

# Bis(ethylene)( $\eta$ -pentamethylcyclopentadienyl)cobalt as a Precursor to Heteronuclear Metal Clusters: X-Ray Crystal Structure of $[\text{Co}_2\text{Mo}_2(\mu\text{-CO})_3(\mu_3\text{-CO})(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$ ; a Model for CO Activation on a Stepped Metal Surface

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U.v. irradiation of  $[\text{Co}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$  with the compounds  $[\text{M}_2(\text{CO})_4(\eta\text{-C}_5\text{R}_5)_2]$  ( $\text{M} = \text{Fe}$  or  $\text{Ru}$ , and  $\text{R} = \text{H}$ ;  $\text{M} = \text{Fe}$ ,  $\text{R} = \text{Me}$ ) or  $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  affords the cluster complexes  $[\text{CoM}_2(\mu\text{-CO})_3(\mu_3\text{-CO})(\eta\text{-C}_5\text{Me}_5)(\eta\text{-C}_5\text{R}_5)_2]$  and  $[\text{Co}_2\text{Mo}_2(\mu\text{-CO})_3(\mu_3\text{-CO})(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$ ; the molecular structure of the latter species, established by X-ray diffraction, reveals a novel bonding mode for a CO ligand.

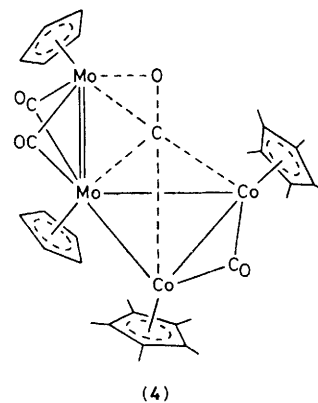
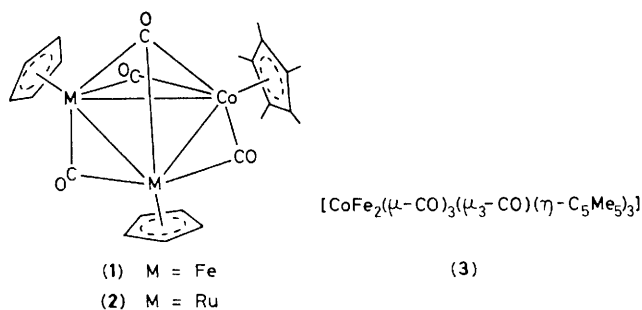
A convenient synthesis of  $[\text{Co}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$  has recently been reported,<sup>1</sup> allowing the mononuclear cobalt species to be used as a precursor to heteronuclear metal clusters containing  $\text{Co}(\eta\text{-C}_5\text{Me}_5)$  fragments. Previously, we have employed<sup>2</sup> the compounds  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$  as a method of introducing  $\text{Pt}(\text{CO})(\text{PR}_3)$  groups into metal clusters with carbonyl ligands. It was proposed that  $\text{PtPR}_3$  fragments, formed by release of ethylene, attack the metal carbonyl linkages so that transfer of CO to platinum takes place, and heteronuclear metal-metal bonds are formed. It was thought that  $\text{Co}(\eta\text{-C}_5\text{Me}_5)$  groups, derived from  $[\text{Co}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$ , might behave similarly.

Irradiation of  $[\text{Co}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$  and  $[\text{Fe}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (1:1) in toluene with ultraviolet light gave black crystals of (1). The ruthenium analogue (2), and the cobalt-iron compound (3), were similarly prepared from reactions between  $[\text{Co}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$  and  $[\text{Ru}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  or  $[\text{Fe}_2(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2]$ , respectively. The spectroscopic data<sup>†</sup> for (1)–(3) are in accord with the structures proposed.<sup>‡</sup> In particular, the i.r. spectra of the three compounds show a band near  $1650\text{ cm}^{-1}$  due to the  $\mu_3\text{-CO}$  ligand, as well as bands in the range  $1830\text{--}1750\text{ cm}^{-1}$  due to  $\mu_2\text{-CO}$  groups. A similar band pattern is observed in the i.r. spectra of the structurally related compounds  $[\text{Co}_2\text{Cr}(\mu\text{-CO})_3(\mu_3\text{-CO})(\eta\text{-C}_6\text{H}_5\text{Me})(\eta\text{-C}_5\text{Me}_5)_2]$ ,  $[\text{Co}_2\text{Mn}(\mu\text{-CO})_3(\mu_3\text{-CO})(\eta\text{-C}_5\text{H}_4\text{Me})(\eta\text{-C}_5\text{Me}_5)_2]$ , and  $[\text{Co}_2\text{Fe}(\mu\text{-CO})_3(\mu_3\text{-CO})(\eta\text{-C}_4\text{H}_4)(\eta\text{-C}_5\text{Me}_5)_2]$ .<sup>3</sup> Examination of the  $^{13}\text{C}$  { $^1\text{H}$ } n.m.r. spectra of (1)–(3) showed<sup>†</sup> three resonances for the CO ligands, and thus site-exchange does not occur at room temperature.

Ultraviolet irradiation of a mixture (1:1) of  $[\text{Co}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$  and  $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  in toluene at  $50\text{--}60^\circ\text{C}$

afforded (20%) compound (4), the structure of which was established by an X-ray diffraction study.<sup>§</sup>

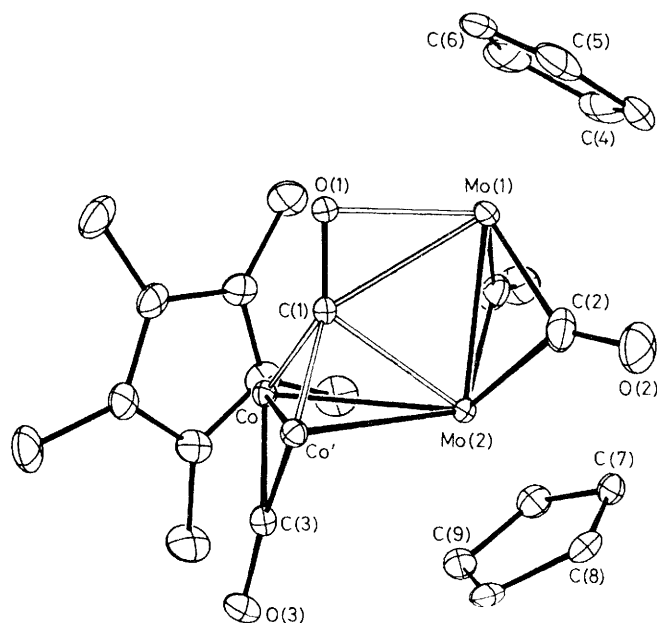
The molecule (Figure 1) lies at a site of crystallographic mirror symmetry, with the mirror plane passing through Mo(1), Mo(2), C(1), O(1), C(3), and O(3). The metal core is open, with an isosceles triangular  $\text{Co}_2\text{Mo}$  fragment attached to a



<sup>†</sup> Selected spectroscopic data, i.r. spectra measured in tetrahydrofuran,  $^1\text{H}$  n.m.r. in  $\text{C}_6\text{D}_6$ , and  $^{13}\text{C}$  { $^1\text{H}$ } n.m.r. in  $\text{CD}_2\text{Cl}_2$ . Compound (1):  $\nu_{\text{CO}}$  at  $1829\text{vs}$ ,  $1778\text{s}$ ,  $1771\text{s}$ , and  $1665\text{s cm}^{-1}$ ; n.m.r.:  $^1\text{H}$ ,  $\delta$  4.46 (s, 10 H,  $\text{C}_5\text{H}_5$ ) and 1.40 (s, 15 H,  $\text{C}_5\text{Me}_5$ );  $^{13}\text{C}$  { $^1\text{H}$ },  $\delta$  288.6 ( $1 \times \mu_3\text{-CO}$ ), 268.8 ( $1 \times \mu\text{-CO}$ ), and 258.0 p.p.m. ( $2 \times \mu\text{-CO}$ ). Compound (2):  $\nu_{\text{CO}}$  at  $1830\text{vs}$ ,  $1775\text{s}$ , and  $1660\text{s cm}^{-1}$ ; n.m.r.:  $^1\text{H}$ ,  $\delta$  4.72 (s, 10 H,  $\text{C}_5\text{H}_5$ ) and 1.22 (s, 15 H,  $\text{C}_5\text{Me}_5$ );  $^{13}\text{C}$  { $^1\text{H}$ },  $\delta$  261.8 ( $1 \times \mu_3\text{-CO}$ ), 247.7 ( $2 \times \mu\text{-CO}$ ), and 243.7 p.p.m. ( $1 \times \mu\text{-CO}$ ). Compound (3):  $\nu_{\text{CO}}$  at  $1806\text{vs}$ ,  $1757\text{s}$ ,  $1745\text{s}$ , and  $1644\text{s cm}^{-1}$ ; n.m.r.:  $^1\text{H}$ ,  $\delta$  1.51 (s, 30 H,  $\text{C}_5\text{Me}_5$ ) and 1.44 (s, 15 H);  $^{13}\text{C}$  { $^1\text{H}$ },  $\delta$  295.0 ( $1 \times \mu_3\text{-CO}$ ), 276.0 ( $1 \times \mu\text{-CO}$ ), and 262.8 p.p.m. ( $2 \times \mu\text{-CO}$ ). Compound (4):  $\nu_{\text{CO}}$  at  $1750\text{s}$ ,  $1711\text{vs}$ ,  $1696\text{vs}$ , and  $1633\text{vw cm}^{-1}$ ; n.m.r.:  $^1\text{H}$ ,  $\delta$  5.46 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 4.62 (s, 5 H,  $\text{C}_5\text{H}_5$ ), and 1.59 (s, 30 H,  $\text{C}_5\text{Me}_5$ );  $^{13}\text{C}$  { $^1\text{H}$ },  $\delta$  294.1 ( $2 \times \text{CO}$ ), 281.4 ( $1 \times \text{CO}$ ), 268.1 ( $1 \times \text{CO}$ ), 100.8 ( $\text{C}_5\text{Me}_5$ ), 95.7 ( $\text{C}_5\text{H}_5$ ), 92.5 ( $\text{C}_5\text{H}_5$ ), and 8.9 p.p.m. (Me).

<sup>‡</sup> The structure proposed for (1) has been confirmed by a single-crystal X-ray diffraction study (D. Hodgson, K. Marsden, and P. Woodward, unpublished work).

<sup>§</sup> Crystal data for (4):  $\text{C}_{34}\text{H}_{30}\text{Co}_2\text{Mo}_2\text{O}_4$ ,  $M = 822.4$ , orthorhombic, space group  $Pnma$ ,  $a = 10.548(3)$ ,  $b = 16.723(7)$ ,  $c = 17.183(6)\text{Å}$ ,  $U = 3030(2)\text{Å}^3$ ,  $Z = 4$ ,  $F(000) = 1656$  electrons,  $D_c = 1.80\text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 19.0\text{ cm}^{-1}$ , Mo-K $\alpha$  X-radiation,  $\lambda = 0.71069\text{Å}$ . The structure was solved by heavy atom (Patterson and Fourier) methods and refined in the centrosymmetric space group  $Pnma$  using blocked-cascade full-matrix least-squares. For 3875 unique absorption and extinction-corrected observed data [ $I \geq 2\sigma(I)$ ], measured at 230 K on a Nicolet P3m diffractometer, the current residual  $R$  is 0.024. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 1.** Molecular structure of  $[\text{Co}_2\text{Mo}_2(\mu\text{-CO})_3(\mu_4\text{-CO})(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$  shown with all hydrogen atoms and the  $\text{C}_5\text{Me}_5$  ring attached to  $\text{Co}'$  omitted for clarity. Important geometrical parameters:  $\text{Mo}(1)\text{-Mo}(2)$  2.574(1),  $\text{Mo}(2)\text{-Co}$  2.709(1),  $\text{Co}\text{-Co}'$  2.404(1),  $\text{Co}\text{-C}(1)$  1.869(2),  $\text{Mo}(1)\text{-C}(1)$  2.404(3),  $\text{Mo}(2)\text{-C}(1)$  2.281(3),  $\text{O}(1)\text{-Mo}(1)$ , 2.088(2),  $\text{C}(1)\text{-O}(1)$  1.283(3),  $\text{Co}\text{-C}(3)$  1.867(3),  $\text{C}(3)\text{-O}(3)$  1.187(4),  $\text{Mo}(1)\text{-C}(2)$  2.052(3),  $\text{Mo}(2)\text{-C}(2)$  2.154(3), and  $\text{C}(2)\text{-O}(2)$  1.188(3) Å;  $\angle \text{C}(1)\text{-O}(1)\text{-Mo}(1)$  87.6(1)°.

second molybdenum by a  $\text{Mo}=\text{Mo}$  double bond [2.574(1) Å nearly perpendicular to the trimetal plane [ $\text{Mo}(1)\text{-Mo}(2)$  is at 94.2° to this plane]. On simple electron counting grounds, (4) is unsaturated (62 valence electrons) even if  $\text{C}(1)\text{O}(1)$  is regarded as a six-electron donor, and the unsaturation appears to reside in  $\text{Mo}(1)\text{-Mo}(2)$ . Such a metal array models the co-ordinatively unsaturated sites to be found on 'stepped' metal surfaces<sup>4</sup> [*e.g.* at the intersection of the (111) and (001) planes in a face-centred cubic metal]. An  $\eta^2\text{-}(\mu_4\text{-CO})$  ligand is bound to the  $\text{Co}_2\text{Mo}_2$  fragment such that the  $\text{C}(1)\text{O}(1)$  vector is almost perpendicular (at 88.5°) to the  $\text{Co}_2\text{Mo}(2)$  plane. Bonding of CO to four metal atoms has been observed<sup>5</sup>

in  $[\text{Fe}_4\text{H}(\text{CO})_{13}]^-$  where one CO bridges a saturated  $\text{Fe}_4$  'butterfly' cluster which, in contrast to (4), resembles sites at the intersection of two close-packed face-centred cubic metal planes [*e.g.* (111) and  $(\bar{1}\bar{1}\bar{1})$ ]. The edgewise or  $\eta^2$  bonding of  $\text{C}(1)\text{O}(1)$  to  $\text{Mo}(1)$  in (4) is highly asymmetric. Although a localized bonding description would be overly simplistic, it is clear that the  $\text{C}(1)\text{O}(1)$  bond [1.283(3) Å] is substantially activated, being longer than the most precisely characterised four-electron  $\eta^2\text{-CO}$  ligands, *viz.*  $[\text{MoZr}(\mu\text{-}\eta^1, \eta^2\text{-CO})\{\mu\text{-OC}(\text{Me})\}(\text{CO})(\eta\text{-C}_5\text{H}_5)_3]$  [1.241(4) Å]<sup>6</sup> and  $[\text{CoZr}(\mu\text{-}\eta^1, \eta^2\text{-CO})(\mu\text{-CO})(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2]$  [1.200(9) Å],<sup>7</sup> and very similar to that observed for the six-electron donor CO ligand in  $[\text{Nb}_3\{\eta^2\text{-}(\mu_3\text{-C}, \mu_2\text{-O})\text{-CO}\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_3]$  [1.303(14) Å].<sup>8</sup> Alternative saturated geometries, *e.g.* *closo*-tetrahedral with a four-electron CO ligand may be sterically untenable owing to the bulky  $\text{C}_5\text{Me}_5$  groups. Thus  $\text{Co}(\eta\text{-C}_5\text{Me}_5)$  fragments, with cluster core angles<sup>9</sup> > 120°, may favour open cluster geometries, with unsaturation and highly activated four- or six-electron CO ligands.

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## References

- 1 R. G. Beevor, S. A. Frith, and J. L. Spencer, *J. Organomet. Chem.*, 1981, **221**, C25.
- 2 F. G. A. Stone, *Inorg. Chim. Acta*, 1981, **50**, 33; and references therein.
- 3 L. M. Cirjak, J-S. Huang, Z-H. Zhu, and L. F. Dahl, *J. Am. Chem. Soc.*, 1980, **102**, 6623.
- 4 E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91; and references therein.
- 5 M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 1976, 919.
- 6 B. Longato, J. Norton, J. C. Huffman, J. A. Marsella, and K. G. Caulton, *J. Am. Chem. Soc.*, 1981, **103**, 209.
- 7 P. T. Barger and J. E. Bercaw, *J. Organomet. Chem.*, 1980, **201**, C39.
- 8 W. A. Herrmann, H. Biersack, M. L. Ziegler, K. Weidenhammer, R. Siegel, and D. Rehder, *J. Am. Chem. Soc.*, 1981, **103**, 1692.
- 9 D. M. P. Mingos, *Inorg. Chem.*, 1982, **21**, 464.