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REACTIONS OF GROUP VI METAL CARBONYLS WITH SOME TERDENTATE NITROGEN DONOR LIGANDS AND THE OXIDATION OF THE PRODUCTS WITH IODINE

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SUMMARY

The hexacarbonyls of chromium, molybdenum and tungsten react with three terdentate nitrogen donor ligands, T, to give *fac*-$M(CO)_3T$ derivatives, where T = bis(2-pyridylmethyl)amine, bis(2-pyridylmethyl)methylamine and bis(2-pyridylethyl)amine. $Mo(CO)_3$(cycloheptatriene) and $W(CO)_3(\text{acetonitrile})_3$ have also been used to prepare two of these products. The action of iodine on the *fac*-$Mo(CO)_3T$ and *fac*-$W(CO)_3T$ derivatives has also been investigated. In all cases the products are seven-co-ordinate divalent metal compounds of the type $[M(CO)_3(T)I]^+I^-$. These iodo derivatives are the first of this type to contain terdentate nitrogen ligands.

INTRODUCTION

A number of octahedral substituted Group VI metal carbonyls of general formula $M(CO)_3T$ (M = Cr, Mo or W; T = terdentate ligand) have been characterised[1]. The most extensive studies have used terdentate phosphorus[2,3] and arsenic[4-6] donor molecules. It is conceivable that both *mer*- and *fac*-$M(CO)_3T$ complexes can be isolated. On replacing carbonyl groups of a metal hexacarbonyl with ligands which are poorer π-acceptors than carbon monoxide, the π-bonding of the remaining carbonyl groups will be greatest if all the carbonyl groups are mutually *cis*, *i.e.* are situated *trans* to the incoming ligand atoms. Thus *fac*-$M(CO)_3T$ will be the expected configuration for a hexacarbonyl substituted by a terdentate ligand. For nitrogen donor molecules this arrangement is known where T = diethylenetriamine[7], tri-2-pyridylamine[8], and some substituted hexahydrotriazines[9]. However, features associated with the particular ligand chosen for study may affect the nature of the product. Thus, repulsions between non-bonded atoms when the substituents on the co-ordinated atom of the ligand are large might destabilise the *fac*-structure and favour the *mer*-arrangement. The IR spectrum of $Cr(CO)_3[Et_2N(CH_2)_2NH(CH_2)_2NEt_2]$ is said to be consistent with a *mer*-arrangement[10] and this is attributed to large repulsions which would develop between the ethyl groups in a *fac*-configuration. Alternatively, the ligand chosen may be insufficiently flexible to span the facial positions. Such an example is 2,2′,2″-terpyridyl, (terpy), the unstable *mer*-$Mo(CO)_3$terpy having been prepared[11] from $Mo(CO)_3$(mesitylene). Somewhat surprisingly however this ligand is more inclined to form $M(CO)_4$terpy, ($M = Cr$, Mo or W), compounds, one nitrogen atom remaining unco-ordinated. We have recently studied[12] the co-ordinating ability of the potentially terdentate *E*-pyridine-2-carbaldehyde 2′-pyridylhydrazone, (*E*-paphy), which is also restricted to a meridional type of co-ordination. Some evidence was found for the formation of the unstable *mer*-$Mo(CO)_3$(*E*-paphy). The usual products are of the type $M(CO)_4$(paphy), ($M = Cr$, Mo or W), and, interestingly, in these compounds the *E*-paphy isomerises to the *Z*-isomer which, due to strong intramolecular hydrogen bonding, cannot act as more than a bidentate ligand.

Ligands such as 2,2′,2″-terpyridyl possess good co-ordinating ability and this may be attributed to the presence of $-N{=}C{-}C{=}N-$ systems which permit the formation of conjugated chelate ring systems, these providing a facile pathway for back-donation of metal t_{2g} electrons into empty antibonding molecular orbitals of the ligand. Saturated aliphatic triamines, such as diethylenetriamine, cannot operate in this way and must rely solely on the strength of the metal–nitrogen σ-bonds produced.

We report here the results of a study of the reactions of Group VI metal hexacarbonyls with the terdentate nitrogen donor ligands, bis(2-pyridylmethyl)amine (dpma), bis(2-pyridylmethyl)methylamine (Me.dpma), and bis(2-pyridylethyl)amine (dpea). These ligands are sufficiently flexible to co-ordinate facially so the steric constraints associated with the α-di-imino type of ligand are avoided, and the ligands may be regarded as "half-way" situations between the extremes of 2,2′,2″-terpyridyl and diethylenetriamine mentioned above. Thus, it is possible to study the effect of disrupting the chelate ring conjugation whilst retaining pyridine ring nitrogens in the ligands. Two identical five-membered rings may be formed using dpma and Me.dpma, but the rings will be six-membered with dpea. The methyl group attached to the aliphatic nitrogen of Me.dpma should improve the σ-donor ability of the ligand compared with dpma, but may well have an adverse steric influence.

These ligands have previously been used in reactions with transition metal compounds of conventional oxidation states. Thus, for example, octahedral iron and nickel $[M(dpma)_2]^{2+}$ and $[M(Me.dpma)_2]^{2+}$ ions have been prepared[13]. A number of five-co-ordinate $MX_2(T)$ complexes, ($M = Zn^{II}$, Cd^{II}, or Hg^{II}; $X = Cl$, Br or I; $T =$ dpma or Me.dpma) have also been isolated[14]. With dpea a wide range of structural types have been characterised[15,16]: (*i*) five-co-ordinate $MX_2(T)$, ($M = Ni^{II}$, Co^{II}, Cu^{II}, Mn^{II} or Cd^{II}; $X = Cl$, Br or CNS); (*ii*) square planar $[PdX(T)]^+$, ($X = Cl$, Br or I); (*iii*) tetrahedral $ZnX_2(T)$, ($X = Cl$, Br or I) in which one nitrogen of dpea is unco-ordinated, and (*iv*) octahedral halogen-bridged $[MCl_2(T)]_n$ ($M = Mn^{II}$ and Cd^{II}). Complexes of first row transition metal ions with dpma have also been studied potentiometrically[17,18] and formation constants reported.

The oxidation of Group VI metal tricarbonyl–tritertiary arsine complexes by halogens has been extensively studied by Nyholm and his co-workers[4,5,19]. The products are usually divalent seven-co-ordinate metal compounds, but of two distinct types, either ionic $[M(CO)_3(triars)X]^+Y^-$, ($X = Br$ or I; $Y = Br$, I or BPh_4), or neutral $[M(CO)_2(triars)X_2]$, ($X = Cl$, Br or I). The compounds $M(CO)_3(TP)$, {$M = Mo$ or W; TP = bis[2-(diphenylphosphino)phenyl]phenylphosphine} give some analogous compounds[3] on oxidation with bromine or iodine. Since halogen oxidations of metal tricarbonyl–terdentate nitrogen donor complexes appear not to have been attempted, we have also investigated the reactions between iodine and some of the $M(CO)_3T$ compounds isolated in this study.

EXPERIMENTAL

IR spectra above 375 cm^{-1} were recorded on Perkin–Elmer 237 and Unicam SP 100 spectrophotometers. Below 400 cm^{-1} spectra were obtained from samples dispersed in polyethylene using an R.I.I.C. FS 720 interferometer. The Fourier transforms of the resulting interferograms were computed on an I.C.L. 4-50 computer, giving an effective resolution of 2.5 cm^{-1}. Conductance measurements at 25° were made in nitromethane using a Wayne–Kerr Autobalance bridge and a dip-type cell with platinum electrodes. A Gouy balance was used for room temperature magnetic susceptibility measurements.

Iodine estimations[20] used a thiosulphate titration after oxidation of samples by a Schöniger oxygen flask method. Bis(2-pyridylmethyl)amine[13], bis(2-pyridylmethyl)methylamine[13], and bis(2-pyridylethyl)amine[21] were prepared by literature methods. All solvents used in reactions and measurements were dried by appropriate desiccants before use. Reactions were carried out in an atmsophere of dry oxygen-free nitrogen.

Since the preparations of the M(CO)$_3$T compounds are all similar and straightforward only a typical preparation is described. Other products are shown in Table 1.

TABLE 1

GROUP IV METAL TRICARBONYL-TERDENTATE NITROGEN DONOR COMPLEXES

Starting material	Conditions	Product	Yield (%)	Analysis, found (calcd.) (%)		
				C	H	N
Mo(CO)$_6$/dpma	Benzene 12 h	Mo(CO)$_3$dpma yellow	80	47.2 (47.6)	3.43 (3.18)	11.0 (11.1)
W(CO)$_6$/dpma	Mesitylene 6 h	W(CO)$_3$dpma yellow	75	38.6 (38.6)	3.05 (2.80)	8.9 (9.0)
Cr(CO)$_6$/Me.dpma	Toluene 24 h	Cr(CO)$_3$Me.dpma red	70	54.3 (55.0)	4.39 (4.30)	11.7 (12.0)
Mo(CO)$_6$/Me.dpma	Benzene 24 h	Mo(CO)$_3$Me.dpma yellow	87	48.8 (48.9)	3.70 (3.82)	10.6 (10.7)
Mo(CO)$_3$cht^a/Me.dpma	Benzene 1½ h	Mo(CO)$_3$Me.dpma yellow	68	49.1 (48.9)	3.66 (3.82)	11.3 (10.7)
W(CO)$_6$/Me.dpma	Mesitylene 6 h	W(CO)$_3$Me.dpma yellow	75	38.6 (39.9)	3.08 (3.14)	8.9 (8.7)
W(CO)$_3$(MeCN)$_3$/Me.dpma	Benzene 2 h	W(CO)$_3$Me.dpma yellow	77	39.9 (39.9)	3.28 (3.14)	8.4 (8.7)
Cr(CO)$_6$/dpea	Mesitylene 2 h	Cr(CO)$_3$dpea orange	80	56.2 (56.3)	4.69 (4.79)	11.6 (11.4)
Mo(CO)$_6$/dpea	Benzene 16 h	Mo(CO)$_3$dpea yellow	75	50.2 (50.1)	4.16 (4.17)	10.2 (10.3)
W(CO)$_6$/dpea	Mesitylene 6 h	W(CO)$_3$dpea yellow	80	41.9 (41.2)	3.66 (3.44)	8.3 (8.5)

[a] cht = cycloheptatriene.

fac-Tricarbonyl[bis(2-pyridylmethyl)amine]chromium(0)

Chromium hexacarbonyl (0.2 g) and dpma (0.2 g) were heated together in mesitylene (10 ml) under gentle reflux for 2 h. After cooling, the orange crystals were filtered off, washed repeatedly with small portions of ethanol and dried *in vacuo*. Yield 90%. (Found: C, 54.0; H, 4.00; N, 12.3. $C_{15}H_{13}CrN_3O_3$ calcd.: C, 53.6; H, 3.89; N, 12.5%.)

Iodine oxidation reactions

The preparations of $[M(CO)_3(T)I]^+I^-$ compounds were all carried out by similar procedures. The $M(CO)_3T$ (0.3 g) was stirred in dichloromethane or chloroform (15 ml) and over 10 min two equivalents of iodine dissolved in dichloromethane or chloroform (25 ml) were added. The temperature of the solution was kept below 10°. The solvent was then reduced to low volume at 20°/10 mm and excess petroleum ether (30–40°) added. The resulting yellow precipitate was washed with petroleum ether and dried *in vacuo*. Details of individual compounds are given in Table 2.

TABLE 2

IODINE OXIDATION PRODUCTS

Complex (0.3 g)	Iodine (g)	Product yield (%)	Analysis, found (calcd.) (%)			
			C	H	N	I
$Mo(CO)_3dpma$[a]	0.20	$[Mo(CO)_3(dpma)I]^+I^-$ 86	28.0 (28.4)	2.26 (2.06)	6.47 (6.65)	39.8 (40.2)
$W(CO)_3dpma$[b]	0.17	$[W(CO)_3(dpma)I]^+I^-$ 60	23.4 (25.0)	2.29 (1.80)	5.79 (5.82)	35.0 (35.2)
$Mo(CO)_3Me.dpma$[a]	0.20	$[Mo(CO)_3(Me.dpma)I]^+I^-$ 67	29.2 (29.6)	2.54 (2.32)	6.22 (6.49)	39.7 (39.2)
$W(CO)_3Me.dpma$[b]	0.16	$[W(CO)_3(Me.dpma)I]^+I^-$ 46	24.9 (26.2)	2.16 (2.04)	5.63 (5.74)	34.8 (34.6)
$Mo(CO)_3dpea$[a]	0.19	$[Mo(CO)_3(dpea)I]^+I^-$ 65	30.1 (30.8)	2.66 (2.57)	6.12 (6.35)	37.1 (38.4)
$W(CO)_3dpea$[b]	0.16	$[W(CO)_3(dpea)I]^+I^-$ 63	26.1 (27.2)	2.61 (2.28)	6.04 (5.61)	35.0 (33.9)

[a] In CH_2Cl_2. [b] In $CHCl_3$.

Iodotricarbonyl[bis(2-pyridylmethyl)methylamine]tungsten(II) tetraphenylborate

$W(CO)_3(Me.dpma)$, (0.2 g), was suspended in chloroform (15 ml) at 10° and iodine (0.11 g) in chloroform (20 ml) added dropwise with stirring over a period of 10 min. Silver nitrate (0.08 g) in water (0.5 ml) and ethanol (5 ml) was added with stirring and the resulting silver iodide filtered off. To the filtrate was added sodium tetraphenylborate (0.15 g) in ethanol (5 ml). The solution was reduced to 10 ml at 20°/10 mm and the resulting orange precipitate washed with ethanol and dried *in vacuo*. Yield 40%. (Found: C, 49.2; H, 3.69; I, 13.0; N, 4.81. $C_{40}H_{35}BIN_3O_3W$ calcd.: C, 51.7; H, 3.77; I, 13.7; N, 5.52%.)

RESULTS AND DISCUSSION

The reactions of Group VI metal hexacarbonyls with the potentially terdentate ligands dpma, Me.dpma and dpea in refluxing solvents lead to the formation of crystalline $M(CO)_3T$ derivatives, (Table 1). The molybdenum compounds were conveniently prepared in benzene whereas, in order to achieve a reasonable reaction rate, the chromium and tungsten compounds were best prepared in mesitylene. Two of the derivatives have also been prepared by substitution of more labile ligands, namely $Mo(CO)_3$(Me.dpma) from $Mo(CO)_3$(cycloheptatriene) and $W(CO)_3$(Me.dpma) from *fac*-$W(CO)_3$(acetonitrile)$_3$. No significant differences in stability of the products were evident which could be related to a change in chelate ring size from five-membered in dpma and Me.dpma derivatives to six-membered in dpea derivatives. Also the methyl group attached to the central nitrogen of Me.dpma appeared not to noticeably affect the stability of this group of derivatives, either favourably by enhanced σ-donation, or adversely by steric interaction.

TABLE 3

PHYSICAL DATA FOR $M(CO)_3T$ DERIVATIVES

Compound[a]	Λ_M[b] (ohm$^{-1}\cdot$cm^2)	Infrared spectra (cm^{-1})								
		ν(NH)	Ring deformations		ν(CO)[c]					
			8a	8b	Nujol			CHCl$_3$ soln.		
$Cr(CO)_3$dpma	2.2	3322	1607	1570	1905 sh 1892	1770	1735			
$Mo(CO)_3$dpma	1.7	3332	1605	1570	1905 sh 1895	1768	1740			
$W(CO)_3$dpma	2.1	3315	1608	1571	1890	1755 br				
$Cr(CO)_3$Me.dpma	2.3		1603	1568	1892	1775	1740	1908	1790	1768
$Mo(CO)_3$Me.dpma	4.2		1604	1569	1897	1785	1750	1910	1792	1770
$W(CO)_3$Me.dpma	3.0		1603	1567	1887	1767	1742	1900	1785	1760
$Cr(CO)_3$dpea	3.4	3317	1604	1568	1892	1772	1732	1908	1778	1755
$Mo(CO)_3$dpea	2.2	3285	1602	1566	1898	1773	1733	1911	1782	1762
$W(CO)_3$dpea	3.0	3260	1603	1568	1893	1770	1725	1900	1765 br	

[a] All compounds diamagnetic. [b] 10^{-3} *M* in nitromethane. [c] All bands strong.

All the compounds are diamagnetic and non-conducting in nitromethane (Table 3). IR evidence (Table 3) shows that in all cases both pyridine ring nitrogens and the central aliphatic nitrogen are attached to the metal. As expected, ν(N–H) frequencies of the $M(CO)_3$(dpma) and $M(CO)_3$(dpea) complexes are lower than ν(N–H) of the uncomplexed ligands. It has been shown[14] for these ligands that the highest energy pyridine ring deformation (8a) increases in frequency on co-ordination, whilst the next-highest frequency mode (8b) remains virtually unchanged. Complexes with both pyridine nitrogens co-ordinated therefore should show two bands in the 1550–1650 cm^{-1} region, whereas complexes with one pyridine nitrogen unco-ordinated will show three bands in this region, the middle one being at virtually the same frequency as 8a of the free ligand. All the present compounds show just two deformation modes in this region, 8a showing an increase of 15±2 cm^{-1} compared with the appropriate free ligand, the frequency change of 8b being no more than ±2 cm^{-1}. The structures of the compounds are therefore based on an octahedral shape, but could involve either facial or meridional co-ordination of the terdentate ligands. Molecular models of the three ligands show clearly that they are all sufficiently flexible to span either a face or a meridion of an octahedron. Molecular models of each of the $M(CO)_3T$ compounds have been constructed using the M–C and M–N bond distances of $Cr(CO)_3(dien)$[22] and $Mo(CO)_3(dien)$[23] with some adjustment to allow for possible metal $d_\pi \rightarrow$pyridine ring π^* donation. In each case very little strain or steric interaction developed irrespective of whether the stereochemistry was facial or meridional. In view of the fact that π-bonding of the three carbonyl groups will be greatest for the facial arrangement this stereochemistry was expected to be favoured, especially since *mer*-$Mo(CO)_3(terpy)$[11] and *mer*-$Mo(CO)_3$(*E*-paphy)[12] are unstable, bidentate co-ordination of the ligands being favoured with metal carbonyls. It was surprising to find, therefore, that the compounds showed three strong bands in the $\nu(CO)$ region in the solid state (with occasionally a further shoulder), and likewise three bands in chloroform solution, although here the lowest frequency bands are perhaps better described as very pronounced shoulders on the low frequency side of the second bands. The more definite separation of the lower two bands in the solid compared with solution spectra may, in part, be due to site symmetry effects in the crystal lattice. The spectra of $Mo(CO)_3$(dpea), a typical example, are shown in Fig. 1. The dpma compounds decompose rather readily in solution so solution spectra were not obtained for these compounds.

These results are at first sight compatible with the unexpected *mer*-arrangement (C_{2v} local symmetry; $2A_1+B_1$) and mitigate against the formation of *fac*-$M(CO)_3T$ derivatives (C_{3v} local symmetry; A_1+E). Such an argument implies equivalence of the three donor nitrogens. However, the central nitrogen is aliphatic and will act solely as a σ-donor whereas the two pyridine ring nitrogens have π-acceptor ability utilising vacant anti-bonding molecular orbitals of the rings. The local

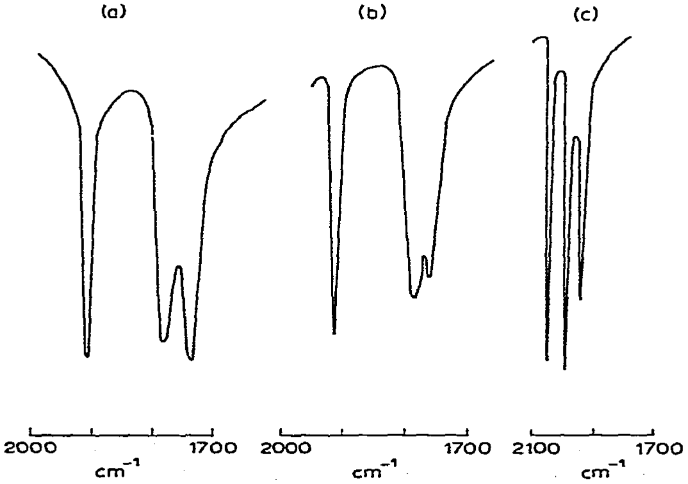

Fig. 1. Infrared spectra: (a) $Mo(CO)_3$dpea, Nujol mull; (b) $Mo(CO)_3$dpea, chloroform solution; (c) $[Mo(CO)_3(dpea)I]^+I^-$, chloroform solution.

symmetry of these compounds can therefore be effectively regarded as lowered to C_s. The degeneracy of the E mode in C_{3v} symmetry is lifted giving $A'+A''$ in C_s symmetry and the highest frequency A_1 mode (C_{3v}) corresponds to a second A' mode (C_s). This effect has previously been reported[24–26] for several *fac*-$M(CO)_3BL$ compounds, where B is a bidentate and L a monodentate ligand. Should L and B have very similar σ- and π-bonding abilities then the local symmetry can be regarded as C_{3v} and two ν(CO) bands are observed (*e.g.* $Mo(CO)_3$(phen)py[25], 1902 and 1782 cm^{-1}), but if L has a very different π-acceptor ability to B then C_s symmetry is appropriate and three ν(CO) bands are observed (*e.g.* $Mo(CO)_3(phen)NHEt_2$[24], 1891, 1769 and 1742 cm^{-1}). The more dissimilar the bonding properties of B and L, the greater will be the splitting of the E mode. Although this effective symmetry lowering has not been observed before whilst using a single terdentate ligand, since there can be no conjugation throughout the ligands in question the IR ν(CO) results are not incompatible with the expected facial co-ordination.

Although several $M(CO)_3T$ compounds[3–5,19] have been oxidised with iodine no such reactions have used metal carbonyls substituted by terdentate nitrogen donor ligands. However, $Mo(CO)_4$(*E*-paphy), in which the potentially terdentate ligand leaves one nitrogen unco-ordinated, reacts with iodine[12] to give the non-electrolyte $Mo(CO)_2$(*E*-paphy)I_2 in which *E*-paphy is thought to act in a terdentate manner. The

TABLE 4

PHYSICAL DATA FOR $[M(CO)_3(T)I]^+I^-$ DERIVATIVES

Compound	Λ_M[a] (ohm$^{-1}\cdot$cm^2)	Infrared spectra (cm^{-1})					
		ν(NH)	Ring deformations		ν(CO)[b]		ν(MI)
			8a	8b	Nujol	$CHCl_3$	
$[Mo(CO)_3(dpma)I]^+I^-$	97	3170	1611	1570	2040 1965 1945	2050 1990 1957	139 m
$[W(CO)_3(dpma)I]^+I^-$	84	3227	1612	1568	2030 1945 1918	2045 1962 1935	139 s
$[Mo(CO)_3(Me.dpma)I]^+I^-$	91		1609	1574	2040 1987 1945	2045 1980 1960	139 s
$[W(CO)_3(Me.dpma)I]^+I^-$	89		1608	1570	2030 1968 1925	2040 1962 1940	142 s
$[W(CO)_3(Me.dpma)I]^+BPh_4^-$			1609	1573	2042 1968 1906		
$[Mo(CO)_3(dpea)I]^+I^-$	94	3195	1612	1569	2040 1965 1930	2045 1980 1935	142 m
$[W(CO)_3(dpea)I]^+I^-$	82	3205	1610	1565	2030 1955 1928	2045 1970 1940	139 m

[a] 10^{-3} M in nitromethane. [b] All bands strong.

reactions of iodine with molybdenum and tungsten tricarbonyl-dpma, Me.dpma and dpea compounds in either chloroform or dichloromethane at 10° give complexes (Table 2) which may be formulated as ionic seven-co-ordinate divalent metal species, $[M(CO)_3(T)I]^+I^-$. These complexes decompose slowly on standing and are somewhat air and moisture sensitive. Molar conductances in nitromethane (Table 4) are consistent with the presence of 1/1 electrolytes and it has been shown in one case, $[W(CO)_3(Me.dpma)I]^+I^-$, that the anion can be exchanged for tetraphenylborate. The virtual diamagnetism of the compounds is consistent with a spin-paired d^4 configuration, the number of valence electrons thereby being in agreement with the noble gas formalism.

An examination of the IR spectra (Table 4) of these iodo derivatives in the pyridine ring deformation region[14] shows the presence of only two bands, 8a being 21 ± 2 cm^{-1} increased in frequency compared with the uncomplexed ligand and 8b being virtually unshifted (at most an increase of 4 cm^{-1}). Thus all three nitrogens of the ligands remain co-ordinated to the metal on oxidation, in agreement with a seven-co-ordinate formulation. The mull and chloroform solution IR spectra (Table 4 and Fig. 1) show three ν(CO) bands, but this feature does not enable a conclusion to be drawn as to structure, since any low-symmetry tricarbonyl species would give a three band ν(CO) pattern. However, the shifts of 150–200 cm^{-1} to higher ν(CO) frequencies compared with the $M(CO)_3T$ compounds can be related to an increase in positive charge carried by the metal in these divalent species.

The far IR spectra of these compounds contain a band at ca. 140 cm^{-1} which is absent in the ligands. We attribute these bands to ν(M–I) frequencies and we believe no previous ν(M–I) values reported refer to seven-co-ordinate species. There is no significant difference between the ν(Mo–I) and ν(W–I) frequencies and this feature has previously been observed[27] for other halogeno carbonyl species, *e.g.* ν(M–Cl) of $Mn(CO)_5Cl$ and $Re(CO)_5Cl$. The expected decrease in the metal–halogen stretching frequency as the mass of the metal increases can even be reversed, as for $[Mo(CO)_5Cl]^-$ [ν(Mo–Cl), 248 cm^{-1}] and $[W(CO)_5Cl]^-$ [ν(W–Cl), 258 cm^{-1}][27]. This may indicate an increasing M–I bond strength from molybdenum to tungsten. Some metal–chlorine and metal–bromine stretching frequencies for dpea complexes have recently been reported[28].

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