthesis and Chemical Characterization of $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe(CO)_7(\mu_3\text{-}O)$ (1). An initial attempt to add photolytically generated $Fe(CO)_4$ fragments to the acetylene-like molybdenum dimer 2 under what were thought to be air-free conditions gave the oxo-capped 1 as a major product instead of the simple cycloaddition products that were predicted for this reaction (Scheme I). Subsequent attempts to synthesize 1 under rigorously air-free conditions did not lead to the isolation of 1 but instead gave a highly intriguing 62-electron butterfly dimolybdenum–diiron cluster, $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe_2(CO)_9(\mu_2\text{-}CO)(\eta^2\text{-}\mu_4\text{-}CO)$, containing a molybdenum-coordinated Π-bound carbonyl ligand; its synthesis and stereochemistry are described elsewhere.[11,12b] Since the preparation of 1 could not be reproduced under rigorously air-free conditions, we postulated that the original isolation of 1 resulted from a reaction which had been inadvertently exposed to air, possibly as a result of inadequate deoxygenation of the reaction solvent.

In an attempt to mimic inadequately deoxygenated toluene, we saturated the solvent with air and then ran the reaction in a manner which was identical with the original preparation of 1. (As in the original reaction, a slow stream of N_2 was bubbled through the mixture throughout the course of the reaction.) By this procedure, we were able to isolate 1 as the only isolable mixed-metal organometallic product in overall yields ranging from 16 to 24%. The reaction was repeated with pretreatment of the reaction solvent with dry chemically pure O_2 in order to rule out the possibility that the production of 1 resulted from the introduction of traces of water into the solvent from air.[31,32] The products of the reaction as well as the yield of 1 were identical for reactions run following pretreatment with either air or dry prepurified O_2. An attempt to increase the yield of 1 by bubbling air through the reaction vessel throughout the photolysis did not result in the production of significant quantities of 1 as indicated by the lack of infrared absorbences attributable to 1 in spectra taken during the course of the reaction. Careful attempts to isolate 1 by exposing $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe_2(CO)_9(\mu_2\text{-}CO)(\eta^2\text{-}\mu_4\text{-}CO)$ to air under ambient conditions failed to produce 1. No further attempts were made to optimize the yield of 1.

The new oxo-capped dimolybdenum–iron cluster 1 crystallizes as black plates which dissolve in most common organic solvents to give brown solutions. This compound is relatively air-stable in the solid state but somewhat less so in solution. The sharp ^1H resonance at δ 1.89 obtained for 1 in $CDCl_3$ was assigned to the two pentamethylcyclopentadienyl ligands. Its solution infrared spectrum consisting of strong, sharp bands at 2027 cm^{-1} and 1978 cm^{-1}, a shoulder at 1960 cm^{-1}, and a broad peak of moderate intensity at 1817 cm^{-1} is compatible with the solid-state molecular structure containing both terminal and

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highly asymmetric carbonyl ligands. With use of the experimental conditions herein described, we were able to isolate 1 in nonoptimized overall yields of 16–24%. In addition to unreacted starting materials, the only other organometallic compounds that were isolated from the reaction were $Fe(CO)_5$ and the Mo–Mo single-bonded $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6$ dimer, which is produced by the reaction of liberated CO with 2.[45]

Mixed-metal organometallic clusters such as 1 are of particular interest due to the extensive use of molybdenum-based heterogeneous catalysts. Our current research involving the synthesis and physicochemical properties of molybdenum-containing mixed-metal clusters has shown that 2 can react with $Fe_2(CO)_9$ to give such molybdenum-containing species. In subsequent articles, we will report the reaction of 2 with a assortment of carbonyl- and/or nitrosyl-containing organometallic compounds. Such reactions have resulted in the isolation of a wide variety of unusual new organometallic clusters, some of which are formed with concomitant N–O or C–O bond activation.[11-13,32]

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Registry No. 1, 102342-15-4; 2, 12132-04-6; $Fe_2(CO)_9$, 15321-51-4; Mo, 7439-98-7; Fe, 7439-89-6.

Supplementary Material Available: Tables giving calculated positions and isotropic temperature factors for all hydrogen atoms, anisotropic thermal parameters for all non-hydrogen atoms, and a listing of observed and calculated structure factor amplitudes (44 pages). Ordering information is available on any current masthead page.

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Peralkylcyclopentadienyl Tungsten Polyhydride Complexes

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$[WCp^*H_4]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) has been prepared by the reaction of $[WCp^*Cl_4]_2$ with $LiAlH_4$ followed by treatment with methanol. Analogous $\eta^5\text{-}C_5Me_4Et$, $\eta^5\text{-}C_5Me_4\text{-}n\text{-}Pr$, $\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu$, $\eta^5\text{-}C_5Et_5$, and $\eta^5\text{-}C_5Et_4\text{-}t\text{-}Bu$ complexes have been prepared similarly. Reaction of $[WCp^*H_4]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with CO under pressure gives the known dinuclear hydrido carbonyl complex $[WCp^*H(CO)_2]_2$, whereas with PMe_3 a hydrido phosphine complex $W_2Cp^*_2H_6(PMe_3)$ is formed. The dimeric unit is retained when $[WCp^*H_4]_2$ is mixed with $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ and during the reaction of this mixture with CO or PMe_3. A trimeric trihydride complex, $[WCp^*H_3]_3$, forms together with a small amount of $[WCp^*H_4]_2$ upon high-pressure hydrogenation of WCp^*Me_4. Reaction of $WCp^*Cl_4(PMe_3)$ with $LiAlH_4$ gives the monomeric phosphine hydride complex $WCp^*H_5(PMe_3)$. $[WCp^*H_4]_2$ can be protonated cleanly by HBF_4 to give $[W_2Cp^*_2H_9]BF_4$. With use of analogous methodology several hydride complexes containing the two-carbon-linked cyclopentadienyl ligand $\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4$ have been prepared. The octahydride complex $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ crystallizes as a toluene solvate in the triclinic space group $P\bar{1}$ with $a = 14.828$ (3) Å, $b = 15.963$ (5) Å, $c = 7.854$ (3) Å, $\alpha = 93.03$ (3)°, $\beta = 98.04$ (2)°, $\gamma = 110.91$ (2)°, and $Z = 2$. Diffraction data (Mo Kα) were collected at −50 °C with a CAD4F-11 diffractometer, and the structure was refined to $R_1 = 4.3\%$ and $R_2 = 4.7\%$ for 4595 absorption corrected reflections having $3° \leq 2\theta \leq 50°$ and $F_o > 4\sigma(F_o)$. The complex shows a dinuclear structure with a W–W distance of 2.591 (1) Å and slightly distorted bridging ligand system. The hydride ligands could not be located, even using a data set collected at −180 °C. An interesting difference in the reactivity of $[WCp^*H_4]_2$ and $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ is that the latter does not react readily with CO. ^1H NMR data for all neutral hydride complexes show intramolecular hydride exchange to be rapid on the NMR time scale under most conditions, while the exchange of terminal and bridging hydrides in $[W_2Cp^*_2H_9]^+$ is slow at −30 °C (400 MHz).

Introduction

Several years ago we discovered that a tantalum complex with the composition $[Ta(\eta^5\text{-}C_5Me_5)Cl_2H]_2$ would react readily with carbon monoxide to give a μ-hydrido μ-η^2,η^2-formyl complex, $Ta_2(\eta^5\text{-}C_5Me_5)_2Cl_4(\mu\text{-}H)(\mu\text{-}CHO)$.[1] This is a rare example of the reduction of carbon monoxide by a transition-metal hydride complex under mild conditions. Formation of a complex containing a formyl ligand is thought to be the first step in homogeneous systems in which CO is reduced.[2] Although we could show that methane could be obtained by hydrogenation in the presence of $AlCl_3$ and methanol by hydrolysis, we felt that the inherent oxophilicity of tantalum ultimately would prevent any catalytic reduction of CO to C_1 or, more desirably, C_2 products. We decided to move toward less oxophilic metals to the right of tantalum and continue to explore the possibility of bimetallic activation of carbon monoxide.

Our exploration of the reactions of alkylidyne complexes led to the discovery of $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$.[3] We found

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