

Synthesis and Characterization of the Cluster Acid $\text{Co}_3(\text{CO})_9\text{C}-\text{OH}$: a Metal Carbonyl Complex in which a Carbonyl Oxygen-bonded Hydrogen is Converted into a Metal-bonded Hydrogen

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Summary The acid $\text{Co}_3(\text{CO})_9\text{C}-\text{OH}$ was prepared and characterized, and its quantitative conversion into $\text{HCo}(\text{CO})_4$ and $\text{Co}_4(\text{CO})_{12}$ was established spectroscopically.

In the preceding communication¹ the formation of $\text{Li}[\text{Co}_3(\text{CO})_{10}]$ by two reactions was reported. When considering the metal species only, reactions (1) and (2)[†] may be regarded as 'redox condensations.'² On the other hand, owing to the formation of a new Co-C(apical) bond, these reactions may also be regarded as oxidation-reductions involving one of the carbonyl groups. In view of the current interest in the reduction of CO by molecular

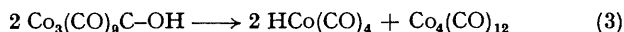
hydrogen,³ the synthesis of the still unknown⁴ $\text{Co}_3(\text{CO})_9\text{C}-\text{OH}$ was investigated.

By operating under a strictly controlled Ar atmosphere, addition of excess of dry HCl to a stirred suspension of $\text{Li}[\text{Co}_3(\text{CO})_{10}]\cdot\text{Et}_2\text{O}^\dagger$ (0.15 g) in n-hexane (30 ml) at -20°C resulted in the formation of a dark red solution whose i.r. spectrum showed $\tilde{\nu}_{\text{CO}}$ bands at 2090m-w, 2040vs, 2025s, 2000m, and 1995wsh cm^{-1} , comparable with the absorptions for $\text{Co}_3(\text{CO})_9\text{C}-\text{OMe}$ reported⁵ at 2108m, 2065vs, 2040s, 2020w, and 1985w cm^{-1} (CCl_4). Evaporation at ca. -20°C of a concentrated hexane solution of the compound, followed by dissolution of the solid residue in $\text{C}_6\text{D}_6\text{CD}_3$, gave

[†] For reactions (1) and (2), see preceding communication.

a ca. 10% solution, whose ^1H n.m.r. spectrum at -35°C showed a sharp resonance at $+11.25$ p.p.m. downfield from Me_4Si attributed to the O -bonded proton. The solutions of the acid are air-, moisture-, and temperature-sensitive. The solid compound, isolated as red crystals by a sequence of low-temperature operations, rapidly decomposed at room temperature. The thermal decomposition of the hexane solution of the product was used for its further characterization. After 70 min at ca. 40°C quantitative final conversion of the acid into $\text{HCo}(\text{CO})_4$ and $\text{Co}_4(\text{CO})_{12}$ (by i.r. comparison with standard solutions) was observed. The formation of $\text{Co}_4(\text{CO})_{12}$ took place through the intermediacy of an unidentified carbonyl species (presently under investigation) with a characteristic absorption at 1880 cm^{-1} .

The thermal decomposition of the tricobalt acid can therefore be represented by equation (3). Reaction (3)



appears to be the first well established example of hydrogen migration from a carbonyl oxygen to the metal within a metal carbonyl complex. While this work was in progress, the isolation of $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ containing both O -bonded and Fe -bonded hydrogens and 'isoelectronic' with the acid of this study, was reported.⁶ Since $\text{HCo}(\text{CO})_4$ is likely^{7,8} to be in equilibrium with $\text{Co}_2(\text{CO})_8$ and H_2 , the reverse of reaction (3) may be regarded as the reduction of a co-ordinated carbonyl group by molecular hydrogen. Attempts are now being made to ascertain the possibility of reversing reaction (3). The relevance of these observations to the hydroformylation⁹ and Fischer-Tropsch¹⁰ processes is under investigation.

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