Pentamethylcyclopentadienyl Cobalt Carbonyl Dimers containing Multiple Metal–Metal Bond Character: Preparation, Structural Analysis (Including *X*-Ray Crystallographic Determinations), and Bonding Implications of $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]^n$ ($n = -1$ or 0)

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Summary Syntheses and structural characterizations (including *X*-ray crystallographic determinations) of $[Na(2,2,2\text{-crypt})]^+[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]^{\dot{-}}$ [where (2,2,2-crypt) = $N(C_2H_4OC_2H_4OC_2H_4)_3N$] and $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$ have resulted in (at least) a partial resolution of the contradiction between previously available structural data and theory in correlating metal–metal bond-length differences and bond orders (B.O.) for structurally analogous nitrosyl- and carbonyl-bridged cyclopentadienyl metal dimers; a distinct contraction of 0·034 Å in the Co–Co bond length is observed upon going from the paramagnetic $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]^{\dot{-}}$ monoanion [2·372(1) Å; B.O. = 1·5] to its oxidized neutral dimer [2·338(2) Å; B.O. = 2·0], which is consistent with the presumed removal of the unpaired electron from an M.O. primarily composed of out-of-plane antibonding $d\pi^*$ dimetal character.

The first example of a cyclopentadienyl cobalt carbonyl anion was the $[Co_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}CO)_2]^{\dot{-}}$ radical anion (**1**) which was synthesized and structurally characterized as its $[(Ph_3P)_2N]^+$ salt (**1a**)[1] and independently as its $[Ph_4As]^+$ salt (**1b**).[2] This dimeric monoanion (**1**) is of particular interest not only in terms of its possible chemical utility [*e.g.*, it reacts with MeI to produce $Co_2(\eta^5\text{-}C_5H_5)_2Me_2(\mu_2\text{-}CO)_2$

$[X]^+[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)_2Co(C_5H_5\text{-}\eta^5)]^{\dot{-}}$

(**1**)

a; X = $(Ph_3P)_2N$
b; X = Ph_4As

$[Na(2,2,2\text{-crypt})]^+[(\eta^5\text{-}C_5Me_5)Co(\mu\text{-}CO)_2Co(C_5Me_5\text{-}\eta^5)]$

(**2**)

2,2,2-crypt = $N(C_2H_4OC_2H_4OC_2H_4)_3N$

$[(\eta^5\text{-}C_5Me_5)Co(\mu\text{-}CO)_2Co(C_5Me_5\text{-}\eta^5)]$

(**3**)

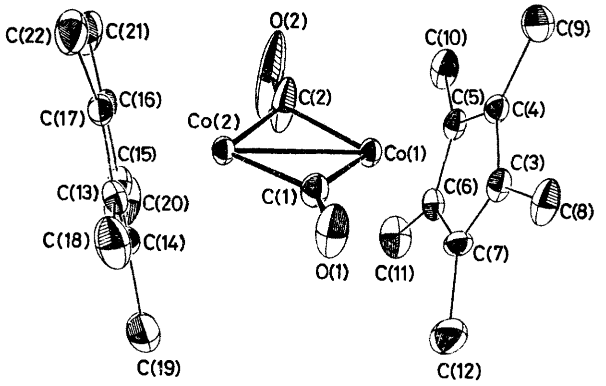
which thermally decomposes to acetone in 85% yield[3]] but also from a theoretical viewpoint in that from electronic considerations it may be considered to possess a multiple metal–metal bond order (B.O.) of 1·5. Our attempts to obtain crystals of its oxidized neutral dimer[1,4] for a structural analysis were not successful. On the basis of other work, we believed that replacement of the C_5H_5 ligands of (**1**) with C_5Me_5 would significantly change its redox and solubility properties so as to allow the isolation and characterization of the dimeric monoanion and its oxidized neutral analogue. We have now prepared the complexes (**2**) and (**3**), and the new tetrameric cluster $[Co_4(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu_2\text{-}CO)(\mu_3\text{-}CO)_2]$.[5] Here we report the syntheses, structures, and properties of (**2**) and (**3**).

The pentamethylcyclopentadienyl monoanion of (**2**) was prepared by the reduction of $[Co(\eta^5\text{-}C_5Me_5)(CO)_2]$ with sodium in tetrahydrofuran (THF). The red solid isolated from the decanted liquid was washed with 7:1 Et_2O–hexane to remove the $NaCo(CO)_4$ by-product. Crystals of (**2**) were obtained by solvent diffusion with hexane over a glyme solution, to which 2,2,2-crypt had been added, of the foregoing red sodium salt; spectral data: i.r.: ν_{CO}(THF), 1670s; ν_{CO} (Nujol mull), 1715w and 1655s cm^{-1}; e.s.r.(THF): 15-line dicobalt hyperfine pattern centred at 3200 G, A_{iso} = 45 G, and g_{iso} = 2·10.

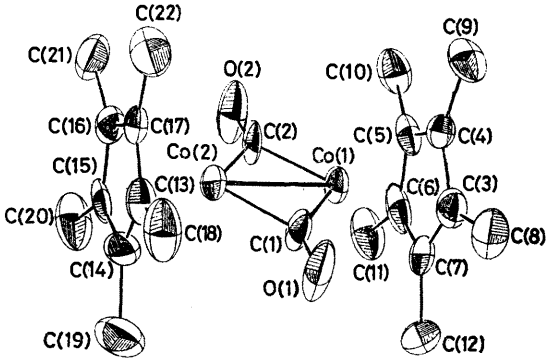
Slow oxidation of the red sodium salt by anhydrous $FeCl_3$ in THF produced the green neutral dimer (**3**), which was recrystallized by slow evaporation from hexane: i.r.: ν_{CO}(hexane), 1760s; ν_{CO}(Nujol mull): 1750s, br cm^{-1}; ^1H n.m.r. (C_6D_6): τ8·60s; mass spectra (70 eV; inlet temp., 150 °C): M^+ *m/e* 444(34·3%). Complex (**3**) was also found to be a minor product in the synthesis of $[Co(\eta^5\text{-}C_5Me_5)(CO)_2]$ by the reaction of $Co_2(CO)_8$ with C_5Me_5H in refluxing CH_2Cl_2.

Crystal data: (**2**), $C_{40}H_{66}Co_2N_2NaO_8$, M = 843, monoclinic, $P2_1/a$, a = 17·364(8), b = 17·948(4), c = 13·903(3) Å, β = 90·82(3)°, U = 4332(2) $Å^3$, D_c = 1·29 g cm^{-3}, Z = 4. For 4033 diffractometry-collected reflections $[I \geqslant 2{\cdot}0\sigma(I)]$, $R_1(F)$ = 0·060 and $R_2(F)$ = 0·069.† (**3**), $C_{22}H_{30}Co_2O_2$, M = 443·8, monoclinic, $P2_1/c$, a = 9·693(5), b = 14·722(7), c = 14·912(6) Å, β = 101·86(4)°, U = 2083(2) $Å^3$, D_c = 1·42 g cm^{-3}, Z = 4. For 1720 independent reflections $[I \geqslant 2{\cdot}0\sigma(I)]$, $R_1(F)$ = 0·072 and $R_2(F)$ = 0·078.†

The configuration of the pentamethylcyclopentadienyl monoanion of (**2**) shown in the Figure is considerably different from the centrosymmetric C_{2h}–$2/m$ geometry of the corresponding cyclopentadienyl monoanion (**1**) [of crystallographic C_i–$\bar{1}$ site symmetry in both (**1a**) and (**1b**)] which has a planar D_{2h} $Co_2(CO)_2$ core with perpendicular C_5H_5 ligands. Firstly, the $Co_2(CO)_2$ core in (**2**) is nonplanar as shown by torsion angles of 168·0° between the two fused CoC_2 planes and of 169·6° between the two fused CCo_2 planes. Secondly, the C_5Me_5 ligands are inclined with an angle of 153·5° between the ring normals. Thirdly, one of the two bridging carbonyl ligands exhibits extremely large out-of-plane thermal ellipsoids indicative of an averaged structure in which this one bridging carbonyl ligand occupies at least two bent orientations in the crystalline state.



Monoanion of (2)



(3)

FIGURE. Configurations of the $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]^{\overline{\cdot}}$ monoanion of (**2**) and its oxidized neutral dimer (**3**). The considerable geometrical differences between (**2**) and (**3**) include the distinctly non-perpendicular *vs.* essentially perpendicular dispositions, respectively, of the two C_5Me_5 rings relative to their $Co_2(CO)_2$ cores. The unusually elongated out-of-plane thermal ellipsoids of C(2) and O(2) in (**2**) relative to those of the other bridging atoms in either (**2**) or (**3**) have been interpreted in terms of a disorder-averaged structure of this one carbonyl ligand. Interatomic distances (in Å) with e.s.d.'s in parentheses are given for each $Co_2(CO)_2$ core: for the monoanion of (**2**): Co(1)–Co(2) 2·372(1); Co(1)–C(1) 1·820(6); Co(2)–C(1) 1·834(6); Co(1)–C(2) 1·800(7); Co(2)–C(2) 1·792(7); C(1)–O(1) 1·204(6); and C(2)–O(2) 1·204(8); for structure (**3**): Co(1)–Co(2) 2·338(2); Co(1)–C(1) 1·860(12); Co(2)–C(1) 1·856(12); Co(1)–C(2) 1·841(11); Co(2)–C(2) 1·847(12); C(1)–O(1) 1·190(13); and C(2)–O(2) 1·188(13).

In contrast, the configuration of the neutral pentamethylcyclopentadienyl dimer (**3**) depicted in the Figure closely conforms to an ideal C_{2v}–*2mm* geometry with the C_5Me_5 ligands being eclipsed and bisected by one of the two pseudo vertical mirror planes which are perpendicular to the mean $Co_2(CO)_2$ plane. The eclipsed (rather than the normally staggered) C_5Me_5 rings together with the observed small but significant puckering of the $Co_2(CO)_2$ core (corresponding to the above-mentioned torsional angles of 176·3 and 175·4°, respectively) may be attributed to a minimization of steric interactions between the C_5Me_5 rings and the bridging carbonyl ligands.

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† 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.

The presence in the solid-state i.r. spectra of two bridging carbonyl frequencies for (**2**) and only one frequency for (**3**) is in accordance with their different crystalline configurations, while the one solution i.r. band for both (**2**) and (**3**) is in harmony with an essentially planar centrosymmetric $Co_2(CO)_2$ core, which in the absence of crystal packing forces is stabilized by the multiple Co–Co bonding. The 15-line e.s.r. spectra of (**3**) in THF, glyme, acetone, and acetonitrile are analogous to those previously found[1,2] for (**1**) and are characteristic of a hyperfine interaction of the unpaired electron with both ^{59}Co nuclei (100% abundance, $I = 7/2$).

The salient structural feature emerging from this comparative study is that the observed 0·034 Å decrease between the Co–Co bond length of 2·372(1) Å in the monoanion (**3**) (with assumed B.O. of 1·5) and that of 2·338(2) Å in its oxidized neutral dimer (**4**) (with assumed B.O. of 2·0) provides direct experimental support for the multiple metal–metal bond-order model[1,6] over the previously untested bond-order range of 1·5—2·0 for the same metal atoms. The near constancy in the metal–metal bond lengths determined from prior *X*-ray studies by Bernal *et al.*[7] of $[Co_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}NO)_2]$ [2·372(1) Å, B.O. = 1·0] and the paramagnetic $[Co_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}NO)(\mu_2\text{-}CO)]$ [2·370(1) Å, B.O. = 1·5], which are both isomorphic and isostructural in the crystalline state with $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}NO)_2]$ [2·326(4) Å, B.O. = 2·0],[8] had led to the conclusion[7] that 'the successive increase in bond order predicted by the EAN rule is not observed.' Despite this insensitivity of Co–Co bond lengths to an alteration of B.O. from 1·0 to 1·5, the (bond length)–(bond order) correlation predicted by theory[6] is observed in the two directly related dimers (**2**) and (**3**) for a change of B.O. from 1·5 to 2·0. It is apparent that the analogously short M–M distances in this series of dimers are mainly influenced by the particular electronic and steric constraints of the carbonyl- and nitrosyl-bridged ligands (*i.e.*, the direct M–M interactions are much weaker), which thereby effectively resist a further shortening in the M–M distance upon an increase in metal–metal B.O. > 1·0.

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