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Isolation of the All-Bridging CO Isomer of $Cp_3Co_3(CO)_3$ and Observations Concerning a Highly Deformable Small Metal Cluster

Matthew P. Robben and William E. Geiger*

Department of Chemistry, University of Vermont, Burlington, Vermont 05405

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

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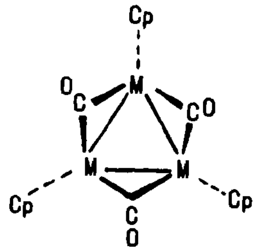
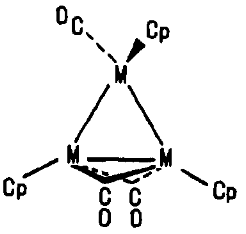
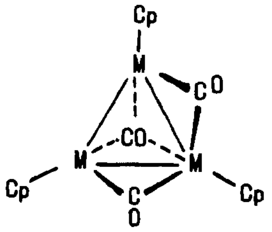
Metal clusters of the cobalt group with the formula $Cp_3M_3(CO)_3$, Cp = η^5-cyclopentadienyl, display an intriguing structural diversity. Four types of isomers (structures **A**−**D**) have been previously reported.[1−6] Characterization of the tricobalt system has been particularly challenging. Indeed, questions about the solution structure(s) of $Cp_3Co_3(CO)_3$ are reminiscent of the classic $Co_2(CO)_8$ problem,[7] and this cluster has been called an "exceptionally deformable molecule".[4] Early controversies[1,2] involving the cluster were partially resolved when isomer **C**, featuring a triply-bridging CO, was identified by crystallography as the favored isomer in the solid state.[4,8] The existence of the all-bridging isomer **A** has been the subject of considerable speculation,[1−3] but detailed studies[8] failed to identify it in either solid state or solution. This is surprising, since the all-bridging CO isomer is known for the analogous Rh system,[9] and since bridging structures are usually preferred for first row metals compared to the heavier congeners.[10] We now report the isolation of isomer **A** and its characterization by physical methods, including X-ray crystallography. We also shed light on the behavior of isomer **C** in solution, showing that, contrary to previous claims,[4,8] the apparent equilibrium between isomers **C** and **B** does not appear to be significantly dependent on solvent polarity.



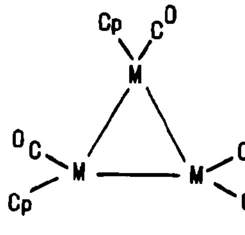
A, M=Rh



B, M=Rh,Co



C, M=Co



D, M=Ir

The preparation of the cluster was carried out by photolysis of 2 g of $CpCo(CO)_2$ in toluene,[11] consistent with earlier methods.[1−4] The reaction residue, eluted with 1:1 pentane/CH_2Cl_2 on alumina, gave (sequentially) red-brown $CpCo(CO)_2$, green $Cp_2Co_2(\mu\text{-}CO)_2$,[12] and 630 of mg of $Cp_3Co_3(\mu_2\text{-}CO)_2(\mu_3\text{-}CO)$ (isomer **C**), in accordance with earlier workers. An additional pair of brown bands eluted with CH_2Cl_2. The first of these afforded 50 mg of the new cluster $Cp_3Co_3(\mu_2\text{-}CO)_3$, isomer **A**, which was characterized by mass spectrometry (EI, m/z = 456, M^+), IR (ν_{CO} = 1839, 1784 cm^{-1}), NMR (^1H, $CDCl_3$, δ = 5.05) and elemental analysis (C, 47.35, calc 47.40; H, 3.08, calc 3.32). X-ray-quality crystals grown by slow evaporation of CH_2Cl_2 solutions of the complex at 273 K showed the expected all-bridging arrangement of the three carbonyl groups (Figures 1 and 2).[13]

The title compound possesses near-C_{3v} symmetry, with three Co atoms forming an isosceles triangle, one metal−metal bond being 1.2 pm shorter than the other two. Like the trirhodium analogue,[9] all three Cp ligands are displaced to one side of the Co_3 plane (average elevation 32.6°), with the three carbonyls displaced to the other side (average tilt 55.4°). The metal core is slightly smaller than that of isomer **C**, with an average Co−Co distance of 240.4 pm compared to 247.3 pm for **C**.

The present result brings to 3 the number of isomers identified with $Cp_3Co_3(CO)_3$, all differing in the arrangement of the CO

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(11) Photolysis under N_2 for 96 h, followed by solvent removal and extraction with CH_2Cl_2, gave a dark brown residue after evaporation of CH_2Cl_2. All operations were conducted under N_2, although C_{3v}-$Cp_3Co_3(CO)_3$ appears to be reasonably air-stable as a solid.

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(13) Crystal data for $Cp_3Co_3(CO)_3$: $C_{18}H_{15}Co_3O_3$, orthorhombic, $Pmn2_1$, a = 13.656(3) Å, b = 8.941(2) Å, c = 6.742(1) Å, V = 821.0(5) Å^3, Z = 2, D_x=1.845 g cm^{-3}, μ(Mo Kα) = 30.07 cm^{-1}, T = 238 K. Of 2590 reflections collected in two octants (Siemens P4, $2\Theta_{max}$ = 60°), 1345 were used to solve and refine the structure. The noncentrosymmetric space group choice was supported by E statistics, the value of Z, and the chemically and computationally well-behaved results of refinement. A Rogers test supports the reported enantiomorph [η = 1.7(4)]. With all non-hydrogen atoms anisotropic and hydrogen atoms idealized, $R(F)$ = 5.29% and $R(wF)$ = 6.14%.

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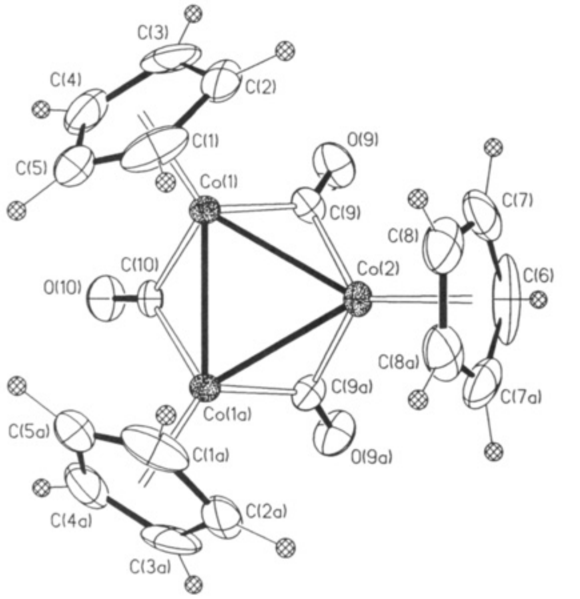

Figure 1. Molecular structure of $Cp_3Co_3(\mu_2\text{-}CO)_3$ with 40% thermal ellipsoids. Co(1)−Co(2) = 2.408(1), Co(1)−Co(1a) = 2.396(1), CNT−Co(1) = 1.740(9), CNT−Co(2) = 1.750(9) Å.

groups on the metal framework (besides the crystallographically characterized[4] **C**, isomer **B**, with one terminal and two doubly-bridging CO's, also seems firmly established[4,8]). Of the various structural types known for $Cp_3M_3(CO)_3$ complexes, only the all-terminal isomer **D** has not been identified for M = Co. Given the strong preference for bridging CO's in the first-row metals, **D** is unlikely to be isolable for $Cp_3Co_3(CO)_3$.

In the process of these studies we discovered that the composition of dissolved samples of **C** was not completely in accord with previous reports. Dissolving pure **C** in mildly polar solvents such as CH_2Cl_2 or THF produces a mixture of **C** and **B**, as previously reported,[4,8] characterized by five IR bands in the CO stretching region [ν_{CO} (cm^{-1}) = 1960, 1840, 1810, 1750, 1710]. A very similar pattern is observed for solutions in nonpolar solvents such as benzene. Although we cannot rule out the possibility that the **B/C** equilibrium has a minor solvent dependence, we see no evidence that, as earlier stated,[8] **B** is the exclusive isomer in benzene. We note that quantitative measurement of isomer **B** in benzene is inherently difficult owing to spectral interferences arising from rather intense benzene absorptions at 1960 and 1810 cm^{-1}.

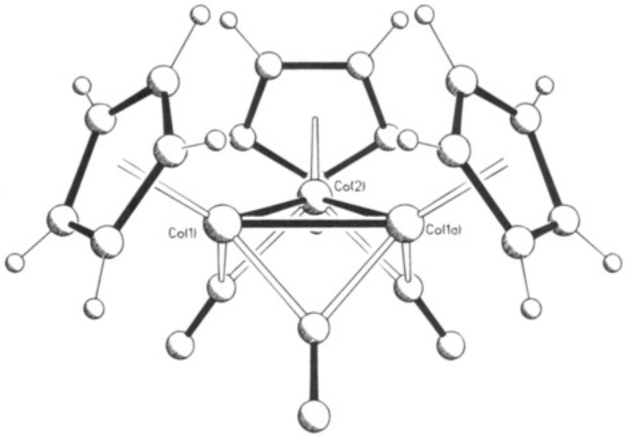

Figure 2. View of $Cp_3Co_3(\mu_2\text{-}CO)_3$ showing the elevation of the Cp rings (average 32.6°) and the CO groups (average 55.5°) with respect to the Co_3 plane.

The redox properties of the new isomer **A** are distinctly different than those of the **B/C** mixture. Whereas the latter is subject to rapid fragmentation upon one-electron reduction,[14] the former undergoes *two* reversible one-electron reductions ($E°$ = −1.34 V, −2.41 V vs ferrocene$^{0/+}$), showing that the all-bridging CO arrangement significantly stabilizes the lower cluster oxidation states. We will report on the electron-transfer-induced isomerizations of the systems **A**, **B**, and **C** in a subsequent paper.

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Supplementary Material Available: Tables giving crystal structure determination details, atomic coordinates, bond lengths, bond angles, and thermal parameters and figures showing a unit cell packing diagram and IR spectra of $Cp_3Co_3(CO)_3$ (isomers **B/C**) in CH_2Cl_2 and benzene (10 pages). For ordering information see any current masthead page.

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