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SOME CYCLOPENTADIENYLCOBALT CYANIDES AND ISOCYANIDES*

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SUMMARY

The cyclopendatienyl di- and tri-cyanides of cobalt, $C_5H_5Co(CN)_2PPh_3$ and $[C_5H_5Co(CN)_3]^-$ have been prepared by reaction of cyanide with $C_5H_5Co(PPh_3)I_2$ and $C_5H_5Co(CO)I_2$ respectively. The anionic tricyanide has been isolated as its potassium and its benzyl triphenylphosphonium salt and has been alkylated to yield the neutral mono- and dicationic tris-(alkylisocyanide) complexes $C_5H_5Co(CN)_2$-CNMe and $[C_5H_5Co(CNEt)_3]^{2+}$.

Continued interest in cyanide and isocyanide metal complexes[3,4] prompts us to report some initial results obtained in the cyclopentadienylcobalt series. Although these ligands are formally iso-electronic with carbon monoxide only relatively few of their analogues of the numerous hydrocarbon metal carbonyls have become known. Some years ago we showed[2] that in the direct reaction of dicarbonylcyclopentadienyliron halides with phenylisocyanide, the extent of replacement of carbon monoxide and halide can be controlled by the choice of halogen and solvent, and that the tris-(isocyanide) complex $[C_5H_5Fe(CNPh)_3]^+Cl^-$ is readily obtained from the chloride. But the reaction with cyanide of the same complex has only been found to yield[5] $C_5H_5Fe(CO)_2CN$ and $[C_5H_5Fe(CO)(CN)_2]^-$, and the tricyanide $[C_5H_5Fe(CN)_3]^{2-}$ is as yet unknown. Similarly in the analogous molybdenum and tungsten series only the mono- and/or dicyanides $[C_5H_5M(CO)_3CN]$ and $[C_5H_5M(CO)_2(CN)_2]^-$ have been described[5].

Since cyanide and isocyanide ligands are known to favour higher oxidation states than carbonyl groups, it appeared likely that the molybdenum(IV) complex[6] $C_5H_5Mo(CO)_2Br_3$ and the cobalt(III) complex[7] $C_5H_5Co(CO)I_2$ should be particularly good starting materials for the preparation of polycyanides. In agreement with this consideration we describe here the ready conversion of the latter complex into the tricyanocyclopentadienylcobalt(III) anion, $[C_5H_5Co(CN)_3]^-$, whereas we have so far failed to isolate stable products from the reaction of cyanide with the cobalt(I) complex $C_5H_5Co(CO)_2$, in agreement with earlier observations[5].

Reaction of the di-iodide (I) with potassium cyanide proceeded readily in methanol solution. Evidence that it causes replacement of carbon monoxide before replacement of iodide is obtained from the lack of CO-stretching frequency in the

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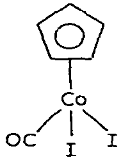
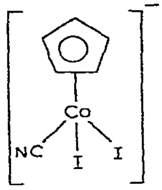
* Part III of the series: Organo-cobalt complexes (for part II see ref. 1); as well as part II of the series: Cyanide and isocyanide metal complexes (for part I see ref. 2).

solutions obtained with only one molar equivalent of cyanide. However, the intermediate complexes (II) and (III) proved too unstable for ready isolation, when one or two moles of potassium cyanide were employed. With three equivalents of this reagent, the anion (IV) was the exclusive product and whereas isolation as the potassium salt was rather wasteful (37 % yield), benzyltriphenylphosphonium chloride precipitated the anion in satisfactory yield (64 %).



(I)



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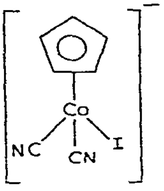

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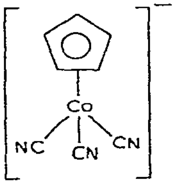
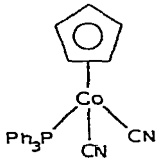
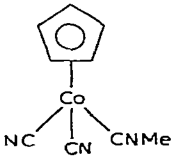


(IV)

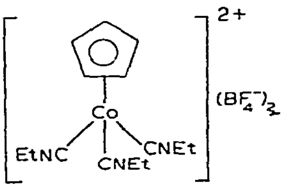
By contrast with these results, the triphenylphosphine analogue[7] of (I), $C_5H_5Co(PPh_3)I_2$, reacts readily with two equivalents of cyanide to give the neutral dicyano complex (V) and even excess of cyanide gives this as the major product with only traces of the tricyano complex (IV). According to spectroscopic evidence the related complexes[7] $C_5H_5Co(C_5H_5N)I_2$ and $C_5H_5Co[P(OEt)_3]I_2$ behaved similarly with cyanide, but the products from these reactions have not been isolated. Thus there is evidence for the following order of reactivity towards cyanide in this series: CO > I > PPh_3 (C_5H_5N, $P(OPh)_3$).



(V)



(VI)



(VII)

Most metal cyanides[8], including cobalticyanide[9] $[Co^{III}(CN)_6]^{3-}$ can be alkylated on nitrogen to yield alkyl isocyanide complexes. The contrasting alkylation on metal of the pentacyanocobaltate ion $[Co^{II}(CN)_5]^{3-}$ may be ascribed, like its catalytic

TABLE 1

IR AND NMR DATA

Complex	*ν(CNR)*[a] *(cm⁻¹)*	*ν(CN)*[a] *(cm⁻¹)*	*τ(C_5H_5)*	*Solvent for NMR*	*τ(other)*
(V)		2120, 2110	4.82	$CDCl_3$	2.5 (Ph)
(VI)	2250	2122	4.45	$CDCl_3$	6.42 (Me)
			4.2	D_2O	6.39 (Me)
(VIII)	2270, 2250		3.59	D_2O	5.95 (q, CH_2)
	2215 (sh)			D_2O	8.51 (t, Me)
$[C_5H_5Fe(CO)(CNEt)_2]I$	2215, 2195	2010[b]	4.79	$CDCl_3$	6.05 (q, CH_2)
				$CDCl_3$	8.55 (t, Me)

[a] As Nujol mulls, [b] ν(CO) (cm^{-1}).

activity[10], to its coordinative unsaturation. However, this speculation requires confirmation from additional examples. In the present work we have therefore examined the alkylation of the tri-cyano complex (IV) with two alkylating agents. Both caused the expected alkylation on nitrogen. Methyl iodide gave the neutral, monoalkylated product (VI) while the more powerful alkylating agent (*cf.* ref. 11), triethyloxonium tetrafluoroborate, gave the fully alkylated salt (VII). This shows one of the lowest-field cyclopentadienyl ^{1}H NMR signals so far recorded (τ 3.59 in D_2O) ($C_5H_5MoO_2Cl$ resonates[12] at τ 3.40 in $CDCl_3$ and τ 3.15 in acetone). This and other spectral data for complexes (V)–(VII) are given in Table 1 which includes data for $[C_5H_5Fe(CO)(CNEt)_2]I$ prepared for comparison following the general method of Coffey[5].

EXPERIMENTAL

All reactions were conducted under nitrogen in dry, redistilled solvents, purged with nitrogen.

Tricyanocyclopentadienylcobalt(III) salts (IV)

(*a*). *Potassium salt.* The iodide (I) (4.06 g, 10 mmole) and potassium cyanide (2.0 g, 30 mmole) were refluxed in methanol (100 ml) overnight. The resultant solution was filtered through Kieselguhr and evaporated under reduced pressure. The residue was chromatographed on neutral alumina, initially using ether/methanol (1/1). Methanol eluted an orange solid. Recrystallisation from methanol gave the potassium salt of (I) (37% yield). M.p. 210° (decomp.), ν(CN) 2120, 2110 and 2090 (sh) cm^{-1}; $\tau(D_2O)$ 4.48; soluble in water, alcohols, chloroform and acetonitrile. (Found: C, 39.55; H, 2.1; N, 17.2. $C_8H_5CoKN_3$ calcd.: C, 39.8; H, 2.1; N, 17.4%).

(*b*). *Benzyltriphenylphosphonium salt*: The crude product from the above reaction, after evaporation of the initial solution, was dissolved in water. Addition of aqueous benzyltriphenylphosphonium chloride precipitated the orange salt (64%), m.p. 240° (decomp.). Its infrared spectrum was identical with that of a sample similarly precipitated from an aqueous solution of the purified potassium salt; ν(CN) 2115, 2120 and 2130 cm^{-1}. It is soluble in alcohols and in acetonitrile, sparingly soluble in dichloromethane. (Found: C, 71.2; H, 4.9; N, 7.4. $C_{33}H_{27}CoN_3P$ calcd.: C, 71.3; H, 4.9; N, 7.6%).

Triphenylphosphinedicyanocyclopentadienylcobalt(III), (V)

To a saturated methanol solution of triphenylphosphinecyclopentadienyldiiodocobalt (1.0 g, 15.6 mmole) was added dropwise a methanol solution of potassium cyanide (0.203 g, 31.2 mmole) and the mixture was stirred overnight at room temperature. The solution was filtered, evaporated under reduced pressure and the residue chromatographed on neutral alumina using ether/methanol (initially 4/1 later 1/9) mixtures as solvent. The major, orange, fraction on evaporation gave the neutral complex (V) (60 mg, 9%), crystallising from methanol as a yellow solid, m.p. 196° (decomp.), soluble in alcohols, ether, benzene and chloroform. (Found: C, 68.7; H, 4.7; N, 6.2. $C_{25}H_{20}CoN_2P$ calcd.: C, 68.5; H, 4.6; N, 6.4%). A later fraction gave a trace of the anion (IV).

Methylisocyanidecyclopentadienyldicyanocobalt(III), (VI)

The benzyltriphenylphosphonium salt of (I) (0.555 g, 1 mmole) was dissolved in the minimum amount of acetonitrile; methyl iodide (4 ml) was added and the solution refluxed overnight, then filtered and evaporated under reduced pressure. The residue was dissolved in dichloromethane and light petroleum was added to the filtered solution to precipitate an orange-yellow powder. Recrystallisation from acetonitrile yielded the neutral complex (VI) (0.15 g, 70%), m.p. 175° (decomp.). (Found: C, 49.9; H, 3.7; N, 19.3. $C_9H_8CoN_3$ calcd.: C, 49.8, H, 3.7; N, 19.4%). Extended reaction (40 h) with twice as much methyl iodide gave the same product.

Tris(ethylisocyanide)cyclopentadienylcobalt(III) tetrafluoroborate (VII)

The benzyltriphenylphosphonium salt of (I) (0.277 g, 0.5 mmole) was dissolved in a minimum amount of dichloromethane and freshly prepared triethyloxonium tetrafluoroborate (0.57 g, 3 mmole) added and the mixture refluxed for 4–6 h. The precipitated product (III) (0.116 g, 52%) was collected by filtration and washed with ether, dichloromethane and chloroform. It was recrystallised from ethanol as a dark brown solid, m.p. 110° (decomp.) (Found: C, 36.5; H, 4.3; N, 9.2. $C_{14}H_{20}B_2CoF_8N_3$ calcd.: C, 36.3; H, 4.4; N, 9.1%).

Carbonylbis(ethylisocyanide)cyclopentadienyliron(II) iodide

Potassium carbonyldicyanocyclopentadienyliron^5 (0.96 g, 4 mmole) and iodoethane (8 ml) were refluxed in acetonitrile (30 ml) for 20 h. The solution was then filtered and evaporated under reduced pressure. The residue was dissolved in dichloromethane, the solution filtered, and light petroleum (b.p. 40–60°) added to precipitate the product (1.06 g, 70%), yellow crystals, m.p. 140° (decomp.) [from chloroform/hexane] soluble in water and in polar organic solvents (Found: C, 37.6; H, 4.0; N, 7.45. $C_{12}H_{15}FeIN_2O$ calcd.: C, 37.3; H, 3.9; N, 7.3%).

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