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Preliminary communication

Dynamic stereochemistry in $[(C_5H_5)Mn(CO)NO]_2$

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Recent work[1] has demonstrated that in $[(C_5H_5)Fe(CO)_2]_2$ rapid intramolecular positional interchange occurs between bridging and terminal CO groups. That such kinds of ligand rearrangements may have considerable generality is provided by the following work on the isoelectronic molecule $[(C_5H_5)Mn(CO)NO]_2$ [2]. Here both CO and NO groups undergo a topologically and energetically similar rearrangement; in addition, a dynamic process not observed for the iron analog is reported.

The low temperature NMR spectrum of $[(C_5H_5)Mn(CO)NO]_2$ (Fig.1) and solution infrared spectra are in best agreement with a mixture of dissymmetric *cis* and *trans* isomers (Scheme 1), structurally similar to those of the iron system[3,4] and related manganese[5] and chromium[6] systems[*]. Note here that the two C_5H_5 groups in each isomer are magnetically non-equivalent. Addition of polar solvents[1] causes the high field doublet (the *cis* isomer) to increase in relative intensity. The solution infrared spectrum (cyclohexane) shows bands at (cm^{-1}) 1992 m, 1970 s, [terminal $\nu(CO)$]; 1813 s [bridge $\nu(CO)$]; 1732 s [terminal $\nu(NO)$[7]]; and 1534 m [bridge $\nu(NO)$[7]], with the 1992 band growing and the 1813 and 1534 bands sometimes splitting upon addition of polar solvents. This is best explained if each isomer contains one of the following: terminal CO, bridging CO, terminal NO, bridging NO, with overlapping[3] of some bands. Solid state infrared spectra show the presence of only the lower frequency terminal $\nu(CO)$ isomer; low temperature PMR spectra of solutions prepared at $-70°$ verify that this is, as expected, the *trans* isomer. We have as yet been unable to crystallize the *cis* form.

As the temperature of the NMR sample (Fig.1) is raised, the cyclopentadienyl rings on each isomer begin to equilibrate. At still higher temperatures, *cis–trans* interconversion is observed. All lineshape changes are reversible and independent of concentration. The low temperature exchange is readily achieved via non-bridged isomers as depicted in Scheme 1. As found for the iron system, bridge–terminal ligand interchange

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[*] Further proof of structure is derived from molecular weight measurements (cryoscopic) in benzene: Found 321; calcd. 356. We are unable to detect the paramagnetism described in ref. 2.

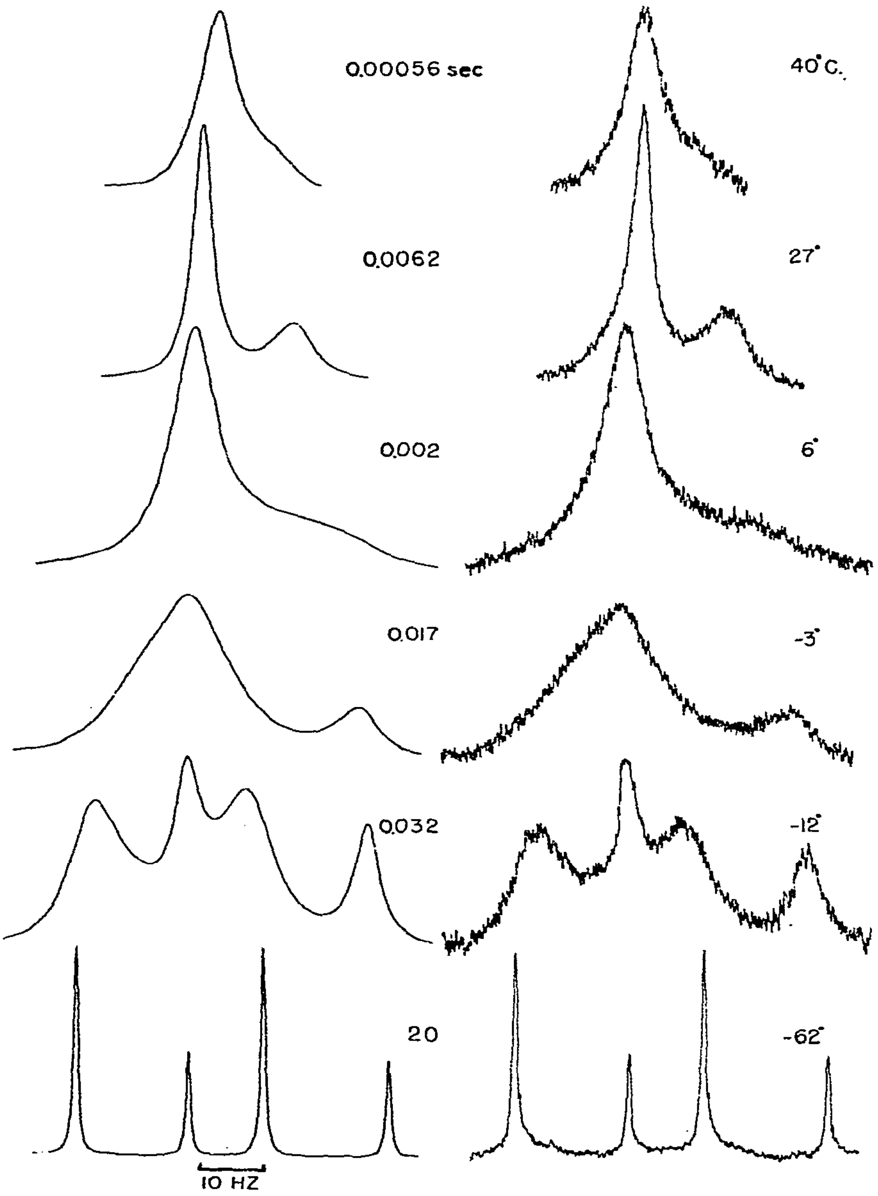
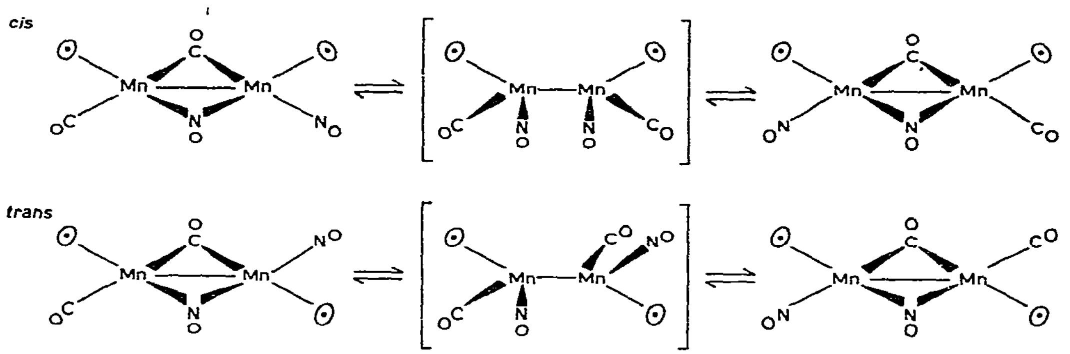


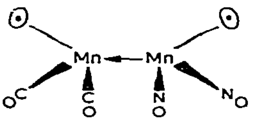
Fig.1. Right: 90 MHz proton NMR spectra of a toluene-d_8 solution of $[(C_5H_5)Mn(CO)NO]_2$ as a function of temperature. Left: Computer generated spectra. The representative mean lifetimes given are those for bridge–terminal exchange in the *trans* isomer.

occurs more rapidly for the *trans* isomer[1b]. However, unlike the iron dimer, the stereochemistry of the manganese system is such that the expected non-bridged intermediates for the bridge–terminal exchange (and concurrent racemization) *cannot* serve for *cis*–



Scheme 1

trans interconversion. Simple rotation about the metal–metal bond does not produce a common intermediate. The most reasonable mechanism for *cis–trans* exchange would appear to be configurational inversion[8] at the metal atom or equilibration via an intermediate such as A.



(A)

The computer simulation shown in Fig.1 confirms that three dynamic processes are occurring and yields Arrhenius activation parameters. The bridge–terminal exchange occurs for the *trans* isomer with E_a = 13.5 ± 0.6 kcal/mol, log A = 12.7 ± 0.5, and for the *cis* isomer with E_a = 13.8 ± 0.6 kcal/mol and log A = 12.6 ± 0.5. The *cis–trans* equilibrium constant (2.3) was, within the accuracy of the data, independent of temperature. The high temperature process takes place with E_a = 19.0 ± 2.4 kcal/mol and log A = 14.6 ± 1.7. The activation energy for the latter process is considerably lower than that found for inversion in similar pseudo-four-coordinate systems[8], and suggests that possibly a dative-bonded (in valence-bond terms) intermediate such as A, for which there is some precedent[9], may be involved. Further studies on this compound and other isoelectronic systems are in progress.

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