The Bonding of Aliphatic Dinitriles in Halogeno(dinitrile)tricarbonyl-manganese(I) and -rhenium(I) Complexes

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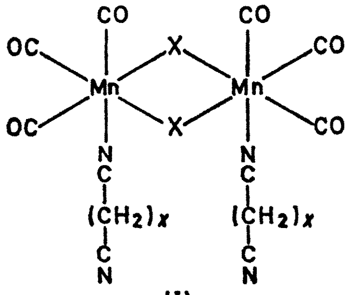
Summary Spectroscopic evidence indicates that aliphatic dinitriles σ-bond in $M(CO)_3(dinitrile)X$ complexes (M = Mn and Re; X = Cl, Br, and I) using one donor nitrogen atom only, and do not act as π-bonding chelates as previously suggested.

Aliphatic dinitriles normally act as σ-bonding bridging ligands in complexes using both nitrogen donor atoms. *X*-Ray crystallographic studies have shown such bonding to be present in, for example, $SnCl_4 \cdot NC(CH_2)_3CN$,[1] and $AgClO_4 \cdot 2NC(CH_2)_4CN$.[2] However, evidence has been presented[3,4] suggesting that dinitriles co-ordinate in a unique chelating manner through the two nitrile π-systems in a series of $M(CO)_3(dinitrile)X$ compounds, (M = Mn and Re; X = Cl and Br). The results supporting such a formulation were: (i) the monomeric nature of $Mn(CO)_3[NC(CH_2)_2CN]X$ in sulpholane; (ii) the complexes did not have bands in the 2250—2350 cm^{-1} region of the i.r. as would be expected for N-bonded nitriles; (iii) the 2100—1800 cm^{-1} region of the i.r. consisted of four bands, the highest of which was assigned to π-bonded nitrile, the other three being carbonyl stretches, in agreement with C_s symmetry.



(I)

X = Cl, Br and I; x = 1, 2 and 3

Whilst using these complexes, $M(CO)_3[NC(CH_2)_xCN]X$ (M = Mn and Re; X = Cl, Br and I; x = 1, 2, and 3) as intermediates, we have obtained results, listed below, which cast doubt on the validity of such a formulation. (i) The i.r. spectrum of $Mn(CO)_3[NC(CH_2)_2CN]Br$ in sulpholane was examined under nitrogen over 4 h. The ν(CO) band pattern and positions changed considerably indicating reaction with the solvent. (ii) Two weak bands were found in the 2250—2350 cm^{-1} region of the i.r. for all the complexes, the position of the higher frequency band (2300 ± 5 cm^{-1}) being characteristic of an N-bonded nitrile group, the position of the lower band being very close to ν(CN) of the unco-ordinated dinitrile. The weakness or even absence of ν(CN) in the i.r. spectra of nitrile complexes has been reported before. Thus no ν(CN) was apparent in the i.r. of $ReCl_3(PPh_3)_2MeCN$,[5] but a single-crystal *X*-ray study[6] showed the presence of a linear Re–N–C system. As further evidence of the presence of both N-bonded and unco-ordinated nitrile, the Raman spectrum of $Re(CO)_3[NC(CH_2)_2CN]Cl$ shows a very strong band at 2302 cm^{-1} and a medium intensity band at 2277 cm^{-1}. (iii) Mull i.r. spectra of the manganese complexes show two sharp, strong bands above 2000 cm^{-1} and one very broad, strong, band below 2000 cm^{-1}, *e.g.*, $Mn(CO)_3[NC(CH_2)_2CN]Br$: 2072, 2046, and 1941 cm^{-1}. In acetonitrile the broad lowest frequency band is resolved into three bands giving a total of five bands in this region, *e.g.*, $Mn(CO)_3[NC(CH_2)_2CN]Br$: 2066m, 2043s, 1975m, 1956s, 1935s cm^{-1}. Such solution spectra show no changes after 1 h and at least 80% of the original complex could be recovered by removal of the solvent.

We have also prepared the isotopic mixture $Mn(CO)_{5-x}(C^{18}O)_xBr$ (x = 0—5),[7] and from this $Mn(CO)_{3-x}(C^{18}O)_x[NC(CH_2)_2CN]Br$ (x = 0—3). Thirteen bands are found in the i.r. between 2100 and 1850 cm^{-1} for this isotopically substituted complex. If the assignment[4] for $Mn(CO)_3[NC(CH_2)_2CN]Br$ of the highest frequency ν(CO) at 2043 cm^{-1}, with ν(CN) at 2066 cm^{-1}, is correct, the increased complexity of the spectrum due to isotopic substitution will occur only below 2043 cm^{-1}. However, a new band of approximately equal intensity to that of the band at 2066 cm^{-1} is clearly evident at 2054 cm^{-1}. The 2066 cm^{-1} band must therefore also be assigned to a carbonyl stretching vibration and cannot be related to a π-bonded nitrile group.

The identification of five i.r. ν(CO) bands ($2A_1 + 2B_1 + B_2$), N-bonded and unco-ordinated nitrile groups, and in some cases, *e.g.*, $Mn(CO)_3[NC(CH_2)_2CN]Cl$: 287, 278, and 237 cm^{-1}, three i.r. ν(M–X) bands ($A_1 + B_1 + B_2$) is consistent with the dimeric structure (I), of C_{2v} symmetry, for these complexes. Chelating bidentate ligands, (B), such as 2,2′-bipyridyl, react with these compounds, cleaving the halogen bridges and liberating the dinitrile, to give $M(CO)_3BX$ complexes. The dimeric halogen-bridged metal tetracarbonyl halides are known to react in a similar fashion.

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