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Stabilization of Carbonyl Clusters by a Carbide Atom. Synthesis and Characterization of $[Co_8(CO)_{18}C]^{2-}$ and of Paramagnetic $[Co_6(CO)_{14}C]^-$ Anions

Sir:

The synthesis of the dianion $[Co_6(CO)_{15}C]^{2-}$, which is isostructural with the trigonal prismatic $[Rh_6(CO)_{15}C]^{2-}$, has previously been reported.[1] We now wish to report the ^{13}C NMR spectra of $[Co_6(CO)_{15}C]^{2-}$, and to report on its transformation into the new anions $[Co_6(CO)_{14}C]^-$ and $[Co_8(CO)_{18}C]^{2-}$.

Samples of $[Co_6(CO)_{15}C]^{2-}$ (ca. 30% ^{13}CO) have been prepared both starting from equally enriched $Co_3(^{13}CO)_9CCl$ and $Na[Co(^{13}CO)_4]$ and also from $Co_3(CO)_9CCl$ and $Na[Co(^{13}CO)_4]$. In both cases the ^{13}C NMR spectra at −70° in perdeuterioacetone are very similar and consist of three signals of relative intensities 3:6:1.4 assigned to edge-bridging (δ 252 and 234.9 ppm; $\omega_{1/2}$ 76 Hz) and terminal carbonyls (δ 224.9 ppm; $\omega_{1/2}$ 13 Hz), respectively. In agreement with the similarity in the solution ir spectra of the two dianions,[1,2] this pattern is similar to that previously found for $[Rh_6(CO)_{15}C]^{2-}$.[3] The considerable deviation from the expected intensities (3:6:6) is probably related to the anomalous relative intensities found in $Co_4(CO)_{12}$,[4] and confirms that intensities in the ^{13}C NMR spectra of cobalt compounds should be interpreted with care.

The ^{13}C NMR spectrum of $[Co_6(CO)_{15}{}^{13}C]^{2-}$ (ca. 90% $^{13}C_{carbide}$)[5] in perdeuterioacetone at −70° is similar to those reported above except for the presence of the carbide resonance at 330.5 ppm ($\omega_{1/2}$ 43 Hz), thus proving the source of the carbide atom ($^{13}CCl_4$) and showing a considerable shift to lower field in comparison with the corresponding rhodium analogue (δ 266.7 ppm).[3]

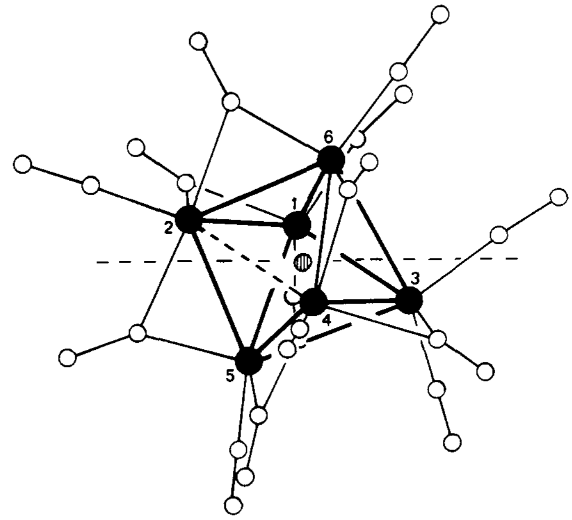

Figure 1. Structure of the $[Co_6(CO)_{14}C]^-$ anion. The idealized twofold axis is shown. The cobalt-cobalt distances have the following values (Å): 2-4, 2.96 (1); 1-2, 2-5, 2-6, 3-4, 4-5, and 4-6, 2.53 (mean); 1-3, 1-5, 1-6, 3-5, and 3-6, 2.75 (mean).

Solutions of the Na^+ or $[NMe_3(CH_2Ph)]^+$ salts of $[Co_6(CO)_{15}C]^{2-}$ in THF react with carbon monoxide (1 atm, 25°)[6] to give a mixture of compounds containing the anion $[Co(CO)_4]^-$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, some $Co_3(CO)_9CX$ derivatives (X not yet identified), and the new dark brown paramagnetic anion $[Co_6(CO)_{14}C]^-$. More conveniently this new anion has been isolated (10–20% yield) in a pure form as the Na^+, $[NMe_4]^+$, and $[NEt_4]^+$ salts by reaction of $Co_3(CO)_9CCl$ with 2 mol of $Na[Co(CO)_4]$ in diethyl ether; the ir spectrum (THF) shows carbonyl stretching absorptions due to both terminal (2070 vw, 2020 vs, and 1990 sh cm^{-1}) and bridging (1857 s cm^{-1}) groups. The ESR spectrum (THF) shows a strong signal at $g = 2.0128$ and the paramagnetism has been confirmed using Evans' method[7] ($\mu_{eff} \simeq 1.37\ \mu_B$).

Since there are no previous reports of stable hexanuclear paramagnetic carbonyls, we have carried out an x-ray structural determination.[8] The structure is shown in Figure 1 and provides further evidence for the presence of an unpaired electron in excess to the usual 86 found in hexanuclear carbonyl clusters of octahedral structure.[9] The metal atom cluster is a distorted octahedron of idealized molecular symmetry C_{2v}. The 12 cobalt-cobalt interactions can be divided into three sets: one stretched edge 2.96 (1) Å, six carbonyl-bridged edges of mean length 2.53 Å, and five edges of intermediate lengths (mean 2.75 Å). The Co–C carbide distances are in the range 1.84–1.94 (2) Å, with mean value of 1.88 Å.

The reaction of the dianion $[Co_6(CO)_{15}C]^{2-}$ with $Co_4(CO)_{12}$ provides a further example of a redox condensation reaction:[9]

$$2[Co_6(CO)_{15}C]^{2-} + Co_4(CO)_{12} \xrightarrow[i\text{-}Pr_2O]{60^\circ} 2[Co_8(CO)_{18}C]^{2-} + 6CO$$

The diamagnetic octanuclear dianion has been isolated (~80% yield) as pure Na^+ and $[NMe_3(CH_2Ph)]^+$ salts; the ir spectrum (THF) shows carbonyl stretching absorptions at 2055 vw, 1990 vs, 1950 w, and 1810 m cm^{-1}.

The structure[10] of the dianion $[Co_8(CO)_{18}C]^{2-}$ is shown in Figure 2. The metal atom polyhedron can be described as a tetragonal antiprism elongated along one of the two-fold symmetry axes, resulting in the idealized symmetry D_2. The Co–Co distances are in the range 2.47–2.59 (1) Å with mean value of 2.52 Å; there are no significant differences between the basal and the interbasal distances. The carbide atom is in the center of the cluster but, due to the previously mentioned

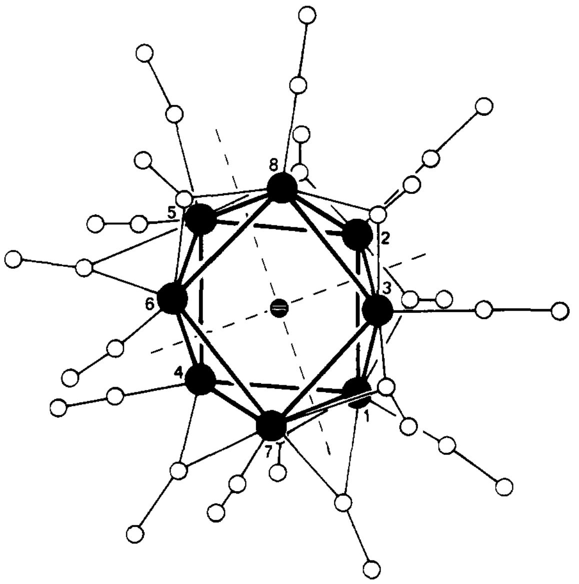

Figure 2. Structure of the $[Co_8(CO)_{18}C]^{2-}$ dianion. The twofold axes apply only to the metal atoms cluster and are indicated by dotted lines: one bisects Co_5–Co_8 and Co_1–Co_7, the other Co_2–Co_3 and Co_4–Co_6. The third axis is normal to the paper.

distortion, it is not equidistant from the cobalt atoms, the Co–C carbide distances being in the range 1.95–2.20 (2) Å with a mean value of 2.07 Å. The deformation of the antiprism and the long Co–$C_{carbide}$ distances probably represent a compromise situation in which bonding of the carbide atom is still possible in the large cavity of this polyhedron. The carbonyl groups can be divided into two sets of nine terminal and nine edge-bridging, although some of the bridging groups are markedly asymmetric. It is worth noting that the isoelectronic $Rh_8(CO)_{19}C$ has a different structure in which a trigonal prism of rhodium atoms has been capped both along a square face and along one of the triangular edges.[1]

The series of anions $[Co_6(CO)_{15}C]^{2-}$, $[Co_6(CO)_{14}C]^-$, and $[Co_8(CO)_{18}C]^{2-}$ provides a further example of the unusual stability of carbide carbonyl clusters,[1] which we attribute to the presence of additional bonds with the central carbon atom.

Further details of this and other studies of cobalt and rhodium[11] carbonyl carbide clusters will be reported later.

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(10) The salt $[NMe_3CH_2Ph]_2[Co_6(CO)_{18}C]$ crystallizes in the $P\bar{1}$ space group with cell constants a = 19.02 (2) Å, b = 10.37 (1) Å, c = 12.81 (1) Å, α = 116.43 (9)°, β = 88.90 (9)°, γ = 95.53 (9)°, and Z = 2. The structure has been solved using 3560 diffraction intensities collected by counter methods. The refinement is in progress, the present conventional value of R being 8.9%.
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Chromium(II) Porphyrins and an Irreversible Dioxygen Complex

Sir:

We have recently been interested in the discovery of clean, high yield synthetic routes to low valent metalloporphyrins and more particularly in the generation of coordinatively unsaturated metalloporphyrins which are precursors to dioxygen complexes. The reaction of $Cr(acac)_2$[1] with $M^{III}Cl$(porphyrin) complexes, presumably occurring via a bridged chlorine transfer redox mechanism,[2] has proved to be a key step en route to dioxygen complexes derived from Fe(II)[3] and Mn(II)[4] species. We now report that this and another method can be exploited to reduce Cr(III) porphyrins and present evidence that distinguishes the Cr(II) d^4 formulation of the reduced products from the possible alternative, namely, a Cr(III) radical anion derived from porphyrin ring reduction. We also report the first example of a dioxygen complex derived from Cr(II).

Under scrupulously oxygen-free conditions, green CrCl(TPP)[5] is reduced by $Cr(acac)_2$ in toluene or THF to give red-brown solutions from which purple crystals of Cr(TPP) can be isolated.[7] Magnetic susceptibility measurements (Faraday method at 25 °C under an argon atmosphere) on these crystals and on the related Cr(OEP) are consistent with a high-spin d^4 configuration ($\mu_{eff}{}^{corr}$ = 4.8 μ_B). The $M^{III/II}$ reduction potential for Cr is expected to be considerably more negative[8] than those of Co, Fe, and Mn raising the possibility of porphyrin ring reduction in preference to metal reduction. One criterion for distinguishing between metal and ligand redox reactions in metalloporphyrins, which apparently has wide generality,[9] is that the numerical difference between the half-wave potential of the first ligand oxidation in nitrile solvents and the first ligand reduction in Me_2SO, $\Delta E_{1/2}{}^{ox/red}$, is 2.25 ± 0.15 V. As with Cr(OH)(OEP),[10] cyclic voltammetry at Pt on CrCl(TPP) in benzonitrile and in Me_2SO (Figure 1) reveals six half-wave potentials relative to SCE. We have assigned these potentials as follows: +1.15 and −1.23 V to the first ligand oxidation and reduction, respectively; −0.86 V to $Cr^{III/II}$; +0.95 V tentatively to $Cr^{III/IV}$; +1.41 V to the second ligand oxidation; and −1.70 V to the second ligand reduction. We note that $\Delta E_{1/2}{}^{ox/red}$ is 2.38 V, and moreover, the differences between the first and second ligand reductions (0.47 V) and the first and second ligand oxidations (0.26 V) both lie in the normal ranges, 0.49 ± 0.08 and 0.29 ± 0.05 V, respectively.[11,12] Exhaustive coulometry at −1.0 V consumed one