Effect of the Countercation and Solvent on the Formation of Anionic Tricobalt Carbonyl Clusters

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Summary The formation of the anionic cluster $[Co_3(CO)_{10}]^-$ from $[Co(CO)_4]^-$ and $Co_2(CO)_8$, or $Co_4(CO)_{12}$ was optimized using lithium as countercation and di-n-butyl ether as solvent; analytically pure $Li[Co_3(CO)_{10}] \cdot Et_2O$ was obtained in Et_2O.

THE role of the alkali metal countercation in the solid state[1] and solution[2] chemistry of carbonylmetallate anions is of increasing interest. The stabilising effect of the alkali metal cation on the co-ordination of CO_2 to cobalt was also recently reported.[3] The effect of the countercation and solvent on the formation of anionic carbonyl metal clusters has apparently not yet been investigated in depth, however.

It has now been found that the formation of one of the simplest anionic metal clusters,[4,5] $[Co_3(CO)_{10}]^-$, is strongly influenced by both the countercation and the solvent.

First, it has been established that the trinuclear cluster can be prepared by the 'redox condensation'[6] of $[Co(CO)_4]^-$ with $Co_2(CO)_8$. This was proved as follows. When an $8 \cdot 5 \times 10^{-3}$ M solution of $Co_2(CO)_8$ in di-n-butyl ether (Bu_2O) was treated under a strictly controlled Ar atmosphere with 1 equiv. of thf-free (thf = tetrahydrofuran) LiCo-$(CO)_4$† in Bu_2O at 15 °C for 40 min under reduced pressure (*ca.* 20 mmHg), an $8 \cdot 5 \times 10^{-3}$ M solution of $Li[Co_3(CO)_{10}]$ was obtained. The reaction was monitored by i.r. spectroscopy, and the final spectrum had $\tilde{v}_{CO}$ bands at 2071w, 2006vs, 1999s, 1975m, 1865w, and 1584 cm^{-1}, consistent with the spectrum reported[4] for $[Co_3(CO)_{10}]^-$. Analytically pure $Li[Co_3(CO)_{10}].Et_2O$† was isolated from a similar reaction in diethyl ether followed by slow evaporation under reduced pressure. When a 10^{-2} M solution of $Li[Co_3(CO)_{10}]$ was treated with CO at atmospheric pressure, i.r. bands attributable to $Co_2(CO)_8$ and $LiCo(CO)_4$ became evident, which disappeared when the CO was pumped off. Moreover, gas-volumetric monitoring of reaction (1) in Bu_2O showed the equilibrium constant (M = Li) to be $K_c/[CO]^2 = 143$ l mol^{-1} at 16 °C, $P_{(CO)}+P_{(Bu_2O)} = 1$ atm. Addition of 3% thf (v/v) to the mixture in equilibrium (1)

$$MCo(CO)_4 + Co_2(CO)_8 \rightleftharpoons M[Co_3(CO)_{10}] + 2CO \qquad (1)$$

(M = Li) resulted in decomposition of $Li[Co_3(CO)_{10}]$ and formation of $LiCo(CO)_4$ and $Co_2(CO)_8$. Formation of Li-$[Co_3(CO)_{10}]$ and disappearance of $Co_4(CO)_{12}$ were observed (i.r.) in the reaction of a slight excess of $LiCo(CO)_4$ with $Co_4(CO)_{12}$ in Bu_2O under Ar, thus showing that reaction (2), M = Li, is shifted to the right under these conditions.

$$2 MCo(CO)_4 + Co_4(CO)_{12} \longrightarrow 2 M[Co_3(CO)_{10}] \qquad (2)$$
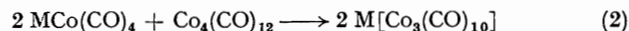
Similar experiments with $NaCo(CO)_4$[7] instead of $LiCo(CO)_4$ led to substantially different results. Under CO, the equilibrium constant for equation (1) (M = Na) was $7 \cdot 8$ l mol^{-1} at 16 °C, $P_{(CO)}+P_{(Bu_4O)} = 1$ atm. Attempts to shift equilibrium (1) by pumping the CO off resulted in the appearance of $Co_4(CO)_{12}$, thus showing that formation of $Na[Co_3(CO)_{10}]$ according to equation (2) was unfavourable under these conditions.

The results of this study suggest that the formation of an anionic metal carbonyl cluster may result from a delicate balance of competitive co-ordination by the countercation to the carbonyl groups or the solvent. This work reports a case of cluster stabilisation by the smaller of two cations. Other clusters may be destabilised by smaller cations because of their polarizing effect. Countercation effects may become less important with 4*d* and 5*d* transition elements, which have larger metal–metal bond strengths.[8]

† Satisfactory elemental analyses were obtained.

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