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REACTIONS OF MANGANESE AND RHENIUM HALOGENOPENTACARBONYLS WITH 1,2-DICYANOBENZENE

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Summary

Manganese and rhenium halogenopentacarbonyls react with 1,2-dicyanobenzene, L, to afford either monomeric $M(CO)_3XL_2$ complexes containing monodentate dinitrile ligands, or polymeric $[Re_2(CO)_6X_2L]_n$ complexes in which the dinitrile is thought to bridge $Re_2(CO)_6X_2$ units. Spectroscopic evidence indicates that the nitrile groups are σ-bonded in both types of complexes.

Introduction

The substitution reactions of Group VII metal carbonyl halides with ligands containing nitrile groups has recently been a subject of some interest. The products $M(CO)_4X(NCMe)$ [1], $M(CO)_3X(NCR)_2$ [1,2], and $M_2(CO)_6X_2(NCMe)_2$ [3] (M = Mn and Re; X = Cl, Br, and I; R = Me, Et, Ph, and $CH_2{=}CH$) have been isolated using mononitriles. Aliphatic dinitriles were reported [2,4] to give $M(CO)_3X[NC(CH_2)_xCN]$, (x = 1,2, or 3) complexes, the ligands chelating by π-donation. We have however reported [5] additional spectroscopic studies including the use of $C^{18}O$ isotopic substitution which suggest that these complexes should be formulated as halogen-bridged dimers with monodentate σ-bonded dinitrile ligands. Farona et al. [6] subsequently indicated that both types of dinitrile complexes can be isolated, the π-bonded type being the kinetically controlled, and the σ-bonded type the thermodynamically favoured species.

The ligands $Ph_2P(CH_2)_2CN$ and $Ph_2PC_6H_4CN$ have also been utilised. The former ligand gives $Re_2(CO)_6X_2[Ph_2P(CH_2)_2CN]_2$ complexes in which the cyanophosphine ligands bridge the metal atoms by forming Re—P and Re—N σ-bonds [7]. The latter ligand is chelating in $Mn(CO)_3X(Ph_2PC_6H_4CN)$ complexes [8,9], forming Mn—P σ-bonds and Mn—nitrile π-bonds. In the $Re_2(CO)_6X_2(Ph_2PC_6H_4CN)_2$

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complexes isolated [9] the ligand was held to be bridging by phosphorus lone pair donation and nitrile π-donation. However this mode of bonding has recently been questioned and evidence presented [10] to show that the ligand acts in an identical manner to $Ph_2P(CH_2)_2CN$ in these rhenium dimers.

Only one such complex containing 1,2-dicyanobenzene has been reported, namely $Mn(CO)_3Br[o\text{-}C_6H_4(CN)_2]$. The nitrile is said to be chelating by π-donation from both nitrile groups [2]. In view of the paucity of information on 1,2-dicyanobenzene complexes and the possibility that such complexes may actually involve σ-bonded nitrile groups, we have examined some further reactions of Group VII metal halogenopentacarbonyls with this ligand.

Experimental

All reactions were performed under prepurified, dried nitrogen using anhydrous solvents. Molecular weight determinations were carried out ebullioscopically in chloroform. Infrared spectra were recorded using a Perkin—Elmer 621 spectrophotometer and a Beckman—R.I.I.C. FS 720 interferometer. Raman spectra were recorded with a Coderg PHO spectrophotometer equipped with a krypton—argon ion laser.

Preparation of $Mn(CO)_3Br[o\text{-}C_6H_4(CN)_2]_2$

$Mn(CO)_5Br$ (0.20 g) and 1,2-dicyanobenzene (0.38 g) were stirred in 20 ml of 2,2-dimethoxypropane at 60°C for $1\frac{1}{2}$h. The yellow solid product was filtered, washed with warm 2,2-dimethoxypropane and dried in vacuo. Yield: 70%. (Found: C, 48.0; H, 1.45; Br, 17.0; N, 12.0. Mol. wt. 487. $C_{19}H_8BrMnN_4O_3$ calcd.: C, 48.0; H, 1.68; Br, 16.8; N, 11.8%. Mol. wt. 475.)

Preparation of $Mn(CO)_3I[o\text{-}C_6H_4(CN)_2]_2$

The deep yellow solid product was prepared from $Mn(CO)_5I$ (0.20 g) and 1,2-dicyanobenzene (0.32 g) in a similar manner, using a reaction time of 3 h. Yield: 58%. (Found: C, 43.6; H, 1.60; I, 25.1; N, 10.9. $C_{19}H_8IMnN_4O_3$ calcd.: C, 43.6; H, 1.53; I, 24.3; N, 10.9%.)

Preparation of $Re(CO)_3Br[o\text{-}C_6H_4(CN)_2]_2$

$Re(CO)_5Br$ (0.20 g) and 1,2-dicyanobenzene (0.25 g) were reacted in refluxing chloroform for 48 h. The solvent was then removed at room temperature under reduced pressure to give a pale yellow solid which was well washed with warm 2,2-dimethoxypropane before drying in vacuo. Yield: 48%. (Found: C, 36.9; H, 1.41; Br, 13.5; N, 9.03. $C_{19}H_8BrN_4O_3Re$ calcd.: C, 37.8; H, 1.32; Br, 13.3; N, 9.24%.)

Preparation of $Re_2(CO)_6X_2[o\text{-}C_6H_4(CN)_2]$, *(X = Cl, I)*

$Re(CO)_5X$ (0.20 g) and 1,2-dicyanobenzene (X = Cl, 0.20 g; X = I, 0.23 g) were reacted in refluxing chloroform for 3 h. The lemon yellow crystals which deposited were filtered, washed with chloroform and dried in vacuo. Yields: X = Cl, 33%; X = I, 30%. (Found for the chloro product: C, 22.9; H, 0.75; Cl, 9.63; N, 3.73. $C_7H_2ClNO_3Re$ calcd.: C, 22.9; H, 0.54; Cl, 9.65; N, 3.82%. Found for the iodo product: C, 18.5; H, 0.69; I, 26.8; N, 3.08. $C_7H_2INO_3Re$ calcd.: C, 18.3; H, 0.44; I, 27.8; N, 3.06%.)

Results and discussion

The reaction of $Mn(CO)_5Br$ with a 2.5-fold excess of 1,2-dicyanobenzene in refluxing hexane for 14 days is known [2] to afford $Mn(CO)_3Br[o\text{-}C_6H_4(CN)_2]$. On the basis of spectroscopic evidence, (Table 1), it was proposed that the dinitrile acted as a chelating ligand by π-donation from both nitrile groups. We now report complexes of two different stoichiometries, namely $M(CO)_3X[o\text{-}C_6H_4(CN)_2]_2$ (M = Mn, X = Br, I; M = Re, X = Br) and $Re_2(CO)_6X_2[o\text{-}C_6H_4(CN)_2]$ (X = Cl, I). All reactions employed approximately a four-fold excess of dinitrile, the former type being produced in 2,2-dimethoxypropane or by a prolonged reaction period in chloroform, the latter type being prepared using a shorter reaction time in chloroform.

The $M(CO)_3X[o\text{-}C_6H_4(CN)_2]_2$ complexes are stable on storage under nitrogen and soluble in solvents such as chloroform and acetone, $Mn(CO)_3Br[o\text{-}C_6H_4(CN)_2]_2$ being found to be monomeric in the former solvent. It would seem therefore that these complexes are further examples of the extensive group of octahedral $M(CO)_3XL_2$ (M = Mn, Re; X = halogen) compounds. If this assumption is correct the dinitriles must be monodentate, either by nitrogen lone pair or nitrile π-donation. Coordination of both nitrile groups of each dinitrile would lead to an eight coordinate structure in which the 18 electron formalism would be exceeded. In this unlikely event, chelation could only be achieved by π-donation, σ-bond chelation being impossible due to the linearity of the $-C-C\equiv N \rightarrow M$ moieties.

IR spectroscopic results (Table 1) are in agreement with a *fac*-octahedral structure involving two monodentate nitrogen-bonded dinitrile ligands. Two weak bands are found in the $\nu(CN)$ region, the lower frequency band being

TABLE 1

INFRARED SPECTRA (cm^{-1})

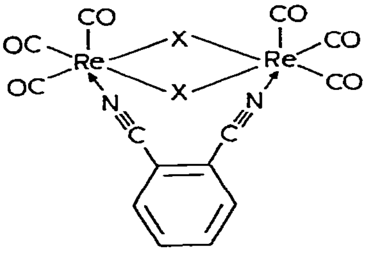
Compound	Coordinated $\nu(CN)$	Uncoordinated $\nu(CN)$	$\nu(CO)$	$\nu(MX)$
$o\text{-}C_6H_4(CN)_2$, L		2237m		
$Mn(CO)_3BrL^a$	2049(sh)		2039s, 1976s, 1946s^b	
$Mn(CO)_3BrL_2$	2252w	2235mw	2050s, 1980s, 1945s^b 2055s, 1978s, 1943s^c	186s
$Mn(CO)_3IL_2$	2255w	2240mw	2050s, 1967s, 1938s^c	156s
$Re(CO)_3BrL_2$	2260w	2237m	2045s, 1960s, 1925s^b 2050s, 1953s, 1917s^c	188s
$Re_2(CO)_6Cl_2L$	2260w		2060s, 2040s, 1965m, 1950m 1920s^b	283s, 237s
	2261s^d		2048m, 2039m, 1944m, 1932w, 1912m, 1901m^d	
$Re_2(CO)_6I_2L$	2255w		2050s, 2030s, 1967s, 1945s, 1920s^b	161s, 149s

[a] Ref. 2. [b] $CHCl_3$ solution. [c] Nujol mull. [d] Raman spectrum.

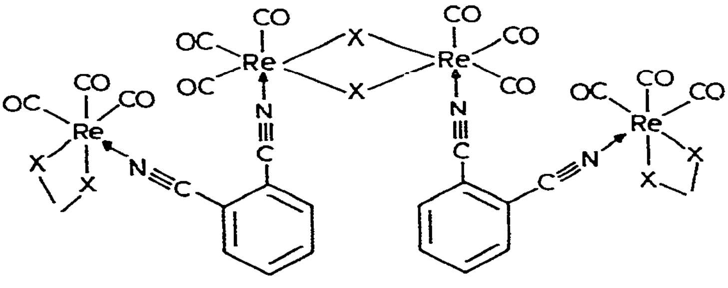
shifted no more than 3 cm^{-1} from the position of the ν(CN) band of the uncomplexed ligand. The higher frequency band is found at a position typical of a σ-bonded nitrile, it being accepted [11] that σ-bonding is normally accompanied by an increase in ν(CN) over that observed for the free ligand. In contrast π-donation shifts ν(CN) to lower frequencies and no bands are observed for these complexes which could be so assigned. The very low intensity of the coordinated ν(CN) IR bands is a feature observed for the $M_2(CO)_6X_2$(dinitrile)$_2$ [5] and all the cyanophosphine complexes [10] previously reported. The complexes exhibit three intense ν(CO) bands in the IR spectra, the pattern being similar to that observed for complexes in which the CO groups are known to be in a *fac*-arrangement [12]. The positions are very similar to those of $Mn(CO)_3Br(NCMe)_2$ [2].

The mid IR region is not useful in complementing this structural assignment. Three ν(MC) and six δ(MCO) modes are IR active for these complexes of C_s point group, but up to fifteen bands are observed due to the additional presence of ligand bands. The far IR spectra each contain one intense band assignable to ν(MX) in agreement with the proposed structure.

The $Re_2(CO)_6X_2[o\text{-}C_6H_4(CN)_2]$ complexes are also stable under nitrogen, but, in contrast to the $M(CO)_3X[o\text{-}C_6H_4(CN)_2]_2$ type, are virtually insoluble in a range of organic solvents. They exhibit only one band assignable to σ-bonded ν(CN) in their IR or Raman spectra, (Table 1). The absence of other bands in this region together with the lack of bands assignable to π-bonded nitrile groups suggests that both nitrile groups of the 1,2-dicyanobenzene ligand are σ-bonded. As before, the IR ν(CN) bands are of very low intensity, but in the Raman spectrum of the chloro-complex the ν(CN) band is of comparable intensity to that



(I)



(II)

of the strongest ν(CO) band, making the assignment of σ-bonded nitrile quite certain. Solution IR spectra of the ν(CO) region show five bands for each complex, whilst the Raman spectrum of the chloro-complex shows six bands in this region. The frequency shifts on comparing the IR and Raman spectra of the chloro-complex presumably result from a change of phase from solution to solid state respectively. These results point to the isolation of complexes possessing a C_{2v} point group [ν(CO), IR active $2A_1 + B_1 + 2B_2$; Raman active $2A_1 + A_2 + B_1 + 2B_2$]. Both I and II fit this requirement, but we strongly favour the polymeric structure II since the dimeric structure I can only be attained with unacceptably long Re—X bonds since the two linear —C—C≡N → Re groups are restricted to the trigonal sp^2 angle. The mid IR spectra of the complexes contain more than the expected five ν(ReC) and nine δ(ReCO) bands due to the presence of ligand vibrations, but in the far IR bands at 283 and 237 cm^{-1} for the chloro-complex and 161 and 149 cm^{-1} for the iodo-complex support the formation of halogen-bridged species. These ν(ReX) bands appear at similar frequencies to those of $Re_2(CO)_8Cl_2$ (288 and 240 cm^{-1}) and $Re_2(CO)_8I_2$ (163 and 142 cm^{-1}) [13].

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