Contribution from the Department of Chemistry,
State University of New York at Albany, Albany, New York 12203, U.S.A.

Transition Metal Complexes of Cyanocyclopentadienides. II. Tricyanocyclopentadienyl and Pentacyanocyclopentadienyl Complexes of Manganese(I), Rhenium(I) and Iron(II)

R.E. Christopher* and L.M. Venanzi**

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The behaviour of the 1,2,3-tricyanocyclopentadienide ('123-TP'), 1,2,4-tricyanocyclopentadienide ('124-TP'), and pentacyanocyclopentadienide ('PP') anions as ligands towards manganese(I), rhenium(I) and iron(II) has been investigated. Spectroscopic and other evidence indicates that the manganese and rhenium complexes $[M(L)(CO)_3]_n$ *(M = Mn and Re; L = 124-TP and PP), and the iron complex* $[Fe(PP)_2 . H_2O]_n$*, have polymeric structures containing N-bonded bridging cyanocyclopentadienyl groups. There is no evidence for the formation of pentahapto (or 'π-bonded') complexes with these ligands.*

Introduction

In Part I[1] we described the behaviour of the mono- and 1,2-dicyanocyclopentadienide anions, $[C_5H_{5-n}(CN)_n]^-$ with n = 1 and 2, as ligands towards manganese(I), rhenium(I) and iron(II). We now report the preparation and characterisation of some manganese(I), rhenium(I) and iron(II) complexes of the 1,2,4-tricyanocyclopentadienide (n = 3, 124-TP') and 1,2,3-tricyanocyclopentadienide (n = 3, '123-TP') anions, and of the percyanocarbon anion pentacyanocyclopentadienide (n = 5, 'PP').

Experimental Section

Starting Materials. Potassium 1,2,3- and 1,2,4-tricyanocyclopentadienides were prepared by cyanation of sodium cyclopentadienide.[2] Silver 1,2,4-tricyanocyclopentadienide was prepared by mixing warm aqueous solutions of the potassium salt and silver nitrate. The resulting precipitate was washed with water and dried *in vacuo.* Tetraethylammonium pentacyanocyclopentadienide was obtained by a cyclisation route from malononitrile.[3] Silver pentacyanocyclopentadienide was prepared from the tetraethylammonium salt by a method similar to that used in the preparation of silver chlorotetracyanocyclopentadienide.[4] Potassium pentacyanocyclopentadienide was supplied by Dr. O.W. Webster of E.I. du Pont de Nemours, Wilmington, Delaware. Bromopentacarbonylmanganese (I) and -rhenium(I), and anhydrous ferrous chloride, were obtained as described in Part I.[1] The methyl cyanide complexes *fac*-$[M(CO)_3(CH_3CN)_3]^+ClO_4^-$ (M = Mn or Re) were prepared by refluxing the appropriate bromopentacarbonyl with silver perchlorate in methyl cyanide, and recrystallised from methyl cyanide/ether.[5] All preparations were done under nitrogen and, for the manganese complexes, with the exclusion of light.

Preparation of Manganese and Rhenium 124-TP and PP Complexes. (a) *Direct precipitation of the complexes.* For the *manganese* complexes, filtered solutions of bromopentacarbonylmanganese(I) (1.00 g, 3.64 mmoles) and either potassium 1,2,4-tricyanocyclopentadienide (0.65 g, 3.64 mmoles) or tetraethylammonium pentacyanocyclopentadienide (1.16 g, 3.64 mmoles) in tetrahydrofuran were mixed and refluxed for 20 h. The resulting bright yellow precipitate was washed with water to remove potassium or tetraethylammonium bromide, and dried *in vacuo.* The yield of $[Mn(L)(CO)_3]_n$ was about 75% for the 124-TP complex, and 35% for the PP complex. For the *rhenium* complexes, filtered tetrahydrofuran solutions of *fac*-$[Re(CO)_3(CH_3CN)_3]^+ClO_4^-$ (0.49 g, 1.00 mmoles) and either potassium 1,2,4-tricyanocyclopentadienide (0.18 g, 1.00 mmoles) or potassium pentacyanocyclopentadienide (0.22 g, 1.00 mmoles) were mixed and refluxed for 20 h. The resulting white precipitate was washed with water, and dried *in vacuo.* The yields of $[Re(L)(CO)_3]_n$ (L = 124-TP or PP) were *ca.* 80 percent.

(b) *Preparation via methyl cyanide camplexes.* For the *manganese* complexes, a mixture of bromopentacarbonylmanganese(I) (1.00 g, 3.6 4mmoles) and either silver 1,2,4-tricyanocyclopentadienide (1.09 g, 4.37 mmoles) or silver pentacyanocyclopentadienide (1.30 g, 4.37 mmoles) was refluxed in methyl cyanide (200

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* Present address: The Radiochemical Centre, Amersham, Bucks, England.

** Present address: Department of Chemistry, University of Delaware, Newark, Delaware 19711, U.S.A.

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(2) O.W. Webster, *J. Amer. Chem. Soc.,* 88, 3046 (1966).

(3) O.W. Webster, *J. Amer. Chem. Soc.,* 88, 4055 (1966), and references therein.

(4) O.W. Webster, *J. Org. Chem.,* 32, 39 (1967).

(5) R.E. Christopher, D. Phil. Thesis, Oxford University, 1971.

mls) for 4 h. The infrared spectrum of the resulting solution showed that complete formation of the methyl cyanide complex *fac*-$[Mn(CO)_3(CH_3CN)_3]^+$, with 124-TP or PP as the anion, had occured. The 124-TP or PP complex was obtained from the filtered solution either (i) by complete removal of solvent at 80°C *in vacuo*, followed by washing with cold methyl cyanide and vacuum drying, or (ii) by evaporating the solution to a viscous oil (infrared spectroscopy showed that this contained coordinated methyl cyanide), and then diluting with tetrahydrofuran or 1,2-dimethoxyethane and refluxing for 1 h, thereby precipitating the complex. The average yield was 70-80%. For the *rhenium* complexes, a mixture of bromopentacarbonylrhenium(I) (0.50 g, 1.23 mmoles) and silver pentacyanocyclopentadienide (0.44 g, 1.48 mmoles) was refluxed in 50 mls of methyl cyanide for 18 h. The infrared spectrum of the resulting solution indicated that complete conversion to *fac*-$[Re(CO)_3(CH_3CN)_3]^+$ had occured, with PP as the counter-anion. The filtered solution was evaporated at 80°C *in vacuo* to give a pale yellow solid; infrared spectroscopy showed that this contained coordinated methyl cyanide. The solid was dissolved in the minimum of tetrahydrofuran, and the filtered solution diluted with ethanol. The resulting precipitate was dried *in vacuo* (yield 60%).

Attempted Preparation of Manganese 123-TP Complexes. On refluxing a mixture of potassium 1,2,3-tricyanocyclopentadienide (0.50 g, 2.78 mmoles) and bromopentacarbonylmanganese(I) (0.76 g, 2.79 mmoles) in tetrahydrofuran (50 mls) for 4 days, we obtained a precipitate of potassium bromide and a yellow solution with ν(CO) at 2062, 2054 and 1971 cm^{-1}. Evaporation of the solution to 4 mls precipitated a yellow solid. This was redissolved in the minimum of hot tetrahydrofuran and the solution kept under nitrogen for 4 days. Yellow crystals were obtained, with ν(CO) at 2062 and 1969, and ν(CN) at 2245 cm^{-1} (in tetrahydrofuran), and a mull spectrum (1900-700 cm^{-1}) very similar to that of potassium 1,2,3-tricyanocyclopentadienide. In view of the discussion below and in Part I,[1] it is likely that this complex contained N-bonded 123-TP groups; however, no reasonable formulation can be proposed on the basis of the analytical results obtained (C 49.1, H 4.8, N 12.0%). A second complex, with ν(CO) at 2054 and 1971 and ν(CN) at 2246 cm^{-1} in tetrahydrofuran, was obtained by evaporating the concentrated reaction solution (after precipitation of the first complex) to dryness. As attempts to recrystallise this product were unsuccessful, it was not further studied.

Preparation of the Iron Complexes. The iron PP complexes were prepared by methods similar to those described by Webster.[3] All operations were performed in a nitrogen-filled glove-bag, using deoxygenated solvents. Silver pentacyanocyclopentadienide (0.94 g, 3.15 mmoles) and anhydrous ferrous chloride (0.20 g, 1.57 mmoles) were added to 10 mls of methyl cyanide. The suspension was stirred at room temperature for 30 mins., and then filtered from the precipitated silver chloride. The pale yellow solution was evaporated to 2 mls and allowed to stand for 1 h. The white crystals which formed were washed with cold methyl cyanide and dried *in vacuo* at room temperature (20 h). This product contained coordinated methyl cyanide (see discussion below). On heating for 20 h at 110°C *in vacuo*, a pale yellow-green product, $[Fe(PP)_2 . H_2O]_n$, was obtained. Attempts to prepare the 124-TP analogues of these PP complexes were not successful.

Elemental analyses and physical measurements were performed as described in Part I.[1]

Results and Discussion

Analytical data for the complexes prepared are given in Table I, and infrared spectra are summarised in Table II and III.

Manganese and Rhenium Complexes. The manganese and rhenium 124-TP and PP complexes were obtained as powdery precipitates, and further purification was nôt possible as the complexes are insoluble in all solvents except those with which they react. Although in some cases the analytical data are not completely satisfactory, the analytical compositions $[M(L)(CO)_3]$ are indicated for the manganese and rhenium 124-TP and PP complexes.

Infrared Spectra 2500-700 cm^{-1}. The main spectral change which accompanies coordination of the 124-TP anion is a shift of ν(CN), by *ca.* 40 cm^{-1}, to higher frequencies (see Table II). Otherwise the spectra of potassium 1,2,4-tricyanocyclopentadienide and its complexes are very similar in this region, apart from some differences in band splittings. In particular, the intense bands at 812 and 830 cm^{-1} in the potassium salt assigned to C-H out-of-plane deformation modes (*c.f.* 710, 740 and 750 cm^{-1}, respectively, for the $[C_5H_5]^-$, MP and DP anions[1]), do not shift to higher frequencies in the complexes. In view of the discussion in reference 1, these results indicate that the 124-TP ligands are bonded *via* their nitrilic nitro-

Table I.

	Analyses [%found(%reqd.)]			
Complex	C	H	N	Metal
$[Mn(124\text{-}TP)(CO)_3]_n$	47.0(47.3)	0.9(0.7)	14.6(15.1)	20.3(19.7)
$[Re(124\text{-}TP)(CO)_3]_n$	33.1(32.2)	1.0(0.5)	9.4(10.2)	
$[Mn(PP)(CO)_3]_n$[a]	46.7(47.4)	0.3(0.0)	20.8(21.3)	16.4(16.7)
$[Re(PP)(CO)_3]_n$	34.7(33.9)	0.6(0.0)	15.4(15.2)	
$[Fe(PP)_2 . H_2O]_n$	53.4(52.9)	0.5(0.4)	30.6(30.8)	12.0(12.3)

[a] %0: found 14.2, required 14.6%.

Table II. Infrared Spectral Data (2500-700 cm^{-1}) for the Manganese and Rhenium 124-TP and PP Complexes [a].

[Mn(124-TP)(CO)$_3$]$_n$	[Re(124-TP)(CO)$_3$]$_n$	K[124-TP]	[Mn(PP)(CO)$_3$]$_n$	[Re(PP)(CO)$_3$]$_n$	K[PP]
2240vs	2236vs	2238m [b]			
		2202vs [b]	2260s	2251s	2246s [c]
		2196sh [b]	2225vs	2230vs	2231sh [c]
		2148m [b]			2222vs [c]
2057vs	2046vs		2069vs	2056vs	
1968vs	1937vs		1977vs	1951vs	
		1610m			1627m
1495s	1493vs	1495vs	1466m	1463m	1470vs
1443s	1440s	1445vs		1429sh	1424w
1396w	1397sh		1381br,w	1385m	1384s
1334m	1331m	1339s		1364sh	1370sh
1170m	1172m	1173s		1134vw	1118m
1131s	1135s	1140m	879vw	878w	880vw
		1128m			814w
		1115m			
1033vw	1044br,w	1025w			
968m	967m	962m			
821m	824m	830s			
		812vs			
750vw		745vw			

s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [a] KBr discs 2500-2300 and 1800-700 cm^{-1}, nujol mulls elsewhere. [b] In tetrahydrofuran solution these bands collapse to a single band at 2200 cm^{-1}. [c] 2218 and 2238(sh) cm^{-1} in tetrahydrofuran.

gen atoms in these complexes. The absence of infrared bands at *ca.* 2200 cm^{-1} in the 124-TP complexes means that all three nitrile groups of the ligand are coordinated to metal atoms. As 124-TP cannot act as a 'chelate', polymeric structures with bridging ligands are proposed for the complexes. These structures, based on the repeating unit shown in the Figure, are related to those of the 1,2-dicyanocyclopentadienyl complex anions [M$_2$(DP)$_3$(CO)$_6$]$^-$;[1] addition of a third nitrile group to the DP ring allows each ligand to bridge three metal atoms. The dimeric structure of the DP complexes is thereby extended to a polymeric array in the 124-TP complexes. The polymeric structures also account for the insolubility of the complexes in all solvents other than those in which they solvolyse.

Table III. Far Infrared Spectral Data for the 124-TP Complexes [a].

[Mn(124-TP)(CO)$_3$]$_n$	[Re(124-TP)(CO)$_3$]$_n$	K[124-TP]
678s		662m
659m	660w	658m
	645m	
627s	625m	620m
616s	613m	613vs
581vw	586vw	568m
534m	536m	542vs
497s	498m	504s
485sh	475m	489vs
454m		
385vw		
		218m
		174vs
		147vs
		90s

s = strong, m = medium, w = weak, v = very, sh = shoulder. [a] Nujol mulls, 700-70 cm^{-1}.

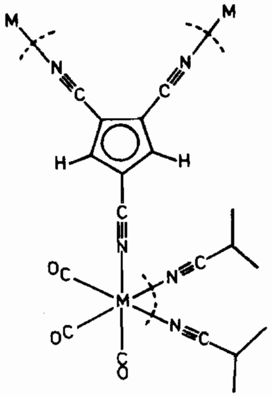

Figure 1. Structure of the manganese and rhenium complexes [M(124-TP)(CO)$_3$]$_n$ (the repeating unit appears inside the broken lines).

The manganese and rhenium PP complexes appear to have structures similar to those of the 124-TP complexes, but with each PP ligand having two non-bonded nitrile groups in addition to the three N-bonded groups. Thus the PP complexes have two strong infrared bands in the ν(CN) region, at *ca.* 2225 cm^{-1} due to free nitrile groups (*c.f.* 2222 cm^{-1} in K[PP]), and at *ca.* 2255 cm^{-1} arising from N-bonded nitrile grousp. Furthermore the spectra of the PP complexes in the 1500-700 cm^{-1} region are very similar to that of K[PP] itself. If the PP anion were *pentahapto* bonded (in the nomenclature of Cotton[6]), a marked increase in the complexity of the infrared spectrum in this region would be expected, because of the lowered symmetry of the PP moiety (compare pentahapto coordination of the [C$_5$H$_5$]$^-$ anion[7]). Although N-coordination must also result in a formal lowering of the PP symmetry, it is unlikely to give marked spectral changes for the vibrations mainly localised on the ring carbon atoms. By analogy with the 124-TP complexes, it is assumed that the coordinated nitrile groups in the PP complexes are at the 1-, 2- and

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(6) F.A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968).

(7) D.M. Adams, « Metal-Ligand and Related Vibrations », Arnold, 1967.

4-positions. This is supported by the observation that the 123-TP anion does not form highly insoluble polymeric complexes under the conditions used in the preparation of the 124-TP and PP complexes (see experimental section).

Far infrared spectra 700-70 cm^{-1} The 218 cm^{-1} band of potassium 1,2,4-tricyanocyclopentadienide (Table III) may be assigned to a CN out-of-plane deformation as the corresponding modes in the 1,2-dicyanocyclopentadienide salts occur at about 220 cm^{-1}.[1] Coordination of the 124-TP anion appears to be accompanied either by a large frequency shift or by a marked intensity reduction of the 218 cm^{-1} band, as no absorptions were observed in the 220 cm^{-1} region in the complexes. This behaviour is in accordance with N-bonding of the 124-TP anion, as similar spectral changes accompany N-coordination (but not pentahapto coordination) of 1,2-dicyanocyclopentadienide and benzonitrile.[1]

We were unable to convert the complexes into products of pentahapto structure by refluxing their tetrahydrofuran or diglyme suspensions with manganese or rhenium bromopentacarbonyls (*c.f.* the behaviour of the manganese 1,2-dicyanocyclopentadienyl complexes[1]). The inertness of the polymeric complexes may result from their very low solubilities in these solvents. Spectroscopic and conductivity studies showed that on refluxing the complexes in methyl cyanide, dissociation of the cyanocyclopentadienide ligand occured with formation of *fac*-$[M(CO)_3(CH_3CN)_3]^+$ (M = Mn or Re).[5] As described in the experimental section, the polymeric complexes $[M(L)(CO)_3]_n$ (L = 124-TP or PP) can be recovered from these solutions.

Iron Complexes. Webster[3] obtained a complex $[Fe(PP)_2 . H_2O]$, which he termed 'decacyanoferrocene', by allowing anhydrous ferrous chloride to react with silver pentacyanocyclopentadienide in methyl cyanide. We have found that the white solid which crystallises from the cold reaction solution[3] contains coordinated methyl cyanide (after vacuum drying at room temperature). Thus the infrared spectrum (4000 -1400 cm^{-1}) showed bands at 3009, 2945, 2316 and 2287 cm^{-1} from methyl cyanide, at 3400 and 1650 from water, and at 2250, 2223, 1474 and 1461 cm^{-1} from PP. The methyl cyanide ν(CN) bands are 20-30 cm^{-1} higher than in liquid methyl cyanide, indicating N-coordination of the methyl cyanide.[8] Furthermore, the infrared spectrum in the PP ν(CN) region was similar to that of the manganese and rhenium complexes, indicating that the complex contained N-bonded PP groups. On drying at 110°C *in vacuo*, a pale yellow-green product, of composition $[Fe(PP)_2 , H_2O]$, was obtained; this appears to be identical to the complex obtained by Webster.[3] The infrared spectrum confirmed the absence of methyl cyanide. Bands were observed at 2251, 2219 and 1467 cm^{-1} from PP, and at 3360 and 1634 cm^{-1} from water. As ν(CN) bands characteristic of both coordinated (2251 cm^{-1}) and uncoordinated (2219 cm^{-1}) nitrile groups were observed, then, by analogy with the manganese and rhenium PP complexes, it is proposed that in this complex each PP group bridges three iron atoms, giving a polymeric structure in which the iron is in an approximately octahedral environment. The proposed structure is similar to that of the iron tricyanomethanide (TCM) complex $[Fe(TCM)_2 . H_2O]_n$.[9] The effective magnetic moment of the PP complex, 5.54 B.M. at room temperature is similar to that of the TCM complex, 5.17 B.M.[9a] The conductivity of $[Fe(PP)_2 . H_2O]_n$ in methyl cyanide is *ca.* 270 mhos per gram-atom of iron, within the range 220-280 mhos normally found for a 1:2 electrolyte in this solvent.[10] Thus complete dissociation of the ligand occurs on dissolving the complex in methyl cyanide.

Attempts to prepare iron 124-TP complexes gave products of uncertain composition which were not further investigated.

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(9) (a) J.H. Enemark and R.H. Holm, *Inorg. Chem.*, 3, 1516 (1964). (b) W.H. Baddley, *Inorg. Chim. Acta Revs.*, 2, 7 (1968).

(10) R.A. Walton, *Quart. Revs.*, *19*, 126 (1965).