$\Delta H^\circ = +1.04 \pm 0.10$ kcal/mol, $\Delta S^\circ = +3.46 \pm 0.29$ cal/(mol deg), $\Delta G^\circ_{298} = +0.00 \pm 0.19$ kcal/mol.

The pmr resonances at 134° show significant broadening. At 155° the resonances from the two isomers have coalesced. At higher temperatures decomposition becomes significant. Analysis of the changes in line shapes which occur up to the coalesence temperature allowed estimation of exchange rates which obeyed the standard Arrhenius and absolute rate theory equations. The activation parameters in Table VIII have been obtained. These values are very similar to those obtained for the corresponding phosphine complexes[24] and suggest that replacement of a phosphine ligand with an isocyanide ligand has very little effect on the polytopal rearrangement barriers in these complexes.

Table VIII

Rearrangement	E_a, kcal/mol	Log A	$\Delta H^{\ddagger}$, kcal/mol
cis → trans	21.5 ± 1.0	12.33 ± 1.0	20.8 ± 1.0
trans → cis	22.7 ± 1.0	13.40 ± 1.0	21.9 ± 1.0
	$\Delta S^{\ddagger}$, eu		$\Delta G^{\ddagger}_{298}$, kcal/mol
cis → trans	−4.7 ± 2.4		22.2 ± 1.0
trans → cis	0.2 ± 2.4		21.8 ± 1.0

The high energy barrier determined for the polytopal rearrangement in this molybdenum isocyanide complex further supports the belief that the predominant cis–trans rearrangement pathway in the dimer is through the doubly carbonyl-bridged intermediate, *i.e.*, pathways 2 and 3 or 2′ and 3′.

The spectra of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ in toluene solvent are complicated by the trace concentrations of several isomers. As with the spectra in acetone, absolute assignments of the resonances cannot be made, except for the isomer found in the solid state. No further discussion of the possible rearrangements and various exchange processes would be justified by the data now available. Suffice it to say that the exchanges observed in toluene solvent are consistent with the observations made on the acetone solutions.

Although much more can still be done to delineate in greater detail the structural and dynamic properties of this system, it is appropriate to conclude by pointing out that the most important feature of the system has been established unambiguously. That feature is the rapid scrambling of CO and $CNCH_3$ ligands between the metal atoms. The work reported here also shows beyond any reasonable doubt that scrambling occurs through the intermediacy of transient species having either two bridging CO ligands or one bridging CO ligand and one bridging $CNCH_3$ ligand.

Acknowledgments. We are very grateful to both the National Science Foundation (Grant No. 33142X) and the Robert A. Welch Foundation (Grant No. A494) for generous financial support of this work.

Structural and Dynamic Systematics in the Isoelectronic Series $[(C_5H_5)ML_2]_2$, Where M = Cr, Mn, and Fe and L = CO and NO

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Abstract: This work reports a detailed comparison of solution and solid-state structural properties for the isoelectronic series $[(C_5H_5)Cr(NO)_2]_2$, $[(C_5H_5)Mn(CO)(NO)]_2$, and $[(C_5H_5)Fe(CO)_2]_2$. The structure of $[(C_5H_5)Mn(CO)(NO)]_2$ has been determined from three-dimensional X-ray data collected by counter methods. The opaque compound crystallizes in space group $C_{2h}^5\text{-}P2_1/c$ of the monoclinic system with two dimeric molecules in a cell of dimensions $a = 7.002$ (1) Å, $b = 12.491$ (3) Å, $c = 8.023$ (2) Å, and $\beta = 108.07$ (1)°. The observed and calculated densities are 1.75 (1) and 1.772 g cm^{-3}, respectively. Full-matrix least-squares refinement gave a final value of the conventional R factor (on F) of 0.040 for the 1197 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of discrete dimeric ligand-bridged molecules with trans cyclopentadienyl rings. The dimers have an imposed crystallographic center of symmetry which makes the bridging (B) as well as the terminal (T) carbonyl and nitrosyl ligands disordered. Some important bond lengths (in Å) are Mn–Mn, 2.571 (1); Mn–B (av), 1.906 (5); Mn–T (av), 1.723 (4); and Mn–C (av C_5H_5), 2.13 (1). Comparisons with similar bridged dimeric molecules such as the iron carbonyl analog are made. In solution, all three compounds exist as a mixture of cis and trans ligand-bridged dimers, the ratio [cis]:[trans] following the order Fe > Mn > Cr. The activation energy for cis–trans interconversion and bridge–terminal ligand interchange decreases in the order Cr > Mn > Fe. For both the iron and the manganese compounds, bridge–terminal ligand interchange is more rapid for the trans than for the cis isomers; for manganese, both processes are more rapid than cis–trans interconversion, and this result is interpreted in terms of the stereochemistry of the system. Activation parameters and thermodynamic data are reported for all three systems.

It is now well-established that the molecule $[(C_5H_5)Fe(CO)_2]_2$ undergoes rapid intramolecular rearrangement at room temperature.[1] In solution the molecule exists as an equilibrating mixture of isomeric

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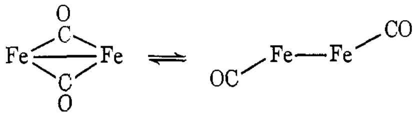
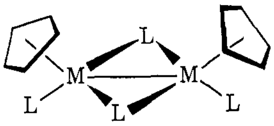
(1) (a) K. Noack, *J. Organometal. Chem.*, 7, 151 (1967); (b) A. R. Manning, *J. Chem. Soc. A*, 1319 (1968); (c) R. F. Bryan, P. T. Greene,

structures I, III, IV, and probably a gauche structure such as V.[1e] The mechanistic pathway for interconversion of these isomers is believed to involve bridge–terminal carbonyl equilibration,[1d,e] and rotation about the iron–iron bond.


(A)

In the solid state either structure I (cis bridged) or III (trans bridged) is found,[1c,2] depending upon the solvent employed for crystallization. Since this iron compound is a member of the isoelectronic series $[(C_5H_5)Cr(NO)_2]_2$,[3] $[(C_5H_5)Mn(CO)(NO)]_2$,[3] and $[(C_5H_5)Fe(CO)_2]_2$, we felt it would be of interest to extend the investigation of structural and dynamic properties to all members of this series. The effects on the molecular structure and on molecular dynamics of substitution of NO for CO were unknown. Such molecular properties are manifestations of the potential energy surfaces which $[(C_5H_5)ML_2]_2$ molecules occupy, and in this paper we investigate how the shapes of thse surfaces depend upon metal and ligands.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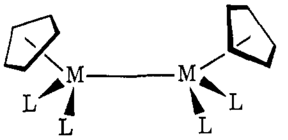
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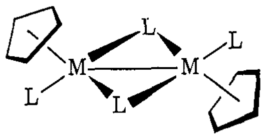
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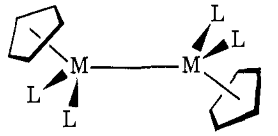
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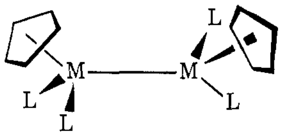
V

L = CO, NO

A recent report from this laboratory[4] described preliminary proton nmr and infrared results on the manganese member of the series and indicated that instantaneous structures and interconversion processes were surprisingly similar to the iron system despite change of metal and substitution of two carbonyls by nitrosyls. X-Ray results[5] on an isomer of $[(C_5H_5)Cr(NO)_2]_2$ indicate that it has structure III. We present in this paper the X-ray structure determination of the major isomer of $[(C_5H_5)Mn(CO)(NO)]_2$ and an examination of solution structural thermodynamics and kinetics for the entire isoelectronic series.

Experimental Section

Syntheses. Solutions of all organometallics were handled with rigorous exclusion of oxygen in solvents that had been carefully dried and deoxygenated. Solid samples could be briefly handled in air without deleterious effects. The compounds $[(C_5H_5)Mn(CO)(NO)]_2$ and $[(C_5H_5)Cr(NO)_2]_2$ were prepared as previously described.[3] Crystals suitable for X-ray work were grown by slow diffusion of hexane into saturated toluene solutions at −15°.

Spectroscopy. Infrared spectra were recorded on Beckman IR-5 and IR-9 spectrophotometers and were calibrated with polystyrene film. Solutions were prepared in Schlenk apparatus and were transferred *via* syringe to matched, nitrogen-flushed IRtran-2 cells or to the sealed cell described previously.[6] Solid-state spectra were recorded as Nujol mulls (various amounts of grinding had no apparent effect on the spectra). The manganese compound was additionally studied by evaporating a solution and studying the resulting film by attenuated total reflectance techniques. Samples were always monitored for possible decomposition (or isomerization) by observing whether changes took place in the spectrum during the course of several scans.

Nuclear magnetic resonance spectra were recorded on Perkin-Elmer Hitachi R20-B (60 MHz) or Bruker HFX-90 (90 MHz) spectrometers. Samples for low-temperature or room-temperature studies were prepared with degassed solvents in serum-capped tubes. For high-temperature work samples were prepared on a vacuum line and were sealed off under high vacuum. Spectral calibration was achieved *via* frequency counter, and temperature controllers were calibrated with the same Wilmad nmr thermometers. Generally, ample time (*ca.* 15 min) was allowed for sample equilibration at each new temperature. For $[(C_5H_5)Cr(NO)_2]_2$ at temperatures in excess of +100°, because of thermal instability, the sample could not be inserted until the spectrometer had equilibrated. Here sample equilibration time had to be held to the time necessary to tune the instrument (2–3 min).

Treatment of Nuclear Magnetic Resonance Data. Computer simulation of pmr line shapes for the dynamic molecules was performed with a local version of the program EXCNMR, originally written by G. M. Whitesides.[7] For the kinetic analysis of $[(C_5H_5)Mn(CO)(NO)]_2$ several nonroutine procedures were necessary. First, because the exchanging resonances were close together in frequency, normally small changes in chemical shifts with temperature seriously interfered with the simulation procedure. This was remedied by graphing the chemical shifts *vs.* temperature in regions below and just above the slow-exchange limit, extrapolating these curves to higher temperature regions (the plots were approximately linear), and using the corrected chemical shifts for line-shape computation at the higher temperatures. The three independent kinetic processes could be easily accommodated by the kinetic exchange matrix.[7a] For the C_5H_5 exchange within the cis and trans isomers, the ratios of the appropriate matrix elements (exchange probabilities corresponding to the two rate processes) varied slightly with temperature for optimum fit. The high-temperature process, at the point where the two low-temperature processes had nearly reached the fast-exchange limit, was simulated by extrapolating the Arrhenius plots of the latter processes to this region and then including elements for cis–trans exchange in the kinetic exchange matrix. The ratio of this exchange probability to either of the low-temperature interchanges had to be varied considerably to achieve a suitable match. Another complication which also occurred in the iron system[1e] was a small temperature dependence of the cis–trans equilibrium constant; the dependence was even smaller for the manganese system and could similarly be taken into account by minor changes in relative populations.

The kinetic analysis of $[(C_5H_5)Cr(NO)_2]_2$ in the dynamic region was somewhat more straightforward. However, owing to rapid thermal decomposition, the entire range of spectral temperature dependence was not available for simulation. Additional rate data could be obtained for lower temperatures by equilibrating the system in acetonitrile at room temperature, evaporating the solvent as quickly as possible, and redissolving the sample in toluene-d_8 in the cold spectrometer probe. The slow rate of decrease of the cis isomer could then be followed and analyzed by

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(6) T. J. Marks, *J. Chem. Educ.*, **48**, 167 (1971).

(7) (a) G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967); (b) R. Kubo, *Nuovo Cimento, Suppl.*, **6**, 1063 (1957); (c) R. A. Sack, *Mol. Phys.*, 1, 163 (1958).

classical equilibration methods.[8] Arrhenius and log K *vs.* $1/T$ plots were computer-fitted by the method of least squares. Standard deviations reported are those derived from the fitting procedure.

Molecular Weight Studies. The molecular weight of $[(C_5H_5)Mn(CO)(NO)]_2$, which had not been reported, was determined cryoscopically in benzene using an apparatus described previously[9] (calcd, 356 for a dimer; found, 321).

X-Ray Study of the Manganese System. Preliminary Weissenberg and precession photography of the *hkl*, 0*kl*, and *hk*0 nets showed that the opaque crystals of $[(C_5H_5)Mn(CO)(NO)]_2$ belong to the monoclinic system. The systematic absences observed for the reflections *h*0*l* with *l* odd and 0*k*0 with *k* odd are consistent with group $C_{2h}{}^5$-$P2_1/c$. For the crystal chosen for subsequent data collection, the faces were identified from optical goniometry as belonging to the forms {100} and {011}. The distances between the faces of these forms were approximately 0.2 mm. Cell parameters were determined at 22° from a least-squares refinement[10,11] of 21 intense high-order reflections, hand-centered on a Picker four-circle automatic diffractometer using monochromatized Mo Kα radiation (λ 0.70930 Å) and employing a tube takeoff angle of 1.1°. The cell parameters are a = 7.002 (1) Å, b = 12.491 (3) Å, c = 8.023 (2) Å, and β = 108.07 (1)°. The density calculated for two formula weights per unit cell is 1.772 g cm^{-3} and agrees with that of 1.75 (1) g cm^{-3} measured by flotation in aqueous $ZnCl_2$. A crystallographic center of symmetry is imposed on the dimer molecule.

The mosaicity of the crystal was examined by means of the narrow-source, open counter, ω-scan technique. The peak width at half height for a typical strong reflection was found to be approximately 0.1°. Scans of 2θ and ω showed minor splitting of peaks for 0*k*0 reflections but no splitting for *h*00 or 00*l* reflections. The crystal was mounted on the diffractometer with the b^* axis slightly offset from the spindle axis.

Data were collected using monochromatic Mo Kα radiation in a manner similar to that previously described.[12] The intensities of six standard reflections showed an average deviation from their average intensity of about $\pm 3\sigma$. Intensity data were collected for the unique *hkl* planes up to 2θ (Mo Kα) = 127.0°, yielding 1783 reflections. In addition 199 Friedel-pair reflections were collected. The data were processed in the normal manner[10,11] using a value for p of 0.04. The average deviation among the Friedel-pairs is 1.4%. Of the unique reflections observed, 1197 reflections have $F^2 > 3\sigma(F^2)$ and only these reflections were included during the refinement of the structure. The linear absorption coefficient for the compound for Mo Kα radiation is 18.1 cm^{-1}. The data were corrected for absorption.[13] The maximum–minimum transmission factors were 0.774 and 0.586, respectively.

Preliminary experiments on the $[(C_5H_5)Mn(CO)(NO)]_2$ system suggested a trans stereochemistry of ligand groups, similar to the structure known for the related *trans*-$[(C_5H_5)Fe(CO)_2]_2$ system.[2,14] The manganese dimer was assumed to be structurally isomorphous with the iron dimer since the space groups and crystal habits found for both systems are identical while the cell constants are very similar. Atomic parameters from the structure of the iron dimer[2] were used as a starting trial structure for the present work.

One cycle of isotropic refinement of the positions for all non-hydrogen atoms with the cyclopentadienyl atoms treated as a rigid group[13] of D_{5h} symmetry (C–C = 1.42 Å) gave the agreement indices

$$R = \sum |F_o| - |F_c|| / \sum |F_o|$$

and

$$R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum wF_o{}^2\}^{1/2}$$

of 0.22 and 0.28. Weights, w, were taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. In this and succeeding full-matrix least-squares refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors were taken from the new tabulation,[15] except for hydrogen atom factors which were those of Stewart, Davidson, and Simpson.[16] Anomalous dispersion effects were included in the calculation of F_c[13] using the values of $\Delta f'$ and $\Delta f''$ for manganese calculated by Cromer and Liberman.[17]

Isotropic least-squares refinement (with the presumed disordered carbon and nitrogen atoms assigned nitrogen scattering factors) was continued until convergence was achieved (R = 0.131 and R_w = 0.172). At this point a three-dimensional difference Fourier map revealed significant amounts of residual electron density in a torus about the cyclopentadienyl ring. Thus the thermal motion of this ring was not satisfactorily accounted for by the use of an overall group temperature factor. Therefore all atoms were allowed to refine individually with anisotropic temperature factors and agreement indices R = 0.085 and R_w = 0.129 were obtained after one cycle of refinement. A subsequent three-dimensional difference Fourier map revealed three of the five cyclopentadienyl hydrogen atoms in reasonable positions. All five hydrogen atoms were idealized (D_{5h} symmetry, C–H = 1.0 Å, and temperature factor, B = 6.0 Å,^{2} equal to the final rigid group overall temperature factor) and included in this and ensuing refinements as a fixed-atom structure factor addition. The least-squares refinement was continued until convergence was achieved, giving the agreement indices R = 0.044, R_w = 0.058, and a goodness of fit, the standard deviation of an observation of unit weight, of 1.92e. At this point difference Fourier calculations with the disordered atoms left out of the structure factor calculation gave electron density peaks that were featureless and not resolvable into contributions from the separate nitrosyl and carbonyl groups. We thus assigned to the superimposed carbon and nitrogen atoms "hybrid" scattering factors obtained from an averaging of those values for nitrogen and carbon. Two final cycles of refinement with individual anisotropic parameters for all atoms and the "hybrid" scattering factor for the disordered nitrogen-carbon atoms led to a significant improvement of the agreement indices over the previous model which used the nitrogen scattering factor for the disordered atoms. The final agreement factors are R = 0.040, R_w = 0.051, and a goodness of fit of 1.69e. In the final cycle no parameter shifted more than 0.10 of its standard deviation.

A comparison of $\Sigma w(|F_o| - |F_c|)^2$ for various classes of reflections based upon $|F_o|$, Miller indices, and the setting angles shows no unusual trends. A final difference Fourier map reveals no peak greater than 0.41 (8) e/Å^3, which is approximately 5% the height of an oxygen atom in previous difference maps. The peaks above background are in regions associated with the manganese atom or the cyclopentadienyl ring. There is no significant electron density residue in the region of the disordered groups. Of the 586 reflections omitted from the refinement for which $F_o{}^2 < 3\sigma(F_o{}^2)$, only 19 had $|F_o{}^2 - F_c{}^2| > 3\sigma(F_o{}^2)$.

The positional and thermal parameters obtained from the last cycle of least-squares refinement are given in Table I, along with the associated standard deviations as estimated from the inverse matrix. Root-mean-square amplitudes of vibration are given in Table II. Intermolecular and intramolecular contact distances are given in Table III. In the above tables the superimposed nitrogen and oxygen atoms resulting from the disorder problem have been labeled as X. Table II, Table III, and final values of $10|F_o|$ and $10F_c$ in electrons have been deposited.[18]

The Crystal Structure of *trans*-$[(C_5H_5)Mn(CO)(NO)]_2$

The crystal structure of $[(C_5H_5)Mn(CO)(NO)]_2$ consists of the packing of discrete, centrosymmetric, dimeric molecules (Figure 1). The intermolecular contacts are normal, the shortest being the O(2)–H(5) distance of 2.51 Å.

A perspective view of a single dimeric molecule showing the atom labeling scheme is presented in

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[8] H. S. Gutowsky, J. Jonas, and T. H. Siddall, III, *J. Amer. Chem. Soc.*, **89**, 4300 (1967); K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, New York, N. Y., 1965, p 20.

[9] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 159.

[10] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[11] R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

[12] See, for example, R. M. Kirchner and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 1095 (1973).

[13] Programs and procedures used were as described previously,[12] with the addition of the Dunitz–White TMA program for librational corrections based upon the Trueblood–Schomaker algorithms.

[14] O. S. Mills, *Acta Crystallogr.*, 11, 620 (1958).

[15] D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography," Vol. 4, Kynoch Press, Birmingham, England, in press, Table 2.2A.

[16] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[17] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

[18] See paragraph at end of paper regarding supplementary material.

Table I. Positional and Thermal Parameters for $[(C_5H_5)Mn(CO)(NO)]_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	0.08577 (8)[b]	0.06759 (4)	0.12082 (6)	0.01733 (12)	0.00604 (4)	0.01097 (9)	0.00094 (6)	−0.00066 (7)	−0.00102 (5)
X(1)[c]	−0.0931 (6)	0.1672 (3)	0.0647 (5)	0.0228 (9)	0.0068 (3)	0.0217 (8)	0.0023 (4)	−0.0007 (6)	−0.0023 (4)
X(2)	0.1012 (5)	0.0458 (3)	−0.1091 (4)	0.0193 (7)	0.0075 (3)	0.0120 (5)	0.0009 (3)	0.0017 (5)	0.0006 (3)
O(1)	−0.2083 (6)	0.2365 (3)	0.0327 (6)	0.0391 (12)	0.0090 (3)	0.0464 (13)	0.0090 (5)	0.0003 (9)	−0.0026 (5)
O(2)	0.1868 (5)	0.0836 (3)	−0.2028 (4)	0.0300 (8)	0.0135 (3)	0.0168 (5)	−0.0046 (4)	0.0081 (6)	0.0015 (3)
C(1)	0.4067 (7)	0.0813 (10)	0.2117 (7)	0.0170 (10)	0.0311 (13)	0.0162 (9)	−0.0035 (10)	−0.0010 (7)	−0.0032 (10)
C(2)	0.3569 (12)	−0.0114 (7)	0.2702 (12)	0.0367 (21)	0.0132 (6)	0.0407 (21)	0.0120 (9)	−0.0244 (16)	−0.0126 (10)
C(3)	0.2499 (11)	0.0087 (8)	0.3754 (10)	0.0388 (20)	0.0163 (8)	0.0258 (14)	−0.0099 (10)	−0.0169 (12)	0.0114 (9)
C(4)	0.2258 (8)	0.1150 (9)	0.3830 (7)	0.0274 (14)	0.0240 (9)	0.0143 (9)	0.0045 (10)	−0.0010 (8)	−0.0091 (8)
C(5)	0.3239 (10)	0.1619 (4)	0.2805 (10)	0.0426 (20)	0.0079 (4)	0.0326 (15)	−0.0059 (7)	−0.0188 (14)	0.0007 (6)
H(1)	0.4933[d]	0.0865	0.1321						
H(2)	0.3926	−0.0866	0.2391						
H(3)	0.1908	−0.0460	0.4414						
H(4)	0.1470	0.1536	0.4525						
H(5)	0.3370	0.2403	0.2539						

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The numbers given in parentheses here and in succeeding pages are estimated standard deviations in the least significant figures. [c] X refers to the disordered hybrid, a combination carbon–nitrogen atom. [d] Hydrogen atoms are in calculated positions which were not refined. All hydrogen atoms were assigned an isotropic temperature factor of $B = 6.0$ Å^2.

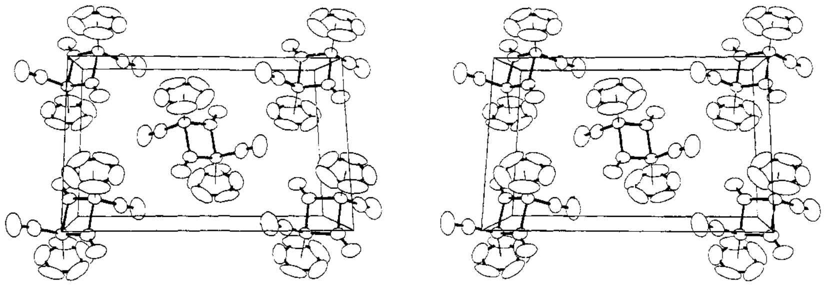

Figure 1. Stereoscopic packing diagram of $[(C_5H_5)Mn(CO)(NO)]_2$. The view is approximately down z. Cyclopentadienyl hydrogen atoms have been omitted for clarity. The 50% probability vibrational ellipsoids are shown.

Figure 2. The molecule in the solid state has a crystallographic center of symmetry. This center gives an identical chemical environment about each Mn atom of the dimer and requires the two Mn atoms and two bridging X atoms to be coplanar and the cyclopentadienyl ligands to be trans. As will be discussed in detail later, there is convincing chemical evidence that, of the bridging ligands and hence of the terminal ligands, one is a carbonyl and the other a nitrosyl. The crystallographically imposed center of symmetry thus leads to disordered bridging and terminal ligand groups. Nevertheless the overall geometry of $[(C_5H_5)Mn(CO)(NO)]_2$ is clearly defined as structure III, as can be seen in Figure 2.

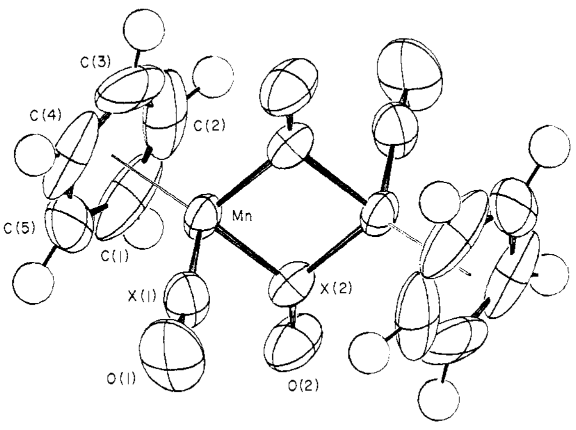

Figure 2. Perspective view of a single molecule of $[(C_5H_5)Mn(CO)(NO)]_2$ with the atom labeling scheme. The disordered carbon and nitrogen atoms are labeled X. The 50% probability vibrational ellipsoids are shown. For reasons of clarity the cyclopentadienyl hydrogen atoms are shown at one-half their thermal B values.

Selected bond angles and distances are given in Table IV. The Mn–Mn distance of 2.571 (1) Å does not compare to values found in other manganese dimers. Manganese dimers are known to exist with only a ligand-bridging interaction, $[Mn(CO)_4(\mu\text{-}Br)]_2$[19] and $Mn_2(CO)_6(\mu\text{-}N_3)_3$[20] (Mn–Mn = 3.743 (8), 2.893 (4) Å); with only a metal–metal interaction, $[Mn(CO)_5]_2$[21] and $[Mn(CO)_4(P(CH_2CH_3)_3)]_2$[22] (Mn–Mn = 2.923 (3), 2.913 (6) Å); and with both ligand-bridging and metal–metal interactions, $Mn_2(CO)_8(\mu\text{-}H)(\mu\text{-}P(C_6H_5)_2)$,[23] $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$,[24] and $(C_5H_5)_2Mn_2(NO)(NO_2)(\mu\text{-}NO)_2$[25] (Mn–Mn = 2.937 (5), 2.871 (2), and 2.53 Å, respectively). In general for inorganic binuclear complexes, the length of the metal–metal interaction is not directly related to its strength.[26, 27] Also, the geometry of these

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Table IV. Selected Bond Distances and Angles

Bond lengths (Å)			Bond angles (deg)		
Mn–Mn′[a]	2.571 (1)		Mn–X(1)–O(1)	177.2 (4)	
Mn–X(1)	1.723 (4)		Mn–X(2)–O(2)	138.1 (3)	
Mn′–X(2)	1.911 (4)		Mn–X(2)–Mn′[a]	84.8 (1)	
Mn–X(2)	1.901 (3)		Mn′–X(2)–O(2)	137.1 (3)	
X(1)–O(1)	1.157 (5)		X(2)–Mn–X(2′)	95.2 (1)	
X(2)–O(2)	1.194 (4)		Mn′–Mn–X(1)	98.4 (1)	
Mn–cg[b]	1.800 (6)		Mn′–Mn–cg[b]	136.0 (3)	
Mn–C(1)	2.144 (5)	2.131 (16)[c]	X(1)–Mn–X(2)	96.0 (2)	
Mn–C(2)	2.145 (5)		X(1)–Mn–cg	125.6 (4)	
Mn–C(3)	2.140 (5)		X(1)–Mn–X(2′)	95.2 (2)	
Mn–C(4)	2.111 (4)		X(2)–Mn–cg	119.7 (3)	
Mn–C(5)	2.117 (4)		X(2′)–Mn–cg	118.4 (3)	
C(1)–C(2)	1.336 (10)	1.342 (18)	Mn–cg–C(1)	90.7 (5)	
C(2)–C(3)	1.315 (11)		Mn–cg–C(2)	91.1 (6)	
C(3)–C(4)	1.342 (10)		Mn–cg–C(3)	90.8 (6)	
C(4)–C(5)	1.356 (9)		Mn–cg–C(4)	88.7 (5)	
C(5)–C(1)	1.361 (9)		Mn–cg–C(5)	88.7 (5)	
			C(1)–C(2)–C(3)	108.8 (6)	108.0 (9)
			C(2)–C(3)–C(4)	108.8 (7)	
			C(3)–C(4)–C(5)	107.8 (6)	
			C(4)–C(5)–C(1)	106.6 (6)	
			C(5)–C(1)–C(2)	107.9 (6)	

[a] Atoms related by the center of symmetry have a prime. [b] cg denotes the center of gravity of the cyclopentadienyl ring. [c] The number in parentheses is the standard deviation of a single observation estimated on the assumption that the quantities averaged are from the same population.

binuclear complexes varies widely depending upon the presence and types of bridging ligands. Comparisons of trends in geometry for bridged binuclear molecules with and without metal–metal interactions have been made elsewhere.[24,27,28] In a later section comparisons will be made between the present work and other similar non-manganese dimers.

The Mn–(XO) terminal distance of 1.723 (4) Å falls in the middle of the range of values expected for a superimposed CO and NO group. For example, terminal Mn–(CO) distances range from 1.68 to 1.93 Å with a mean value of 1.80 Å for the manganese dimers[22–27] and $(C_5H_5)Fe(CO)_2Mn(CO)_5$.[29] The only terminal Mn–(NO) distance known for a manganese dimer is 1.652 Å in $(C_5H_5)_2Mn_2(NO)_3(NO_2)$,[25] but values from 1.57 to 1.73 Å have been reported for Fe–(NO) bonds[30] while values from 1.56 to 1.80 A are given in a recent review[31] for metal–nitrogen distances of approximately linear M–N–O groups.

Comparisons of the bond lengths and angles of the bridging XO group of this study with bridging CO groups in similar dimeric manganese molecules cannot be made because no others are known. There is one dimeric manganese structure reported with bridging NO groups, $(C_5H_5)_2Mn_2(NO)(NO_2)(\mu\text{-}NO)_2$,[25] that has markedly unsymmetrical bridging NO groups as a result of the different formal oxidation numbers of +2 and 0 for the manganese atoms. The bridging Mn–(NO) distances reported are 1.78 and 1.94 Å. However, there are some similar isoelectronic iron and chromium dimeric species known, and comparisons between them will be made in a following section.

It has been commonly found for both carbonyl and nitrosyl ligands that the groups with longer metal–ligand distances, M–(XO), have shorter X–O distances. This is true in the present study. The terminal group X–O distance of 1.157 (5) Å compares well with the mean value of 1.165 Å found for 19 other terminal N–O distances[32] and the mean value of 1.159 Å found for terminal C–O distances in similar complexes.[1c,2,21,22,33,34] The bridging group X–O length of 1.194 (4) Å compares well with the mean value of 1.184 Å found for bridging CO groups in similar complexes.[1c,2,34] Bond distances have been reported for bridging nitrosyl ligands as 1.193 (4) Å in $[(C_5H_5)Cr(NO)_2]_2$,[5] 1.205 Å in $(C_5H_5)_2Mn_2(NO)_3(NO_2)$,[25] and 1.12 (2) Å in $(C_5H_5)_2Cr_2(NO)_3(NH_2)$.[35] Except for the last value, the agreement with the present results is good.

The carbon atoms of the cyclopentadienyl ring show no deviation from planarity. The carbon atoms lie in a weighted least-squares plane defined by the equation

$$4.342x + 0.596y + 4.429z - 2.747 = 0$$

(in monoclinic coordinate system). The maximum deviation of an atom from the plane is 0.008 (5) Å; the mean deviation is 0.005 (5) Å. The manganese to cyclopentadienyl plane distance is 1.799 (5) Å. The mean Mn–C(ring) distance is 2.13 (2) Å, which compares favorably with other similar mean Mn–C(ring) distances of 2.13 Å in $[(C_5H_5)Mn(CO)_2]_2(C_4H_6)$,[36] and 2.15 (2) Å in $(C_5H_5)Mn(CO)_3$.[33] The mean C(ring)–C(ring) distance is 1.34 (1) Å, which compares with the mean values of 1.42 Å[36] and 1.39 Å.[33] The short mean

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Table V. Comparison of Mean Geometrical Parameters of the Isoelectronic Series $[(C_5H_5)ML_2]_2$ and Other Similar Ligand Bridged Dimers with Metal–Metal Bonds[a]

				Distance, Å					Angle, deg		
	Molecule	B	Ref	M–M	M–B	B···B	M–T	M–C(Cp)	M–B–M′	B–M–B′	*b*
A	*cis*-$[(C_6H_8)Co(CO)_2]_2$	$(CO)_2$	40c	2.559 (3)	1.91 (1)	2.84 (2)	1.79 (1)	2.08 (4)[g]	84 (1)	95 (1)	175
B	*trans*-$[CpFe(CO)_2]_2$	$(CO)_2$	1c	2.534 (2)	1.914 (4)	2.87 (1)	1.75 (1)	2.11 (2)	82.9 (2)	97.1 (4)	180
C	*cis*-$[CpFe(CO)_2]_2$	$(CO)_2$	2	2.531 (2)	1.92 (1)	2.85 (1)	1.75 (2)	2.11 (2)	82.6 (2)	96.0 (3)	164
D	(*cis*)$[CpRCp]Fe_2(CO)_2$[c]	$(CO)_2$	34	2.510 (2)	1.92 (1)	na[d]	1.70 (1)	na	81.8 (4)	96.1 (4)	160
E	*trans*-$[CpMn(CO)(NO)]_2$	CO, NO	Present work	2.571 (1)	1.91 (1)[e]	2.82 (1)	1.723 (4)[e]	2.13 (1)	84.8 (1)	95.2 (1)	180
F	*trans*-$[CpCr(NO)_2]_2$	$(NO)_2$	5	2.615 (1)	1.91 (1)	na	1.690 (3)	2.21 (1)	86.7 (1)	93.3 (1)	180
G	*trans*-$(Cp)_2Cr_2(NO)_3(NH_2)$	NO, NH_2	35	2.650 (4)	1.94 (1)[e]	na	1.65 (3)	2.24 (5)	86.4 (5)	93.1 (8)	
H	*trans*-$[CpCr(NO)(NMe_2)]_2$	$(NMe_2)_2$	41	2.67 (1)	2.00 (1)	na	1.63 (2)	2.26 (1)	84.3 (5)	85.7 (5)	180
I	*cis*-$[CpCr(NO)(NMe_2)]_2$	$(NMe_2)_2$	41	2.72 (1)	2.01 (1)	na	1.63 (1)	2.26 (1)	85.0 (4)	95.1 (4)	na[f]

[a] Key: M = metal, B = bridging ligand, T = terminal ligand other than (C_5H_5), Cp = (π-C_5H_5), Me = CH_3. [b] Dihedral angle between normals of M–B–M′ and M–B′–M′ planes, in deg. A value of 180 indicates a planar M_2B_2 geometry. [c] CpRCp is (π-C_5H_4)CH(N$(CH_3)_2$)-CH(N$(CH_3)_2$)(π-C_5H_4), which forces a cis configuration. [d] Not reported. [e] Composite value resulting from disorder problem. [f] Report fold about N–N vector is 178°. [g] Average value for the carbon atoms of the bonding butadiene moiety of the π-cyclohexa-1,3-diene group.

C(ring)–C(ring) value is probably a result of large librational effects within the ring itself, a partial description of which is given by the vibrational amplitude values in Table II. Inspection of the individual bond length values in Table IV shows that there is a systematic trend in the variation of the Mn–C(ring) and C(ring)–C(ring) distances. The shorter Mn–C(ring) distances have carbon atoms that have longer C(ring)–C(ring) distances, and this trend goes around the ring in a smooth fashion. This would imply that some localization of electron density in the ring has occurred. It is possible, but unlikely, that the X-ray experiment may have underestimated the standard deviations as a result of an approximate model for the thermal motion of the cyclopentadienyl ring. Correction of the coordinates of the ring carbon atoms for librational effects[13] increased the M–C(ring) and C(ring)–C(ring) distances by approximately 0.020 and 0.015 Å, respectively, but did not change any of the trends in bond distances noted above. Pro and con arguments for electron localization have been discussed in review articles.[37,38] More recent work[39] on $(C_5H_5)_2Mo(NO)(CH_3)$ presents further evidence for possible electron localization, as evidenced by skewing of the ring–metal interaction.

Comparison of the Crystal Structures in the Isoelectronic Series $[(C_5H_5)ML_2]_2$. Mean geometric parameters in the isoelectronic series $[(C_5H_5)ML_2]_2$ and other very similar complexes are given in Table V. The complexes listed have either the cis or trans configuration. All of the trans complexes have a crystallographically imposed center of symmetry giving a plana- M_2B_2 geometry (B = bridging ligand). For the trans complexes E and G where there are two different bridging ligands, the structures are disordered. The cis complexes do not have a planar M_2B_2 geometry but have a buckling of the M_2B_2 moiety with the bridging ligands bending away from the cyclopentadienyl (Cp) rings. Otherwise the complexes A through I are remarkably similar.

A planar M_2B_2 geometry in bridged dinuclear complexes has been suggested[40] to be more stable than a nonplanar M_2B_2 geometry. This results from the possibility of delocalized π-electron density in a planar bridge[40a] and the minimization of repulsive effects between bridging groups in the limit of a planar geometry.[40b] For those complexes where the information has been reported, crystals were only obtained or, in some cases, more easily obtained for the planar or nearly planar complexes.

Within the isoelectronic series (B, C, E, and F) there is a smooth trend in the M–M distance that correlates with the size of the metal atom. As the metal covalent radius decreases (Cr > Mn > Fe), the M–M distance decreases. Complex A has a Co–Co distance longer than expected from the M–M trend noted presumably as a result of having larger and bulkier terminal ligands cis to each other. This is another example of the insensitivity of the M–M bond length to bond order. D has its Cp rings linked together and perhaps this helps close down the M–M distance. Although an insufficient amount of information is given in the communication[41] to determine why the cis form (I) of $[(C_5H_5)Cr(NO)(NMe_2)]_2$ has a longer M–M bond than the trans form (H), presumably the planar trans form suffers less from repulsive effects between the bridging groups.

The M–B distances at 1.92 Å remain the same throughout the series despite the diverse radii of the metal atoms. The complexes H and I, which have appreciably bulkier bridging ligands (NMe_2), have slightly longer but equal M–B lengths. The smooth variation in M–B–M′ and B–M–B′ angles is a result of having the M–B distances remain constant while the M–M distances change. There is no difference in these trends between cis and trans isomers.

The M–T distance is shorter when the terminal group (T) is a nitrosyl ligand. This might reflect the stronger π-electron acceptor properties of a linear nitrosyl group, formally NO^+, compared with a carbonyl group. As discussed earlier, in general M–(NO) distances are shorter than M–(CO) distances. In addition, with increasing metal atomic number the metal atoms become weaker π-electron donors. This

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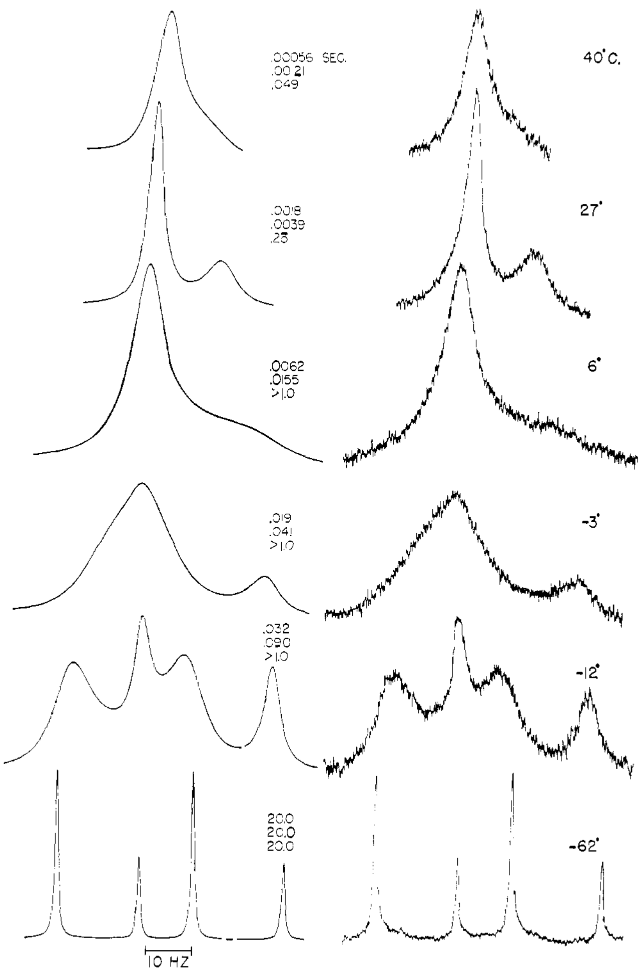

Figure 3. (Right) The 90-MHz proton nmr spectra of a toluene-d_8 solution of $[(C_5H_5)Mn(CO)(NO)]_2$ as a function of temperature. (Left) Computer generated spectra for the mean lifetimes (top to bottom): bridge–terminal ligand interchange, trans isomer; bridge–terminal ligand interchange, cis isomer; cis–trans isomer exchange, trans isomer.

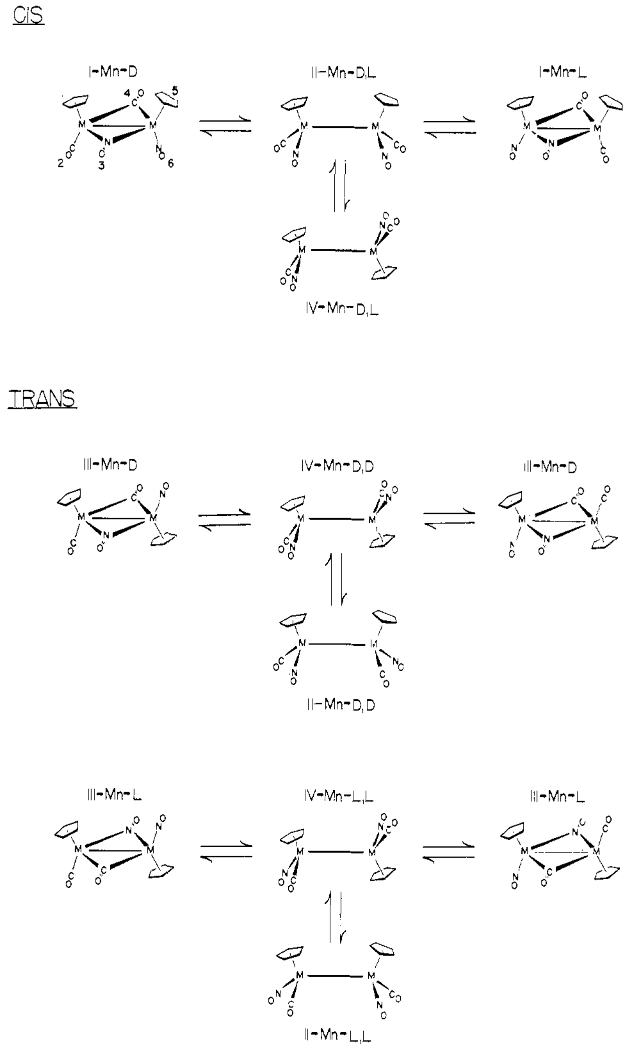

Figure 4. Possible structures of $[(C_5H_5)Mn(CO)(NO)]_2$ and interconversions executed by symmetrical bridge cleavage followed by rotation about the metal–metal bond. Roman numerals denote geometrical isomers and D and L specify opposite chirality.

effect would reinforce the M–T trend observed. The apparent trend in M–C(Cp) distances, which decrease with decreasing M–M distances, is a result of the decreasing metal atomic radii. Other factors such as close contacts and the relative amount of π-electron density donation from the cyclopentadienyl ring to the metal must also be important to some extent.

Spectral Results. $[(C_5H_5)Mn(CO)(NO)]_2$ in Solution. The proton nmr spectra of $[(C_5H_5)Mn(CO)(NO)]_2$ as a function of temperature are shown in Figure 3. It is apparent that the limiting low-temperature spectrum consists of two doublets, each corresponding to an isomer with magnetically nonequivalent cyclopentadienyl rings. The isomers are not present in equal proportions. If a toluene-d_8 solution of this compound is prepared by dissolving the crystals at −65° in the nmr spectrometer, only the low-field doublet is observed. This is assigned to the enantiomorphous trans structures III–Mn–D and III–Mn–L (Figure 4);[42] such a conclusion is in agreement with the X-ray results. The exact disposition of the carbonyl and nitrosyl ligands follows from the magnetic nonequivalence of the C_5H_5 rings and from the vibrational data (*vide infra*). Returning to the low-temperature nmr spectrum in Figure 3, it is also apparent that the second isomer has nonequivalent cyclopentadienyl rings. Addition of polar solvents (*e.g.*, CD_2Cl_2, acetone) causes the higher field doublet to grow in relative intensity. By analogy with the $[(C_5H_5)Fe(CO)_2]_2$ system,[1] we assign the more polar isomer the enantiomorphous cis structures I–Mn–D and I–Mn–L. In both iron and manganese systems, the cis isomer C_5H_5 protons resonate to higher field than those of the trans.

Further support for the above structures is derived from vibrational data. The infrared spectrum of $[(C_5H_5)Mn(CO)(NO)]_2$, as a solution in cyclohexane, is shown in Figure 5. If we neglect for the moment the weaker band at 1992 cm^{-1}, the spectrum requires the presence of terminal CO (1970 cm^{-1}), bridging CO (1813 cm^{-1}), terminal NO[43] (1732 cm^{-1}), and bridging NO[43] (1534 cm^{-1}) groups. The solid-state infrared spectrum is similar in appearance, with well-resolved bands at 1955, 1782, 1709, and 1509 cm^{-1}.

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[42] D and L are only used here to indicate that enantiomers of a given geometrical isomer have opposite configurations. No information about absolute configuration or the sign of optical rotation is implied.

[43] B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 277 (1966); W. P. Griffith, *Advan. Organometal. Chem.*, 7, 231 (1968).

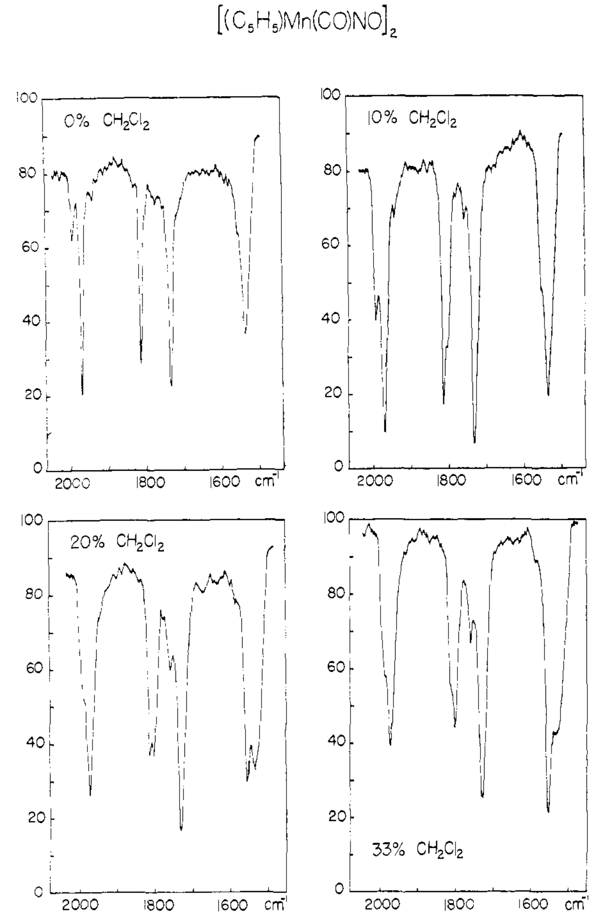

Figure 5. Infrared spectra of $[(C_5H_5)Mn(CO)(NO)]_2$ in cyclohexane solution as a function of added methylene chloride.

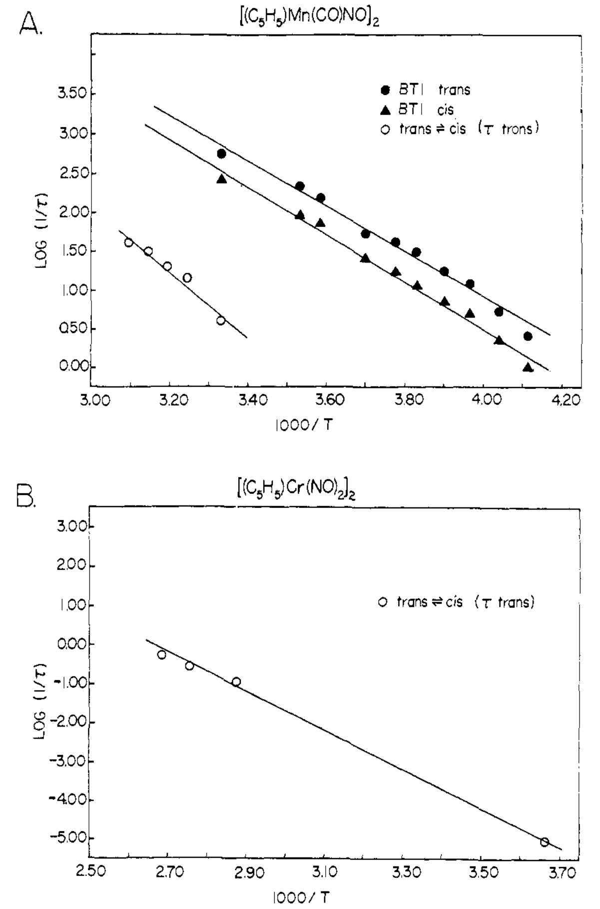

Figure 6. Arrhenius plots for the exchange processes studied. BTI refers to bridge–terminal ligand interchange.

This pattern is in excellent accord with structure III-Mn and is impossible to reconcile with a more symmetrical structure without invoking unreasonable band positions[44a] and/or unreasonable factor group splitting.[44b,c] Additional support for this assignment is derived from observation of weak ^{13}CO bands[45] in the mull at 1920 and 1745 cm^{-1}. The CO stretching band at 1992 cm^{-1} in the solution spectrum is assigned to the cis isomer (overlap obscures the other expected bands), and that this isomer also contains one terminal CO, one bridging CO, one terminal NO, and one bridging NO group is supported by the result of progressively increasing the solvent polarity. Figure 5 clearly shows, at the least, three of the four expected bands for the polar isomer growing in. This kind of behavior, including near-overlapping of bands for cis and trans isomers, closely parallels the $[(C_5H_5)Fe(CO)_2]_2$ system.[1] No bands were observed for the manganese compound which could be confidently assigned to a nonbridged isomer (II, IV, or V). The assignment of these very weak bands in the iron system followed from strong bands observed in the ruthenium analog.[1a]

Returning to the variable temperature nmr spectra in Figure 3, we see that rapid interchange of the cyclopentadienyl rings within each isomer begins above *ca.* −30°. Furthermore, the rate of ring interchange for the trans isomer is greater than that for the cis isomer. At still higher temperatures a third discrete process becomes rapid, interconversion of cis and trans isomers. All changes in the pmr spectra are reversible upon lowering the temperature and are independent of concentration. Computer simulation (see Experimental Section) shown in Figure 3 confirms that three discrete, independent rate processes are occurring and allows extraction of activation parameters (Table VI). Figure 6 illustrates Arrhenius plots derived from such data.

Attempts to crystallize the cis isomer from a variety of polar solvents[2] were unsuccessful. In all cases only the trans isomer could be isolated.

Spectral Results. $[(C_5H_5)Cr(NO)_2]_2$ in Solution. The room temperature pmr spectrum for this molecule is shown in Figure 7. The small singlet resonance to high field was at first thought to result from an impurity, but neither repeated slow crystallization from any number of solvent systems nor careful chromatography could detectably alter the intensity in toluene-d_8 of the small peak relative to the larger low-field C_5H_5 resonance. Addition of polar solvents (*e.g.*, acetone, acetonitrile) causes the high-field peak to grow in intensity (several minutes are required for complete equilibration). Table VII gives some equilibrium constants as a function of solvent; the amount of cis isomer present is roughly proportional to the dielectric constant of the solvent. Similar behavior is observed

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[44] (a) The frequencies for the iron dimer also occur *ca.* 20 cm^{-1} lower in the solid state than in solution. (b) J. G. Bullitt and F. A. Cotton, *Inorg. Chim. Acta*, 5, 637 (1971). (c) S. F. A. Kettle, *Pure Appl. Chem.*, 27, 113 (1971).

[45] L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, 12, 53 (1969).

Table VI. Activation Parameters[a]

Compound and isomer	Bridge–terminal ligand interchange E_a[b]	Log A	Cis ⇌ trans E_a[b]	Log A
$[(C_5H_5)Fe(CO)_2]_2$				
Cis	11.0 ± 1.0[c]	13.0 ± 1.0[c]	12.0 ± 1.0[d]	13.0 ± 1.0[d]
Trans	8.0 ± 1.0[c]	13.0 ± 1.0[c]	12.0 ± 1.0[d]	13.0 ± 1.0[d]
$[(C_5H_5)Mn(CO)(NO)]_2$				
Cis	13.8 ± 0.6	12.6 ± 0.5	19.1 ± 2.4	14.9 ± 1.7
Trans	13.5 ± 0.6	12.7 ± 0.5	19.1 ± 2.4	14.6 ± 1.7
$[(C_5H_5)Cr(NO)_2]_2$				
Cis			21.5 ± 1.3	13.3 ± 1.3
Trans			23.4 ± 1.2	13.6 ± 1.2

[a] Standard deviations are those obtained from the least-squares fitting procedure. [b] In kcal/mol. [c] Calculated from data of ref 1d, assuming log A = 13.0. [d] Reference 1e.

Table VII. Cis–Trans Equilibrium Constants[a] for $[(C_5H_5)Cr(NO)_2]_2$ as a Function of Solvent

Solvent	Solvent dielectric constant[b]	K[c]
Cyclohexane	2.02	21.8
Carbon disulfide	2.64	19.2
Toluene-d_8	2.38	15.4
Nitrobenzene	34.6	5.0
Acetone-d_6	20.7	3.2
Acetonitrile	36.2	3.0
Dimethyl-d_6 sulfoxide	47.6	2.1

[a] At +35°. K = [trans]/[cis]. [b] At +25°. [c] Estimated error ±5%.

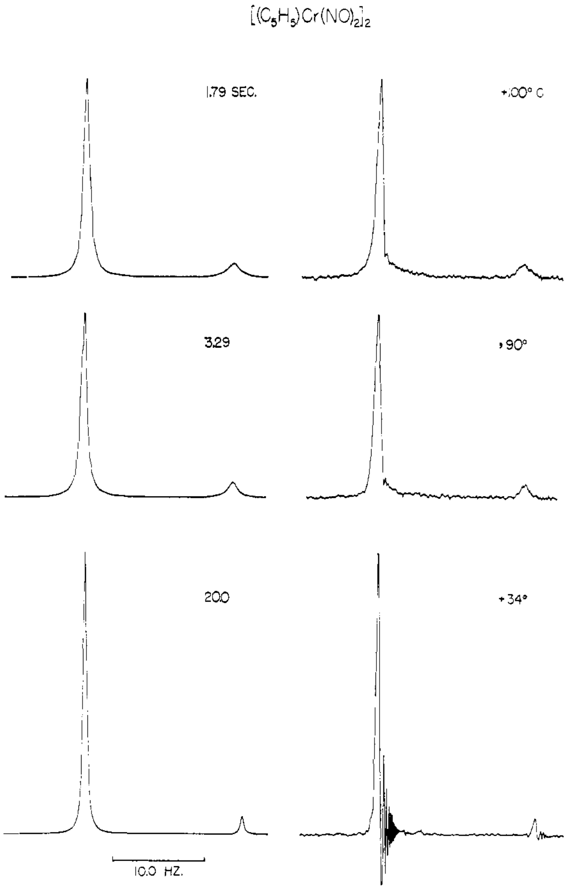

Figure 7. (Right) The 60-MHz proton nmr spectra of a toluene-d_8 solution of $[(C_5H_5)Cr(NO)_2]_2$ as a function of temperature. (Left) Computed spectra for the mean lifetimes of the trans isomer indicated.

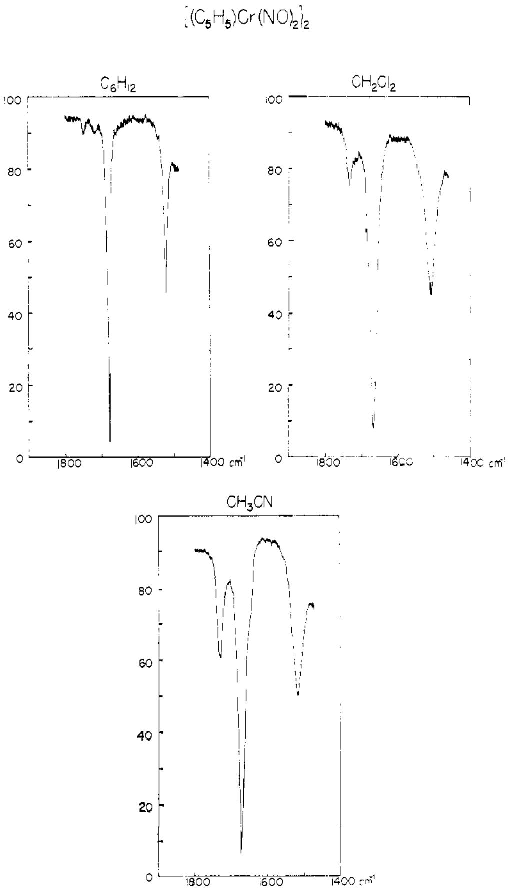

Figure 8. Infrared spectra of $[(C_5H_5)Cr(NO)_2]_2$ in the solvents indicated.

for $[(C_5H_5)Fe(CO)_2]_2$[1b,e] and $[(C_5H_5)Mo(CO)_3]_2$.[46] Evaporation of the polar solvent and dissolution of the residue in toluene-d_8 produces the original toluene-d_8 spectrum after an equilibration time of several minutes. Furthermore, at higher temperatures the onset of rapid exchange between the two species is observed; the rate of this process is independent of concentration. No change in the room temperature pmr spectra is observed on cooling to −95°. Based upon this information and vibrational data (*vide infra*), we assign the more and less intense resonances to NO-bridged trans (III) and cis (I) isomers, respectively.

The infrared spectrum of $[(C_5H_5)Cr(NO)_2]_2$ as a solution in cyclohexane is presented in Figure 8.

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(46) R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, 7, 153 (1973).

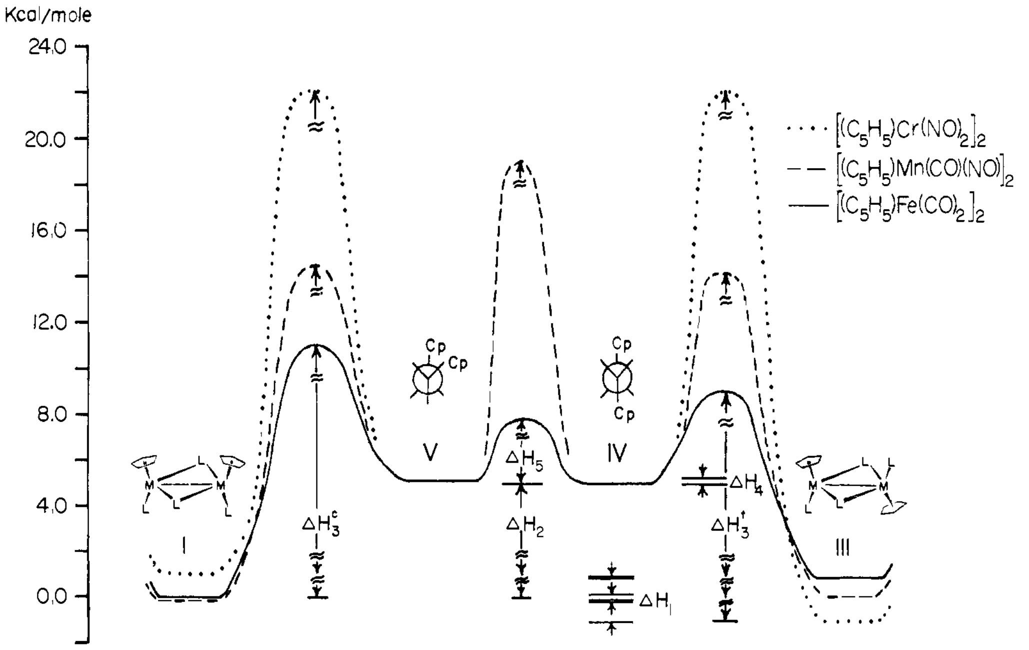

Figure 9. Schematic representation of the reaction coordinate for structural interconversions of $[(C_5H_5)ML_2]_2$ molecules. Data for the three compounds have been adjusted to the same zero point.

Table VIII. Thermodynamic Parameters for the Equilibrium[a] Cis Bridged $\rightleftharpoons$ Trans Bridged

Compound	ΔH_1[b]	ΔS_1[c]	ΔG_1[b] at 298 °K
$[(C_5H_5)Fe(CO)_2]_2$	0.9 ± 0.1	3.5 ± 0.5	−0.15 ± 0.1
$[(C_5H_5)Mn(CO)(NO)]_2$	−0.16 ± 0.1	0.93 ± 0.4	−0.44 ± 0.3
$[(C_5H_5)Cr(NO)_2]_2$	−2.1 ± 0.3	−1.7 ± 1.0	−1.6 ± 0.3

[a] K = [trans]/[cis]. [b] In kcal/mol. [c] In eu.

The type of pattern observed and the dependence on solvent polarity are again strikingly reminiscent of the iron system.[1] We assign the bands at 1679 and 1521 cm^{-1}, respectively, to the antisymmetrically coupled terminal and bridging N–O stretches[43] in the centrosymmetric trans structure, III. The symmetric stretches, since they are infrared inactive, should be quite weak. The weak band at 1747 cm^{-1} is assigned to the totally symmetric terminal N–O stretch of the cis structure, I. As in the iron system,[1] the antisymmetric stretch is obscured by the trans isomer. Addition of polar solvents (Figure 8) displaces the equilibrium in favor of the cis isomer. Any structure having all terminal N–O groups would exhibit a more complex spectrum (two or three terminal N–O stretches[1]) and can be discounted as the second major isomer. No bands securely attributable to a nonbridged structure were observed. The solid-state (Nujol mull) infrared spectrum of samples of $[(C_5H_5)Cr(NO)_2]_2$, obtained by slow crystallization, exhibits strong bands at 1662 and 1504 cm^{-1}. The spectrum does not exhibit the large correlation field splitting seen for *trans*-$[(C_5H_5)Fe(CO)_2]_2$ in accord with the crystallographic data,[5] which indicate a triclinic crystal system ($P\bar{1}$) with only *one* molecule per unit cell.

Interconversion takes place between the cis and trans bridged isomers of $[(C_5H_5)Cr(NO)_2]_2$, but it is considerably slower than in the iron and manganese compounds. Appreciable line broadening does not occur until *ca.* +90° at 60 MHz (Figure 7). Thermal decomposition greatly reduces the temperature range over which dynamic spectra can be recorded for line shape analysis; an additional point for the Arrhenius plot (Figure 6) was obtained by classical equilibration methods at 0° (see Experimental Section). As can be seen from the activation parameters in Table VI, the barrier to isomer interconversion is higher than in the iron and manganese compounds.

Solution Structural Thermodynamics. Figure 9 portrays a reaction coordinate for structural interconversions of $[(C_5H_5)ML_2]_2$ molecules. The thermodynamic parameters (ΔH_1, ΔS_1) for the cis–trans equilibrium (I $\rightleftharpoons$ III), obtained from the pmr data, are given in Table VIII. It is apparent that moving to the right in the periodic table progressively stabilizes the cis isomer with respect to the trans isomer. The trend appears to result from both enthalpy and entropy effects. At first glance this progression would appear to contradict the structural data which indicate more short intramolecular nonbonded contacts in the cis structure and more severe interactions as the M–M distance decreases. A possible explanation may be that puckering of the four-membered ring in the cis form is better able to relieve increasing strain as the metal–metal distance decreases (note the contraction of MBM′ angles in Table V).

The enthalpy difference between bridged and nonbridged structures is given by ΔH_2. This quantity could be obtained for the iron and ruthenium $[(C_5H_5)M(CO)_2]_2$ systems,[1a] where nonbridged isomers were detected in the infrared spectra. No evidence for such species was obtained for the manganese and chromium compounds, and we conclude that ΔH_2 must be at least as great as in the iron system, 4 kcal/mol. This is especially plausible since trends in ΔH_2 seem to parallel those in ΔH_3 (*vide infra*). One interesting conclusion which emerges from these results is that the NO ligand shows no less tendency to form bridge bonds than CO.

Solution Molecular Dynamics. The postulated[1d,e] intermediacy for the iron system of the nonbridged isomer (II, IV, or V) (reaction A) in the cis–trans isomer equilibration (I $\rightleftharpoons$ III) was inferred from several persuasive observations. First, the nonbridged isomer was known[1a] to be present in small quantities in solution. Secondly, it was present in considerably greater proportions in the ruthenium analog, $[(C_5H_5)Ru(CO)_2]_2$,[1a] and, as might be expected from a reaction coordinate such as in Figure 9 (*i.e.*, lower ΔH_2), the barrier to cis–trans interconversion (ΔH_3^c, ΔH_3^t) was correspondingly lower. Thirdly, the ^{13}C nmr studies of Gansow[1d] indicate that bridge–terminal exchange of CO in the cis iron isomer, I, occurs at a rate comparable with cis–trans isomer equilibration. Bridge–terminal CO exchange is somewhat faster in the trans isomer than exchange with the cis.[1d] Several recent experiments implicate this ligand interchange pattern in second-row metal carbonyl[47] and also isocyanide[48] systems. As is usually the case, the choice of a mechanism such as A is made in an attempt to interpret an observed set of site permutations in terms of a chemically reasonable redistribution of electrons and nuclei.[49]

The isoelectronic compound $[(C_5H_5)Mn(CO)(NO)]_2$ provides an opportunity both to investigate the generality of reaction A and to introduce several new perturbations into the system. Figure 4 indicates that cis and trans bridged isomers are dissymmetric. The result of cleaving the bridge bonds *via* reaction A so as to leave the same ligands on each manganese (a "symmetrical cleavage") followed by bridge closure in the same manner is indicated. Note that cis enantiomers I–Mn–D and I–Mn–L are interconverted at the same rate as C_5H_5 groups; however, racemization does not accompany C_5H_5 exchange for the trans species. The results of this process along with those of other feasible[50a] (though chemically less reasonable) ligand position permutations[50b] which interchange C_5H_5 rings in one step are presented for the sake of completeness in Table IX using the general numbering scheme for skeletal positions shown at the upper left of Figure 4. Operation 1 can be interpreted as the symmetrical bridge cleavage process. As can be seen in Table IX, it should ideally be possible using ^{13}C and ^{15}N nmr and chiral or diastereotopic probes to differentiate 1 unequivocally from any one of the other permutations,[51] but it is also apparent that alternative operations 2 through 8 seem chemically far less reasonable than a symmetrical cleavage of the bridging ligands to yield a short-lived nonbridged intermediate. Further mechanistic studies are in progress.

Table IX. Consequences of Indicated Permutations in Cis- and Trans-Bridged $[(C_5H_5)Mn(CO)(NO)]_2$[a]

Operation	C_5H_5 exchange	D $\rightleftharpoons$ L	$CO_B \rightleftharpoons CO_T$ $NO_B \rightleftharpoons NO_T$
	Cis (I–Mn–D)		
1 (2463)	Yes	Yes	Yes
2 (23)(46)	Yes	No	Yes
3 (26)	Yes	Yes	No
4 (2346)	Yes	No	CO only
5 (34)(26)	Yes	No	No
6 (263)	Yes	Yes	NO only
7 (246)	Yes	Yes	CO only
8 (2643)	Yes	No	NO only
	Trans (III–Mn–D)		
1 (2453)	Yes	No	Yes
2 (23)(54)	Yes	Yes	Yes
3 (25)	Yes	No	No
4 (2345)	Yes	Yes	CO only
5 (34)(25)	Yes	Yes	No
6 (253)	Yes	No	NO only
7 (245)	Yes	No	CO only
8 (2543)	Yes	Yes	NO only

[a] See Figure 4 for skeletal position numbering scheme.

In discussing the high-temperature process which interconverts cis and trans $[(C_5H_5)Mn(CO)(NO)]_2$ isomers, it is important to note (Figure 4) that the corresponding nonbridged isomers are diastereomeric. Thus, unlike the iron system,[1] symmetrical bridge cleavage followed by rapid rotation[52] about the metal–metal bond should not in itself provide a pathway for isomer equilibration. Just such a situation is observed and the process which does interconvert cis and trans isomers requires considerably more energy than bridge-terminal ligand interchange or cis–trans exchange in the iron system. Two pathways out of a large number of possible permutations appear most likely: inversion of configuration at manganese[53] in II–Mn, and IV–Mn interconverts cis and trans isomers and also racemizes trans enantiomers. An argument against inversion is that barriers in pseudo-four-coordinate $(C_5H_5)M<$ molecules are usually in excess of 30 kcal/mol, *e.g.*, 31 kcal/mol in $(C_5H_5)Mn(CO_2CH_3)(NO)P(C_6H_5)_3$,[53b] whereas the barrier in the

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(47) F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, **94**, 6191 (1972); J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 79 (1973).

(48) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **94**, 6193 (1972); F. A. Cotton, private communication.

(49) I. Ugi, D. Marquarding, H. Klusacek, and P. Gillespie, *Accounts Chem. Res.*, **4**, 288 (1971); P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971); S. S. Eaton, J. R. Hutchinson, R. H. Holm, and E. L. Mutterties, *ibid.*, **94**, 6411 (1972); W. G. Klemperer, *ibid.*, **94**, 8360 (1972); *Inorg. Chem.*, **11**, 2668 (1972).

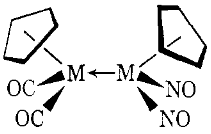
(50) (a) H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963); J. T. Hougen, *Pure Appl. Chem.*, 11, 481 (1965). (b) The operations in Table IX represent site permutations of ligands occupying the indicated skeletal positions. Since it is reasonable that cyclopentadienyl rings remain bonded to the same metal during rearrangements, we have recast orthodox permutations of the same species as equivalent operations which are mechanistically realistic Hence, (15)(24)(36)* → (2463), as an example.

(51) (a) Studies employing chiral lanthanide shift reagents have so far failed to impart resolvable chemical shift differences to enantiomeric pairs. (b) The ^{13}C nmr spectrum of a 40% ^{13}CO enriched sample at −40° in 4:1:1 toluene:CH_2Cl_2:C_6F_6 exhibits resonances at (*vs.* TMS) −217 and −268 ppm (trans isomer) and −214 and −267 ppm (cis isomer). Raising the temperature causes broadening and finally coalescence of the resonances at *ca.* 27–37°. From these data we estimate $\Delta G^{\ddagger} \approx 13.0\text{–}13.5$ kcal/mol, or, assuming $\log A = 13$, $E_a \approx 13.3\text{–}13.8$ kcal/mol. This result is in good agreement with the data of Table VI and the predictions of Table IX. Temperature-dependent ^{55}Mn quadrupolar relaxation hinders more detailed line shape analysis.[51c] (c) O. A. Gansow and A. R. Burke, *J. Chem. Soc., Chem. Commun.*, 456 (1972).

(52) The exact magnitude of this barrier (ΔH_5) remains undetermined and could be larger than portrayed in Figure 9. More crowded systems have substantial barriers.[46]

(53) (a) H. Brunner, *Angew. Chem., Int. Ed. Engl.*, 10, 249 (1971), and references therein; (b) H. Brunner and H.-D. Schindler, *Chem. Ber.*, 104, 2467 (1971); (c) H. Brunner, *Proc. Int. Conf. Organometal. Chem.*, 6, P7 (1973).

present case is probably less than 15 kcal/mol (19 kcal/mol − ΔH_2). However, it has been noted[54] that variation of R has a marked effect on rates of cis–trans isomerization in $(C_5H_5)Mo(CO)_2(L)R$ compounds, and it is conceivable that the adjacent transition metal could lower the barrier to polytopal isomerization in $[(C_5H_5)ML_2]_2$ systems. The second plausible mechanism for cis–trans equilibration is an *unsymmetrical* cleavage of the bridging ligands, to leave two carbonyls on one manganese and two nitrosyls on the other (VI). In valence bond terms, this



VI

intermediate contains a metal–metal dative bond, for which there is some precedent.[55]

The kinetic parameters follow a smooth trend across the periodic table, as can be seen in Table VI. The activation energies for bridge–terminal ligand interchange and cis–trans equilibration decrease in the order Cr > Mn > Fe. For the latter two systems bridge–terminal ligand interchange is more rapid for the trans than for the cis isomer ($\Delta H_3^t < \Delta H_3^c$). It was not possible to obtain such information for $[(C_5H_5)Cr(NO)_2]_2$. The trend in ΔH_3 may well represent the decrease in energy necessary to break nitrosyl as compared with carbonyl bridges, although changes in ΔH_2 as well as strain in the bridge must also be important. These data are incorporated in the comparative reaction coordinates of Figure 9.

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Supplementary Material Available. Tables II and III and final values of $|F_o|$ and $|F_c|$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6602.

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(54) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

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Mössbauer Spectra of Iron Complexes with Macrocyclic Ligands. Partial Center Shifts and Partial Quadrupole Splittings

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Abstract: Mössbauer spectra have been measured and interpreted in detail for 37 iron complexes with synthetic macrocyclic tetradentate ligands. Most of the complexes are six-coordinate derivatives of the composition $Fe^{II-III}(MAC)X_2^{n+}$. The macrocyclic ligands (MAC) vary in ring size and in the extent and arrangement of unsaturated linkages; the axial ligands X may be CH_3CN, imidazole, NCS^-, CN^-, NO_2^-, Cl^-, Br^-, I^-, or $CH_3CO_2^-$. Two oxo bridged dimers $(MAC)FeOFe(MAC)^{n+}$ were also studied. The center shift, δ, and quadrupole splitting, ΔE_q, for the ligating groups involved in the six-coordinate low-spin iron(II) complexes have been separated into additive quantities, the partial center shift (pcs) and the partial quadrupole splitting (pqs). These quantities correlate with spectrochemical parameters determined for other ions (Co^{III} and Ni^{II}) and with the limited data available for iron(II) itself; from these correlations, spectrochemical parameters or ligand field strengths that are not directly measurable can be estimated for a number of ligands that form important complexes with iron. The pcs and pqs values indicate the importance of π bonding in Fe^{II} complexes with the α-diimine linkage and support the view that ΔE_q is largely a function of $Dq_{xy} - Dq_z$. The relationship of Mössbauer data on iron hemes to that of the relatively simple model system of this report is discussed.

Iron complexes of synthetic macrocyclic ligands have been produced and characterized recently.[2–7] Although similar macrocyclic compounds of copper, nickel, and cobalt are well-known and have been

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(1) (a) Evans Chemical Laboratory, The Ohio State University. (b) Savannah River Laboratory, E. I. du Pont de Nemours and Co.

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Busch, et al. / *Mössbauer Spectra of Iron Complexes with Macrocyclic Ligands*