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Transition Metal Complexes of Cyanocyclopentadienides. I. Monocyanocyclopentadienyl and 1,2-Dicyanocyclopentadienyl Complexes of Manganese(I), Rhenium(I) and Iron(II)

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Manganese(I), rhenium(I) and iron(II) complexes of the monocyanocyclopentadienyl ('MP') and 1,2-dicyanocyclopentadienyl ('DP') anions have been prepared and characterised. Spectroscopic and other evidence indicates that the complexes formulated $[M(L)(CO)_3]$ *(M=Mn, L=MP and DP; M=Re, L=MP) and* $[Fe(MP)_2]$ *have pentahapto (or 'π-bonded') structures. In the complexes of type* $[Me_4N][M_2(DP)_3(CO)_6]$ *(M=Mn and Re), however, the dimeric anions contain N-bonded bridging ligands. The interconversion of the manganese N-bonded and pentahapto complexes has been studied by infrared spectroscopy.*

Introduction

One area of organo-transition metal chemistry which is receiving increasing attention concerns the behaviour as ligands of unsaturated hydrocarbons substituted with highly electronegative groups. Many fluorocarbons,[1] and a few cyanocarbons[2] have been investigated. Both types of ligand have yielded interesting results, in terms of the complexes isolated and their properties. Baddley[2] has summarised the results obtained with the 'percyanocarbons' tricyanomethanide, tetracyanoethylene and dicyanoacetylene. All known complexes of the tricyanomethanide anion contain N-bonded ligands. With the exclusion of charge-transfer adducts and complexes in which the ligand is polymerised, all but one[2b] of the tetracyano-ethylene and dicyanoacetylene complexes known contain centrally π-bonded (or 'dihapto' in the nomenclature of Cotton[3]) cyanocarbon ligands.

We have investigated the behaviour of the cyanocyclopentadienide anions, of general type $[C_5H_{5-n}(CN)_n]^-$ (where n=1,2,3 and 5), as ligands towards manganese(I), rhenium(I) and iron(II). We report here the results obtained with the monocyanocyclopentadienide (n=1, 'MP'), and 1,2-dicyanocyclopentadienide (n=2, 'DP') anions.

Experimental Section

Starting Materials. Potassium monocyanocyclopentadienide and tetramethylammonium 1,2-dicyanocyclopentadienide were prepared by the stepwise cyanation of sodium cyclopentadienide.[4] Bromopentacarbonylmanganese(I) and rhenium(I) were prepared by bromination of the dimetal decacarbonyls,[5] or purchased from Pressure Chemicals. Anhydrous ferrous chloride was obtained from Alpha Inorganics. All preparations were done in a nitrogen atmosphere and, for the manganese complexes, with the exclusion of light.

Preparation of $[M(MP)(CO)_3]$ (M=Mn and Re). These complexes were prepared by methods similar to those described by Nesmeyanov et al.,[6] and recrystallised from cyclohexane. Melting points were in good agreement with literature values.[6]

Preparation of $[Fe(MP)_2]$. Potassium monocyanocyclopentadienide (1.00 g, 7.74 mmoles) was refluxed with a suspension of anhydrous ferrous chloride (0.61 g, 4.84 mmoles) in tetrahydrofuran (50 mls) for 24 h. The dark solid obtained on evaporating the filtered reaction solution to dryness was extracted with 100 mls of hot benzene, and the resulting solution taken to dryness. The product was purified by recrystallisation from benzene (15 mls), or cyclohexane (900 mls), or by the slow addition of cyclohexane to a saturated benzene solution of the complex. The complex melted at 168°C, with decomposition (lit.[7] 166-167°C).

Preparation of $[Mn(DP)(CO)_3]$ *and* $[Me_4N][Mn_2(DP)_3(CO)_6]$. An equimolar mixture of bromopentacarbonylmanganese(I) (2.00 g, 7.28 mmoles) and tetramethylammonium 1,2-dicyanocyclopentadienide (1.38 g, 7.28 mmoles) in tetrahydrofuran (150 mls) was refluxed for 11 h. After removing the precipitated potassium bromide, the yellow solution was concentrated to 10 mls, and then diluted with 100 mls of ether. The precipitated $[Me_4N][Mn_2(DP)_3(CO)_6]$ was collected, washed with water and hexane, and recrystallised several times from tetrahydrofuran or aceto-

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ne (10 mls) by the addition of ether (100 mls). [$Mn(DP)(CO)_3$] was obtained from the diluted reaction solution (after precipitation of the dimeric complex) by evaporating to dryness, washing with water and then hexane, and recrystallising the resulting solid from ethanol (2 mls).

Preparation of [Me_4N][$Re_2(DP)_3(CO)_6$]. A mixture of bromopentacarbonylrhenium(I) (1.00 g, 2.46 mmoles) and tetramethylammonium 1,2-dicyanocyclopentadienide (0.47 g, 2.46 mmoles) in diglyme (30 mls) was refluxed for 22 h. Infrared spectroscopy in the carbonyl stretching region showed that the resulting solution contained the dimeric complex (absorptions at 2033 and 1935 cm^{-1}), and a second product with a strong band at 2022 cm^{-1}. The mixture of products was precipitated from the reaction mixture by the addition of hexane, and the dimeric complex separated from the second product by briefly boiling the mixture with ethanol (20 mls). The dimeric complex remained in suspension and was collected and recrystallised from tetrahydrofuran (3 mls) by the addition of 50 mls of ethanol. Attempts to obtain the second product in a pure form were not successful. Since refluxing for shorter periods gave a higher proportion of this product, relative to that of the dimeric complex, and also gave a lower yield of precipitated tetramethylammonium bromide, it is very unlikely that the second product is a pentahapto complex [$Re(DP)(CO)_3$]; presumably it is a bromide-containing precursor of the dimeric complex.

Analyses. Elemental analyses of the complexes were performed by Instranal Laboratories, Rensselaer, N.Y. (carbon, hydrogen and nitrogen), and by Galbraith Laboratories, Knoxville, Tenn. (carbon, hydrogen, nitrogen and oxygen). Manganese and iron were determined in N,N-dimethylformamide solution by atomic absorption spectroscopy, at 280 nm. and 248 nm., respectively, using a Perkin-Elmer model 303 instrument. Purified cyclopentadienyltricarbonylmanganese(I) and ferrocene were used as primary standards.

Spectroscopic Methods. Infrared Spectra in the 3200-700 cm^{-1} region were recorded on a Beckman IR 12 instrument, calibrated with indene, carbon monoxide and carbon dioxide,[8] and with carbon tetrachloride solutions of chromium and molybdenum hexacarbonyls.[9] Prominent features in the 3200-700 cm^{-1} region are considered accurate to 1-2 cm^{-1}, and to 0.3-0.5 cm^{-1} for solution spectra in the carbonyl stretching region. *Far infrared spectra* in the 800-70 cm^{-1} region were recorded on a Beckman IR 11 spectrometer ,calibrated with carbon dioxide[8] and water vapour.[10] The positions of intense bands in this region are considered accurate to 1 cm^{-1}. *Visible and ultraviolet spectra* (45,000-10,000 cm^{-1}) were recorded with a Cary 14 instrument. *Proton magnetic resonance spectra* were recorded using a 100 MHz Varian HA-100 instrument. Saturated solutions in perdeuteromethyl cyanide (containing 5% tetramethylsilane) were made up in an inert atmosphere. *Mass spectra* were recorded on an AEI MS-902 instrument using an ionising voltage of 70 eV. *Conductivities* of 10^{-3} *M* solutions in methyl cyanide were measured using a conventional conductivity cell, equipped with platinised platinum electrodes, and a Wayne Kerr bridge. The cell constant was obtained using standard aqueous solutions of potassium chloride.[11]

Results and Discussion

Analytical and other data for the monocyanocyclopentadienyl ('MP') and 1,2-dicyanocyclopentadienyl ('DP') complexes are given in Table I. Brief reports on the preparation of the MP complexes have previously appeared. Thus, Nesmeyanov et al.[6] obtained [$Mn(MP)(CO)_3$] and [$Re(MP)(CO)_3$] from potassium monocyanocyclopentadienide and the appropriate metal chloropentacarbonyl. The iron(II) complex, [$Fe(MP)_2$] ('1,1'-dicyanoferrocene'), has previously been prepared by the cyanation of ferrocene,[12] and by other indirect methods,[7,12a] but not directly from a monocyanocyclopentadienide salt. We have characterised the MP and DP complexes shown in Table I by spectroscopic and other methods. The MP complexes, which are shown to have expected pentahapto (or 'π-bonded') structures, serve as model compounds for the interpretation of the spectra of the DP complexes. We have concluded that one of the DP complexes has a pentahapto structure, while the other two contain dimeric anions in which the DP ligands are attached to the metal *via* their nitrilic nitrogen atoms.

Monocyanocyclopentadienyl Complexes. The MP complexes are diamagnetic crystalline solids which are soluble in most organic solvents and which give non-conducting solutions in methyl cyanide. Spectroscopic studies indicate that in all cases the metal-MP bonding mode is of the "pentahapto" type.

Infrared Spectra 3200-700 cm^{-1}. The spectra of the manganese and rhenium complexes in carbon tetrachloride and carbon disulphide solutions showed only minor differences from the solid state spectra listed in Table II, except in the carbonyl stretching region; spectra in the latter region were obtained for cyclohexane solutions. The main spectral changes which accompany coordination of the MP anion in these complexes are: (a) the disappearance of the intense bands at about 740 cm^{-1} and the observation of new bands in the 850 cm^{-1} region. The *ca.* 740 cm^{-1} bands of potassium monocyanocyclopentadienide may be assigned to C-H out-of-plane deformation modes (denoted "γ(CH)"), related to the umbrella mode, ν_4 (710 cm^{-1}), of $[C_5H_5]^-$;[13] (b) the shift of ν(CN), by about 40 cm^{-1}, to higher frequencies in the complexes; and (c) smaller shifts of the bands in the

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Table I.

Complex	Colour	Yield(%)	λ_M [a]	M [b]	Analyses [% found (% reqd.)]				
					C	H	N	O	Metal
$[Mn(MP)(CO)_3]$	yellow	58	0	229(229)	47.1(47.2)	1.8(1.8)	6.1(6.1)	20.3(20.9)	24.2(24.0)
$[Re(MP)(CO)_3]$	white	56	0	361 [c](361)	30.1(30.0)	1.2(1.1)	3.8(3.9)	13.3(13.3)	
$[Fe(MP)_2]$	orange	54	0	236(236)	61.1(61.1)	3.5(3.4)	12.0(11.9)		24.1(23.7)
$[Mn(DP)(CO)_3]$ [d]	yellow-orange	14	0	254(254)	47.2(47.3)	1.1(1.2)	11.0(11.0)	19.3(19.0)	21.4(21.6)
$[Me_4N][Mn_2(DP)_3(CO)_6]$ [e]	yellow	23	152	—	52.8(53.4)	3.1(3.0)	14.1(14.1)	13.1(13.8)	16.4(15.8)
$[Me_4N][Re_2(DP)_3(CO)_6]$	white	20	125	—	39.1(38.8)	2.3(2.2)	10.1(10.2)		

[a] Molar conductivity ($ohm^{-1}cm^2mole^{-1}$), for *ca.* $10^{-3}M$ solutions in methyl cyanide at 25°C. [b] Molecular weight from mass spectral data, with calculated value in parentheses. [c] ±1. [d] nmr(ring protons): 3.38d,4.05t (J=4.0), c.f. $[Me_4N][DP]$ 3.63d,4.14t (J=3.8). [e] nmr(ring protons): 4.26d,4.94t, on γ scale.

1500-1200 cm^{-1} region (attributed to ν(C-CN) and ν(CC) [ring] modes), and in the C-H stretching region.

At first sight, the coordination shifts of the C-N stretching mode might be interpreted in terms of N-bonding of the MP anion in these complexes, as similar shifts generally occur on N-coordination of an organic nitrile to a transition metal,[14] due mainly to an increase in the C-N stretching force constant.[15] However, N-coordination is unlikely to be also accompanied by large frequency shifts of the γ(CH) modes. For example, in the N-bonded benzonitrile complexes *cis*-$[Re(CO)_3(PhCN)_2X]$ (X = Cl, Br) the C-N stretch occurs 40 cm^{-1} higher than in liquid benzonitrile, but only slight coordination shifts (12 cm^{-1} or less) are observed for all other benzonitrile modes,[16] including those assigned to γ(CH) vibrations.[17]

Pentahapto coordination of the MP anion, however, *is* expected to result in large increases in the γ(CH) frequencies as similar shifts occur on pentahapto coordination of $[C_5H_5]^-$;[18] these are probably due largely to kinematic coupling of the γ(CH) and metal-ring skeletal modes.[19] In view of these expectations, and the other results discussed below, we conclude that the MP complexes contain pentahapto coordinated ligands and that the observed coordination shifts of ν(CN) are due to other effects. Kinematic coupling of ν(CN) and metal-ring skeletal modes is not possible in a penta-hapto complex. Furthermore, it is unlikely that coupling of the ν(CN) and ν(CO) modes *via* their interaction force constants would produce a shift as large as 40 cm^{-1} in ν(CN), and in any case this could not explain the ν(CN) shift in the ferrocene derivative. It therefore seems likely that the observed shift of ν(CN) on coordination of MP is the result of an increased C-N stretching force constant. This may be rationalised in terms of the results of Huckel calculations on the pentacyanocyclopentadienide anion.[16] These calculations indicate that the interaction of ring and nitrile π orbitals decreases the C-N bond order. Similar effects are expected to occur in MP and the other cyanocyclopentadienides, and may account for the low ν(CN) frequencies observed for the ligand salts. On pentahapto coordination of the ligand, however, the overlap between ring $p\pi$ and metal orbitals may reduce the extent of the ring-nitrile π-interaction, thus increasing the C-N bond order and hence the stretching force constant. In cyclohexane solution, three intense carbonyl stretching bands are observed for the manganese and rhenium complexes. This indicates that the method of local symmetry (which appears to account for the vibrational spectrum of cyclopentadienyltricarbonylmanganese(I)[20]) is an inadequate approximation for these complexes, as a tricarbonyl group with C_{3v} local symmetry should give only two carbonyl stretches (a_1+e). Similar effects have been observed for other ring-substituted cyclopentadienyltricarbonylmanganese and rhenium derivatives.[21]

Far infrared spectra 700-70 cm^{-1}. The spectra of carbon tetrachloride and carbon disulphide solutions of the manganese and rhenium complexes showed only slight differences from the mull spectra listed in Table III. The discussion which follows considers the 700-250 cm^{-1} region only, as the spectrum of potassium monocyanocyclopentadienide was not obtained below 250 cm^{-1}. In the spectrum of 1,1′-dicyanoferrocene, intense bands appear at 472 and 456 cm^{-1} (the latter band having a shoulder at *ca.* 450 cm^{-1}) which are not observed in the spectrum of potassium monocyanocyclopentadienide. These features may be assigned to the asymmetric ring tilting and asymmetric ring-metal stretching modes, respectively, of a "sandwich" compound. The corresponding modes in ferrocene occur at 490 and 477 cm^{-1}.[19] In addition, the 356 cm^{-1} band may be the symmetric ring tilt or symmetric ring-metal stretch. These latter modes are infrared inactive in ferrocene (they appear in the Raman at 390 and 301 cm^{-1} respectively[19]), but should become infrared active in the ring substituted derivative. In the spectra of the manganese and rhenium complexes, the region 700-450 cm^{-1} is crowded and contains metal-carbon stretching and metal-carbon-oxygen deformation modes of the tricarbonyl group, as well as internal ligand modes. Below 450 cm^{-1} the manganese complex has bands at 365 and 360 cm^{-1} (358 cm^{-1} in solution), and at 344 cm^{-1}, which are not observed in the spectrum of potassium monocyanocyclopentadienide. These features may be assigned respectively to ring tilting

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and ring-metal stretching modes. The corresponding modes in cyclopentadienyltricarbonylmanganese(I) are at 372 and 354 cm^{-1}.[22] In the rhenium complex, bands assigned to the ring tilting and ring-metal stretching modes appear at 341 and 312 cm^{-1}. Thus the far infrared spectra of the MP complexes may be readily interpreted in terms of the proposed pentahapto structures. If, however, the complexes contained N-bonded MP groups, the corresponding metal-ligand vibrations (ν(MN) and δ(MNC)) would be expected to occur at much lower frequencies than observed here. Thus in the N-bonded benzonitrile complexes *cis*- and *trans*-[$MX_2(PhCN)_2$] (M = Pd, Pt; X = Cl, Br), the ν(MN) modes have been assigned in the 110-90 cm^{-1} region.[23] Furthermore, the complexes *cis*-[$Re(CO)_3(PhCN)_2X$] (X = Cl, Br) show no infrared features above 100 cm^{-1} which may be assigned to ν(MN) modes.[16]

Mass Spectra. The most intense peaks in the mass spectra of the MP complexes correspond to the bare metal ions. The molecular ion peak was observed with medium or low intensity for all the complexes. The main fragments from [$Fe(MP)_2$] corresponded to metal-containing ions with one or two MP rings in various stages of fragmentation. With the manganese and rhenium complexes, initial stepwise loss of the carbonyl groups occured and no ions containing both carbonyl groups and ring fragments were observed. The fragmentation patterns of the complexes are similar to those observed from other ring-substituted derivatives of ferrocene[24] and cyclopentadienyltricarbonylmanganese(I).[25]

Electronic Spectra. The *ca.* 23,000 and 31,000 cm^{-1} bands of ferrocene show marked intensity enhancement in the 1,1′-dicyano- derivative (see Table IV). Whereas the former band shows no significant frequency shift, the *ca.* 31,000 cm^{-1} band occurs 1,200 cm^{-1} lower in the dicyanoferrocene. The intensity enhancement is in accordance with the assignment of these bands to electronic transitions which are orbitally forbidden (and largely *d-d*, but with appreciable charge transfer character) in ferrocene, but which become orbitally allowed in ring-substituted derivatives with molecular symmetry lower than D_{5d} (or D_{5h}).[26] The much greater shift of the *ca.* 31,000 cm^{-1} band on ring substitution, compared with that of the *ca.* 23,000 cm^{-1} band, can be attributed to the more "d-d" like nature of the latter band.[26] In the ultraviolet region, cyano-substitution of the ferrocene rings is accompanied by the appearance of an intense band at 40,200 cm^{-1}. Ferrocene has weak shoulders in this region, assigned to symmetry forbidden bands,[26,27] which become formally allowed in ring-substituted ferrocenes. Potassium monocyanocyclopentadienide itself has a band in the ultraviolet at 37,900 cm^{-1} (ε = 16,000—in water[4]) which, on the basis of its position and intensity, may be characterised as a π-π* transition.[28] Pentahapto coordination of the MP anion results in the "loss" of this band (either by a large shift to higher frequency, or by a reduction in its intensity) as no absorption band is observed in the 38,000 cm^{-1} region of [$Mn(MP)(CO)_3$].

1,2-Dicyanocyclopentadienyl Complexes. The manganese and rhenium DP complexes listed in Table I were obtained by the prolonged reflux of the metal bromopentacarbonyl and a 1,2-dicyanocyclopentadienide salt in tetrahydrofuran or diglyme. Complexes of analytical composition [$Mn(DP)(CO)_3$] and [Me_4N][$Mn_2(DP)_3(CO)_6$] were obtained from the manganese reaction. Although infrared spectroscopy indicated that the rhenium reaction yielded at least two products, only one complex, of composition [Me_4N][$Re_2(DP)_3(CO)_6$], was isolated. Whereas [$Mn(DP)(CO)_3$] gave a non-conducting solution in methyl cyanide, the complexes [Me_4N][$M_2(DP)_3(CO)_6$] had molar conductivities (see Table I) in the range 120-160 mhos, as expected for 1:1 electrolytes in methyl cyanide.[14a] The analytical data and conductivity measurements, with the spectroscopic results discussed below, indicate that the metal-DP linkage in [$Mn(DP)(CO)_3$] is of the pentahapto type, as in the analogous MP complex. The [$M_2(DP)_3(CO)_6$]$^-$ anions, however, contain N-bonded bridging ligands and are assigned the structures shown in the Figure.

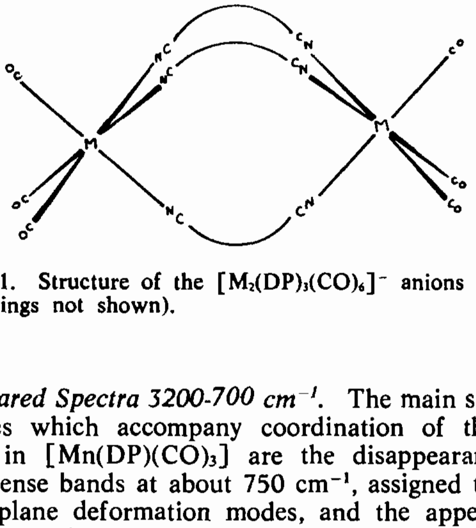

Figure 1. Structure of the [$M_2(DP)_3(CO)_6$]$^-$ anions (5-membered rings not shown).

Infrared Spectra 3200-700 cm^{-1}. The main spectral changes which accompany coordination of the DP anion in [$Mn(DP)(CO)_3$] are the disappearance of the intense bands at about 750 cm^{-1}, assigned to C-H out-of-plane deformation modes, and the appearance of new bands in the 840 cm^{-1} region (see Table II). In addition, there are band shifts and intensity changes in the 1500-900 cm^{-1} region, and the ν(CH) and ν(CN) modes shift to higher wavenumbers in the complex. These spectral changes are very similar to those observed on coordination of MP, and the complex [$Mn(DP)(CO)_3$] is therefore assigned an analogous pantahapto structure. As with the corresponding MP complexes, the coordination shift of ν(CN) presumably arises from the effect of pentahapto coordination on the ring-nitrile π-interactions. In the carbonyl stretching region, three intense absorptions are observed for [$Mn(DP)(CO)_3$] in cyclohexane solution; the two lowest frequency bands (which may be considered to be derived from the e-mode of a

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Table II. Infrared Spectral Data (2500-700 cm^{-1}) for the MP and DP Complexes (KBr Discs).

$[Mn(MP)(CO)_3]$	$[Re(MP)(CO)_3]$	$[Fe(MP)_2]$	K[MP]	$[Mn(DP)(CO)_3]$	$[Me_4N][Mn_2(DP)_3(CO)_6]$	$[Me_4N][Re_2(DP)_3(CO)_6]$	Na[DP]
2237s	2236s	2227vs	2197vs	2242s	2232vs	2227vs	2216vs
			2180vs				
2040.6vs^a	2042.1vs^a						2197vs
1967.4vs^a	1958.4vs^a			2187vw	2180sh	2174sh	2180s
1962.8vs^a	1954.0vs^a			2051.4vs^a	2050.3vs^b	2036.5vs^b	
1456m	1448w	1445w	1461m	1988.9vs^a	1962.2vs^b	1937.3vs^b	
1418w	1411w	1441w	1451s	1976.6vs^a			1582m
1384w		1396w	1370w	1451w	1480s	1480vs	1474m
1376m	1365m	1380w	1349s		1438m	1437s	1438s
1326vw	1313w		1334w		1396w*	1404vw*	
1247m	1242m	1233m	1265m	1383m	1360vs	1357vs	1361vs
1066m	1064m	1053w	1059sh	1273m	1297m	1298s	1290m
1045m	1042m	1048m	1948s	1204m	1222m	1224s	1214m
1038m	1032m	1033m	1034s		1128s	1129s	1116m
916m	910m	914m	922s	1098w	1090w	1089vw	1086w
868w	854w	863m		1043m	1058s	1059s	1049s
	844w	856sh		1013w	1027sh	1034m	1027w
841s	829s	828s	824s			1025m	1015w
		819sh		942w	943w*	945m*	
			743sh	910vw	878w	885w	892w
			734vs	860m		859w	865w
				843m	807w	816w	807vw
					732vs	740vs	759vs
					725sh	733sh	750vs

s = strong, m = medium, w = weak, v = very, sh = shoulder. Bands due to the tetramethylammonium cation in the dimeric complex are marked *. ^{a} Cyclohexane solution. ^{b} Methyl cyanide solution.

C_{3v} tricarbonyl group) are separated by about 10 cm^{-1}, compared with *ca.* 5 cm^{-1} in $[Mn(MP)(CO)_3]$. In the series of complexes $[Mn(C_5H_5)(CO)_3]$, $[Mn(MP)(CO)_3]$ and $[Mn(DP)(CO)_3]$, corresponding ν(CO) bands progressively increase in frequency by 10-20 cm^{-1}. The direction of this shift is as expected since the substitution of nitrilic groups on the cyclopentadienyl ring should decrease the electron density at the metal atom, leading to smaller metal-CO(π*) interactions and hence to higher CO stretching force constants.

The main spectral changes accompanying ligand coordination in the complexes $[Me_4N][M_2(DP)_3(CO)_6]$, where M = Mn and Re, are the *ca.* 40 cm^{-1} shifts of ν(CN) to higher wavenumber. Otherwise the spectra of the complexes closely resemble that of the free ligand. In particular, the C-H out-of-plane deformation modes at *ca.* 750 cm^{-1} in Na[DP] (714 cm^{-1} in the tetramethylammonium salt) do not show large coordination shifts. These spectral changes indicate that the DP ligands are bonded *via* (both) their nitrilic nitrogen atoms. The geometry of the DP ligand requires the two nitrile groups to be bonded to different metal atoms, and the structure shown in the Figure is proposed for these anions. The spectra in the carbonyl stretching region are in accordance with the proposed structures. Thus, with a suitable (trigonal) arrangement of the five-membered rings, the anions have the molecular symmetry D_{3h}, giving rise to carbonyl stretches in the species $a_1'+e''+a_2''+e'$; of these the a_1' and e'' modes are expected to be Raman active, and the a_2'' and e' modes infrared active. (Since the coupling between carbonyl groups attached to different metal atoms is expected to be very slight, the a_1' and a_2'' modes (and the e' and e'' modes) are expected to occur at essentially the same frequencies). The observation of two ν(CO) bands in the infrared spectra of the manganese and rhenium complexes in solution is in accordance with these expectations, although spectra could only be obtained in polar solvents where ν(CO) linewidths are rather large.

Far Infrared Spectra 700-70 cm^{-1}. The far infrared spectra of the DP salts and complexes are listed in Table III. In all cases the 700-450 cm^{-1} region is complicated and contains internal ligand modes and, in the complexes, metal-carbon stretching and metal-carbon-oxygen bending modes of the tricarbonyl groups. Both the sodium and tetramethylammonium salts of DP have an intense band at about 220 cm^{-1} which is probably due to a CN out-of-plane deformation modes (either γ(C-CN) or γ(CCN), in the nomenclature of reference 17); compare *ca.* 170 cm^{-1} in benzonitrile.[17] The DP salts also have a series of intense bands in the 200-110 cm^{-1} region, whose positions are highly cation dependent; these presumably arise from lattice modes. In $[Mn(DP)(CO)_3]$ the CN out-of-plane deformation mode appears as a strong band at 207 cm^{-1}. In addition, new bands, not observed in the DP salts or in the dimeric complexes, occur at 341 and 329 cm^{-1}, and may be assigned respectively to the ring tilting and ring-metal stretching modes. The 167 cm^{-1} band of $[Mn(DP)(CO)_3]$ may be the ring torsional mode (163 cm^{-1} in $[Mn(C_5H_5)(CO)_3]$[29]). The N-bonded dimeric DP complexes have only weak absorptions below 450 cm^{-1}. In particular, the CN out-of-plane bending mode of DP appears to be either drasticaly reduced in intensity, or shifted out of the 450-70 cm^{-1} region, in the complexes. We have noticed similar spectral changes in some N-bonded benzonitrile complexes. Thus *cis*-$[Re(CO)_3(PhCN)_2Cl]$ has only very weak bands in the 240-140

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(29) R.E. Christopher, unpublished observations.

Table III. Far Infrared Spectral Data (700-70 cm.$^{-1}$ for the MP and DP Complexes (Nujol Mulls).

[Mn(MP)(CO)$_3$]	[Re(MP)(CO)$_3$]	[Fe(MP)$_2$]	K[MP] [a]	[Mn(DP)(CO)$_3$]	[Me$_4$N][Mn$_2$-(DP)$_3$(CO)$_6$]	[Me$_4$N][Re$_2$-DP)$_3$(CO)$_6$]	Na[DP]	[Me$_4$N][DP]
688sh	604s	638w	636m	668s	685s	651sh	646sh	633s
671vs	598s	593w	568w	651sh	643m	646s	634s	602s
632vs	563s	566s	523w	642s	630vs	629m	610s	534vs
568s	543w	563sh		629s	591s	589m	607sh	502m
547m	507s	508m		616sh	546m	565vw	569m	497s
530vs	499s	*472*s		611s	534s	552m	537vs	489m
509w	443vw	*456*s		606s	507vs	534s	509m	454m [c]
492w	404vw	*450*sh		534sh	496sh	511vs	502s	436sh
*365*m [b]	375w	356w		526s	483m	486s	492sh	414sh
*360*m [b]	*341*s	218w		484m	465s	188vw	372w	373vw
*344*w	*312*m	196m		474m	354w	148sh	293m	301vw
183m	185m	179sh		458w	284vw	111sh	223s	220s
162m	136mvw	121w		409vw	208w		204s	194w
114w	121vw			352w	150w		187s	176vw
88vw	97w			*341*m			151s	130sh
				*329*m				110s
				207s				
				*167*m				
				134w				
				103w				

s = strong, m = medium, w = weak, v = very, shoulder. Bands in italics are assigned to skeletal modes. [a] 700-250 cm^{-1} only. [b] These two bands collapse to a single band at 358 cm^{-1} in CCl$_4$ solution. [c] Due to tetramethylammonium cation (456 cm^{-1} in [Me$_4$N]Br).

cm.$^{-1}$ region,[29] whereas the CN out-of-plane bending modes in liquid benzonitrile give intense infrared absorptions (at *ca.* 170 cm^{-1}).[17] As in the benzonitrile complexes, no bands due to metal-ligand modes are observed in the spectra of the dimeric DP complexes.

Nmr Spectra. Table I gives proton magnetic resonance data for the manganese DP complexes, and the tetramethylammonium DP salt. The complexes give sharp line spectra, confirming that they are diamagnetic. The integrated peak areas in the spectrum of [Me$_4$N][Mn$_2$(DP)$_3$(CO)$_6$] correspond approximately to the required [DP]:[Me$_4$N] ratio of 3:1. Compared with the free DP anion, the ring protons resonate at somewhat lower field (0.1-0.25 τ) in the N-bonded dimeric complex. For [Mn(DP)(CO)$_3$] a larger upfield shift (0.6-0.8 τ) occurs on coordination of the ligand; this is in accordance with the proposed pentahapto structure of this complex, as upfield shifts normally accompany pentahapto coordination of [C$_5$H$_5$]$^-$ and its derivatives, or hexahapto coordination of benzene and its derivatives.[30]

Mass spectra. The mass spectrum of [Mn(DP)(CO)$_3$] revealed a fragmentation pattern very similar to that of the corresponding MP complex. Thus the bare metal ion was the most intense peak in the spectrum, the molecular ion was seen with low intensity, and a stepwise loss of the carbonyl groups occured. The dimeric complex [Me$_4$N][Mn$_2$(DP)$_3$(CO)$_6$] showed, in addition to very intense peaks at m/e below 75 due to cation fragments, weak peaks in the 254-80 region. Some of the latter peaks corespond to those of [Mn(DP)(CO)$_3$], and may arise from the presence of a small amount of this compound in the dimeric complex, or from thermal rearrangement of the dimeric complex in the spectrometer. In addition, some peaks were observed from ions containing both ring fragments and carbonyl groups. This fragmentation pattern contrast with that observed in the mass spectra of the pentahapto complexes.

Table IV. Electronic Spectra of the MP and DP Complexes (in Methyl Cyanide).

[Fe(C$_5$H$_5$)$_2$]		[Fe(MP)$_2$]	
ν [a]	ε [b]	ν	ε
22,650	94 [c]	22,600	240 [d]
31,120	52	29,900	226
		40,200	8150
[Mn(C$_5$H$_5$)(CO)$_3$]		[Mn(MP)(CO)$_3$]	
ν	ε	ν	ε
30,600	1110	29,800	1160
[Mn(DP)(CO)$_3$]		[Me$_4$N][Mn$_2$(DP)$_3$(CO)$_6$]	
ν	ε	ν	ε
29,280	1140	29,900sh	*ca.*11,000
34,480	1640	34,720	64,600

[a] Peak position (cm^{-1}). [b] Molar extinction coefficient (l.mole^{-1}cm^{-1}). [c] Oscillator strength = 0.0021. [d] Oscillator strength = 0.0054.

Electronic Spectra. [Me$_4$N][Mn$_2$(DP)$_3$(CO)$_6$] has an intense absorption band at 34,720 cm^{-1}, with a pronounced shoulder at *ca.* 30,000 cm^{-1} (see Table IV). The former band is probably a modified internal ligand transition, as [Me$_4$N][DP] has bands at 36,400 ($\varepsilon = 12,900$) and 35,300 cm^{-1} ($\varepsilon = 14,500$),[4] most likely due to π-π^* transitions. Pentahapto coordination of DP drastically reduces the intensity of the *ca.* 35,000 cm^{-1} band. Thus [Mn(DP)(CO)$_3$] has a band at 34,480 cm.$^{-1}$ with a molar extinction coefficient of only 1,640. In addition, the pentahapto complex has a second band at 29 280 cm.$^{-1}$ ($\varepsilon = 1,140$), corresponding to the 29,800 and 30,600 cm.$^{-1}$ bands of [Mn(DP)(CO)$_3$] and [Mn(C$_5$H$_5$)(CO)$_3$] respectively.

Reactions of the DP complexes. The interconver-

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(30) R.V. Emmanuel and E.W. Randall, *J. Chem. Soc. (A)*, 3002 (1969).

sion of the two manganese DP complexes was studied by infrared spectroscopy (2300-1800 cm.$^{-1}$). No conversion to the pentahapto complex was observed on prolonged reflux (50 hours) of a tetrahydrofuran solution of $[Me_4N][Mn_2(DP)_3(CO)_6]$. However, refluxing a 1:1 molar mixture of the dimeric complex and bromopentacarbonylmanganese(I) in tetrahydrofuran (48 hours) gave extensive conversion into $[Mn(DP)(CO)_3]$. Infrared studies showed that in the 1:1 reaction of $[Me_4N][DP]$ and $[Mn(CO)_5Br]$ used to prepare the two manganese DP complexes (see experimental section), the N-bonded dimeric complex was formed first, and that on extended reflux the excess $[Mn(CO)_5Br]$ (or a species derived from it, as $[Mn(CO)_5Br]$ itself reacts slowly with THF) effected a partial conversion into $[Mn(DP)(CO)_3]$. No method of converting the pentahapto complex to the N-bonded complex was found, the pentahapto complex being unchanged after extended reflux (75 hours) in THF, either alone or in the presence of added DP salts. Thus the pentahapto complex appears to be the more stable product under the reaction conditions used, but it is formed more slowly than the N-bonded dimeric complex. It is possible that in the reaction with the dimeric complex the $[Mn(CO)_5Br]$ (or a species derived from it) becomes bonded to the π-electron system of a DP ring in the $[Mn_2(DP)_3(CO)_6]^-$ anion, and that this is followed by Mn-N bond cleavage to give eventually the pentahapto product. Attempts to convert the dimeric rhenium complex to a pentahapto complex, by refluxing with rhenium carbonyl compounds, were unsuccessful, giving products of unknown composition. The N-bonded DP ligands are readily displaced from $[Me_4N][Mn_2(DP)_3(CO)_6]$ by methyl cyanide and other coordinating solvents. Thus complete conversion to $[Mn(CH_3CN)_3(CO)_3]^{+}$[16] and free ligand occured on refluxing a methyl cyanide solution of the dimeric complex for one hour, as indicated by the infrared and electronic spectra and specific conductivity of the resulting solution. The pentahapto DP complex, in contrast, does not react with refluxing methyl cyanide or with other coordinating solvents.

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