Synthesis, Crystal Structure, and Stereochemical Characterization of $[Co_4(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu_2\text{-}CO)(\mu_3\text{-}CO)_2]$: a Completely Bonding Tetrahedral Cobalt Cluster formed from a Cobalt–Cobalt Multiple-bonded Dimer

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Summary A new type of tetrahedral metal cluster, $[Co_4(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu_2\text{-}CO)(\mu_3\text{-}CO)_2]$ (**1**), has been prepared by the reaction of neutral $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]$ (**2**) with dicobalt octacarbonyl as well as by the oxidation of the monoanion of (**2**) with toluene-*p*-sulphonic acid in the presence of $NaCo(CO)_4$; a structural analysis by *X*-ray diffraction revealed that (**1**) may be viewed, at least conceptually, as an adduct formed by the net insertion of a $Co_2(CO)_4(\mu_2\text{-}CO)$ fragment across the Co–Co double bond of (**2**).

IN the course of our investigation of the physicochemical properties of the $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]^{\cdot-}$ monoanion,[1] it was found that its oxidation in the presence of $NaCo(CO)_4$ produces the title compound (**1**). An *X*-ray diffraction analysis of this green molecular compound revealed a new type of tetrahedral metal cluster containing both doubly and triply bridging carbonyl ligands as well as terminal carbonyl and C_5Me_5 ligands. Further studies have shown that (**1**) may also be prepared from the reaction of the neutral $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]$ (**2**) and dicobalt octacarbonyl.

$[Co_4(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu_2\text{-}CO)(\mu_3\text{-}CO)_2]$

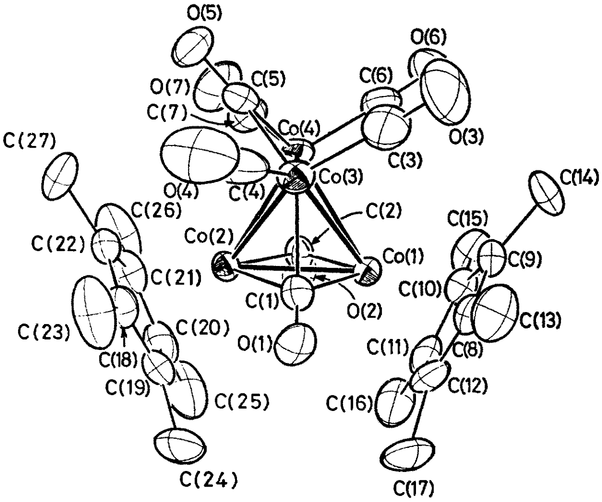
(**1**)

$[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]$

(**2**)

The preparation of (**1**) is of particular interest in that its formation may be envisaged as resulting from the net insertion of a $Co_2(CO)_4(\mu_2\text{-}CO)$ fragment across the Co–Co double bond of (**2**). Such additions of substrates across a metal–metal multiple bond are uncommon,[2–5] one example being the recently reported $[Rh_3(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu_3\text{-}CO)_2]^-$ monoanion.[2]

Complex (**1**) was first isolated from the reaction of $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ with Na sand. The mixture containing primarily $Na[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]$ and $NaCo(CO)_4$ was slowly added to toluene-*p*-sulphonic acid to give, upon extraction, an air-sensitive green product which was crystallized from hexane solution. Complex (**1**) was also produced from the reaction of (**2**) with $Co_2(CO)_8$ in hexane. I.r. spectrum (Nujol mull): ν_{CO} 2005s, 1995s, 1980s, 1970s, 1950s, 1830s,br, 1760s, 1710sh, and 1695s cm^{-1}; ^1H n.m.r. spectrum (C_6D_6) τ 8·50s; *X*-ray diffraction analysis: $Co_4C_{27}O_7H_{30}$, M = 701·7, monoclinic, $C2/c$, a = 43·186(15), b = 9·739(2), c = 20·553(7) Å, β = 102·71(3)°, U = 8433(4) $Å^3$, D_c = 1·66 g cm^{-3}, Z = 12. The crystal structure was solved by direct methods[6] and refined to $R_1(F)$ = 0·064 and $R_2(F)$ = 0·070 for 6220 diffractometry-collected reflections [$I \geqslant 2{\cdot}0\sigma(I)$].† With $C2/c$ symmetry 8 of the 12 cobalt molecules per unit cell lie on general positions; the other 4 molecules each lie on a crystallographic twofold axis which results in the doubly bridging carbonyl ligand and the four independent terminal carbonyl ligands of the $Co_2(CO)_4(\mu_2\text{-}CO)$ fragment being randomly disordered between two twofold-related orientations. All molecular parameters presented here are based upon the independent crystal-ordered C_1 molecule.



(1)

FIGURE. Molecular configuration of $[Co_4(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu_2\text{-}CO)(\mu_3\text{-}CO)_2]$ which approximately conforms to $C_s\text{–}m$ symmetry in possessing a completely bonding cobalt tetrahedron encapsulated by two face-bridged carbonyl, one edge-bridged carbonyl, four terminal carbonyl, and two terminal pentamethylcyclopentadienyl ligands.

This tetracobalt cluster (Figure) of idealized $C_s\text{–}m$ geometry may be viewed as an addition product produced by the formal insertion of a $Co_2(CO)_4(\mu_2\text{-}CO)$ fragment across the double bond of (**2**). The linkage *via* both Co–Co and Co–CO interactions gives rise to a completely bonding cobalt tetrahedron as well as the conversion of two doubly bridging carbonyl ligands of (**2**) into triply bridging ones in (**1**). Based upon its electronic equivalence to tetracobalt dodecacarbonyl[7] and the conformity of the four cobalt atoms to the EAN rule, the expected diamagnetism of (**1**) is in accordance with the observed sharp ^1H n.m.r. signal of the methyl hydrogen atoms.

One salient structural feature is that the tetrahedral cobalt core contains Co–Co bonds with a varying range of single-bond lengths which closely conform only to the $C_s\text{–}m$ molecular symmetry. The unique Co(1)–Co(2) and Co(3)–Co(4) bond lengths are 2·455(1) and 2·386(1) Å, respectively; the chemically equivalent Co(1)–Co(3) and Co(1)–Co(4) bond lengths of 2·540(1) and 2·554(1) Å, respectively, are distinctly longer than the chemically equivalent Co(2)–Co(3) and Co(2)–Co(4) bond lengths of 2·502(1) and 2·490(1) Å, respectively. The overall variation of 0·17 Å among the six Co–Co electron-pair bonds, which may be readily ascribed to the different environmental effects (steric and electronic) of the ligands, emphasizes the inherent danger in simply relating metal–metal bond lengths to assumed bond orders without adequate consideration of differences in ligand geometry. The Co(1)–Co(2) single-bond length of 2·455(1) Å in the $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_3\text{-}CO)_2$ part of (**1**) is 0·12 Å longer than the Co–Co double-bond length of 2·338(2) Å in (**2**).

Upon formal linkage of the $Co_2(CO)_4(\mu_2\text{-}CO)$ fragment with (**2**) (which *per se* possesses $C_{2v}\text{–}2mm$ symmetry), the symmetrically bridging Co–CO bonds in (**2**) of bond-length range 1·841(11)–1·860(12) Å and mean 1·851 Å become asymmetrical [under assumed $C_s\text{–}m$ symmetry in (**1**)] with the equivalent Co(1)–C(1) and Co(1)–C(2) bond lengths of 1·977(6) and 1·978(6) Å, respectively, being distinctly shorter than the Co(2)–C(1) and Co(2)–C(2) bond lengths of 2·034(6) and 2·017(6) Å, respectively. Their interconversion to triply bridging carbonyl ligands gives rise to equivalent Co(3)–C(1) and Co(4)–C(2) bond lengths of 1·942(6) and 1·938(6) Å, respectively, whose relative shortness provides convincing evidence of strong CO electron-acceptor character from the cobalt atoms of the $Co_2(CO)_4(\mu_2\text{-}CO)$ fragment. These observed molecular distortions of the $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_3\text{-}CO)_2$ part of (**1**) from $C_{2v}\text{–}2mm$ symmetry to approximate $C_s\text{–}m$ symmetry are due to the particular arrangement of the carbonyl ligands of the attached $Co_2(CO)_4(\mu_2\text{-}CO)$ fragment which ideally conforms to only mirror plane symmetry.

In order to analyse the possible fluxional character of these carbonyl ligands of (**1**) in solution, temperature dependent ^{13}C n.m.r. studies are in progress. The work presented here indicates that both (**2**) and its monoanion may be useful reagents in the synthesis of new metal cluster systems, and efforts currently underway to prepare

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† The atomic co-ordinates for this work are available on request from the Director of 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.

mixed metal clusters have resulted in the photolytic preparation of $[FeCo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6]$,[8] an electronically equivalent analogue of $[Fe_3(CO)_{10}(\mu_2\text{-}CO)_2]$.

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