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CYANIDE AND ISOCYANIDE METAL COMPLEXES

IV*. ALLYLCOBALT CYANIDES

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Summary

Both σ- and π-allylcobalt(III) polycyanides $K_3[\sigma\text{-}C_3H_4RCo(CN)_5]$, $K_2[\pi\text{-}C_3H_4RCo(CN)_4]$ and $K[\pi\text{-}C_3H_4RCo(CN)_3PPh_3]$ (R = H or Me), have been prepared by reaction of appropriate carbonyls with potassium cyanide and fully characterised.

Introduction

The successful preparation of the cyclopentadienylcobalt tricyanide, $K[C_5H_5Co(CN)_3]$, from cyclopentadienyldicarbonylcobalt(I) [1] or cyclopentadienylcarbonyldiiodocobalt(III) [2] suggested possible application to the corresponding allyl derivatives. The expected products (I) or (II) of such reactions have previously been reported [3] as products from reaction of allyl halides with pentacyanocobaltate(II) according to eqn. (1),

$$2K_3[Co(CN)_5] + CH_2{=}CHCH_2X \rightarrow K_3[\sigma\text{-}C_3H_5Co(CN)_5] + K_3[Co(CN)_5X] \qquad (1)$$

or, in the case of the crotyl complex, from butadiene and the hydrido anion $[Co(CN)_5H]^-$ according to eqn. (2) [3, 4].

$$[Co(CN)_5H]^{3-} + CH_2{=}CH{-}CH{=}CH_2 \rightarrow [Co(CN)_5{-}CH_2CH{=}CHCH_3]^{3-} \qquad (2)$$

In each case [3, 4] the initially formed σ-allyl complex (I) was shown to be reversibly convertible to the π-allylic derivative (II), the latter being favoured in the equilibrium: $[\sigma\text{-}C_3H_4RCo(CN)_5]^{3-} \rightleftharpoons [\pi\text{-}C_3H_4RCo(CN)_4]^{2-} + CN^-$ (where R = H or *syn*-1-methyl), when aqueous solutions were left standing, whereas

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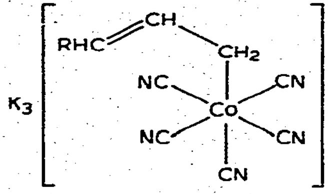
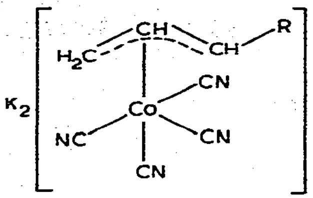
* For Part III, see ref. 1. Also Part V of the series: Organocobalt complexes (for Part IV see ref. 1).

addition of excess potassium cyanide caused reversal with formation of the σ- from the π-complex. Despite the good spectra obtained for these species, which have also been postulated [5, 6] as intermediates in hydrogenation using $[Co(CN)_5H]^{3-}$, none of the complexes was isolated pure and characterised by analysis.


(I)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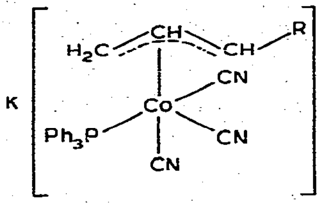
(III)

Results and discussion

Whereas the cyclopentadienyl complex $C_5H_5Co^{III}(CO)I_2$ is readily obtained from the dicarbonyl $C_5H_5Co^{I}(CO)_2$, reaction of either of the π-allyl complexes $\pi\text{-}C_3H_5Co(CO)_3$ or $\pi\text{-}C_3H_5Co(CO)_2PPh_3$ with iodine did not yield iodocobalt(III) complexes of sufficient stability to permit ready isolation. However, direct reaction with a mixture of iodine and cyanide proceeded smoothly to give the expected cyano complexes (II) and (III), according to eqns. (5) and (6),

$$\pi\text{-}C_3H_4RCo(CO)_3 + I_2 + 4KCN \rightarrow K_2[\pi\text{-}C_3H_4RCo(CN)_4] + 3CO + 2KI \quad (5)$$

$$\pi\text{-}C_3H_4RCo(CO)_2PPh_3 + I_2 + 3KCN \rightarrow K[\pi\text{-}C_3H_4RCo(CN)_3PPh_3] + 2CO + 2KI \quad (6)$$

(R = H or Me)

possibly via unstable iodides of the type $\pi\text{-}C_3H_5Co(CO)(L)I_2$ (L = CO or PPh_3). Evidence for such a course is provided by the rapid evolution of carbon monoxide when iodine is added to the tricarbonyl, $C_3H_5Co(CO)_3$, at room temperature and the apparent lack of reaction when the latter is refluxed with potassium cyanide in the absence of such an oxidising agent.

In the phosphine-substituted series, even use of excess potassium cyanide led cleanly to the π-allyl or crotyl complexes (III), but the more ready occurrence of the above-mentioned equilibria [3, 4] made it desirable to employ a deficiency of cyanide in the tricarbonyl series. In this way the potassium salts of the π-allyl and π-crotyl complexes (II), $K_2[C_3H_5Co(CN)_4]$ and $K_2[C_3H_4MeCo(CN)_4]$, were readily isolated as yellow solids. Use of excess cyanide gave the salts of the σ-complexes (I), $K_3[C_3H_5Co(CN)_5]$ and $K_3[C_3H_4MeCo(CN)_5]$, also as yellow solids. All four yield solutions in D_2O whose NMR spectra agree well with those previously reported [3, 4]. Those of the new phosphine substituted complexes (III) are very similar to those of the tetracyano-π-allyl derivatives (II) and hence readily assigned (see Experimental); the greater band multiplicity results from the expected phosphorus—hydrogen splitting and has been observed inter al. for the π-crotyl precursor [7], C_3H_4-

TABLE 1

DATA FOR ALLYLCOBALT(III) POLYCYANIDES

Compound		Infrared spectra (Nujol mulls)		Analysis found (calcd.) (%)		
		ν(CN)	ν(C=C)	C	H	N
$K_3[C_3H_5Co(CN)_5]$	(I: R = H)	2175w, 2125m	1611w	27.9 (27.7)	1.7 (1.4)	19.9 (20.2)
$K_3[C_4H_7Co(CN)_5]$	(I: R = Me)	2178w, 2122m, 2110m	1608w	30.3 (30.1)	2.2 (1.95)	19.2 (19.5)
$K_2[C_3H_5Co(CN)_4]$	(II: R = H)	2120s, 2075m		30.1 (29.8)	2.1 (1.77)	20.1 (19.85)
$K_2[C_4H_7Co(CN)_4]$	(II: R = Me)	2118m, 2068m, 2030w		32.2 (32.4)	2.2 (2.4)	18.8 (19.0)
$K[C_3H_5Co(CN)_3PPh_3]$	(III: R = H)	2120s, 2110m		60.3 (60.1)	4.0 (4.2)	9.1 (8.8)
$K[C_4H_7Co(CN)_3PPh_3]$	(III): R = Me)	2170s, 2145m, 2125s		61.4 (60.9)	4.4 (4.5)	8.5 (8.5)

$MeCo(CO)_2PPh_3$. The only previously recorded IR spectra [3] relate to mixtures and spectral data for all the pure products are therefore given in Table 1 together with analytical results.

Experimental

For general directions see preceding paper [1].

Dipotassium π-allyltetracyanocobaltate(III), (II: R = H)

A solution of allyltricarbonylcobalt(I) [8, 9] (0.55 g, 3 mmol) and potassium cyanide (0.58 g, 9 mmol) in tetrahydrofuran (200 ml) was cooled to ≈ −20°, and iodine (0.76 g, 3 mmol) in tetrahydrofuran (100 ml) added dropwise. The mixture was stirred at this temperature for 3 h and then at room temperature overnight. The filtered solution was then evaporated to dryness under reduced pressure and the residue chromatographed on alumina using methanol as solvent. This eluted the potassium salt (II: R = H) (0.4 g, 47%), a yellow solid, m.p. 128° (dec.), soluble in water and alcohols; $\tau(D_2O)$ 4.5(m), 6.1(d) and 6.9 ppm (d).

Dipotassium π-syn-crotyltetracyanocobaltate(III), (II: R = Me)

This was obtained similarly from crotyltricarbonylcobalt(I) [8, 9] (0.59 g, 3 mmol) as a yellow solid (0.38 g, 43%), m.p. 167° (dec.); $\tau(D_2O)$ 4.9(m), 6.25(m), 6.7(d), 7.5(d), and 8.5 ppm (d).

Tripotassium σ-allylpentacyanocobaltate(III), (I: R = H)

Dropwise addition of iodine (0.76 g, 3 mmol) in tetrahydrofuran (100 ml) at 0° to a stirred solution of allyltricarbonylcobalt(I) [8, 9] (0.55 g, 3 mmol) and potassium cyanide (1.2 g, 18 mmol) in tetrahydrofuran (250 ml) was followed by stirring for 3 h at 0° and overnight at room temperature and then by work-up as above. This procedure gave the σ-complex (I: R = H) (0.5 g, 57%) as a yellow solid, m.p. 195° (dec.), soluble in water and alcohols; $\tau(D_2O)$ 3.4(m), 4.3(d) and 7.6 ppm (d).

Tripotassium σ-crotylpentacyanocobaltate(III), (I: R = Me)

This was obtained similarly to the preceding compound, from crotyltricarbonylcobalt(I) [8, 9] (0.59 g, 3 mmol) as a yellow solid (0.56 g, 52%), m.p. 189° (dec.). $\tau(D_2O)$ 4.0(m), 4.3(m), 7.6(d) and 8.45 ppm (m).

Potassium π-allyl(triphenylphosphine)tricyanocobaltate(III), (III: R = H)

A cooled solution of iodine (0.25 g, 1 mmol) in tetrahydrofuran (100 ml) was added dropwise with stirring to an ice-cooled mixture of allyldicarbonyl(triphenylphosphine)cobalt(I) [8] (0.42 g, 1 mmol) and potassium cyanide (0.39 g, 6 mmol) in tetrahydrofuran (300 ml). After stirring at 0° for 3 h and at room temperature overnight, the solution was filtered, evaporated, and the residue chromatographed on alumina. Methanol eluted the orange-yellow salt (III: R = H) (0.26 g, 55%), m.p. 271° (dec.), soluble in water and in polar organic solvents; $\tau(D_2O)$ 2.7 (m, 5H, Ph), 4.6 (m, 1H, H-2), 6.55 (dd, 2H, *syn*-H-1,3), 6.80 ppm (dd, 2H, *anti*-H-1,3).

Potassium π-crotyl(triphenylphosphine)tricyanocobaltate(III), (III: R = Me)

This was obtained similarly from π-crotyldicarbonyl(triphenylphosphine)-cobalt(I) [8] (0.44 g, 1 mmol) as an orange solid (0.25 g, 50%), m.p. 252° (dec.); $\tau(D_2O)$ 2.7 (m, 5H, Ph), 4.9 (m, 1H, H-2), 6.5 (m, 1H, *anti*-H-3), 6.9 (dd, 1H, *syn*-H-1), 7.2 (dd, 1H, *anti*-H-3) and 8.6 ppm (dd, 3H, Me).

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