THE SYNTHESIS AND SPECTRAL FEATURES OF SOME CATIONIC MANGANESE(I) AND RHENIUM(I) TRICARBONYL COMPLEXES

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(Received September 24th, 1976)

Summary

More than twenty cationic manganese or rhenium tricarbonyl complexes of the types fac-[M(CO)$_3$L$_3$]ClO$_4$ (L = C$_5$H$_5$N or ethylenethiourea; L$_3$ = tri-2-pyridylamine, diethylenetriamine or E-pyridine-2-carbaldehyde-2'-pyridylhydrazone), fac-[M(CO)$_3$X$_2$Y]ClO$_4$ (X$_2$ = 2 C$_5$H$_5$N, 2,2'-bipyridyl, di-2-pyridylamine, 2 PPh$_3$, Ph$_2$PCH$_2$PPh$_2$, Ph$_2$PCH$_2$CH$_2$PPh$_2$, Ph$_2$PCH$_2$CH$_2$AsPh$_2$, or Ph$_2$AsCH$_2$CH$_2$AsPh$_2$; Y = MeCN), or fac-[M(CO)$_3$XY$_2$]ClO$_4$ (X = AsPh$_3$; Y = MeCN) have been prepared by displacement of acetonitrile groups from fac-[M(CO)$_3$(NCMe)$_3$]ClO$_4$. The dicarbonyl cationic complex [Mn(CO)$_2$(PPh$_3$)$_2$(NCMe)$_2$]-ClO$_4$ has also been synthesised. The compounds have been characterised by conductivity measurements, and by infrared (4000—40 cm^{-1}) and ^{1}H and ^{31}P NMR spectroscopy. Trends in Cotton—Kraihanzel CO stretching parameters are discussed.

Introduction

There has been some recent interest in the synthesis of cationic Group VII carbonyl derivatives of the general type [M(CO)$_{6-x}$ (ligand)$_x$]$^+$ (M = Mn and Re; x = 1—4) which are isoelectronic with the well-known neutral Group VI substituted metal carbonyls. The cationic species have been prepared by several routes; (i) the reactions of ligands with the fairly inert hexacarbonyl cations e.g. [Re(CO)$_4$(dppe)]$^+$ from [Re(CO)$_6$]$^+$ [1]; (ii) the reactions of M$_2$(CO)$_{10}$ or M(CO)$_5$X (X = halogen) in a donor solvent e.g. [Re(CO)$_5$(NCMe)]$^+$ from either Re$_2$(CO)$_{10}$ and NO$^+$PF$_6^-$ [2], or Re(CO)$_5$Br and Ag$^+$PF$_6^-$, in acetonitrile [3]; (iii) reactions of M(CO)$_5$X with ligands e.g. cis-[Mn(CO)$_2$(LL')$_2$]Br from Mn(CO)$_5$Br and LL' (LL' = o-Me$_2$AsC$_6$H$_4$NH$_2$ or Ph$_2$AsCH$_2$CH$_2$NH$_2$) [4]; (iv) carbonylation reactions e.g. [Mn(CO)$_4$(o-Me$_2$NC$_6$H$_4$PPh$_2$)]$^+$ from Mn(CO)$_3$Br(o-Me$_2$NC$_6$H$_4$PPh$_2$) and CO in the presence of AlCl$_3$ [5], or [Mn(CO)$_5$L]BF$_4$ from Na[Mn(CO)$_4$L] and ethyl

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chloroformate in the presence of HBF_4 (L = PPh_3, PMe_2Ph, or $P(OPh)_3$) [6]; (v) arene displacement from $[M(CO)_3(arene)]^*$ e.g. $[Mn(CO)_3(\nu\text{-triars})]^*$ from $[Mn(CO)_3(mesitylene)]^*$ (v-triars = $(Me_2AsCH_2)_3CMe$) [7].

Displacement of acetonitrile from $[Mn(CO)_5(NCMe)]PF_6$ by a number of ligands leads to $[Mn(CO)_5L]PF_6$ complexes (L = PR_3 with R = Ph, OPh or p-tol; unidentate dppe or py). Use of longer reaction times and excess of ligands results in the formation of the tricarbonyl cations $[Mn(CO)_3(NCMe)_3]^*$, $[Mn(CO)_3(py)_3]^*$ and $[Mn(CO)_3(py)_2(NCMe)]^*$ by loss of both carbon monoxide and acetonitrile [6,8]. A range of phosphine and phosphite complexes of the types fac-$[Mn(CO)_3L(NCMe)_2]^*$, fac-$[Mn(CO)_3L_2(NCMe)]^*$, cis-$[Mn(CO)_2L_2(NCMe)_2]^*$ and mer,cis-$[Mn(CO)_2L_3(NCMe)]^*$ (L = e.g. PMe_2Ph, $P(OMe)_3$, or $P(OMe)_2Ph$) have also been prepared from fac-$[Mn(CO)_3(NCMe)_3]PF_6$. Such cations may also be formed by treating $[Mn(CO)_{5-x}L_xBr]$ (x = 1—3) with $Ag^*PF_6^-$ in acetonitrile [9]. The only other tricarbonyl cations containing ligands other than phosphorus donors that have been reported are fac-$[Mn(CO)_3(PrNH_2)_3]^*$ and fac-$[Mn(CO)_3(SEt_2)(NCMe)_2]^*$ [3] and fac-$[Mn(CO)_3(bipy)L]NO_3$ (L = py or PPh_3), the latter complexes resulting from reactions of $Mn(CO)_3(bipy)(ONO_2)$ [10].

Apart from fac-$[Re(CO)_3(NCMe)_3]^*$, and our preliminary communication [11] on the ^{31}P NMR coordination shifts of fac-$[Re(CO)_3L_2(NCMe)]^*$ (L_2 = dppm, dppe, or 2 PPh_3) no rhenium tricarbonyl cations have been reported. We describe here the synthesis and spectroscopic properties of a wider variety of manganese tricarbonyl cations than hitherto reported, as well as an extensive range of rhenium analogues. The complexes have been prepared by substitution of acetonitrile ligands from fac-$[M(CO)_3(NCMe)_3]ClO_4$ using nitrogen, phosphorus, arsenic and sulphur donor ligands. The ease of substitution of acetonitrile ligands is well established in metal carbonyl chemistry [12].

Experimental

All reactions were performed under dry nitrogen using anhydrous, deoxygenated, solvents. Ligands were used as received although acetonitrile was distilled several times from phosphorus pentoxide before use. Tri-2-pyridylamine [13] and E-pyridine-2-carbaldehyde-2'-pyridylhydrazone [14] were prepared by literature methods.

Melting points were taken in open capillary tubes and are uncorrected. Routine infrared spectra were recorded on a Perkin—Elmer 735 spectrophotometer. More accurate (± 1 cm^{-1}) spectra, which were subsequently used for CO stretching parameter calculations, were recorded from acetonitrile solutions using a Perkin—Elmer 577 spectrophotometer with abscissa scale expansion and use of an external recorder. Gaseous carbon monoxide and polystyrene were used for frequency standardisation. This instrument was also used to obtain mid-infrared spectra, the far-infrared spectra of samples dispersed in polythene being obtained on a R.I.I.C. FS 720 interferometer. ^1H and ^{31}P NMR spectra were recorded using a Jeol PS-100 spectrometer. For the ^{31}P spectra, the spectrometer was operated at 40 MHz with proton noise decoupling. The chemical shifts are reported in ppm relative to an external 85% phosphoric acid standard placed in a coaxial capillary tube within the NMR tube. Conductance measurements at 298 K were carried

out in acetonitrile using a Wayne—Kerr autobalance universal bridge and a dip-type cell with platinum electrodes.

Preparations *

fac-[M(CO)₃(NCMe)₃]ClO₄ (I, M = Mn; II, M = Re). A solution of the appro-. priate $M(CO)_5Br$ (4 mmol), and $AgClO_4$ (4 mmol) in acetonitrile (20 cm^3) was heated under reflux for 16 h. AgBr was filtered off and the filtrate evaporated to dryness to give the required product which was then recrystallised from acetonitrile/ether, (I: yellow, 83% yield; II: colourless, 92% yield).

These compounds (0.50 mmol in each reaction) were subsequently used in displacement reactions, the abbreviated details of which are listed in Table 1. The manganese products were yellow and the rhenium products colourless, apart from the two *E*-paphy complexes which were red-brown in colour. The prcducts were normally washed with an appropriate solvent to remove any excess ligand and dried in vacuo before analysis. Analytical data are given in Table 2.

Results and discussion

The complexes *fac*-$[M(CO)_3(NCMe)_3]ClO_4$ (I, M = Mn; II, M = Re) have been prepared by minor modifications of literature methods [9,15], and subsequent-ly the substitution of one or more nitrile ligands accomplished by treatment with a variety of Group V and VI donor ligands. The products formed, and the preparative methods, are given in Table 1 and good to excellent yields were ob-tained. As expected, the rate of substitution of nitrile ligands was markedly slower for II than for I. The terdentate ligands tripyam, dien, and *E*-paphy proved to be capable of replacing all three nitrile groups to produce [M(CO)₃-(terdentate)]⁺ cations and no examples were found where the maximum coordi-nation potential of these ligands was not achieved. The reactions of equimolar proportions of I or II and bidentate ligands resulted in the formation of [M(CO)₃-(bidentate)(NCMe)]⁺ cations (bidentate = bipy, dipyam, dppm, dppe, arphos, or dpae). There was, however, some variation in the products of the reactions of I or II with monodentate ligands. Using an excess of pyridine only two nitrile groups were displaced from I, whereas all three nitrile groups were displaced from II. Using even a four-fold excess of $(C_6H_5)_3As$, only one nitrile group was replaced on treatment with either I or II. Since all other ligands used easily re-placed more than one nitrile group, it appears that the inability of the arsine to replace more than one nitrile group must be attributed to steric rather than elec-tronic factors. An excess of ethylenethiourea, (2-imidazolidinethione), forces replacement of all nitrile ligands of both I and II. The substitution reactions using an excess of $(C_6H_5)_3P$ show a significant difference in reactivities between I and II. With II, two nitrile groups are replaced to afford the tricarbonyl cation XIV, whereas with I only one nitrile group is replaced but one carbonyl ligand is also lost to afford the dicarbonyl cation XIII. Similar dicarbonyl cations are products of the reactions of I with other monotertiary phosphines and phos-phites [9].

* Ligand abbreviations used throughout are explained in Table 1.

TABLE 1

PREPARATIONS FROM [M(CO)$_3$(NCMe)$_3$]ClO$_4$ (0.50 mmol; I, M = Mn; II, M = Re)

Ligand	Product	Yield (%)	Reaction conditions	Isolation of product
Pyridine (10.0 mmol)	[Mn(CO)$_3$(py)$_2$(NCMe)]ClO$_4$ (III)	59	Reflux, CHCl$_3$; 3 h	Precipitation by Et$_2$O addition; recryst. from MeCN/Et$_2$O.
Pyridine (2.0 mmol)	[Re(CO)$_3$(py)$_3$]ClO$_4$ (IV)	63	Reflux, Me$_2$CO; 16 h	Precipitation by Et$_2$O addition.
2,2'-Bipyridyl (0.55 mmol)	[Mn(CO)$_3$(bipy)(NCMe)]ClO$_4$ (V)	78	Reflux, CHCl$_3$; 3 h	Precipitation by Et$_2$O addition.
	[Re(CO)$_3$(bipy)(NCMe)]ClO$_4$ (VI)	81	Reflux, CHCl$_3$; 16 h	Insoluble.
Di-2-pyridylamine (0.55 mmol)	[Mn(CO)$_3$(dipyam)(NCMe)]ClO$_4$ (VII)	89	Reflux, CHCl$_3$; 3 h	Insoluble.
	[Re(CO)$_3$(dipyam)(NCMe)]ClO$_4$ (VIII)	79	Reflux, CHCl$_3$; 24 h	Crystallised on cooling.
Tri-2-pyridylamine (0.50 mmol)	[Mn(CO)$_3$(tripyam)]ClO$_4$ (IX)	83	Reflux, Me$_2$CO; 24 h	Evaporation of solvent.
Diethylenetriamine (0.55 mmol)	[Mn(CO)$_3$(dien)]ClO$_4$ (X)	94	Reflux, CHCl$_3$; 0.5 h	Insoluble.
E-Pyridine-2-carbaldehyde 2-pyridylhydrazone (0.55 mmol)	[Mn(CO)$_3$(E-paphy)]ClO$_4$ (XI)	96	Reflux, CHCl$_3$; 0.25 h	Evaporation of solvent.
	[Re(CO)$_3$(E-paphy)]ClO$_4$ (XII)	98	Reflux, Me$_2$CO; 24 h	Precipitation by Et$_2$O addition.
Triphenylphosphine (1.10 mmol)	[Mn(CO)$_2$(PPh$_3$)$_2$(NCMe)$_2$]ClO$_4$ (XIII)	73	Reflux, CHCl$_3$; 4 h	Insoluble; recryst. from MeCN/Et$_2$O.

Reagent	Product	Yield (%)	Conditions	Workup
Triphenylphosphine (1.50 mmol)	$[Re(CO)_3(PPh_3)_2(NCMe)]ClO_4$ (XIV)	47	Reflux, Me_2CO; 16 h	Precipitation by Et_2O addition.
Bis(diphenylphosphino)methane (0.55 mmol)	$[Mn(CO)_3(dppm)(NCMe)]ClO_4$ (XV)	60	Reflux, $CHCl_3$; 3 h	Evaporation of solvent; recryst. from $CH_2Cl_2/EtOH$.
Bis(diphenylphosphino)methane (0.55 mmol)	$[Re(CO)_3(dppm)(NCMe)]ClO_4$, Me_2CO (XVI)	93	Reflux, Me_2CO; 16 h	Evaporation of solvent.
1,2-Bis(diphenylphosphino)ethane (0.55 mmol)	$[Mn(CO)_3(dppe)(NCMe)]ClO_4$ (XVII)	59	Reflux, $CHCl_3$; 3 h	Evaporation of solvent; recryst. from $CH_2Cl_2/EtOH$.
1,2-Bis(diphenylphosphino)ethane (0.55 mmol)	$[Re(CO)_3(dppe)(NCMe)]ClO_4$, Me_2CO (XVIII)	97	Reflux, Me_2CO; 16 h	Evaporation of solvent.
$Ph_2PCH_2CH_2AsPh_2$ (0.55 mmol)	$[Re(CO)_3(arphos)(NCMe)]ClO_4$ (XIX)	82	Reflux, $CHCl_3$; 16 h	Add EtOH and reduce volume.
Triphenylarsine (1.10 mmol)	$[Mn(CO)_3(AsPh_3)(NCMe)_2]ClO_4$ (XX)	89	Room temp. $CHCl_3$; 5 h	Evaporation of solvent; remove excess. $AsPh_3$ by washing with light petroleum.
Triphenylarsine (1.10 mmol)	$[Re(CO)_3(AsPh_3)(NCMe)_2]ClO_4$ (XXI)	93	Reflux, $CHCl_3$; 22 h	Evaporation of solvent left viscous oil. Washed with light petroleum to give solid product.
1,2-Bis(diphenylarsino)ethane (0.55 mmol)	$[Mn(CO)_3(dpae)(NCMe)]ClO_4$ (XXII)	89	Reflux, $CHCl_3$; 3 h	Evaporation of solvent. Recryst. from $CH_2Cl_2/EtOH$.
1,2-Bis(diphenylarsino)ethane (0.55 mmol)	$[Re(CO)_3(dpae)(NCMe)]ClO_4$ (XXIII)	38	Reflux, $CHCl_3$; 16 h	Evaporation of solvent. Washed with light petroleum.
Ethylenethiourea (1.67 mmol)	$[Mn(CO)_3(etu)_3]ClO_4$ (XXIV)	94	Reflux, $CHCl_3$; 3 h	Insoluble, recryst. from CH_2Cl_2.
Ethylenethiourea (1.67 mmol)	$[Re(CO)_3(etu)_3]ClO_4$ (XXV)	89	Reflux, Me_2CO; 16 h	Precipitation by Et_2O addition.

TABLE 2

ANALYTICAL MELTING POINT AND CONDUCTIVITY RESULTS

Complex	M.p. (°C)	Conductivity ^{a} (Ω^{-1} cm^2 mol^{-1})	Analysis (Found (calcd.)) (%)			
			C	H	N	Other
I	146—148	167	29.4 (29.9)	2.88 (2.51)	11.2 (11.6)	
II	104 expl.	162	21.3 (21.4)	1.89 (1.84)	8.30 (8.53)	
III	125—127	156	41.0 (41.2)	3.23 (3.00)	9.63 (9.60)	
IV	107—109 dec.	151	34.4 (35.6)	2.41 (2.49)	6.86 (6.92)	
V	190 dec.	161	41.0 (41.3)	2.56 (2.54)	9.35 (9.65)	
VI		162	30.6 (31.8)	2.05 (1.96)	7.46 (7.41)	
VII	249—251 dec.	171	40.2 (40.0)	2.80 (2.68)	12.2 (12.4)	
VIII	130 expl.	147	31.1 (31.0)	2.59 (2.08)	9.28 (9.63)	
IX	242 dec.	174	44.1 (44.4)	2.62 (2.49)	11.2 (11.5)	
X	250 dec.	145	25.3 (24.6)	4.37 (3.84)	12.6 (12.3)	
XI		152	38.1 (38.5)	3.10 (2.81)	13.2 (12.8)	
XII		109	29.7 (29.6)	2.17 (1.77)	10.0 (9.87)	
XIII	168	146	62.2 (61.8)	4.55 (4.44)	3.22 (3.43)	
XIV	142 dec.	155	52.0 (52.6)	3.65 (3.56)	1.37 (1.50)	
XV	176—178 dec.	140	54.5 (54.3)	4.12 (3.79)	2.19 (2.11)	
XVI	140 dec.	140	47.2 (46.5)	3.75 (3.66)	1.45 (1.64)	6.42 (7.26) ^{b}
XVII	106—108	135	55.6 (54.9)	4.31 (4.01)	1.84 (2.07)	9.59 (9.14) ^{b}
XVIII		132	47.7 (47.1)	3.91 (3.84)	1.49 (1.62)	6.61 (7.14) ^{b}
XIX		135	45.1 (43.6)	3.69 (3.19)	1.15 (1.64)	
XX	148—150	167	46.0 (47.9)	3.40 (3.38)	4.45 (4.47)	
XXI	116—117	145	40.3 (39.6)	2.65 (2.79)	3.08 (3.70)	
XXII	164—166	143	49.1 (48.6)	3.94 (3.55)	1.86 (1.83)	
XXIII		137	41.6 (41.5)	3.14 (3.03)	1.41 (1.56)	
XXIV	123	130	26.6 (26.5)	3.87 (3.33)	15.6 (15.4)	17.0 (17.6) ^{c}
XXV	150—151	124	21.4 (21.0)	2.81 (2.68)	12.2 (12.4)	13.7 (14.2) ^{c}

^{a} 10^{-3} M solutions in acetonitrile. ^{b} P analysis. ^{c} S analysis.

The complexes XVI and XVIII were isolated as acetone solvates, as shown by infrared and NMR spectroscopy. All other complexes were formed without solvent of crystallisation.

The molar conductivities of the complexes, measured as $10^{-3} M$ solutions in acetonitrile at 298 K, fall within the rather wide range 109—174 ohm^{-1} cm^2 mol^{-1}. In this solvent, values as low as 92 and as high as 199 ohm^{-1} cm^2 mol^{-1} have been claimed [16] to characterise 1 : 1 electrolytes.

Infrared spectra

The presence of ionic perchlorate in each complex is further confirmed by the detection (Table 4) of only the t_2 OClO bending mode at ca. 630 cm^{-1} and the t_2 ClO stretching mode at ca. 1095 cm^{-1}, neither showing significant splitting. Lack of perchlorate coordination is also indicated [17] by the absence of the infrared inactive a_1 (ClO) stretching mode at its normal position of ca. 935 cm^{-1}. The data of Table 4 also show that for those complexes retaining some coordinated acetonitrile ν(CN) is ca. 40 cm^{-1} higher in frequency than in the free ligand, such an increase being characteristic of a nitrile bonded through the nitrogen lone pair electrons [18]. A further band some 25 cm^{-1} higher than ν(CN) arises from a combination of the symmetric CH$_3$ deformation and the symmetric CC stretching modes of the coordinated nitrile. Both bands are of low intensity and for a few of the complexes they are so weak as to make their accurate positions uncertain. The low intensity of these bands in the infrared has been noted

TABLE 3

INFRARED ν(CO) BANDS (cm^{-1}) AND CO STRETCHING PARAMETERS

Complex	ν(CO) [a]		Stretching parameters (mdyne/Å)		
	A$_1$ or A'	E or A' + A"	k or k_1	k_2	[a] k_i
I [b]	2064	1975	16.24		0.48
II [b]	2053	1951	15.92		0.55
III [b]	2050	1955	15.95		0.51
IV [b]	2037	1928	15.59		0.58
V [b]	2051	1956	15.96		0.51
VI [b]	2040	1935	15.68		0.56
VII [b]	2047	1950	15.88		0.52
VIII [b]	2051	1951	15.91		0.54
IX [c]	2030	1941			
X [b]	2035	1923	15.53		0.60
XI [d]	2050	1958			
XII [d]	2040	1935			
XIV [b]	2052	1969 1947	15.78	16.41	0.47
XV [c]	2030	1972 1938			
XVI [d]	2052	1975 1952			
XVII [b]	2041	1972 1953	15.79	16.34	0.39
XVIII [b]	2045	1968 1949	15.78	16.31	0.44
XIX [d]	2055	1970 1955			
XX [b]	2058	1960 1981	16.31	15.85	0.46
XXI [c]	2050	1950 1985			
XXII [b]	2042	1971 1953	15.81	16.31	0.41
XXIII [b]	2048	1965 1948	15.80	16.26	0.48
XXIV [d]	2020	1925			
XXV [b]	2022	1912	15.35		0.58

[a] All bands strong. [b] MeCN solution. [c] Nujol mull. [d] CHCl$_3$ solution.

before [19] and on occasions [20] ν(CN) could not be observed at all. The complexes containing coordinated nitrile also exhibit a CCN deformation of somewhat greater intensity at ca. 420 cm^{-1}, this band often being split into two components. This mode is found at 365 cm^{-1} for free acetonitrile.

The carbonyl stretching frequencies of the compounds, except XIII, are listed in Table 3. For many of the compounds ν(CO) bands have been recorded in several solvents and as nujol mulls, but only one set of results is presented in the Table for each compound, the acetonitrile solution results being given where measured. Complexes of the type [M(CO)$_3$X$_3$]$^+$ (X = three identical donor atoms) display two strong ν(CO) infrared bands indicative of C_{3v} symmetry (A$_1$ + E) and hence a *fac*-configuration is appropriate for these cations. Several other cations of the type [M(CO)$_3$X$_2$(NCMe)]$^+$ (X$_2$ = bipy, dipyam, or 2 py), which must have a formal local symmetry lower than C_{3v}, also exhibit only two ν(CO) bands. The same feature is also observed for the cations XI and XII which must have non-identical (pyridyl or azomethine) donor nitrogen atoms. The bonding properties of the chemically different donor nitrogen atoms in these cations cannot therefore be distinguished by monitoring changes in the number of infrared active ν(CO) bands. However for complexes of the type [M(CO)$_3$X$_2$(NCMe)]$^+$ (X$_2$ = dppm, dppe, arphos, dpae or 2 PPh$_3$) as well as the complexes XX and XXI, where X$_2$ or (C$_6$H$_5$)$_3$As are markedly different to acetonitrile, particularly in their π-acceptor abilities, three ν(CO) bands are observed. This implies that these cations either possess the alternative *mer*-configuration (which seems unlikely in view of the rearrangement of the carbonyl groups from their positions in I and II), or more plausibly that the cations retain the *fac*-configuration with C_s local symmetry. In this case, the degeneracy of the E mode of C_{3v} symmetry will be lifted resulting in the two modes A' + A'' [21]. Similar features have been observed for neutral trisubstituted derivatives of Mo(CO)$_6$ [22,23].

The only dicarbonyl complex isolated, XIII, has two strong ν(CO) infrared bands (1960, 1880 cm^{-1}, nujol mull; 1955, 1878 cm^{-1}, MeCN solution) indicative of mutually *cis* carbonyl groups. Some information on the formation of XIII has been obtained by following ν(CO) changes during the course of the reaction between I and a two-fold excess of the phosphine in refluxing chloroform. As the two ν(CO) bands of I diminish in intensity, bands at 2070w, 1977s and 1927s cm^{-1} grow. These bands subsequently slowly decrease in intensity and finally disappear as the bands associated with XIII increase in intensity and finally become the only detectable ν(CO) bands. The one weak and two strong ν(CO) band pattern of the intermediate is consistent [1] with the formation of either *mer,trans*- or *mer,cis*-[Mn(CO)$_3$(NCMe)$_2$(PPh$_3$)]ClO$_4$, but not with the *fac*-isomer for which three strong ν(CO) bands would be expected. Thus, one nitrile group is initially displaced by the phosphine, but a rearrangement of the carbonyl groups must occur. Subsequently one of the mutually *trans*-carbonyl groups is replaced by a further phosphine molecule leaving the two remaining carbonyl groups arranged mutually *cis*.

Although the ν(MC) and δ(MCO) frequencies of many neutral Group VI substituted metal carbonyls have been documented [24,25], little is known of the corresponding modes of substituted metal carbonyls of Group VII [26]. The only information available on these modes for cationic Group VII carbonyl species concerns the hexacarbonyl cations. An extensive vibrational spectroscopic

TABLE 4

MULL INFRARED SPECTROSCOPIC DATA (cm^{-1})

Complex	Nitrile modes		Perchlorate modes		Carbonyl modes
	ν(CN) and δ_{sym}(CH$_3$) + ν_{sym}(CC) [a]	δ(CCN)	ν(ClO) [b]	δ(OClO) [b]	δ(MCO) + ν(MC)
I	2317, 2290	400w	1098	629	683s, 533s, 464s, 435m, 423w
II	2315, 2290	404m	1095	626	592s, 543s, 486s, 438w, 357s
III	2310, 2280	414w	1098	628	686s, 532s, 466m, 451w, 437m
IV			1095	627	603w, 539vs, 488s, 441m, 354m
V	2310, 2280	412m	1095	632	692m, 611m, 534s, 474m, 458m, 422m, 383m
VI	2300vw(br)	415m	1095	628	588w, 543s, 488s, 467m, 424m, 344m
VII	2313, 2287	420mw	1096	626	687s, 533s, 471m, 450m, 441w
VIII	2320, 2295	419m	1102	626	539s, 490s, 442m, 337w
IX			1080	626	687s, 532s, 471m, 461m, 447w
X			1090	626	691s, 531s, 501w, 482w, 463w
XI			1108	626	688w, 532w, 516w
XII			1100	628	594m, 537m, 493m, 349m
XIII	2310vw(br)	421m, 417(sh)	1097	625	689s, 677m, 577s, 461m, 383w, 291m
XIV	2315, 2290	417s, 403(sh)	1095	627	603s, 579vs, 530vs, 484w, 465m, 367s, 276m
XV	2310, 2290		1095		
XVI	very weak	430m(br)	1098	626	603m, 574s, 537vs, 514vs, 371m
XVII	very weak	415m, 403(sh)	1092	629	668vs, 588sh, 552s, 536vs, 476m, 432m
XVIII	2335, 2300	416m, 403(sh)	1098	626	604m, 576s, 544s, 490m, 479w, 460w, 370m
XIX	very weak	415w	1097	626	602m, 578s, 537s, 486m, 465m, 371m
XX	2317, 2290	418m, 407w	1098	628	637vs, 537s, 525m, 497m, 443w
XXI	2320, 2295	416m, 405w	1097	628	603m, 578vs, 540s, 527s, 514s, 430w, 366s
XXII	2310, 2290	420m, 413w	1095	617	665vs, 641s, 578m, 558m, 543m, 526s, 389m
XXIII	2305, 2270	415w(br)	1100	625	601m, 586m, 534s, 515m, 497w, 392m
XXIV			1085	630	682s, 511m, 300w
XXV			1098	627	528w, 506w, 496m, 276w

[a] Weak unless otherwise stated. [b] Strong bands.

study of $[Re(CO)_6]^+$ [27] has shown $\nu(ReC)$ frequencies of 441, 426 and 356 cm^{-1} with $\delta(ReCO)$ bands at 584, 522, 486, and 354 cm^{-1}. The analogous bands of $[Mn(CO)_6]^+$ have been assigned [28] to absorptions at 412, 390 and 384 cm^{-1} [$\nu(MnC)$] and 636, 500 (accidental degeneracy of two modes) and 347 cm^{-1} [$\delta(MnCO)$]. With this information in mind, attempts have been made to assign $\nu(MC)$ and $\delta(MCO)$ bands (Table 4) for the substituted carbonyl cations. Although force constant calculations performed [29] on various metal carbonyls have indicated that $\nu(MC)$ modes usually occur at lower frequencies than $\delta(MCO)$ modes, the above results for the hexacarbonyl cations show that there is some overlap of the ranges. Indeed, coupling between the various vibrations of the same symmetry can be expected, so no attempts have been made for the present compounds to distinguish between $\nu(MC)$ and $\delta(MCO)$ modes. The major difficulty in assigning bands to these modes is the presence of bands in the mid-infrared spectra due to vibrations of ligands other than carbonyl groups. Many can be eliminated from consideration without undue difficulty e.g. $\delta(CCN)$ of coordinated acetonitrile, and the X-sensitive modes of phosphine and arsine ligands, as well as $\delta(OClO)$ of the perchlorate anions. Comparison of the spectra with those of the free ligands in this region has also been of considerable assistance, but caution is needed as ligand frequencies often shift significantly on coordination to a metal. For some compounds we have found that the number of bands which can be assigned to $\nu(MC)$ or $\delta(MCO)$ with some degree of confidence is not consistent with theoretical expectations. This is a situation found previously [24,30] for substituted Group VI metal carbonyls and may be due to accidental degeneracies or very low intensities of some bands. For those cations of C_{3v} local symmetry two $\nu(MC)$ and three $\delta(MCO)$ bands are predicted and for most of the examples five bands can be so assigned, although for XXIV and XXV the number of bands observed is particularly low. Three $\nu(MC)$ and six $\delta(MCO)$ bands are predicted for the cations of C_s local symmetry but only up to seven bands can be so assigned. It is particularly noticeable that for those cations whose local symmetry is C_s but whose effective local symmetry is C_{3v}, on the basis of the number of observed $\nu(CO)$ bands, more than the five $\nu(MC)$ + $\delta(MCO)$ bands expected of C_{3v} local symmetry are found. For example, complexes V and VI display seven and six such bands, respectively. It would appear therefore that a consideration of the number of $\nu(MC)$ + $\delta(MCO)$ bands may be more effective in showing bonding differences of the ligands X and Y in the $[M(CO)_3X_2Y]^+$ cations than is observation of the number of $\nu(CO)$ bands.

The highest frequency $\delta(MCO)$ bands of the hexacarbonyl cations show [27,28] a substantial mass effect, decreasing by 52 cm^{-1} on changing from manganese to rhenium, but for the remaining $\delta(MCO)$ bands this effect is much smaller and is reversed by some 7 cm^{-1} for the lowest frequency $\delta(MCO)$ band. Where direct comparison is possible, a similar mass effect is noticeable for the substituted carbonyl cations. For example, the highest frequency band, presumably $\delta(MnCO)$, of I is found at 683 cm^{-1}, 91 cm^{-1} higher than the analogous band of II. The lower $\delta(MCO)$ and $\nu(MC)$ bands do not generally show such a marked mass effect, although assured comparisons are difficult. It seems that the highest frequency $\delta(MnCO)$ band lies in the range 690—665 cm^{-1} with the analogous $\delta(ReCO)$ being in the range 605—585 cm^{-1}.

A comparison of the $\delta(MCO)$ and $\nu(MC)$ frequencies of the cations I and II

with the corresponding frequencies of the isoelectronic neutral Group VI complexes $[M(CO)_3(NCMe)_3]$ (M = Cr and W) [31] permits a study of the effect of the positive charge on the metal. The $\delta(MCO)$ and $\nu(MC)$ bands of the Group VI complexes are found at higher frequencies than those of the Group VII cations, in line with the reverse trend of substantially higher $\nu(CO)$ frequencies for the cations when compared with the neutral Group VI analogues. Decreased M → C back-bonding and a concommitant increased C—O bond order for the cations compared with the neutral Group VI complexes rationalises these spectroscopic features.

This type of reasoning can be amplified by a consideration of energy-factored approximate force constant values. We have calculated Cotton—Kraihanzel approximate CO force constants [32] (better described as stretching parameters [33]) for a selection of the cations whose $\nu(CO)$ frequencies have been accurately (± 1 cm^{-1}) measured (Table 3). The $\nu(CO)$ frequencies used in the calculations were all obtained from acetonitrile solution spectra, thereby eliminating solvent shift effects. Using the results of references 27 and 28 we have also calculated Cotton—Kraihanzel stretching parameters for the hexacarbonyl cations.

Although calculation of k and k_i for the cations of real or apparent C_{3v} local symmetry (as based on the number of observed $\nu(CO)$ bands) is straightforward with the A_1 fundamental necessarily being of highest frequency so that k_i is positive, some explanation of the $\nu(CO)$ assignments for the fac-$[M(CO)_3X_2Y]^+$ cations is required. The $\nu(CO)$ assignments and subsequent calculations are based on the approach and secular equations of Cotton [34] for fac-$[Mn(CO)_3BrL_2]$ complexes, as corrected by Houk and Dobson [22]. For the cations $[M(CO)_3$-$(NCMe)X_2]^+$ (X_2 = 2 PPh$_3$, dppe, and dpae) stretching and interaction parameters have been calculated using model A with the reasonable assumption that
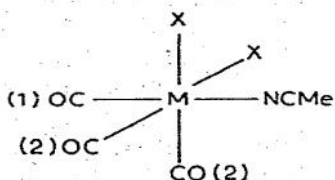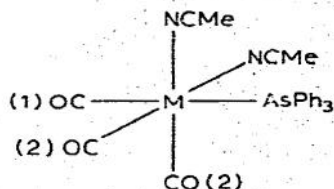
the highest frequency $\nu(CO)$ band will be the A' mode which corresponds to the A_1 mode in C_{3v} symmetry. Since acetonitrile is a poorer acceptor of metal d_π-electrons than phosphine or arsine ligands, the CO(1) bond order will be lower than that of CO(2) and $k_1 < k_2$. With $k_i > 0$, the middle $\nu(CO)$ band must be assigned to the A' mode and the lowest to A'' since a reversal of these assignments makes it impossible to obtain $k_2 > k_1$. For the cations XX and XXI model B has been used so that the unique ligand is consistently $trans$ to CO(1) in all cases. The superior π-acceptor ligand $(C_6H_5)_3$As is thus $trans$ to CO(1) and by similar reasoning $k_1 > k_2$ and the $\nu(CO)$ assignments of Table 3 follow.

The stretching parameters for $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ have been calculated as 18.23 and 18.18 mdynes/Å respectively with stretch—stretch interaction parameters, k_i, of 0.22 and 0.26 respectively. As expected, the k values decrease substantially (by more than 2 mdynes/Å) and the k_i values increase (by more than 0.2 mdynes/Å) as three facial carbonyl groups are replaced by other ligands

which make less demand for metal d_π-electrons. For the complexes of C_{3v} local symmetry a variation of ca. 0.7 mdynes/Å in k is found within the group of tricarbonyl cations for a particular metal, but the variation in k_i is small being ca. 0.1 mdynes/Å.

Differences in k and k_i within a closely related series of compounds should be significant and we are able to make some comments on the values obtained for the Group VII cations and point to comparisons with isoelectronic neutral chromium and tungsten carbonyl compounds. As expected, k and k_i show little, if any, significant variation in complexes which contain ligands of similar bonding abilities, e.g. III, and V or XVII and XXII. Within the series $[Mn(CO)_3N_3]^+$ (N = nitrogen donor ligand) the stretching parameter order is I > III ≃ V ≃ VII > X. Diethylenetriamine is an excellent σ-donor ligand but is not a π-acceptor of metal electrons, so presumably there is a relative strengthening of the π-M—C bonds and a weakening of the π-C—O bonds, leading to a low k value. The heterocyclic nitrogen ligands can form π-M—N bonds to some extent, the π-C—O bonds not being weakened as much as in X, the k value thereby being greater. The high k value of I, and similarly that of II compared with IV must be a consequence of the low ability of acetonitrile to act as a σ-donor, placing relatively little electron density on the metal. Cotton [34] has pointed out that acetonitrile may possess some ability to act as a π-acceptor ligand in competition with carbonyl groups. A similar trend in CO stretching parameters for $[Mn(CO)_5-(NCMe)]^+$ and $[Mn(CO)_5(py)]^+$ (k_1 = 17.05 and 16.97 respectively and k_2 = 17.83 and 17.67, respectively) has been noted [8]. It is unlikely, however, that a nitrile is a significantly better π-acceptor ligand than a heterocyclic nitrogen ligand, so the weak σ-donor ability of acetonitrile will be the major factor in determining the high k values for acetonitrile—carbonyl complexes. Indeed, this work shows that acetonitrile is easily displaced by other more effective σ-donor ligands. Complex XXV has exceptionally low ν(CO) frequencies and a very low k value. Although ethylenethiourea is likely to be a good σ-donor in this complex, it may also act as a π-donor ligand, as had been suggested by Cotton [34] for formamide-type ligands.

The Cotton—Kraihanzel approach has been applied to a number of fac-$[M(CO)_3$-

TABLE 5

CO STRETCHING PARAMETERS OF ISOELECTRONIC CARBONYLS

Compound	k (mdynes/Å)	k_i (mdynes/Å)	Ref.
$Cr(CO)_6$	16.49	0.22	32
$Mn(CO)_6^+$	18.23	0.22	28
$W(CO)_6$	16.41	0.29	32
$Re(CO)_6^+$	18.18	0.26	27
$Cr(CO)_3(NCMe)_3$	13.45	0.64	36
$[Mn(CO)_3(NCMe)_3]^+$	16.24	0.48	This work
$W(CO)_3(NCMe)_3$	13.30	0.53	36
$[Re(CO)_3(NCMe)_3]^+$	15.92	0.55	This work
$Cr(CO)_3(dien)$	13.10	0.70	35
$[Mn(CO)_3(dien)]^+$	15.53	0.64	This work

X_2Y] complexes where M = Group VI element but with only limited success, since quite often where X or Y are good π-acceptor ligands, such as phosphines or arsines, real roots are not obtained [22]. No such problems were encountered in the present work for cations of C_s local symmetry, perhaps because the ν(CO) frequencies are ca. 150 cm^{-1} higher than for the Group VI complexes. Metal—ligand and metal—carbon π-bonding is thus likely to be much weaker for the Group VII cations. In the method used it is assumed that the two kinds of *cis* interaction parameters (a) $k_{i(XX)}$, the coupling of the two carbonyls each *trans* to X in model A or *trans* to acetonitrile in model B, and (b) $k_{i(XY)}$, the coupling of a carbonyl *trans* to X with one *trans* to acetonitrile in model A, or a carbonyl *trans* to acetonitrile with one *trans* to the arsine in model B, are identical. The failure to be able to calculate k_1 and k_2 for the Group VI complexes is probably due to an appreciable difference in $k_{i(XX)}$ and $k_{i(XY)}$, but this difference will be much less significant for the Group VII cations, and the calculations are successfully accomplished. The k_i values for the cations containing phosphine or arsine ligands are somewhat lower than those of the nitrogen-donor complexes, since the better the π-acceptor ability of the ligand the more it is able to compete with carbonyl ligands for metal d_π-electrons, thus reducing the carbonyl interaction effects.

The k values obtained for the cations may be compared with those calculated for isoelectronic neutral substituted Group VI metal carbonyls as an illustration of the effect of the positive charge on the metal. It is to be expected that the stretching parameters of the cations will be greater than those of the neutral complexes since the M—C π-bonding will be lower, with the CO bond order significantly higher. The selection of results shown in Table 5 clearly illustrates this feature, the differences in k values between isoelectronic hexacarbonyls being significantly less than those between isoelectronic trisubstituted carbonyls.

Other infrared bands associated primarily with ligand vibrations show features well established for coordinated ligands and do not merit much comment in the present context. The frequency and intensity of the ν(NH) bands of coordinated paphy (3230m for XI; 3190m for XII), show that the ligand is coordinated in the *E*-isomeric form so that it is able to act as a terdentate ligand. This ligand is known [37] to react with other metal carbonyls by isomerisation to the *Z*-isomer which can act only as a bidentate ligand. The ν(NH) frequency, 3310 cm^{-1}, of both di-2-pyridylamine complexes, VII and VIII, is virtually unchanged from that of the free ligand indicating the non-coordination of this amino-nitrogen atom.

The complexity of the spectra have generally inhibited attempts to assign metal—ligand stretching frequencies. However, bands at 249m and 242m cm^{-1} for III and 222s and 215sh cm^{-1} for IV are likely to be associated with vibrations that involve considerable metal—pyridine nitrogen stretching character. The two low frequency ring vibrations of pyridine found at 604 and 405 cm^{-1} for the free ligand show the usual [38] shifts to higher frequencies on coordination of the ligand to a metal, viz, 635s and 421w cm^{-1} for III and 645s and 434w cm^{-1} for IV. Other workers [30,39] have documented ν(MP) bands for triphenylphosphine substituted metal carbonyls, and, after eliminating from consideration X-sensitive ligand modes, bands at 183ms cm^{-1} for XIII and 161m and 156m cm^{-1} for XIV may be tentatively assigned to this type of vibration. Since

TABLE 6

¹H NMR RESULTS ^{a}

Complex	Solvent	CH₃CN protons	Other protons
I	(CD₃)₂CO	7.47s	
II	(CD₃)₂CO	7.33s	
III	(CD₃)₂CO	7.24s	2.33m (H³, H⁵); 1.88t (H⁴); 1.43d and 1.31d (H², H⁶); $J_{5,6} = J_{2,3} = 5.5$
IV	(CD₃)₂SO		2.30 overlapping triplets (H³, H⁵); 1.78t (H⁴); 1.36d (H²H⁶); $J_{5,6} = J_{2,3} = 5.5$
V	(CD₃)₂CO	7.77s	2.12m (H⁵); 1.64t (H⁴); 1.35dd (H³); 0.68dd (H⁶); $J_{5,6}$ 5.0; $J_{4,6}$ 2.5; $J_{3,4}$ 8.5; $J_{4,5}$ 7.5
VI	(CD₃)₂SO	7.66s	2.10m (H⁵); 1.51t (H⁴); 1.10dd (H³); 0.88dd (H⁶); $J_{5,6}$ 6.0; $J_{4,5}$ 7.5; $J_{3,4}$ 8.0; $J_{4,6}$ 1.5; $J_{3,5}$ 3.0
VII	(CD₃)₂SO	7.68s	2.72m (H³, H⁵); 2.02t (H⁴); 1.43dd (H⁶); $J_{5,6}$ 4.5; $J_{3,4}$ 8.0; $J_{4,5}$ 7.5
VIII	(CD₃)₂CO	7.40s	2.66m (H⁵); 2.32dd (H³); 1.85t (H⁴); 1.22dd (H⁶); $J_{5,6}$ 5.5; $J_{4,6}$ 1.5; $J_{3,4}$ 8.5; $J_{4,5}$ 7.5; $J_{3,5}$ 1.5
IX	CD₃CN		2.62dd (H⁴); 2.12m (H³, H⁵); 1.12d (H⁶); $J_{5,6}$ 5.0; $J_{3,4}$ 8.0; $J_{4,5}$ 6.0
XI	CDCl₃		1.6m (H⁶′); 1.2m (H⁶); 0.1br (NH)
XII	CDCl₃		1.31m (H⁶′); 1.12m (H⁶); 0.19d (NH)
XIII	(CD₃)₂SO	7.99s	2.64m (Ph)
XIV	CDCl₃	8.10s	2.68m (Ph)
XV	CDCl₃	8.58s	2.62m (Ph); 5.40 and 4.54 (AB of CH₂)
XVI	CDCl₃	8.44s	2.58m (Ph); 5.28 and 3.72 (AB of CH₂); 7.87s (Me₂CO).
XVII	CDCl₃	8.44s	2.50m (Ph); 6.96 v.br.m (C₂H₄)
XVIII	CDCl₃	8.32s	2.52m (Ph); 6.95 v.br.m (C₂H₄); 7.86s (Me₂CO)
XIX	CDCl₃	8.28s	2.50m (Ph); 7.10 v.br.m (C₂H₄)
XX	CDCl₃	7.89s	2.53m (Ph)
XXI	CDCl₃	7.75s	2.46m (Ph)
XXII	CDCl₃	8.42s	2.54m (Ph); 7.17 and 6.69 (C₂H₄)
XXIII	CDCl₃	8.23s	2.49m (Ph); 7.41 and 6.82 (C₂H₄)
XXIV	(CD₃)₂SO		6.32s (C₂H₄); 2.04s (NH)
XXV	(CD₃)₂CO		6.04s (C₂H₄); 1.98s (NH)

^{a} τ values relative to TMS; J in Hertz; s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

only one such band is observed for XIII, the phosphine ligands may be mutually *trans* in this dicarbonyl cation as would be sterically preferred.

NMR spectra

¹H and ³¹P NMR results are listed in Tables 6 and 7, respectively. Relative peaks areas are not given, but are in good agreement with expectations. The bands of the spectra of the manganese complexes are broader than those of the rhenium complexes. Both metals have nuclei with large spins (^{55}Mn, 100%, I = 5/2; ^{185}Re, 37%, I = 5/2; ^{187}Re, 63%, I = 5/2) and quadrupole moments. The resulting coupling and relaxation effects introduce some line-broadening effects and from the quality of the spectra obtained it is evident that these effects are more significant for manganese than for rhenium.

(i) *¹H NMR*. The observation of a single resonance for the methyl protons of I and II is further evidence supporting a *fac*-configuration. The presence of co-ordinated acetonitrile in many of the cations prepared is clearly shown by ¹H NMR, although as previously noted [9] there is a large variation in the position of the nitrile proton resonances. This appears downfield from that of the free

ligand for the nitrogen-donor complexes, whereas for the phosphine or arsine donor complexes the resonance position is either essentially unchanged or is shifted upfield of the free ligand position. It has been found [9] for some related acetonitrile complexes that doublet, triplet, or quartet patterns are found when phosphine or phosphite ligands are also present, the splitting being related to the number of such ligands. No such $J(P-H)$ coupling is observed for the phosphine—nitrile complexes reported here.

The methyl protons of the acetone of crystallisation in XVI and XVIII are observed as singlets.

The heterocyclic nitrogen donor complexes generally show well separated individual resonances for the pyridine ring protons [40]. Protons in the 3 and 5 positions to nitrogen are invariably upfield of protons in the 2 (if present) and 6 positions. H^3 and H^5 of III, IV, VII and IX form composite absorptions, but these signals are well separated in V and VI with H^4 protons appearing at an intermediate resonance frequency. For IX, H^4 is found upfield of H^3 and H^5. For a number of the complexes the assignments have been further justified by double resonance experiments. For VI, double irradiation at the H^6 protons causes the multiplet assigned to H^5 to collapse to a doublet whereas the 1 : 2 : 1 triplet assigned to H^4 ($J_{3,4} \simeq J_{4,5}$) is unchanged. The coupling constants listed in Table 6 are then obtained. Similarly for VIII, double irradiation of H^6 protons causes the H^5 multiplet to collapse to a doublet of doublets with $J_{4,5}$ and $J_{3,5}$ being obtained whereas the resonances associated with H^4 (1 : 2 : 1 triplet; $J_{3,4} \simeq J_{4,5}$) and H^3 (doublet of doublets, $J_{3,4} > J_{3,5}$) are unchanged.

The ditertiary phosphine and arsine complexes show some interesting methylene resonance features. The phenyl resonances occur as a broad complex band between τ 2 and 3 ppm and have not been analysed. Whereas heteronuclear coupling with ^{31}P is evident in the spectra of the phosphine complexes no coupling with ^{75}As (100%, $I = 3/2$) is observed for the arsine complexes. The ditertiary arsine complexes XXII and XXIII show two regions of absorption, ν_A and ν_B, associated with the methylene protons, the centres of absorption being at τ 7.17 and 6.69 ppm for XXII and τ 7.41 and 6.82 ppm for XXIII. Clearly the protons are magnetically inequivalent with non-equivalent environments upon formation of the chelate rings. Within each absorption area ν_A or ν_B, splitting gives eight lines for XXIII and seven lines for XXII, the line positions and intensities being symmetric with respect to the centre of the spectra ($\frac{1}{2}(\nu_A + \nu_B) = 6.93$ ppm for XXII and 7.12 ppm for XXIII), the B lines being mirror images of the A lines. The general appearance of the spectrum of XXII is somewhat different from that of XXIII but this is to be expected since the appearance of the spectra will depend on the relative magnitudes of the various couplings involved. The methylene protons are best described as constituting AA'BB' spin systems. Analysis [41] shows that such a system will lead to 12A and 12B transitions, the 24 lines being symmetric with respect to the centre of the spectrum, the 12B lines being mirror images of the 12A lines. The lower number of lines observed in the present examples is probably related to poor resolution owing to quadrupole line-broadening effects mentioned earlier. The spectra cannot therefore be further analysed.

The methylene resonance of free dppe is a deceptively simple triplet [42]. The spectra of the dppe chelate complexes XVII and XVIII are even less well resolved

TABLE 7

^{31}P NMR DATA FOR SOME dppm AND dppe COMPLEXES ^{a}.

Compound	Solvent	$\delta(P)$ (ppm)	$\Delta(P)$ (ppm)	$\Delta(P)$ dppe $-\Delta(P)$ dppm	Ref.
dppm	CHCl$_3$	+22.7			This work
dppe	CHCl$_3$	+13.2			This work
Cr(CO)$_4$(dppm)	CH$_2$Cl$_2$	−25.4	−49.0	42.9	48
Cr(CO)$_4$(dppe)	CH$_2$Cl$_2$	−79.4	−91.9		48
Mo(CO)$_4$(dppm)	CH$_2$Cl$_2$	0.0	−23.6	43.6	48
Mo(CO)$_4$(dppe)	CH$_2$Cl$_2$	−54.7	−67.2		48
W(CO)$_4$(dppm)	CH$_2$Cl$_2$	+23.6	0.0	52.6	48
W(CO)$_4$(dppe)	CH$_2$Cl$_2$	−40.1	−52.6		48
Mn(CO)$_3$Br(dppm)	CH$_2$Cl$_2$	−10.9	−33.6	47.2	This work
Mn(CO)$_3$Br(dppe)	CH$_2$Cl$_2$	−67.6	−80.8		This work
XV	CHCl$_3$	−13.7	−36.4	50.3	This work
XVII	CH$_2$Cl$_2$	−73.5	−86.7		This work
Re(CO)$_3$Br(dppm)	CHCl$_3$	+38.5	+15.8	59.0	This work
Re(CO)$_3$Br(dppe)	CHCl$_3$	−30.0	−43.2		This work
XVI	CH$_2$Cl$_2$	+35.0	+12.3	63.5	This work
XVIII	(CH$_3$)$_2$CO	−38.0	−51.2		This work
PtMe$_2$(dppm)	CH$_2$Cl$_2$	+40.4	+17.4	77.1	45
PtMe$_2$(dppe)	C$_6$H$_6$	−45.4	−59.7		45
PtCl$_2$(dppm)	CH$_2$Cl$_2$	+64.3	+41.3	99.1	45
PtCl$_2$(dppe)	CH$_2$Cl$_2$	−45.3	−57.8		45

^{a} Relative to 85% H$_3$PO$_4$; $\Delta(P) = \delta$(complex) $- \delta$(ligand)

than those of the dpae complexes mentioned above owing to further coupling with the phosphorus nuclei. It is apparent from the general appearance of the spectra that XAA'BB'X or XAA'BB'X' spin systems are present. ^{31}P coupling and relaxation effects result in considerable overlap of the ν_A and ν_B portions of the spectra so only the centres of absorption, $\frac{1}{2}(\nu_A + \nu_B)$, are listed in Table 6. The overall widths of the methylene absorption areas are ca. 1.4 ppm. For comparative purposes we have also examined the spectra of [Mn(CO)$_3$Br(dppe)] and [Re(CO)$_3$Cl(dppe)] and these complexes show similar features to the cations with broad methylene absorptions centred at τ 7.10 and 7.20 ppm respectively.

The methylene resonance of free dppm is a 1 : 2 : 1 triplet (τ 7.23 ppm; ^2J(P—H) 1.5 Hz) [42]. For the two dppm chelate complexes XV and XVI the appropriate spin system is one of the simpler XABX or XABX' systems depending on the equivalence or otherwise of the phosphorus nuclei. Well separated ν_A and ν_B absorptions are evident in the spectra ($\nu_A - \nu_B = 0.86$ ppm; $\frac{1}{2}(\nu_A + \nu_B) = 4.97$ ppm for XV; $\nu_A - \nu_B = 1.56$ ppm; $\frac{1}{2}(\nu_A + \nu_B) = 4.50$ ppm for XVI]. The two protons will be non-equivalent by virtue of the different groups above and below the MP$_2$ plane and also puckering of the chelate rings may well play a significant role. The nuclear spins of the methylene protons will interact to give an AB quartet, each of the four lines being split into a 1 : 2 : 1 triplet if the two phosphorus nuclei are equivalent. Two slightly different J(P—H) coupling constants will be expected for the interaction of non-equivalent protons with equivalent phosphorus nuclei. Although the spectrum of XV is too broadened

to allow successful analysis, approximate coupling constant values of J_{AB} 17 Hz, J_{AP} 11 Hz, and J_{PB} 10 Hz can be obtained for XVI. The spectrum of [Re(CO)₃Br-(dppm)] has also been recorded and is similar except that the methylene protons appear to be less environmentally inequivalent in this compound with ν_A and ν_B centred at τ 5.24 and 4.57 ppm, respectively. Approximate coupling constant values are J_{AB} 15 Hz, J_{AP} 11 Hz and J_{PB} 8 Hz. These values are similar to those found [43] for [CH₃COMn(CO)₃(dppm)] and [CH₃Mn(CO)₃(dppm)].

Methylene proton inequivalence is not observed for XXIV and XXV, the signals being singlets. The NH proton resonances are also singlets but are broad due to the influence of the neighbouring ¹⁴N nuclei.

(ii) ³¹P-{¹H} NMR. Recent ³¹P NMR studies [44] of complexes containing monotertiary phosphine ligands have indicated the existence of a good empirical linear relationship between the chemical shift of the free phosphine, δ(ligand), and the change in chemical shift upon coordination to a metal, Δ(P). With a downfield shift defined as negative, Δ(P) is defined by:

$$\Delta(P) = \delta(\text{complex}) - \delta(\text{ligand}) \tag{1}$$

For several series of transition metal complexes involving monotertiary phosphines e.g. *cis*-PtCl₂L₂ or *fac*-Mo(CO)₃L₃ [44,45] sufficient examples are available to show that the relationship between Δ(P) and δ(ligand) is of the form Δ(P) = Aδ(ligand) + B, with A and B being constants.

The ³¹P chemical shifts of a number of ditertiary phosphine chelate complexes are anomalous in that they do not fit the above relationship. Prior to this work the complexes examined contained Group VI [46—48] or Group VIII (Ni and Pt) [45,49] metals. Representative examples involving dppm or dppe ligands are listed in Table 7, along with our results [11] on the cations XV—XVIII and also for comparison results on [M(CO)₃Br(dppm)] and [M(CO)₃Br(dppe)] (M = Mn and Re). The results show that the anomalous chemical shift behaviour of ditertiary phosphine chelate complexes extends to Group VII compounds. Although three different solvents and solutions of various concentrations were employed to obtain the spectra, concentration and solvent effects were minimal (>1 ppm) and do not affect in any significant way any of the features to be discussed. The resonances appeared as broad singlets owing to coupling and relaxation effects mentioned earlier. Δ(P) decreases in the expected order Mn > Re, the decrease being significantly greater for the dppm complexes than for the dppe complexes. The Mn—Re differences are remarkably constant when considering pairs of complexes involving the same ditertiary phosphine. Thus Δ(P)Mn — Δ(P)Re for the [M(CO)₃Br(dppm)] pair is 49.4 ppm and that for XV—XVI is 48.7 ppm. The use of chelating dppe changes the Δ(P)Mn — Δ(P)Re differences to 37.6 ppm for the [M(CO)₃Br(dppe)] pair and 35.5 ppm for XVII—XVIII. The values listed in Table 7 show that Δ(P) decreases in the similar order Cr > Mo > W for the Group VI examples.

These anomalous chemical shifts are certainly related in some way to chelate ring formation since when acting as bridging ligands the same ditertiary phosphines exhibit chemical shifts of the same magnitude as those of similar monotertiary phosphines [11,47]. Garrou [50] has expressed the anomalous behaviour in terms of an extra "ring contribution" to the coordination chemical shifts. Using the data of Table 7 in a comparison with the δ and Δ(P) chemical shifts

of related monotertiary phosphine complexes, it is apparent that the chemical shift is further downfield than expected for chelating dppe (five-membered ring), whereas for chelating dppm (four-membered ring) it is further upfield than expected. This feature is also illustrated in Table 7 by listing [$\Delta(P)$ dppe complex $- \Delta(P)$dppm complex] for pairs of complexes, the differences being between 40 and 100 ppm. The chemical shift differences are particularly striking for the platinum [45] and rhenium compounds listed, since δ(complex) for the dppm complexes are upfield of δ(ligand) leading to $\Delta(P)$ values of opposite sign to those of the other complexes. As an example of a Group VII monotertiary phosphine complex, the ^{31}P spectrum of XIV in dimethyl sulphoxide has been recorded and δ(complex) and $\Delta(P)$ found to be -8.9 and -14.2 ppm, respectively. The δ(complex) value is, as expected, intermediate between the upfield value of the analogous dppm complex XVI and the downfield value of the analogous dppe complex XVIII. The "ring contribution" to the chemical shift [50] is therefore a deshielding contribution for dppe chelate complexes and a shielding contribution for dppm chelate complexes.

This pronounced ditertiary phosphine chelate effect was first attributed [46] in the five-membered ring complexes [$M(CO)_4(Me_2PCH_2CH_2PMe_2)$] (M = Cr, Mo, or W) to ring strain and it seems reasonable to suggest that reduction of the P—M—P and P—C—P or P—C—C angles from their usual values in the small chelate rings will play an important role in influencing chemical shift values. However such an explanation fails to account for the greater extent of deshielding for five-membered ring systems over the more highly strained four-membered ring systems. Indeed, we have already noted that the $\Delta(P)$ shifts for the four-membered ring systems are substantially less than even those of related monotertiary phosphine complexes. Although we are unable to explain the anomalous chemical shift behaviour of the ditertiary phosphine chelate complexes, it is possible that variable changes in bond angles in forming the complexes resulting in large rehybridization effects, as well as changes in the extent of both $\sigma(P \to M)$ and $\pi(M \to P)$ bonding compared with analogous monotertiary phosphine complexes, may all play a part in determining chemical shift values. The observation of these unusual chemical shifts can be a useful method for characterizing chelate behaviour and eliminating the possibilities of bridging or monodentate modes of bonding for ditertiary phosphines.

Acknowledgment

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