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CYANIDE AND ISOCYANIDE METAL COMPLEXES

III*. FURTHER STUDIES OF THE ALKYLATION OF CYANO GROUPS IN CYCLOPENTADIENYL-COBALT AND -IRON COMPLEXES

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Summary

The extent of alkylation of $[C_5H_5Co(CN)_3]^-$, $C_5H_5Co(CN)_2L$ (L = PPh_3, etc.) and $[C_5H_5Fe(CO)(CN)_2]^-$, is shown to depend critically on the choice of alkylating agent and solvent. IR and NMR spectra of the products are reported and the ^1H NMR spectrum of $C_5H_5Co(CN)(CNMe)(PMe_2Ph)$ is used to demonstrate its chirality.

Introduction

Following our report [1] of the preparation and alkylation of the cyclopentadienyltricyanocobalt(III) anion (I) we have continued the study of alkylations of this and related complexes with a view to elucidating the factors which control the extent of these reactions. The results are now reported together with spectroscopic properties of the cyano and isocyanide complexes.

Results and discussion

Trialkyloxonium salts are powerful alkylating agents and have been independently used by several workers [1—4] to alkylate metal cyanide to isocyanide complexes. In the case of the tricyano complex (I) we reported complete alkylation to the dication (IVc) with triethyloxonium tetrafluoroborate and we now report similar alkylations of the phosphine-substituted complex (V: L = PPh_3) to the dication (VIIc: L = PPh_3) and the anionic iron—cyanide complex (VIII) to the cation (Xc) with this reagent.

On the other hand, we had reported [1] monoalkylation of the tricyanide (I) to the neutral isocyanide complex (IIa) using methyl iodide in acetonitrile

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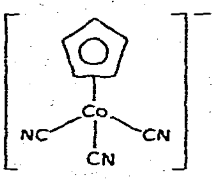
* For Part II see ref. 1. Also Part IV of the series: Organocobalt complexes (for Part III see ref. 1).

and have been unable to force the reaction to proceed beyond this step with a large excess of reagent. Nevertheless ethyl iodide reacted, albeit very inefficiently, with the monomethylated compound (IIa) to give the methyl—ethyl derivative (IIIb). Equally clean monomethylation was observed in the reactions of the phosphine-substituted complexes (V: L = PPh_3) and (V: L = PMe_2Ph) to yield the corresponding cations (VIa). However the iron-containing anion (VIII) is readily dialkylated as reported by Coffey [5], by alkyl halides and we have obtained the dimethyl (Xa), diethyl (Xc) and dibenzyl (Xd) complexes in this way. The greater nucleophilicity of this anion (VIII) may be attributed to the greater electron concentration on Fe^{II} than on Co^{III}, which is partially counteracted by the increased back-bonding to carbonyl compared with cyanide ligands. Hence the dicarbonyl cyanide $C_5H_5Fe(CO)_2CN$, unlike the isocyanide substituted analogues (IX), is comparable with the neutral cobalt(III) complex (II) in its lack of reactivity towards alkyl halides. (It is slowly alkylated by iodomethane but not by other halides tried.) These reactivity differences correlate with the spectral variations discussed below.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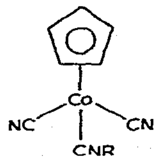
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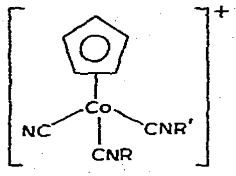
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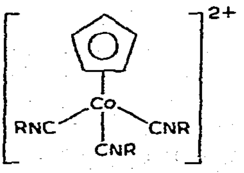
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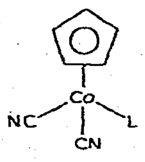
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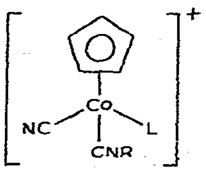
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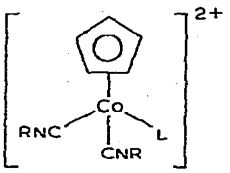
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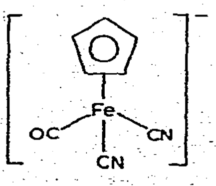
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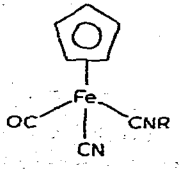
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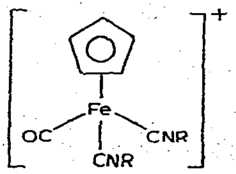
(X)

(a): R = R′ = Me;
(b): R = Me, R′ = Et;
(c): R = Et;
(d): R = $PhCH_2$

The methylation of the anion (VIII) with methyl iodide proved to be remarkably sensitive to solvent effects. Change from acetonitrile [5] to the less polar tetrahydrofuran and dichloromethane caused sharp diminution in yield of the dialkylated product (Xa) (75, 50 and 15% respectively), whereas in methanol solution only the neutral monoalkylated product is formed. Benzyl bromide similarly converts this cyanide (VIII) to the monobenzyl derivative (IXd) in methanol but to the dibenzylated cation (Xd) in acetonitrile as previously described [5].

The importance of the choice of solvent was also evident when the methylation of the cobalt—tricyanide complex (I), using dimethyl sulphate, was compared in methanol and ethanol. In contrast to the apparently clean dimethylation observed in the former solvent, the major product (IIIa) was accompanied by the unreacted (I), mono- (IIa) and tri-methylated compounds (IVa) under otherwise identical conditions in ethanol. It is noteworthy that the various ionic (and neutral) species so formed could readily be separated by column chromatography on neutral alumina, a technique which we have employed extensively for separation and purification of salts throughout this work.

Expecting replacement of either a carbonyl or an isocyanide ligand we photolysed the cationic iron complex (Xa) with potassium cyanide. No displacement could be detected, but with or without added cyanide photolysis in several solvents led ultimately to the cyclopentadienyltris(methyl isocyanide)-iron cation, $[C_5H_5Fe(CNMe)_3]^+$, isolated as the iodide, together with some ferricinium ion. These are secondary products formed by the action of dichloromethane on an intermediate oil of as yet unknown constitution. The details of this process are being studied further, but we describe the photolysis in dioxane as a convenient route to the cation, which has previously been prepared [6], apparently like the phenyl isocyanide analogue [7] from dicarbonylcyclopentadienylchloroiron, $C_5H_5Fe(CO)_2Cl$, and the isocyanide, but has not been described in detail.

Although as mentioned previously [1] we have failed to isolate cyclopentadienylcobalt(I) cyanide or isocyanide complexes from reaction of the dicarbonyl, $C_5H_5Co(CO)_2$, or the carbonylphosphine complex $C_5H_5Co(CO)(PPh_3)$ with potassium cyanide (followed by triethyloxonium tetrafluoroborate), the reaction with cyanide in air provides a fairly efficient direct route to the cobalt(III) complexes (I) and (V: L = PPh_3).

We have also examined briefly the possibility of displacing cyanide ligands from the anionic complex (I) by neutral ligands. Although triphenylphosphine converted the potassium salt of (I) slowly to the neutral substitution product (V: L = PPh_3) in boiling methanol, triethyl phosphite failed to react under the same conditions. Phenylacetylene, tolane and maleic anhydride were also unreactive under these conditions and when irradiated with methanol solutions of the cobalt complex.

IR and NMR spectral data for the compounds prepared in this work are collected in Table 1. They show largely the expected trends as the overall charge or more specifically the charge on the metal is varied. Thus the IR stretching frequencies of the CN, CNR and CO groups all increase slightly, but significantly with increasing positive charge, while the proton resonance signals of both the cyclopentadienyl and isocyanide groups show more marked downfield shifts due to decreased shielding in the same order. For compounds of the same net

TABLE 1

Compound[a]	IR data[b]			NMR data[c]		
	ν(CN)	ν(CNR)	ν(CO)	$\tau(C_5H_5)$	τ[R(of CNR)]	τ(L)
$K^+[CpCo(CN)_3]^-$ (I)	2120, 2110, 2090 (sh)			4.48*		
$CpCo(CN)_2CNMe$ (IIa)	2129, 2121	2250		4.42	6.4	
$\{[CpCo(CN)(CNMe)_2]^+\}_2SO_4^{2-}$ (IIIa)	2138	2258, 2240		4.0	6.3	
$[CpCo(CNMe)_3]^{2+}SO_4^{2=}$ (IVa)		2270, 2256		3.85	6.2	
$[CpCo(CN)(CNMe)(CNEt)]^+I^-$ (IIIb)	2124	2242, 2238		3.96 (4.04*)	6.4(Me), 6.2 (q, CH_2), 8.4(t, CH_3CH_2)	
$[CpCo(CNEt)_3]^{2+}(BF_4^-)_2$ (IVc)		2270, 2250		3.7 (3.59*)	5.95(q, CH_2), 8.51(t, CH_3)	
$CpCo(CN)_2PPh_3$ (V)	2120, 2110			4.82		2.54
$[CpCo(CN)(CNMe)PPh_3]^+I^-$ (VIa)	2122	2248		4.38*	6.2*	2.5*
$CpCo(CN)_2PMe_2Ph$ (V)	2117			4.9		2.4(Ph), 7.9(d, Me)
$[CpCo(CN)(CNMe)PMe_2Ph]^+I^-$ (VIa)	2128	2245		4.4*	6.3*	2.45*(Ph), 7.7*(d, Me), 7.8*(d, Me)
$[CpCo(CNEt)_2PPh_3]^{2+}(BF_4^-)_2$		2265, 2250		3.97	6.0(q, CH_2), 8.5(t, CH_3)	2.45
$CpFe(CO)_2CN$	2118		2056, 2010	4.9		
$[CpFe(CO)_2(CNMe)]^+I^-$		2244	2075, 2022	4.2	6.2	
$K[CpFe(CO)(CN)_2]$ (VIII)	2094, 2080		1970, 1950	5.6*		
$CpFe(CO)(CN)(CNMe)$ (IXa)	2120	2200	2000	5.1	6.54	
$CpFe(CO)(CN)(CNCH_2Ph)$ (IXd)	2129	2200	1995	5.2	4.9(CH_2), 2.7(Ph)	
$[CpFe(CO)(CNMe)_2]^+I^{-d}$ (Xa)		2225, 2217	2004	4.79	6.33	
$[CpFe(CO)(CNEt)_2]^+I^-$ (Xc)		2218, 2185	2007	4.77	6.05(q, CH_2), 8.55(t, CH_3)	
$[CpFe(CO)(CNCH_2Ph)_2]^+Br^{-e}$ (Xd)		2218, 2190	2008	4.72	4.81 (CH_2), 2.68(Ph)	
$[CpFe(CNMe)_3]^+I^-$		2202, 2164		5.26	6.42	

[a] Cp = C_5H_5. [b] All IR spectra in cm^{-1} as Nujol mulls. [c] NMR data in $CDCl_3$ except those asterisked which are in D_2O. [d] Lit. [5]: 2200, 2000 cm^{-1} (as KBr disc). [e] Lit. [5]: 2200, 2010 cm^{-1} (as KBr disc).

charge the ν(CNR) values are consistently higher and the $\tau(C_5H_5)$ values lower in the cobalt than the iron series reflecting the greater positive charge on the metal corresponding to the higher oxidation state of the cobalt(III) compared with the iron(II) compounds. The increasing positive charge on iron that accompanies increasing back-bonding to carbonyl is similarly evident from IR and NMR comparison of e.g. the monocations $[C_5H_5Fe(CNMe)_3]^+$, $[C_5H_5Fe(CO)(CNMe)_2]^+$ and $[C_5H_5Fe(CO)_2(CNMe)]^+$.

The dimethylphenylphosphine complex (VIa: L = PMe_2Ph) was prepared in order to demonstrate the chirality of this type of molecule which possesses a pseudo-tetrahedral metal atom with four different groups attached. As in previous similar examples [8] this feature is clearly evident from the non-equivalence of the *P*-methyl groups in the NMR spectra (see Table 1) whereas they are of course equivalent in the precursor (V: L = PMe_2Ph).

Experimental

All reactions were conducted under nitrogen in carefully dried solvents. Light petroleum refers to the fraction of b.p. 40—60°. Column chromatography was carried out on neutral alumina prepared from Spence's grade 'H' by allowing it to stand under ethyl acetate for 3 days, washing with methanol and water and drying at 160—170° for 8 h.

The potassium (50% yield) and benzyl triphenylphosphonium salts of the anion (I) were prepared as described previously [1], as was the phosphine-substituted cyanide (V: L = PPh_3); the yield of the latter from 1.0 g cyclopentadienyl(triphenylphosphine)diiodocobalt was typically 0.3 g (45%), not 9% as erroneously reported [1]. Alternative preparations of these products are described below.

Potassium cyclopentadienyltricyanocobaltate(III) (I) from cyclopentadienyldicarbonylcobalt(I)

A solution of potassium cyanide (0.33 g, 5 mmol) in ethanol was added to cyclopentadienyldicarbonylcobalt(I) [10] (0.45 g, 2.5 mmol) in ethanol (25 ml) and the mixture stirred at 0° for 4 h. After filtration and evaporation under reduced pressure, the residue was chromatographed to yield the potassium salt of the tricyanide anion (I) [1] (0.35 g, 50%). A similar reaction conducted under nitrogen in carefully deaerated ethanol yielded, on evaporation of the reaction mixture, a very air-sensitive residue showing ν(CN) at 2120 and 2100 cm^{-1}; no pure compound could be isolated from this directly, by addition of various cations, or following subsequent treatment with either benzyl bromide or triethyloxonium tetrafluoroborate.

Cyclopentadienyl(triphenylphosphine)dicyanocobalt(III) (V: L = PPh_3)

(a). From cyclopentadienyl(triphenylphosphine)carbonylcobalt(I). Potassium cyanide (0.33 g, 5 mmol) in methanol (100 ml) was added dropwise to cyclopentadienyl(triphenylphosphine)carbonylcobalt(I) [11] (1.04 g, 2.5 mmol) in methanol (50 ml) and the mixture stirred at 0° for 6 h. After filtration and evaporation under reduced pressure, the residue was chromatographed to yield the complex (V: L = PPh_3) [1] (0.22 g, 20%). As in the preceding experiment,

similar reactions conducted in strict absence of air yielded very air-sensitive material showing cyanide absorption in the infrared (2118 and 2080 cm^{-1}) but no isolable products.

(b). From the tricyanide (I). The potassium salt of the anion (I) (0.5 g, 2.1 mmol) and triphenylphosphine (1.65 g, 6.3 mmol) were refluxed in methanol (150 ml) for three days and the product worked up as in (*a*). Elution with ether/chloroform (1/1) changing gradually to chloroform/methanol (1/1) led to successive isolation of triphenylphosphine (1.3 g, 5 mmol), the complex (V: L = PPh_3) (0.37 g, 40% conversion) and unreacted potassium salt of (I) (0.25 g, 50%).

Cyclopentadienyl(dimethylphenylphosphine)diiodocobalt(III), $C_5H_5Co(PMe_2Ph)I_2$

To a solution of cyclopentadienylcarbonyldiiodocobalt(III) [10] (8.9 g, 22 mmol) in dichloromethane (200 ml) was added dropwise a solution of dimethylphenylphosphine (5 ml, 25.8 mmol) in dichloromethane (60 ml) and the solution stirred overnight at room temperature. It was then treated with charcoal, filtered through Kieselguhr, diluted with hexane (50 ml) and evaporated under reduced pressure until precipitation of dark green crystals appeared complete. The product (11.2 g, 90%) was collected, washed with ether and pentane and recrystallised from dichloromethane/hexane, m.p. 105° (dec.). (Found: C, 29.9; H, 3.0; I, 49.4. $C_{13}H_{16}CoI_2P$ calcd.: C, 30.2; H, 3.1; I, 49.2%.)

Cyclopentadienyl(triethyl phosphite)diiodocobalt(III), $C_5H_5Co[P(OEt)_3]I_2$

This product was obtained by the preceding method from cyclopentadienylcarbonyldiiodocobalt(III) [10] (8.12 g, 20 mmol) and triethyl phosphite (3.65 g, 22 mmol) as black crystals (8.7 g, 80%), m.p. 125° (dec.). (Found: C, 24.4; H, 3.8; I, 46.9. $C_{11}H_{20}CoI_2O_3P$ calcd.: C, 24.3; H, 3.7; I, 46.7%.) Its reaction with cyanide (cf. below) gave a product which could not be obtained pure and was therefore not studied further.

Cyclopentadienyl(dimethylphenylphosphine)dicyanocobalt(III), (V: L = PMe_2Ph)

To a solution of cyclopentadienyl(dimethylphenylphosphine)diiodocobalt (1.0 g, 2 mmol) in methanol (50 ml) was added dropwise a methanol solution of potassium cyanide (0.33 g, 5 mmol). The mixture was stirred at room temperature overnight then filtered, evaporated under reduced pressure and the residue chromatographed using ether/methanol as eluant. The major fraction gave the product (0.38 g, 60%) as yellow crystals, m.p. 187° (dec.) (from methanol), soluble in alcohols, acetonitrile, benzene and chloroform. (Found: C, 57.5; H, 5.4; N, 8.7. $C_{15}H_{16}CoN_2P$ calcd.: C, 57.3; H, 5.1; N, 8.9%.)

Cyclopentadienylpyridinedicyanocobalt(III), (V: L = C_5H_5N)

This product was obtained similarly (40% yield) from cyclopentadienylpyridinediiodocobalt(III) [10] as a rather unstable air-sensitive yellow solid, m.p. 193° (dec.). (Found: C, 56.4; H, 4.2; N, 16.2. $C_{12}H_{10}CoN_3$ calcd.: C, 56.5; H, 3.9; N, 16.5%.)

Reaction of the tricyanide (I) with dimethyl sulphate

(a). In Methanol. Dimethyl sulphate (1.5 g, 12 mmol) was added to a solution of the potassium salt of the anion (I) (0.5 g, 2.1 mmol) in methanol (100 ml) and the mixture was refluxed gently overnight. After filtration and evaporation under reduced pressure, the residue was dissolved in chloroform, filtered, and cyclopentadienylbis(methyl isocyanide)cyanocobalt(III) sulphate (IIIa) (0.6 g, 60%) precipitated by addition of ether as a yellow solid, m.p. 210° (dec.), soluble in water and polar organic solvents. (Found: C, 43.1; H, 4.1; N, 14.8. $C_{20}H_{22}Co_2N_6O_4S$ calcd.: C, 42.8; H, 3.9; N, 15.0%.)

(b) In ethanol. The same procedure was repeated with ethanol in place of methanol. After evaporation of the initial reaction mixture, thin layer chromatography showed the product to be a mixture. It was therefore separated by column chromatography using ether/chloroform (1/1) and later chloroform, chloroform/methanol and finally methanol to elute in succession: cyclopentadienyl(methyl isocyanide)dicyanocobalt(III) [1] (IIa) (92 mg, 20%), then the bis(methyl isocyanide) complex (IIIa) (0.37 g, 48%), unreacted potassium salt of the tricyanide (I) (63 mg, 12.5%) and the orange-yellow cyclopentadienyltris(methyl isocyanide)cobalt(III) sulphate, (IVa) (36 mg, 5%), m.p. 220° (dec.), soluble in water and alcohols. (Found: C, 38.7; H, 3.9; N, 12.5. $C_{11}H_{14}CoN_3O_4S$ calcd.: C, 38.5; H, 4.1; N, 12.2%.)

Cyclopentadienyl(ethyl isocyanide)(methyl isocyanide)cyanocobalt(III), (IIIb)

Excess ethyl iodide (10 ml, 0.12 mol) was added to a solution of cyclopentadienyl(methyl isocyanide)dicyanocobalt(III), (IIa) [1] (0.54 g, 2.5 mmol) in acetonitrile (100 ml) and the solution was refluxed gently overnight. After filtration and evaporation under reduced pressure, the residue was partly soluble in ether. This solution was filtered and evaporated to give unreacted starting material (IIa) (0.43 g, 88%). The ether-insoluble solid was crystallised from methanol giving the dialkylated iodide (IIIb) (95 mg, 10%) as an orange-brown solid, m.p. 170° (dec.), soluble in water, alcohols and chloroform. (Found: C, 35.5; H, 3.75; N, 11.5. $C_{11}H_{13}CoIN_3$ calcd.: C, 35.4; H, 3.5; N, 11.3%.)

Cyclopentadienyl(methyl isocyanide)(triphenylphosphine)cyanocobalt(III) iodide, (VIa: L = PPh_3)

The dicyano complex (V: L = PPh_3) (0.88 g, 2 mmol) was refluxed overnight in methyl iodide (100 ml), the solution filtered, and excess methyl iodide removed under reduced pressure. The residue was dissolved in dichloromethane, filtered, and the product (VIa: L = PPh_3) (0.70 g, 60%) precipitated with light petroleum as an orange solid, m.p. 152° (dec.) soluble in water and in polar organic solvents. (Found: C, 54.1; H, 3.8; N, 5.0. $C_{26}H_{23}CoIN_2P$ calcd.: C, 53.8; H, 4.0; N, 4.8%.)

Cyclopentadienyl(methyl isocyanide)(dimethylphenylphosphine)cyanocobalt(III) iodide, (VIa: L = PMe_2Ph)

This product was obtained in analogous manner to the preceding compound, in 52% yield, as an orange solid, m.p. 171° (dec.). (Found: C, 41.9; H, 4.3; N, 5.9. $C_{16}H_{19}CoIN_2P$ calcd.: C, 42.1; H, 4.2; N, 6.1%.)

Cyclopentadienylbis(ethyl isocyanide)(triphenylphosphine)cobalt(III) bis(tetrafluoroborate), (VIIc: L = PPh_3)

Freshly prepared triethyloxonium tetrafluoroborate (1.9 g, 10 mmol) was added to a saturated dichloromethane solution of the dicyano complex (V: L = PPh_3) (0.44 g, 1 mmol) and the mixture refluxed for 6 h. The dark precipitated solid was collected by filtration, washed with dichloromethane and ether and recrystallised from chloroform to give the brown salt of the dication (VIIc: L = PPh_3) (0.34 g, 60%), m.p. 145° (dec.). (Found: C, 51.9; H, 4.2; N, 4.0. $C_{29}H_{30}B_2CoF_8N_2P$ calcd.: C, 52.0; H, 4.5; N, 4.2%.)

Alkylations of potassium cyclopentadienylcarbonyldicyanoferrate(II), (VIII)

(a). Methylation. Methylation carried out in acetonitrile as described by Coffey [5], gave the bis(methyl isocyanide) derivative (Xa) as the iodide, m.p. 220° (dec.). (Found: C, 33.2; H, 2.9; N, 8.1%) in 75% yield. Identical procedures employing tetrahydrofuran or dichloromethane gave the same product in 50 and 15% yield respectively.

Reaction in methanol ($\approx$ 30 ml) was conducted by refluxing the potassium salt (VIII) (0.48 g, 2 mmol) with a large excess of iodomethane (10 ml, 0.16 mol) for four days. Evaporation of the filtered reaction mixture was followed by chromatography employing ether/chloroform mixtures as eluant. A 2/1 mixture eluted the main fraction which on evaporation yielded cyclopentadienyl(methyl isocyanide)carbonylcyanoiron(II), (IXa) (0.18 g, 40%) as an orange-yellow solid, m.p. 240° (dec.). (Found: C, 49.8; H, 4.0; N, 12.8. $C_9H_8FeN_2O$ calcd.: C, 50.0; H, 3.7; N, 13.0%.) Further elution yielded some unreacted potassium salt (VIII).

(b). Benzylation. Repetition of the last procedure employing benzyl bromide (15 ml, 0.126 mol) in place of iodomethane gave cyclopentadienyl(benzyl isocyanide)carbonylcyanoiron(II) (IXd) (40%) as a yellow solid, m.p. 162° (dec.). (Found: C, 61.4; H, 3.9; N, 9.3. $C_{15}H_{12}FeN_2O$ calcd.: C, 61.7; H, 4.1; N, 9.6%.) This compound has previously been described [5] as a brown oil.

(c). Ethylation. The potassium salt (VIII) (0.48 g, 2 mmol) and triethyloxonium tetrafluoroborate (1.9 g, 10 mmol) were refluxed in dichloromethane (50 ml) for 4 h and the precipitated cyclopentadienylbis(ethyl isocyanide)carbonyliron(II) tetrafluoroborate (Xc) (0.52 g, 75%) collected by filtration and washed with ether and light petroleum, m.p. 127° (dec.). (Found: C, 41.9; H, 4.6; N, 7.9. $C_{12}H_{15}BF_4FeN_2O$ calcd.: C, 41.6; H, 4.3; N, 8.1%.) Its spectra corresponded with those (Table 1) of the known [1] iodide.

Alkylation of cyclopentadienyldicarbonylcyanoiron(II), $C_5H_5Fe(CO)_2CN$

This cyanide [12] (0.4 g, 2 mmol) and iodomethane (10 ml, 0.16 mol) were refluxed in acetonitrile (50 ml) for 64 h. The solution was filtered, evaporated to dryness under reduced pressure and the residue chromatographed. Ether/methanol (5/1) eluted unreacted cyanide (0.2 g, 50%) and ether/methanol (1/1) then eluted cyclopentadienyl(methyl isocyanide)dicarbonyliron(II) iodide, $[C_5H_5Fe(CO)_2(CNMe)]I$, (0.27 g, 40%), a yellow solid, m.p. 105° (dec.), soluble in water and polar organic solvents. (Found: C, 31.1; H, 2.1; N, 4.3. $C_9H_8FeINO_2$ calcd.: C, 31.3; H, 2.3; N, 4.1%.) Similar experiments using iodoethane, 2- and 3-bromopropane or benzyl bromide in place of iodomethane failed to result in alkylation in up to 10 days reflux.

Cyclopentadienyltris(methyl isocyanide)iron(II) iodide, $[C_5H_5Fe(CNMe)_3]I$

A dioxane solution (500 ml) of cyclopentadienylbis(methyl isocyanide)-carbonyliron(II) iodide (Xa) (0.72 g, 2 mmol) was irradiated for 18 h in an annular apparatus employing a 500 W medium pressure mercury lamp (Hanovia 509/12) in a water-cooled quartz tube. The resultant solution was filtered and evaporated to dryness under reduced pressure. The oily residue showed infrared peaks at 2164 and 2135 cm^{-1} (CNMe) and at 1750 and 1727 cm^{-1} (bridging CNR and/or CO ?) and apparently reacted on dissolution in dichloromethane. Immediate addition of light petroleum precipitated cyclopentadienyltris(methyl isocyanide)iron(II) iodide (0.37 g, 78% based on available isocyanide), an orange-yellow solid, m.p. 185° (dec.), soluble in water and polar organic solvents. (Found: C, 35.8; H, 4.0; N, 11.1. $C_{11}H_{14}FeIN_2$ calcd.: C, 35.6; H, 3.8; N, 11.3%.)

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