Preparation of $[Co_3(CO)_{10}]^-$, a New Cobalt–Carbonyl Cluster Anion

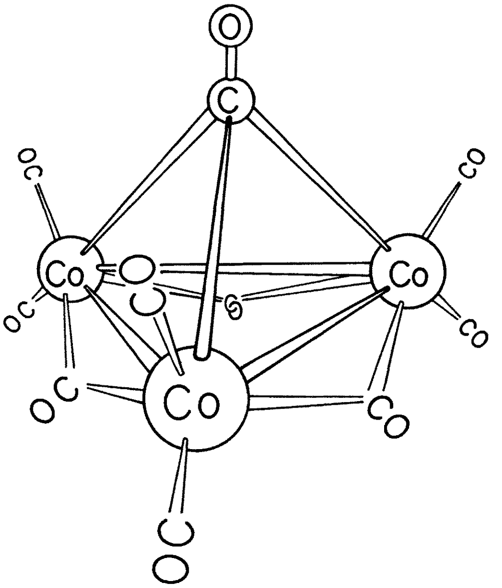
By S. A. FIELDHOUSE, B. H. FREELAND, C. D. M. MANN, and R. J. O'BRIEN*
(*Lash Miller Chemical Laboratories, University of Toronto, Toronto* **181**, *Ontario, Canada*)

Summary The reaction of alkali metals with octacarbonyl dicobalt, in diethyl ether, yields the decacarbonyltricobaltate mono-anion.

THE reduction of cobalt carbonyl complexes is well documented. Octacarbonyl dicobalt is reduced to tetracarbonylcobaltate (−1) by sodium amalgam in diethyl ether[1] or by lithium metal in tetrahydrofuran.[2] In addition, the reduction of dodecacarbonyl tetracobalt by alkali metals in tetrahydrofuran has recently been shown[3] to yield successively the pentadecacarbonylhexacobaltate di-anion $[Co_6(CO)_{15}]^{2-}$ and the tetradecacarbonylhexacobaltate tetra-anion $[Co_6(CO)_{14}]^{4-}$. We report that the reaction of octacarbonyl dicobalt with alkali metals, in diethyl ether, yields the decacarbonyltricobaltate mono-anion.

When a solution of octacarbonyl dicobalt, in diethyl ether, is treated with alkali metals (Li, Na, and K), gas evolution is observed and the solution gradually becomes deep red. The red crystals deposited from the cooled solution turn black upon removal of the solvent, and redissolve in diethyl ether to regenerate a red solution. Analysis of the solid lithium derivative indicates that it has the composition $LiCo_3(CO)_{10}$† and the lithium, sodium, and potassium derivatives have similar i.r. spectra in both solution and the solid state. The i.r. spectra show three distinct types of carbonyl bands in the regions 2080—2000, 1850, and 1600 cm^{-1}. We assign these to terminal, doubly bridging, and triply bridging carbonyl groups respectively, and accordingly suggest the structure shown in the Figure for the $[Co_3(CO)_{10}]^-$ ion. At this stage, however, we cannot rule out the possibility that $[Co_3(CO)_{10}]^-$ also exists in an isomeric form without doubly bridging carbonyl groups.

These results indicate that the reduction of octacarbonyl dicobalt is not as simple a process as earlier work[1,2] would indicate.



FIGURE

Financial support by the National Research Council of Canada is gratefully acknowledged. S.A.F., B.H.F., and C.D.M.M. thank the Government of the Province of

---

† The $Co_3(CO)_{10}$ formulation has been further demonstrated by the preparation of a number of covalent derivatives which will be reported shortly.

Ontario for the award of Province of Ontario Graduate Fellowships. S.A.F. also thanks the University of Manchester, Institute of Science and Technology for the award of the Lionel Blundell Overseas Fellowship.

(*Received, December 4th*, 1969; *Com.* 1846.)

[1] W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, 1958, **7**, 192.
[2] W. R. McClellan, *J. Amer. Chem. Soc.*, 1961, **83**, 1598.
[3] P. Chini, V. Albano, and S. Martinengo, *J. Organometallic Chem.*, 1969, **16**, 471.