Reactions of C_8K with Metal Carbonyls

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Summary The reactions between the readily available C_8K and metal carbonyls provide an easy synthesis of binuclear carbonyls of Cr, Mo, W, and Fe.

BINUCLEAR carbonyl anions of the group VI metals are conventionally synthesised by reduction of metal carbonyls with $NaBH_4$,[1] sodium amalgam,[2] or Na–bipy[3] (bipy = 2,2′-bypiridine). These reactions proceed with contamination of the species $[M_2(CO)_{10}]^{2-}$ with binuclear hydride complexes[2] or mercury derivatives,[4] and many are also slow (18—1400 h). We report here a shorter and highly selective (>99%) route to anionic binuclear complexes.

We have investigated the reaction of metal carbonyls and C_8K by stirring the latter in dry, deoxygenated tetrahydrofuran (THF), adding various molar ratios (1 : 1, 1 : 2, 2 : 1) of metal carbonyls and maintaining the reaction at 20—25 °C for 15—30 min. For metal carbonyl–C_8K ratios of 1 : 1 and 2 : 1 only the binuclear complexes were isolated, in quantitative yield, while the corresponding reactions with excess of $[M(CO)_6]$ (M = Cr, Mo, W) or $[Fe(CO)_5]$ gave a mixture of 50% binuclear complex and 50% starting metal carbonyl.

The reactions were followed by measuring the volume of CO evolved. The amount of CO evolved and the consumption of C_8K suggest the stoicheiometry in equations (1) and (2) for these reactions.

$$2\,[M(CO)_6] + 2\,C_8K \xrightarrow[\text{THF}]{25\,^\circ\text{C}} K_2[M_2(CO)_{10}] + CO + C \quad (1)$$

$$(M = Cr, Mo, W)$$

$$2\,[Fe(CO)_5] + 2\,C_8K \xrightarrow[\text{THF}]{25\,^\circ\text{C}} K_2[Fe_2(CO)_8] + 2\,CO + C \quad (2)$$

The reaction of C_8K with $[Co_2(CO)_8]$ proceeded smoothly, the original very dark brown solution of $[Co_2(CO)_8]$ changing to the colourless solution of $K[Co(CO)_4]$ according to equation (3).

$$[Co_2(CO)_8] + 2\,C_8K \xrightarrow[\text{THF}]{25\,^\circ\text{C}} 2\,K[Co(CO)_4] + \text{graphite} \quad \mathbf{(3)}$$

All the anions have been fully characterised analytically and spectroscopically as tetraethylammonium salts. The absence of hydridic hydrogen in the complexes prepared by this method is indicated by their ^1H n.m.r. spectra and by lack of typical reactions of the hydrogen–metal bond.

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