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Preliminary communication

ISONITRILE DERIVATIVES OF DIMANGANESE DECACARBONYL

I. EVIDENCE FOR METAL—METAL LIGAND EXCHANGE

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Summary

The compound heptacarbonyltrimethylisonitriledimanganese has been prepared and investigated by variable temperature PMR spectroscopy. It has been shown that the isonitrile ligands are rapidly exchanged between the two metal atoms at approximately 100 °C. Comparison of these results with those of the complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)]_2$ shows that the activation barriers are very similar and suggests that geometrical variations may not be very important factors in determining the facility by which bridge-terminal coordination rearrangements occur.

Recent studies have shown that a variety of ligands participate in the dynamical rearrangement whereby terminal (a) and bridging (b) coordination environments are interconverted [1,2]. To a large extent this has been made possible by utilizing the isoelectronic and isostructural $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ geometry as a test system* [1]. Thus, the manner in which geometrical variations in the complex, itself, might impose restrictions or limitations on the rearrangement remains unknown. A system which might be expected to be especially sensitive to such geometrical restraints is that of dimanganese decacarbonyl. In this molecule each manganese atom can be formally regarded as six coordinate [3]. Considerable evidence now substantiates the claim [1a, 4] that bridge—terminal coordination rearrangements occur in a pairwise fashion, eqn.1. Thus, in order for dimanganese decacarbonyl to engage in such a rearrangement it would have to assume a transition state similar to c, which has two bridging carbonyl groups. This intermediate could be formally regarded as seven coordinate, and, on the basis of geometry, might be considered as energetically unfavorable.

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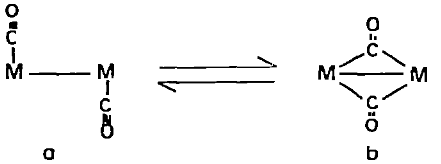
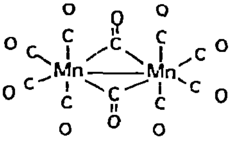
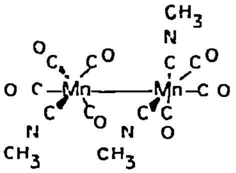
* A number of other systems [2] are simple variations of this one.



a b (1)



c



d

To resolve this question we have examined the more viable system $Mn_2(CO)_7(CNCH_3)_3$*. The compound is conveniently prepared by irradiation of $Mn_2(CO)_{10}$ in the presence of $CNCH_3$. The infrared spectrum shows absorptions at 2162m (CN); 2037w (CO); 2033w (CO), 1984s (CO), 1959s (CO), 1952(sh) (CO), 1931m (CO), 1923m (CO) cm^{-1}. None of these can be assigned to a carbonyl or methylisonitrile ligand in a bridging environment. Cleavage with bromine gives exclusively the two compounds, *cis*-$Mn(CO)_4(CNCH_3)Br$ and *fac*-$Mn(CO)_3(CNCH_3)_2Br$ [5]. Thus, it may be assumed that the dinuclear manganese complex is isostructural to the parent unsubstituted complex and has two isonitrile ligands on one metal atom and one on the other. A plausible structure would be that represented by d**. Consistent with this, the PMR spectrum at room temperature shows two methyl resonances in a two to one intensity ratio. Figure 1 shows the variable temperature PMR spectra of $Mn_2(CO)_7(CNCH_3)_3$ in toluene-d_8 solvent. At higher temperatures, the resonances broaden, coalesce, and finally reform a singlet at ~ 100°. These changes demonstrate the existence of a rearrangement whereby the isonitrile ligands interchange their environments. Additional experiments reveal that the rearrangement is insensitive to the concentration of the complex and the presence of the uncoordinated isonitrile ligand in the sample. This indicates that the rearrangement is both unimolecular and intramolecular. Comparison of experimental and computer simulated spectra yield values for the rates of exchange from which tentative activation parameters have been obtained. As determined from the Arrhenius equation $\log A = 8.9$, and $E_a = 12.9 \pm 1.0$ kcal/mol. $\Delta G^{\ddagger}_{298}$ has been determined as 18.2 ± 1.0 kcal/mol. Although this analysis is not indicative of a unimolecular process [6], it is probable that the data may be subject to systematic error, namely, partial coupling of the methylisonitrile nitrogen nucleus to the methyl protons. This coupling is usually eliminated due to quadrupole induced relaxation, but is occasionally observed in isonitrile molecules [7]. The temperature dependent effects of quadrupolar interactions would result in slight broadening of the spectra at higher temperatures [8]. This would cause the calculated rates of exchange to be artificially slow and lead to a low

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*This compound was briefly mentioned in a recent review [5].

**We recognize that there are several other structures which might be regarded as consistent with this two and one distribution. However, should this be the case, it will not nullify any of the following conclusions.

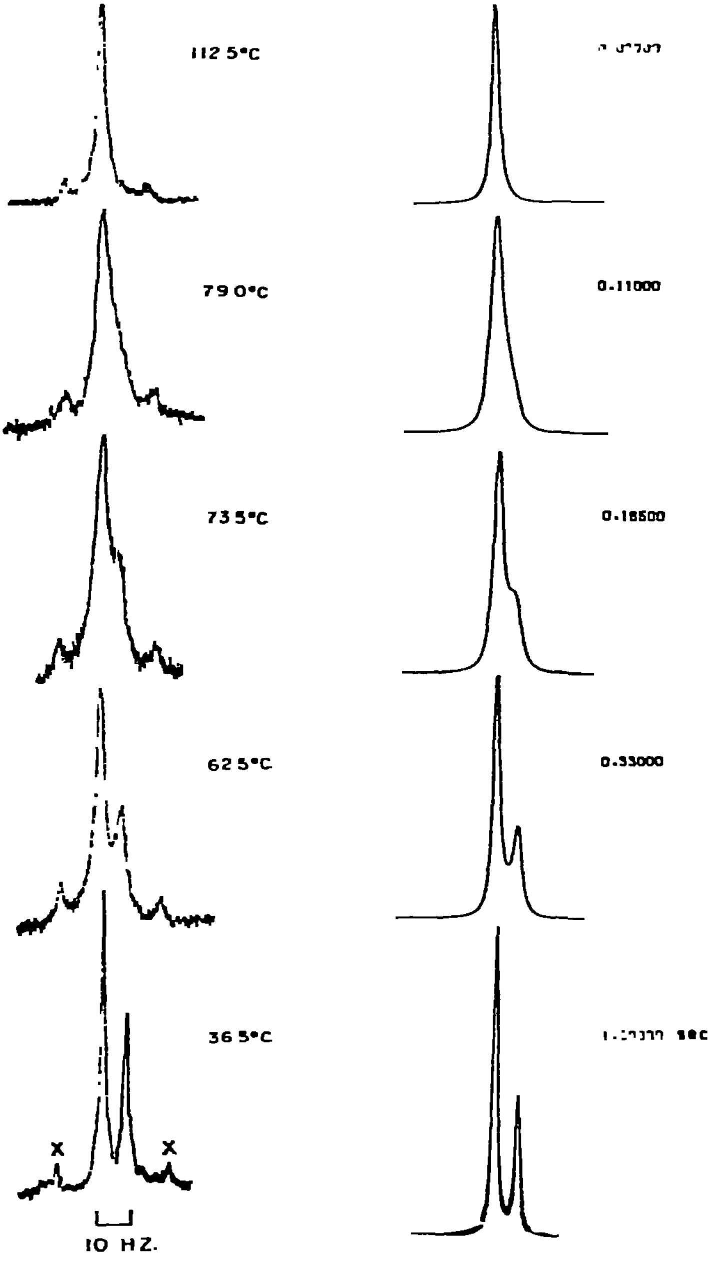

Fig. 1. The variable temperature 100 MHz PMR spectra and corresponding computer simulations for $Mn_2(CO)_7(CNCH_3)_3$ in toluene-d_8 solvent. The computer simulations are identified by average lifetimes in seconds. Peaks marked X are trace impurities.

value of log A. The ΔG function is not particularly sensitive to such error and, therefore, should be a reliable value [9].

A plausible mechanism for the rearrangement would involve a ligand shift in which one isonitrile and one carbonyl or two methylisonitrile ligands assume a bridging environment in an intermediate similar to c. The process would be completed by returning the ligands to terminal positions with a resulting exchange between the metal atoms.

These results show that the rearrangement in $Mn_2(CO)_7(CNCH_3)_3$ is energetically very similar to that in $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)]_2$, [1a] where $\Delta G^{\neq} = 17.5 \pm 1.0$ kcal/mol. It implies that geometrical variations might not be very important factors in determining the facility by which these ligands may move to and from the bridging positions.

Acknowledgement

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References

1 (a) R.D. Adams and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 6589.
  (b) O.A. Gansow, A.R. Burke and W.D. Vernon, J. Amer. Chem. Soc., 94 (1972) 2550.
  (c) R.M. Kirchner, T.J. Marks, J.S. Kristoff and J.A. Ibers, J. Amer. Chem. Soc., 95 (1973) 6602.
  (d) F.A. Cotton, L. Kruczynski and A.J. White, Inorg. Chem., 13 (1974) 1402.
2 (a) R.D. Adams, M.D. Brice and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 6594.
  (b) J. Evans, B.F.G. Johnson, J. Lewis and J.R. Norton, J. Chem. Soc., Chem. Commun., (1973) 79.
3 L.F. Dahl and R.E. Rundle, Acta Crystallogr., 16 (1963) 419.
4 R.D. Adams, M.D. Brice and F.A. Cotton, Inorg. Chem., 13 (1974) 1080.
5 P.M. Treichel, G.E. Dirreen and H.J. Mueh, J. Organometal. Chem., 44 (1972) 339.
6 G. Binsch, Top. Stereochem., 3 (1968) 97.
7 I.D. Kuntz, Jr., P.V.R. Schleyer and A. Allerhand, J. Chem. Phys., 35 (1961) 1533.
8 G.M. Whitesides and H.L. Mitchell, J. Amer. Chem. Soc., 91 (1969) 2245.
9 A. Allerhand, F. Chen and H.S. Gutowsky, J. Chem. Phys., 42 (1965) 3040.