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REACTIONS OF MANGANESE AND RHENIUM PENTACARBONYL HALIDES WITH ACETONITRILE

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SUMMARY

Manganese and rhenium pentacarbonyl halides react with acetonitrile to give binuclear derivatives of the type $[M(CO)_3X(MeCN)]_2$, (X = Cl, Br, I). From IR evidence these compounds are formulated as octahedral dimers of C_{2h} symmetry with bridging halogen atoms and σ-bonded nitrile groups. The reaction between $Mn_2(CO)_8Br_2$ and acetonitrile similarly gives $Mn_2(CO)_6Br_2(MeCN)_2$.

INTRODUCTION

Very recently there has been some interest in Group VII carbonyl–organic nitrile reactions. Manganese and rhenium decacarbonyls react with nitrosonium hexafluorophosphate in acetonitrile[1] to form hexafluorophosphate salts of the cations $[M(CO)_5(MeCN)]^+$. Farona and Kraus[2] have reported that the reactions between manganese and rhenium pentacarbonyl chlorides and bromides and a range or organic dinitriles give $M(CO)_3X[NC(CH_2)_xCN]$ complexes in which the dinitriles are bonded to the metal via the CN π-systems. Also included in this study were the reactions of the pentacarbonyl chlorides and bromides with acetonitrile. With manganese pentacarbonyl chloride the product was the binuclear complex, $Mn_2(CO)_6Cl_2(MeCN)_2$, the other pentacarbonyl halides yielding disubstituted $M(CO)_3X(MeCN)_2$ products.

Using slightly different reaction conditions to those of Farona and Kraus[2] we have found that all 6 $M_2(CO)_6X_2(MeCN)_2$ complexes (M = Mn, Re; X = Cl, Br, I) can easily be prepared from the pentacarbonyl halides. A comprehensive IR study (4000–40 cm^{-1}) of the compounds has been most helpful in elucidating their structural type.

EXPERIMENTAL

Manganese pentacarbonyl halides were prepared by published methods[3] and the rhenium analogues by similar means. Manganese tetracarbonyl bromide dimer was also prepared by a published method[3].

IR spectra in the 4000–350 cm^{-1} region were obtained on a Perkin–Elmer 621 spectrophotometer. The samples were recorded as nujol mulls and also as dispersions in pressed KBr and CsBr discs. The region between 2200 and 1700 cm^{-1} was also investigated using chloroform solutions. Below 400 cm^{-1} spectra were obtained from samples dispersed in low molecular weight polyethylene using a R.I.I.C. FS 720 interferometer. The Fourier transforms of the resulting interferograms were computed using a Fortran IV programme on an I.C.L. System 4–50 computer. The effective resolution was 2.5 cm^{-1}.

All reactions were carried out under a nitrogen atmosphere using acetonitrile previously dried by distillation from phosphorus pentoxide.

Preparation of $Mn_2(CO)_6Cl_2(MeCN)_2$

$Mn(CO)_5Cl$ (0.25 g) was stirred at room temperature for 15 h in 30 ml of 2,2-dimethoxypropane to which had been added acetonitrile (0.045 g). The bright yellow solid product was filtered, washed with 2,2-dimethoxypropane and dried *in vacuo*. Yield: 65%. (Found: C, 27.2; H, 1.52; Cl, 16.2; N, 6.28. $C_5H_3ClMnNO_3$ calcd.: C, 27.8, H, 1.39; Cl, 16.5; N, 6.50%.)

Preparation of $Mn_2(CO)_6Br_2(MeCN)_2$

(*a*). A similar method to that above using $Mn(CO)_5Br$ (0.50 g) and acetonitrile (0.20 g) and a reaction time of 4 days gave a 75% yield of a yellow solid. (Found: C, 23.6; H, 1.46; Br, 30.6; N, 4.96. $C_5H_3BrMnNO_3$ calcd.: C, 23.1; H, 1.15; Br, 30.7; N, 5.38%.)

(*b*). $Mn(CO)_5Br$ (0.20 g) was reacted with acetonitrile (0.06 g) in 20 ml of refluxing petroleum ether (30–40°) for 2½ h. The product was filtered, washed with petroleum ether (30–40°) and dried. Yield: 50%. (Found: C, 23.1; H, 1.42; Br, 31.0; N, 4.86%.)

(*c*). $Mn_2(CO)_8Br_2$ (0.17 g) was stirred at room temperature for 20 h in 30 ml of 2,2-dimethoxypropane to which had been added acetonitrile (0.06 g). Filtration, followed by washing with 2,2-dimethoxypropane and drying *in vacuo* gave a yellow solid (50%). (Found: C, 22.7; H, 1.34; Br, 30.3; N, 5.02%.)

Preparation of $Mn_2(CO)_6I_2(MeCN)_2$

A similar method to (b) above using $Mn(CO)_5I$ (0.30 g) and acetonitrile (0.15 g) and a reaction time of 20 h gave a 65% yield of the desired product. (Found: C, 20.8; H, 1.40; I, 40.9; N, 4.79. $C_5H_3IMnNO_3$ calcd.: C, 19.5; H, 0.98; I, 41.4; N, 4.56%.)

Preparation of $Re_2(CO)_6X_2(MeCN)_2$, ($X = Cl, Br, I$)

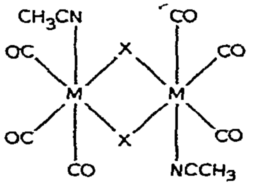
$Re(CO)_5X$ (X=Cl, 0.12 g; X=Br, 0.25 g; X=I, 0.20 g) were reacted with acetonitrile (0.05 g) in 30 ml of refluxing 2,2-dimethoxypropane for 1 h (X=I, 3 h). The colourless fine crystals were filtered, washed with further 2,2-dimethoxypropane and dried. Yields: X=Cl, 75%; X=Br, 72%; X=I, 55%. (Found for the chloro product: C, 17.4; H, 0.88; Cl 10.1; N, 4.12. $C_5H_3ClNO_3Re$ calcd.: C, 17.4; H, 0.87; Cl, 10.3; N, 4.06%.) (Found for the bromo product: C, 15.4; H, 0.81; Br, 19.8; N, 3.63. $C_5H_3BrNO_3Re$ calcd.: C, 15.4; H, 0.77; Br, 20.6; N, 3.60%.) (Found for the iodo product: C, 13.6; H, 0.67; I, 28.6; N, 3.06. $C_5H_3INO_3Re$ calcd.: C, 13.8; H, 0.69; I, 29.1; N, 3.20%.)

RESULTS AND DISCUSSION

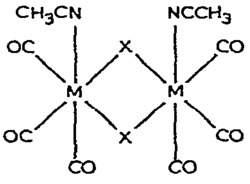
It was expected that the product of a reaction between a Group VII metal pentacarbonyl halide and at least a two molar excess of acetonitrile would be a *cis*-disubstituted complex, $M(CO)_3X(MeCN)_2$. Indeed, Farona and Kraus[2] have very recently isolated such complexes where M = Mn and X = Br (from refluxing hexane) and where M = Re and X = Cl, Br (from refluxing acetonitrile). We have found, however, that by using reaction conditions different and generally more moderate than those of Farona and Kraus the products have the empirical formula $M(CO)_3X(MeCN)$. 2,2-Dimethoxypropane, a solvent previously used[4] for the preparation of anhydrous metal compounds, has been particularly useful in these preparations. Farona and Kraus[2] isolated only the manganese chloro-complex of this type and they presented evidence to suggest a dimeric formulation.

The products are reasonably stable solid compounds, undergoing little decomposition when stored under nitrogen for several weeks. Unfortunately, from a structural standpoint, they are but slightly soluble in organic solvents.

A full IR study of all six compounds leads to the conclusion that they may be formulated as edge-shared binuclear octahedral complexes with bridging halogens [structure (I); point group C_{2h}]. Using its solid state IR spectrum in the ν(CO) region as evidence Farona and Kraus[2] propose the alternative structure (II), point group C_{2v}, for $Mn_2(CO)_6Cl_2(MeCN)_2$.



(I)



(II)

TABLE 1

INFRARED SPECTRA (4000–1800 cm^{-1})

$M_2(CO)_6X_2(MeCN)_2$		ν(CN)[a]	$\delta_{sym}(CH_3) + \nu_{sym}(CC)$[a]	ν(CO)
M	X			
Mn	Cl	2322 w	2300 w	2055 s, 2045 s, 1951 s, 1935 s, 1898 (sh)[b], 2043 s, 1957 (sh), 1946 s[c]
	Br	2322 w	2295 w	2055 s, 1946 (sh), 1932 s, 1896 (sh)[b], 2042 s, 1960 (sh), 1947 s[c]
	I	2313 w	2295 w	2048 s, 2035 (sh), 1955 (sh), 1934 s, 1911 (sh)[b], 2043 s, 1964 (sh), 1952 s[c]
Re	Cl	2322 w	2298 w	2060 s, 1940 (sh), 1920 s, 1876 (sh)[b], 2035 s, 1937 (sh), 1921 s[c]
	Br	2320 w	2297 w	2048 s, 2034 s, 1930 (sh), 1918 s, 1878 (sh)[b] 2039 s, 1938 (sh), 1920 s[c]
	I	2318 w	2295 w	2035 s, 2020 (sh), 1948 s, 1935 (sh), 1893 (sh)[b], 2036 s, 1940 (sh), 1923 s[c]

[a] KBr disc. [b] Nujol mull. [c] $CHCl_3$ solution.

Table 1 shows that the CN stretching frequency of the nitrile increases by ca. 60 cm^{-1} upon co-ordination, such an increase being characteristic[5] of nitriles bonded through the nitrogen lone pair electrons. A further band some 20 cm^{-1} lower than ν(CN) arises from a combination of the symmetric CH_3 deformation and symmetric CC stretching modes of the co-ordinated nitrile.

The solid state IR spectra in the carbonyl stretching region (Table 1) are complex, showing two major bands, the higher usually being resolved into two components and the lower into three components. This led Farona and Kraus[2] to suggest structure (II) for $Mn_2(CO)_6Cl_2(MeCN)_2$ since five IR-active CO bands are predicted ($2A_1+2B_1+B_2$). Although the compounds under consideration are only slightly soluble in organic solvents we have been able to record solution spectra in chloroform in the ν(CO) region by using at least 1 mm path length cells. These spectra (Table 1) show one very strong sharp band followed by a much broader very strong band which always has a very definite shoulder on the higher frequency side. Since solid state spectra are rarely a good guide to structure being often subject to considerable splitting we feel the solution spectra provide strong evidence in favour of structure (I) for which three IR-active ν(CO) bands are expected (A_u+2B_u).

TABLE 2

INFRARED SPECTRA (700–400 cm^{-1}) FROM CsBr DISCS

Compound	ν(MC) and δ(MCO)								
$Mn_2(CO)_6Cl_2(MeCN)_2$	682 s,	637 s,	628 s,	605 w,	519 s,	492 w,	477 w,	462 m,	412 w
$Mn_2(CO)_6Br_2(MeCN)_2$	676 s,	633 s,	625 s,	602 w,	518 s,	490 w,	475 (sh),	465 m,	410 m
$Mn_2(CO)_6I_2(MeCN)_2$	670 s,		618 s,		519 s,	497 vw,	485 w,	468 m,	410 m
$Re_2(CO)_6Cl_2(MeCN)_2$	651 s,	637 m,	628 m,	568 w,	524 s,	508 s,	482 s,		409 m
$Re_2(CO)_6Br_2(MeCN)_2$	649 s,		626 s,	564 w,	526 s,	505 m	492 m,	483 s,	412 m
$Re_2(CO)_6I_2(MeCN)_2$	638 s,		614 s,	559 w,	522 s,	501 m,	488 s,		412 w

TABLE 3

INFRARED SPECTRA (400–40 cm^{-1})

Compound	ν(MX)	ν(MN)	Other deformations
$Mn_2(CO)_6Cl_2(MeCN)_2$	293 s 264 s	234 s	141 m, 125 w, 117 m, 107 w, 93 w, 81 w, 63 w, 46 m
$Mn_2(CO)_6Br_2(MeCN)_2$	191 s 166 s	230 s 220 s	127 m, 120 m, 107 m, 93 m, 66 m, 46 m
$Mn_2(CO)_6I_2(MeCN)_2$	166 s 146 m	220 s	185 w, 122 m, 109 w, 90 s, 78 m, 63 w, 46 m
$Re_2(CO)_6Cl_2(MeCN)_2$	286 s 262 s	229 s	200 m, 129 m, 108 (sh), 105 m, 88 m, 66 w, 44 m
$Re_2(CO)_6Br_2(MeCN)_2$	188 s 161 s	217 (sh) 206 s	105 (sh), 103 s, 88 m, 64 w, 54 w
$Re_2(CO)_6I_2(MeCN)_2$	154 s 134 m	210 s	106 (sh), 90 s, 78 m, 46 m

In the CsBr region of the IR six MCO deformations ($3\ A_u+3\ B_u$) and three MC stretching modes ($A_u+2\ B_u$) are predicted for structure (I). For structure (II) nine MCO deformations ($3\ A_1+3\ B_1+3\ B_2$) and five MC stretches ($2\ A_1+2\ B_1+B_2$) are predicted. Our results (Table 2) again favour structure (I). The asymmetric NCC deformation of the nitrile is also expected in this region.

In the far IR region (Table 3) all six complexes have two strong bands which by comparison with the frequencies observed[6,7] for the related halogen-bridged $M_2(CO)_8X_2$ carbonyl halides (point group D_{2h}) can be assigned to the two metal–halogen stretches (A_u+B_u). One further strong band, sometimes split, is found in the 230–210 cm^{-1} region of the IR in these compounds. Such a frequency appears to be too high for assignment as a deformation mode (CMC, XMC, NMC or XMN), so we favour its assignment as the metal–nitrogen stretch (B_u). There has been some controversy over the assignment of element–nitrile nitrogen stretches in the past, the few established values being 174 cm^{-1} for $ZnCl_2(MeCN)_2$[8], 222 and 207 cm^{-1} for $SnCl_4(MeCN)_2$[9], and 657 cm^{-1} for $BF_3(MeCN)$[10]. Farona *et al.*[11] place the MN stretching modes for $M(CO)_3(MeCN)_3$, where M = Cr, Mo and W, in the 550–480 cm^{-1} region, but these assignments cannot be regarded as unambiguous since ν(MC), δ(MCO) and δ(NCC) also occur around this region.

As further evidence concerning the halogen-bridged nature of the complex we have also prepared $Mn_2(CO)_6Br_2(MeCN)_2$ from $Mn_2(CO)_8Br_2$.

Few other binuclear Group VII carbonyl derivatives involving the C_{2h} point group have been prepared. Abel *et al.*[12] isolated $[Ph_3PMn(CO)_3L]_2$ species where L = the bridging groups –SMe, –SC_6H_4Me-*p*, and –SePh, and Hieber *et al.*[13] have prepared some of the compounds of the series $[LM(CO)_3X]_2$ where M = Tc and Re, X = bridging halogen and L = SR_2, SeR_2, tetrahydrofuran and tetrahydrothiophen. The tetrachloro- and tetrabromohexacarbonyldirhenate(I) anions[7] may also be structurally related. These anions are thought to react with acetonitrile to give $[Re(CO)_3X_2(MeCN)]^-$ anions.

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