σ- and π-Bonded Dinitrile Complexes of Mn^I and Re^I Carbonyl Halides

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Summary The existence of both monomeric π-bonded dinitriles and dimeric σ-bonded dinitriles is postulated and it is suggested that the monomeric π-complexes are the kinetically favoured species, whereas the σ-bonded complexes are the thermodynamically favoured form.

THE syntheses of dinitrile complexes of Mn^I and Re^I carbonyl halides were previously reported,[1,2] and it was shown by i.r. that the nitriles are bidentate, co-ordinating to the metal through the CN triple bonds. Recently,[3] an attempted synthesis of these compounds led to products of the same empirical formula but where the two dinitriles were σ-bonded on one end to the metals and the other end being unco-ordinated [ν_{CN} *ca.* 2300 (*N* co-ordinated) and 2250 cm^{-1} (free nitrile)]. Accordingly, we reinvestigated our complexes and now have evidence for the existence of both types of compounds.

The compounds were identical to those reported previously,[1,2] and no i.r. activity was observed in the 2250—2300 cm^{-1} region. Since Dunn and Edwards report the Raman spectra of the dimeric compounds, we attempted similar studies on our compounds. All the Mn complexes decompose in the laser beam, and the Re complexes show a strong band at 2300 cm^{-1}, but the carbonyl region becomes extremely complicated.

When samples of the π-co-ordinated dinitriles are allowed to stand at 4° for about 4 months two weak nitrile bands are observed at 2300 and 2250 cm^{-1}, and the lowest frequency carbonyl band at 1941 cm^{-1} becomes much broader. Extraction with hot $ClCH_2CH_2Cl$ gives the dimeric product, identified by i.r.[3]

Thus it appears that the π-bonded complexes are the kinetically controlled products, whereas the dimeric σ-bonded complexes are the thermodynamically favoured forms.

Investigation of the metal–halogen stretching frequency region clearly shows the monomeric nature of the proposed π-bonded dinitrile complexes. For $M(CO)_3(NCCH_2CH_2CN)Cl$ (M = Mn, Re), ν (MCl) = 287 and 288 cm^{-1} respectively; for $Re(CO)_3(NCCH_2CN)Cl$, ν (MCl) = 288 cm^{-1}. For $M(CO)_3(NCCH_2CH_2CN)Br$ (M = Mn, Re), ν (MBr) = 220 and 195 cm^{-1}, respectively, and for $M(CO)_3(NCCH_2CN)Br$ (M = Mn, Re), ν (MBr) = 228 and 205 cm^{-1}, respectively. The two or three other bands appearing in this region are independent of the halogen. It is likely that these other bands arise from M–π-CN stretching modes. For the dimeric complexes, Dunn and Edwards report 3 active metal–halogen vibrations, unlike those found for the π-co-ordinated derivatives.

(*Received, 14th February* 1972; *Com.* 232.)

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