structure, the ligand initially in the bridging position could become a terminal ligand. A real example of this might be provided by $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$, which has actually been shown to undergo rapid bridge–terminal exchange.[13]

(4) In binuclear systems where bridged and nonbridged structures have about equal stability and are thus both present in detectable amounts, there will probably be only extremely low activation energies for isomer interconversion and site exchange, since the activation energy to open or close bridges and that for internal rotation would act separately rather than wholly or in part additively. This expectation is consistent with the observation[3] that isomer interconversion for $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$, in which all three isomers, cis bridged, trans bridged, and nonbridged, are present in comparable quantities, is too rapid to broaden the single observed cyclopentadienyl signal even at −100°. It would also appear that the basic reason why only one ^{59}CO signal was observed[5,6] for $Co_2(CO)_8$ is because the isomer interconversion is rapid.

Finally, we want to state very clearly that we do *not* contend that our proposed rearrangement pathway (concerted double opening and reclosing of bridges or *vice versa*, often with internal rotation in between) is universal. There may be cases in which a different pathway is followed. It does appear likely, however, that for a great many important systems, and certainly in the three very representative ones discussed in detail here, our pathway is the correct one.

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Intramolecular Ligand Scrambling *via* Bridged Transition States or Intermediates in Di(*pentahapto*cyclopentadienyl)-(methyl isocyanide)(pentacarbonyl)dimolybdenum

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Abstract: It is shown that in solution $(\eta^5\text{-}C_5H_5)(CO)_3MoMo(CO)_2(CNCH_3)(\eta^5\text{-}C_5H_5)$ exists as a mixture of nonbridged isomers and permutamers and that at room temperature all of these are rapidly interconverted by unimolecular processes. It is especially notable that the isocyanide ligand passes rapidly from one metal atom to the other at room temperature and above. It is further proposed that important transition states, and/or intermediates, in this complex pattern of interconversions are the doubly bridged species $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\mu\text{-}CO)_2Mo(CO)(CNCH_3)(\eta^5\text{-}C_5H_5)$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\mu\text{-}CO)(\mu\text{-}CNCH_3)Mo(CO)_2(\eta^5\text{-}C_5H_5)$. The compound forms crystals consisting exclusively of the trans rotamer of *trans*-$(\eta^5\text{-}C_5H_5)(CO_2)(CNCH_3)MoMo(CO)_3(\eta^5\text{-}C_5H_5)$. The dark maroon crystals are tetragonal, space group $C^4_{4h}\text{-}P4_2/n$ with $a = 21.085\ (3)$ Å, $c = 8.223\ (3)$ Å, and $Z = 8$. Anisotropic refinement of 1874 reflections with intensities at least three times greater than their esd's converged at $R_1 = 0.046$ and $R_2 = 0.060$. The Mo–Mo bond distance is 3.230 (1) Å, which closely resembles that (3.222 Å) in the unsubstituted prototype, $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$, as do all other features of the structure.

It has been shown that carbonyl scrambling reactions in polynuclear metal carbonyls, and such isomerizations as are naturally associated with them, occur quite commonly and are often fast enough to influence nmr line shapes at temperatures of interest, thus making the molecules stereochemically nonrigid, or fluxional.[1-6] In the preceding paper[7] we showed that a common and important rearrangement pathway for some of these systems involves the opening of an existing pair of ligand bridges, some degree of rearrangement of the nonbridged intermediate, and then reclosing of a pair of bridges. We also pointed out that an obvious corollary to this concept is that a molecule which does not have bridges in its stable structure might undergo ligand scrambling reactions *via* intermediates or transition states in which a pair of bridges is formed. It is the purpose of this report to present detailed evidence for such phenomena in a representative system. A very brief, partial preliminary account of some of our observations has been published.[4]

Experimental Section

All preparations were carried out in atmosphere of nitrogen. Solvents were dried over sodium benzophenone and distilled under nitrogen just prior to use. Methyl isocyanide[8] and $(\eta^5\text{-}C_5H_5)$Mo-

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$(CO)_3I$[9] were prepared according to the literature. $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ was purchased from Strem Chemical Co., Danvers, Mass., and used without further purification. Analyses were obtained from Midwest Microlab, Ltd., Indianapolis, Ind.

Preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)I$. The procedure used was similar to that for the preparation of the phenyl derivative.[10] $(\eta^5\text{-}C_5H_5)Mo(CO)_3I$ (1.64 g, 4.6 mmol) was dissolved in 50 ml of THF. CH_3NC (1.45 ml, 27.5 mmol) was added and the solution was refluxed 7.5 hr. The solution was concentrated under vacuum and chromatographed over alumina (5% H_2O) with benzene solvent. Two red bands readily separated. The first band consisted of 0.54 g (33%) of unreacted $(\eta^5\text{-}C_5H_5)Mo(CO)_3I$. The second band was concentrated to yield an oil. After several days at $-25°$ in toluene–hexane solvent orange-red crystals formed. Three crops gave an aggregate yield of 0.58 g (34%) of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)I$. It is stable in the solid state, but solutions decompose over a period of days. It crystallizes as the trans isomer as determined from the infrared spectra. It rearranges to give a 2:1 cis:trans equilibrium mixture over a period of several hours in solution: mp 106.5–107.5° (uncor). The infrared spectra in C_6D_6 contain the following bands (cm^{-1}): trans isomer 2180 (m) $C\equiv N$, 1989 (m) $C\equiv O$, 1919 (s) $C\equiv O$; cis isomer 2180 (m) $C\equiv N$, 1979 (s) $C\equiv O$, 1909 (s) $C\equiv O$. The pmr spectra in *o*-dichlorobenzene contain the following resonances (τ): trans isomer 4.84 (C_5H_5), 6.87 (CH_3); cis isomer 4.70 (C_5H_5), 6.94 (CH_3).

Anal. Calcd for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)I$: C, 28.1; H, 2.09; N, 3.64. Found: C, 28.12; H, 2.19; N, 3.66.

Preparation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$. Method 1. $[\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (2.0 g, 4.1 mmol) was dissolved in 200 ml of toluene in a 300-ml Pyrex flask. CH_3NC (0.34 ml, 6.5 mmol) was added at room temperature. The solution was immediately irradiated with a Hanovia Utility Ultraviolet Quartz lamp. After about 40 min, the evolution of gas ceased, and irradiation was discontinued. The solution was concentrated and filtered. The red filtrate was chromatographed on alumina (5% H_2O) and eluted with benzene. Three red fractions were separated, collected, and evaporated to yield red solids. The first red compound was unreacted $[\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. The small second red band was $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$, yield < 1%. The third red compound, which slowly decomposes on the column, was not characterized.

Method 2. A solution of $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ was prepared by allowing 0.40 g (0.82 mmol) of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ to react with 1% sodium amalgam in THF. The solution was decanted and filtered. To this was added 0.58 g (1.5 mmole) of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)I$. The solution was then refluxed for 21 hr, after which the solvent was removed and the residue dissolved in a small amount of benzene. This solution was chromatographed over alumina (5% H_2O) and eluted with benzene. The first band to be eluted contained $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. A small amount of an unidentified brown compound was eluted next, and then red $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ was eluted. This was recrystallized from a 1:5 toluene:hexane solvent at $-78°$, yield 0.100 g (13%), mp 151.0–151.5°.

Anal: Calcd for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$: C, 40.65; H, 2.60; N, 2.78. Found: C, 40.6; H, 2.72; N, 2.88.

The infrared spectrum in cyclohexane shows absorptions at 2125 cm^{-1} (m), $C\equiv N$; 1978(s), 1966(s), 1937(m), 1925(s), and 1904 (s) cm^{-1}, terminal $C\equiv O$ groups.

The pmr spectrum in toluene-d_8 contains a broad singlet at τ 5.08 (cyclopentadienyl protons) and a broad singlet at τ 7.57 (methyl protons). The mass spectrum contained a parent ion peak at *m/e* 503, plus the dinuclear molybdenum ions $Cp_2Mo_2(CO)_4CNCH_3^+$, $Cp_2Mo_2(CO)_3CNCH_3^+$, $Cp_2Mo_2(CO)_4^+$, $Cp_2Mo_2(CO)_2CNCH_3^+$, $Cp_2Mo_2(CO)_3^+$, $Cp_2Mo_2(CO)CNCH_3^+$, $Cp_2Mo_2(CO)_2^+$, $Cp_2Mo_2CNCH_3^+$, and $Cp_2Mo_2^+$. In addition, the following mononuclear metal ions were prominantly displayed: $CpMo(CO)_2CNCH_3^+$, $CpMo(CO)_3^+$, $CpMo(CO)CNCH_3^+$, $CpMo(CO)_2^+$, $CpMoCNCH_3^+$, $CpMo(CO)^+$, and $CpMo^+$ ($Cp = C_5H_5$).

$[(\eta^5\text{-}C_5H_5)Mo(CNCH_3)_n(CO)_{4-n}{}^+][(\eta^5\text{-}C_5H_5)Mo(CO)_3{}^-]$. The major product from method 1 was from a thermal reaction. It was a mixture of two of the compounds of the above general formula, namely those with $n = 2$ and $n = 3$, in a ratio of about 1:2. This product precipitated as a yellow oil when the reaction was carried out at room temperature but appeared as yellow crystals when the reaction was conducted at 0°. Similar reactions[11] of phosphines with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ have been well characterized. For the crystalline product the following data were obtained. Nmr τ 4.53 (Cp in cation with $n = 3$), 4.25 (Cp in cation with $n = 2$), 5.05 (Cp in anion), 6.18 (CH_3 in cation with $n = 2$), 6.26, 6.31 (CH_3 in cation with $n = 3$). Ir (benzene) in cm^{-1}: 2210, 2180, 2165 (isonitrile ligands); 1915 (CO in cations); 1886, 1760 (CO in anion[11]).

Anal. Calcd for $C_{19}H_{16}O_5N_2Mo_2$: C, 41.93; H, 2.96; N, 5.15. Calcd for $C_{20}H_{19}O_4N_3Mo_2$: C, 43.11; H, 3.44; N, 7.54. Found: C, 42.2; H, 3.41; N, 6.98.

Spectroscopic Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 451 spectrophotometer and calibrated with polystyrene. Pmr spectra were recorded on Varian Associates T-60 or HA-100 spectrometers. Temperature calibrations for the variable temperature spectra were obtained from either methanol or ethylene glycol standards and are expected to be accurate to ±2°. Samples were prepared in an inert atmosphere in serum stopper-adapted nmr tubes. Solvents were vacuum degassed and admitted to the samples from a syringe.

The parameters of the thermodynamic equilibrium between the cis and trans isomers of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)I$ were determined from the equilibrium constants measured by relative pmr resonance intensities at six temperatures in the slow exchange region. The intensities were determined by tracing, cutting out, and weighing the recorded peaks. These data were processed by the method of least squares, which yielded the reported values. The error estimates are equal to one standard deviation.

Line shape calculations were carried out using the program EXCHSYS written by Professor G. M. Whitesides and Dr. J. K. Krieger.[12] Exchange rates for the two isomers in $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)I$ were determined as described previously.[7] Proper account was taken of the equilibrium changes at the different temperatures.

The relative intensities of the pmr resonances in the slow exchange region for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ in acetone-d_8 solutions diluted with toluene-d_8 are shown in Table I. The mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6D spectrometer by Mr. Carl Renner.

Table I. Relative Intensities of the Pmr Resonances

	Relative intensity at peak (τ value)				
	4.49	4.52	4.64	4.66	4.83
In 100% acetone solvent	0.26	0.51	0.26	1.0	1.0
In 5:1 acetone:toluene (v/v)	0.18	0.35	0.18	1.0	1.0
In 2:1 acetone:toluene (v/v)	0.14	0.24	0.14	1.0	1.0

Crystallographic Investigation. Dark maroon, well-formed crystals of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$ were grown over a period of several days from a solution in a mixture of toluene and pentane in 1 to 5 volume ratio, maintained at $-20°$.

The essential crystallographic data are: $Mo_2O_5NC_{17}H_{13}$, FW 503.2; tetragonal crystal system with unit cell dimensions of $a = 21.085$ (3) and $c = 8.223$ (3) Å; $V = 3656$ Å^3; $Z = 8$; $d_{calcd} = 1.83$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 17.2$ cm^{-1}. The observed extinctions, $00l$ for $l = 2n + 1$, $hk0$ for $h + k = 2n + 1$, uniquely indicate the centrosymmetric space group $C^4{}_{4h}-P4_2/n$. Unit cell dimensions and their estimated standard deviations were obtained at room temperature (24 ± 2°) with Mo Kα radiation (λ 0.7107 Å) using the least-squares procedure described previously.[13]

Data were collected in the range $0 < 2\theta < 45°$ using Mo Kα radiation. The θ–2θ scan technique was used with a variable scan rate from 2.0 to 24.0°/min with a scan range from $2\theta(\text{Mo K}\alpha_1) - 0.8°$ to $2\theta(\text{Mo K}\alpha_2) + 0.8°$. The scan rate used was determined by sampling of the peak intensity. Stationary crystal, stationary counter background counts were measured at each end of the scan. The intensities of four standard reflections were monitored periodically during the course of the data collection, and no appreciable loss of intensity was observed.

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Table III. Positional[a] and Thermal[b] Parameters for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	−0.27121 (4)	0.05204 (4)	0.2088 (1)	0.00178 (2)	0.00207 (2)	0.0115 (1)	−0.00016 (2)	−0.00042 (4)	0.00009 (5)
Mo(2)	−0.21600 (4)	−0.04928 (4)	0.4672 (1)	0.00169 (2)	0.00181 (2)	0.0123 (1)	0.00002 (2)	−0.00064 (5)	−0.00053 (5)
O(1)	−0.2477 (5)	−0.0749 (4)	0.023 (1)	0.0065 (4)	0.0032 (2)	0.019 (2)	−0.0001 (3)	0.0001 (7)	−0.0029 (5)
O(2)	−0.3738 (4)	0.0284 (4)	0.472 (1)	0.0030 (2)	0.0036 (2)	0.028 (2)	0.0007 (2)	0.0032 (6)	0.0019 (6)
O(3)	−0.3949 (5)	0.0367 (5)	0.004 (1)	0.0044 (3)	0.0062 (4)	0.039 (3)	−0.0017 (3)	−0.0076 (8)	0.0042 (8)
O(4)	−0.2331 (4)	0.0772 (4)	0.661 (1)	0.0060 (4)	0.0024 (2)	0.018 (1)	0.0004 (2)	−0.0007 (6)	−0.0027 (5)
O(5)	−0.1075 (3)	−0.0283 (4)	0.214 (1)	0.0023 (2)	0.0041 (3)	0.028 (2)	−0.0002 (2)	0.0033 (5)	−0.0007 (6)
N	−0.0929 (4)	−0.0358 (4)	0.696 (1)	0.0034 (3)	0.0025 (3)	0.027 (2)	−0.0004 (2)	−0.0048 (7)	0.0018 (6)
C(1)	−0.2541 (5)	−0.0301 (6)	0.101 (1)	0.0033 (3)	0.0034 (4)	0.011 (2)	−0.0004 (3)	−0.0008 (7)	0.0000 (7)
C(2)	−0.3326 (5)	0.0335 (5)	0.379 (1)	0.0019 (3)	0.0024 (3)	0.020 (2)	−0.0003 (2)	0.0007 (6)	0.0010 (7)
C(3)	−0.3473 (6)	0.0404 (6)	0.0810 (1)	0.0041 (4)	0.0034 (4)	0.021 (2)	−0.0005 (3)	−0.0023 (8)	0.0013 (8)
C(4)	−0.2284 (5)	0.0323 (5)	0.581 (1)	0.0027 (3)	0.0028 (3)	0.011 (2)	0.0001 (2)	−0.0008 (6)	−0.0001 (6)
C(5)	−0.1499 (5)	−0.0325 (5)	0.305 (1)	0.0022 (3)	0.0023 (3)	0.020 (2)	−0.0001 (2)	−0.0009 (7)	−0.0017 (7)
C(6)	−0.1369 (5)	−0.0419 (5)	0.611 (1)	0.0032 (3)	0.0022 (3)	0.018 (2)	0.0000 (3)	−0.0008 (7)	0.0012 (6)
C(7)	−0.0381 (6)	−0.0245 (5)	0.794 (2)	0.0038 (4)	0.0029 (3)	0.034 (3)	0.0001 (3)	−0.008 (1)	0.0004 (8)
C(11)	−0.2732 (5)	0.1617 (4)	0.169 (1)	0.0031 (3)	0.0021 (3)	0.014 (2)	−0.0001 (2)	0.0000 (6)	0.0001 (6)
C(12)	−0.2387 (5)	0.1507 (4)	0.311 (1)	0.0032 (3)	0.0018 (2)	0.018 (2)	−0.0004 (2)	−0.0014 (7)	0.0000 (6)
C(13)	−0.1816 (5)	0.1179 (5)	0.268 (1)	0.0024 (3)	0.0020 (3)	0.030 (3)	−0.0008 (2)	−0.0017 (8)	0.0003 (7)
C(14)	−0.1845 (5)	0.1076 (5)	0.096 (1)	0.0029 (3)	0.0024 (3)	0.026 (3)	−0.0007 (3)	0.0029 (8)	0.0002 (8)
C(15)	−0.2407 (6)	0.1331 (5)	0.036 (1)	0.0033 (3)	0.0024 (3)	0.019 (2)	−0.0006 (3)	0.0015 (8)	0.0018 (7)
C(21)	−0.2436 (5)	−0.1311 (5)	0.643 (1)	0.0034 (3)	0.0019 (3)	0.018 (2)	−0.0003 (2)	0.0015 (7)	0.0012 (6)
C(22)	−0.2133 (5)	−0.1579 (5)	0.508 (1)	0.0026 (3)	0.0020 (3)	0.017 (2)	−0.0002 (2)	−0.0004 (6)	0.0000 (6)
C(23)	−0.2507 (5)	−0.1470 (4)	0.369 (1)	0.0026 (3)	0.0017 (2)	0.019 (2)	−0.0007 (2)	−0.0007 (7)	−0.0009 (6)
C(24)	−0.3062 (4)	−0.1140 (5)	0.420 (1)	0.0017 (3)	0.0020 (3)	0.028 (3)	−0.0005 (2)	−0.0012 (7)	0.0002 (7)
C(25)	−0.3018 (5)	−0.1043 (5)	0.591 (1)	0.0024 (3)	0.0022 (3)	0.024 (3)	−0.0002 (2)	0.0018 (7)	0.0005 (7)

[a] Figures in parentheses in this and following tables are estimated standard deviations in the last significant figure. [b] The expression used for the anisotropic temperature factors is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

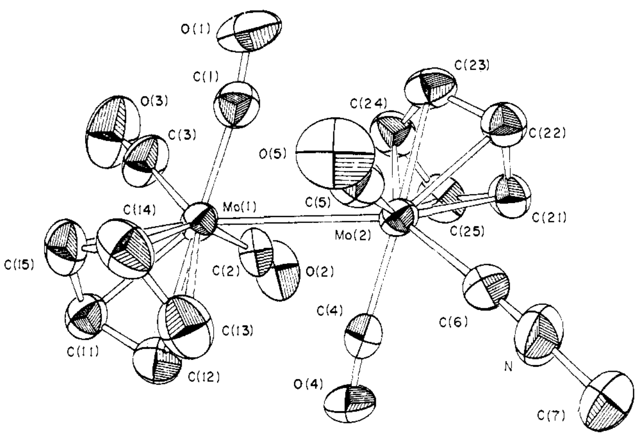

Figure 1. A view of the molecular structure in which the atom numbering scheme followed in the tables is defined. Atoms are represented by thermal vibration ellipsoids enclosing 50% of the electron density.

The intensities of 2785 independent reflections were recorded in this way, of which 1874 had intensities three times greater than their estimated standard deviations, $\sigma(I)$, after Lorentz and polarization corrections were applied to the data. Here $\sigma(I)$ is calculated from the expression

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where S is the scan rate, C is the scan count, R is the ratio of scan time to total background counting time, B is the total background count, and p is a factor introduced to avoid overweighting strong reflections;[14] a value of 0.05 for p was used.

No absorption corrections[15] were made to the data; because of the low linear absorption coefficient it was felt that this correction could be ignored.

Structure Solution and Refinement. The structure was solved using conventional Patterson techniques; the positions of the metal atoms were determined from examination of the appropriate Harker line and section. Preliminary least-squares refinement of the positional and isotropic thermal parameters for the two metal atoms gave values for the agreement factors R_1 and R_2 of 0.224 and 0.240, respectively. All structure factor calculations and least-squares refinements were based on F and the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weights, w, were taken as $4F_o^2/\sigma^2 \cdot (F_o^2)$. The conventional R factor, R_1, and the weighted R factor, R_2, are defined as follows

$$R_1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}$$

$$R_2 = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2}$$

The atomic scattering factors were taken from the tabulations of Cromer and Mann.[16] The effects of anomalous dispersion for Mo were allowed for with corrections[17] made to F_c.

Subsequent difference Fourier syntheses, followed by least-squares refinements, revealed all of the nonhydrogen atoms. Least-squares refinement converged for the anisotropic model with values for R_1 and R_2 of 0.046 and 0.060, respectively. A final difference Fourier synthesis revealed no peaks which could be attributed to hydrogen atoms, and no attempt was made to include these atoms in the model. Shifts in the last cycle of least-squares refinement were all significantly less than their estimated standard deviations. The error in an observation of unit weight is 1.60.

A listing of observed and calculated structure factor amplitudes for those data included in the refinement is given in Table II.[18] The

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

[15] The following computer programs written for the IBM 360 were used: DATARED, a data reduction program by Frenz; AGNOST, an absorption correction program by Cahen based on Coppens' DATAP and Tompa analytical subroutines of Cullen's program; JIMDAP, a version of Zalkin's FORDAP Fourier program modified by Ibers; NUCLS, a least-squares program by Ibers and Doedens which closely resembles Busing and Levy's ORFLS program; SADIAN, a program for calculating atomic distances and angles by Baur; RSCAN, a structure factor analysis program by Doedens; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen; and LIST, a data listing program by Snyder.

[16] "International Tables for X-Ray Crystallography," Vol. IV, in preparation.

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

[18] Table II will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-6594. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

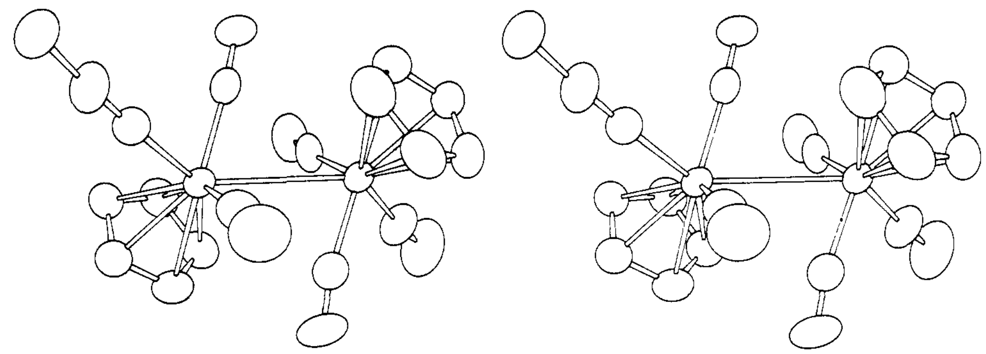

Figure 2. A stereo pair representation of the molecular structure.

Table IV. Root Mean Square Amplitudes of Vibration (Å) for (η^5-C_5H_5)$_2Mo_2(CO)_5(CNCH_3)$

Atom	Min	Int	Max
Mo(1)	0.189 (1)	0.204 (1)	0.221 (1)
Mo(2)	0.182 (1)	0.199 (1)	0.220 (1)
O(1)	0.20 (1)	0.31 (1)	0.38 (1)
O(2)	0.22 (1)	0.27 (1)	0.35 (1)
O(3)	0.22 (1)	0.33 (1)	0.47 (1)
O(4)	0.19 (1)	0.28 (1)	0.37 (1)
O(5)	0.20 (1)	0.30 (1)	0.34 (1)
N	0.20 (1)	0.23 (1)	0.36 (1)
C(1)	0.19 (1)	0.26 (1)	0.29 (1)
C(2)	0.19 (1)	0.24 (1)	0.27 (1)
C(3)	0.24 (1)	0.27 (1)	0.33 (1)
C(4)	0.19 (1)	0.25 (1)	0.26 (1)
C(5)	0.20 (1)	0.23 (1)	0.28 (1)
C(6)	0.21 (1)	0.25 (1)	0.28 (1)
C(7)	0.17 (2)	0.26 (1)	0.41 (1)
C(11)	0.21 (1)	0.22 (1)	0.27 (1)
C(12)	0.19 (1)	0.23 (1)	0.28 (1)
C(13)	0.17 (1)	0.25 (1)	0.33 (1)
C(14)	0.19 (1)	0.26 (1)	0.33 (1)
C(15)	0.18 (1)	0.27 (1)	0.29 (1)
C(21)	0.18 (1)	0.25 (1)	0.29 (1)
C(22)	0.21 (1)	0.23 (1)	0.25 (1)
C(23)	0.17 (1)	0.26 (1)	0.26 (1)
C(24)	0.17 (1)	0.23 (1)	0.32 (1)
C(25)	0.20 (1)	0.23 (1)	0.30 (1)

Table V. Bond Distances (Å) for (η^5-C_5H_5)$_2Mo_2(CO)_5(CNCH_3)$

Mo(1)–Mo(2)	3.230 (1)	C(1)–O(1)	1.15 (1)
Mo(1)–C(1)	1.98 (1)	C(2)–O(2)	1.17 (1)
Mo(1)–C(2)	1.94 (1)	C(3)–O(3)	1.19 (1)
Mo(1)–C(3)	1.93 (1)	C(4)–O(4)	1.15 (1)
Mo(2)–C(4)	1.98 (1)	C(5)–O(5)	1.17 (1)
Mo(2)–C(5)	1.96 (1)	C(6)–N	1.17 (1)
Mo(2)–C(6)	2.05 (1)	N–C(7)	1.43 (1)
Mo(1)–C(11)	2.33 (1)	C(11)–C(12)	1.39 (1)
Mo(1)–C(12)	2.35 (1)	C(12)–C(13)	1.43 (1)
Mo(1)–C(13)	2.40 (1)	C(13)–C(14)	1.44 (1)
Mo(1)–C(14)	2.36 (1)	C(14)–C(15)	1.39 (1)
Mo(1)–C(15)	2.31 (1)	C(15)–C(11)	1.42 (1)
Mo(2)–C(21)	2.32 (1)	C(21)–C(22)	1.40 (1)
Mo(2)–C(22)	2.32 (1)	C(22)–C(23)	1.41 (1)
Mo(2)–C(23)	2.33 (1)	C(23)–C(24)	1.42 (1)
Mo(2)–C(24)	2.37 (1)	C(24)–C(25)	1.42 (1)
Mo(2)–C(25)	2.38 (1)	C(25)–C(21)	1.42 (1)

Table VI. Bond Angles (deg) for (η^5-C_5H_5)$_2Mo_2(CO)_5(CNCH_3)$

Mo(1)–Mo(2)–C(4)	71.9 (3)	Mo(2)–C(4)–O(4)	173 (1)
Mo(1)–Mo(2)–C(5)	71.9 (3)	Mo(2)–C(5)–O(5)	173 (1)
Mo(1)–Mo(2)–C(6)	128.5 (3)	Mo(2)–C(6)–N	177 (1)
Mo(2)–Mo(1)–C(1)	69.4 (3)	C(6)–N–C(7)	176 (1)
Mo(2)–Mo(1)–C(2)	68.6 (3)	C(11)–C(12)–C(13)	108 (1)
Mo(2)–Mo(1)–C(3)	124.9 (4)	C(12)–C(13)–C(14)	106 (1)
C(1)–Mo(1)–C(2)	105.4 (4)	C(13)–C(14)–C(15)	109 (1)
C(1)–Mo(1)–C(3)	78.3 (5)	C(14)–C(15)–C(11)	108 (1)
C(2)–Mo(1)–C(3)	79.2 (5)	C(15)–C(11)–C(12)	109 (1)
C(4)–Mo(2)–C(5)	105.0 (4)	C(21)–C(22(–C(23)	109 (1)
C(4)–Mo(2)–C(6)	76.6 (4)	C(22)–C(23)–C(24)	108 (1)
C(5)–Mo(2)–C(6)	78.4 (4)	C(23)–C(24)–C(25)	108 (1)
Mo(1)–C(1)–O(1)	172 (1)	C(24)–C(25)–C(21)	107 (1)
Mo(1)–C(2)–O(2)	171 (1)	C(25)–C(21)–C(22)	109 (1)
Mo(1)–C(3)–O(3)	176 (1)		

Table VII. Least-Squares Planes for (η^5-C_5H_5)$_2Mo_2(CO)_5(CNCH_3)$

Atom	Dist from plane (Å)	Atom	Dist from plane (Å)
	Plane 1		
	$9.96X + 18.31Y - 1.25Z + 0.01 = 0$		
C(11)	0.02	C(14)	0.01
C(12)	−0.01	C(15)	−0.01
C(13)	0.01		
	Plane 2		
	$9.83X + 18.35Y - 1.31Z - 5.65 = 0$		
C(21)	0.01	C(24)	−0.01
C(22)	−0.01	C(25)	−0.01
C(23)	0.01		

final positional and thermal parameters are listed in Table III, with root-mean-square amplitudes of vibration given in Table IV.

Results

The Structure of the Molecule in the Crystal. The crystal is made up of the discrete molecular unit depicted in Figures 1 and 2. The interatomic distances and internal angles are listed in Table V and VI. Least-squares planes are listed in Table VII. These molecules are packed without any abnormal nonbonded contacts; the closest nonbonded contact, other than those between hydrogen atoms, is 3.20 Å between carbonyl groups.

The molecular structure is extremely similar to that of (η^5-C_5H_5)$_2Mo(CO)_6$.[19] The replacement of one carbonyl group trans to the Mo–Mo bond by $CNCH_3$ causes essentially no change in the rest of the molecular structure. Even the Mo–Mo distance remains essentially identical with a value of 3.230 (1) Å as compared to 3.222 (5) Å in the unsubstituted molecule. This is in itself an important result. It shows that methyl isocyanide, which has the least steric requirement of any isocyanide, can be introduced in place of a CO group as a probe to follow molecular dynamics, without appreciably altering any other structural param-

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(19) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 27, 809 (1957).

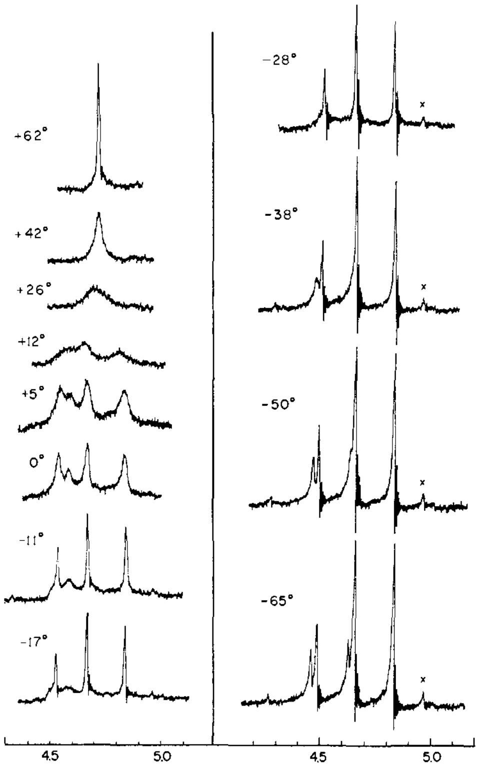

Figure 3. The 100-MHz pmr spectra in the cyclopentadienyl region of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ dissolved in acetone-d_6, at various temperatures. The small peak marked × is due to an unknown impurity.

eters which might in turn alter the dynamic behavior of the system.

This is the first structure to be described in which only one of several terminal CO groups is replaced by an isocyanide ligand. It is even more important and informative because the comparison of substituted and unsubstituted metal carbonyl moieties can be made right within the molecule, by comparing one end with the other, as well as by comparing the entire substituted molecule with the entire unsubstituted one.

The Mo–C–N–C chain does not deviate significantly from linearity. The C≡N distance, 1.17 (1) Å, is essentially the same as that found in CH_3NC itself[20a] (1.161 Å) and those found in the other methyl isocyanide complexes of known structure, namely $Co(CNCH_3)_5ClO_4$[20b] (1.14 Å av) and $Co_2(CNCH_3)_{10}(ClO)_4$[20c] (1.15 Å av). The N–CH_3 distance here, 1.43 (1) Å, is also similar to those found in the three compounds just mentioned, 1.42, 1.44, and 1.50 Å, respectively.

The average Mo–CO distance is 1.96 Å, which is not significantly different from that in the unsubstituted compound.[19] The Mo–$CNCH_3$ bond is much longer than this, however, *viz.* 2.05 (1) Å. This would imply that the isocyanide ligand forms a weaker bond to the metal atom than do the CO ligands.[21] However, the average length of the M–CO bonds on the molybdenum atom to which the isocyanide is bound, 1.97 Å, is, if anything, slightly longer than the average of the M–CO distances on the other molybdenum atom, 1.95 Å (although the difference is, strictly speaking, not statistically significant). Thus, it cannot simply be said that there is less $d\pi \rightarrow p\pi$ back-donation to CH_3NC than to CO, since one would then expect the two CO groups on the substituted atom to make up for this and, thus, to form shorter bonds to Mo than do the three CO groups on the other molybdenum atom. If there is less π bonding there must also be proportionately less σ bonding.

Structure and Dynamics of the Molecule in Solution. The infrared spectrum in cyclohexane shows a single broad absorption at 2125 cm^{-1} attributable to a terminal isocyanide ligand and five strong sharp absorptions at 1978, 1966, 1937, 1925, and 1904 cm^{-1} which can be assigned to terminal carbonyl groups.

The mass spectrum showed a parent ion peak with $m/e = 503$ as well as ions corresponding to the loss of one methyl isocyanide ligand, each of five carbonyl groups, and various combinations of the two ligands. A more complete listing of ion fragments is provided in the Experimental Section.

The room temperature pmr spectrum in acetone-d_6 shows a broad singlet at τ 4.69, due to the cyclopentadienyl protons, and a small broad singlet at 6.28, due to the methyl protons. The temperaure dependence of the cyclopentadienyl resonance is shown in Figure 3. At +62°, it is a sharp singlet. With cooling, it collapses and re-forms as four broad singlets at τ 4.52, 4.57, 4.66, and 4.83 at about 0°. With further cooling, the singlets at 4.52, 4.66, and 4.83 become sharper, but the signal at 4.57 broadens and collapses. At −38° a broad resonance can be seen at 4.47, which sharpens as the temperature is lowered further. At the same temperature it can be seen that the signal at 4.66 is broader at the base and higher than the signal at 4.83. At −50° a shoulder is clearly evident on the low field side of the peak at 4.66 and has sharpened into a separate signal at 4.64 at −65°. The peaks at 4.66 and 4.83 are now of equal intensity and the newly formed peaks at 4.49 and 4.64 are also of equal intensity. The methyl resonance (not shown), showing a sharp singlet at +62°, collapses and re-forms as one large singlet at 6.17 and two small singlets at 6.13 and 6.42. The changes in the spectra were independent of sample concentration over a factor of 4.

In solution the molecule undoubtedly exists as a mixture of interconverting isomers. In addition, *the averaging of all cyclopentadienyl resonances to a sharp singlet at the higher temperatures demonstrates that the isocyanide ligand passes rapidly from one metal atom to the other.*

The intrinsic simplicity of the molecule deprives us of sufficient criteria for a complete assignment of the resonances to specific isomers. However, we have been able to determine which resonances belong to the isomer that exists in the solid state. We shall call this isomer A. By dissolving the crystals in acetone in an nmr sample tube at low temperature, spectra were obtained before rearrangement could occur to the equilibrium mixture. The sample of freshly dissolved crystals showed only two resonances of equal intensity at τ 4.66 and 4.83. With the passage of time all of the other resonances seen in Figure 3 slowly appeared.

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[20] (a) C. C. Costain, *J. Chem. Phys.*, **29**, 872 (1958); (b) F. A Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4**, 318 (1965); (c) *ibid.*, 3, 1495 (1964).

[21] There is no trans effect involving the Mo–Mo bond since on Mo(1) the CO group trans to this bond has an Mo–CO distance which is the same as those for the other two CO groups on Mo(1).

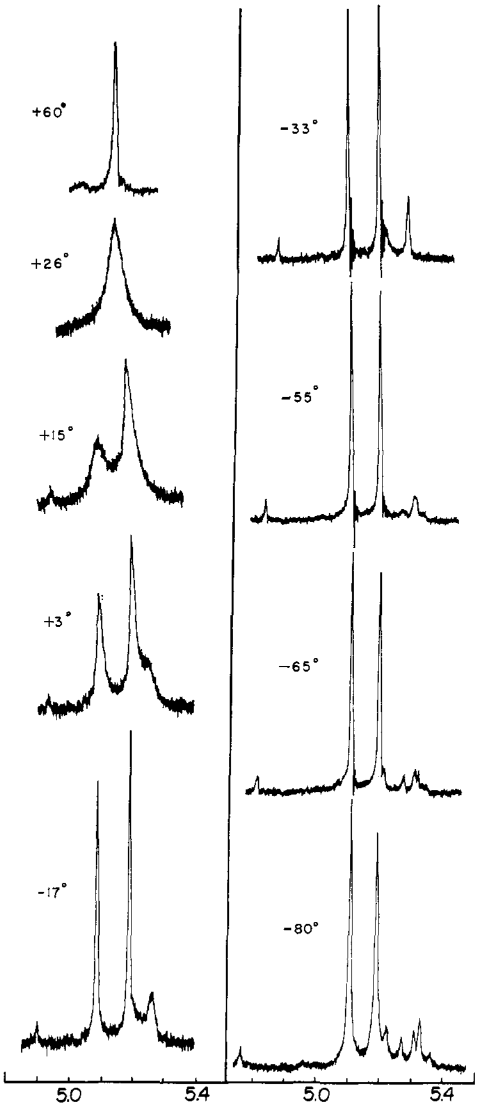

Figure 4. The 100-MHz pmr spectra in the cyclopentadienyl region of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ dissolved in toluene-d_8, at various temperatures.

The pair of smaller resonances at τ 4.49 and 4.64 begin to broaden at a relatively low temperature, and they have already coalesced to a very broad singlet at 4.57 at $-17°$. Since the two individual resonances are of equal intensity at the lower temperatures, it seems reasonable to suppose that they arise from a single isomer which will be called isomer B. The fact that the resonances of isomer B average at the lower temperatures indicates that the isocyanide ligand is more readily exchanged between the metal atoms in isomer B than it is in isomer A. Only ligands cis to the metal–metal bond are appropriately positioned to move directly into bridging positions from which they can then pass to a cis position on the other metal atom. We believe, therefore, that isomer B has the isocyanide substituent cis to the Mo–Mo bond. However, this does not completely specify the structure of isomer B since there are three different rotameric configurations possible for such a cis geometric isomer.

There is a decrease in relative intensity of these two peaks when the sample is diluted with the nonpolar solvent toluene. This behavior is reminiscent of the behavior[22] of the equilibrium between the gauche and trans rotamers of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. It is therefore plausible that isomer B is a gauche rotamer, but this is not rigorously required by the available data.

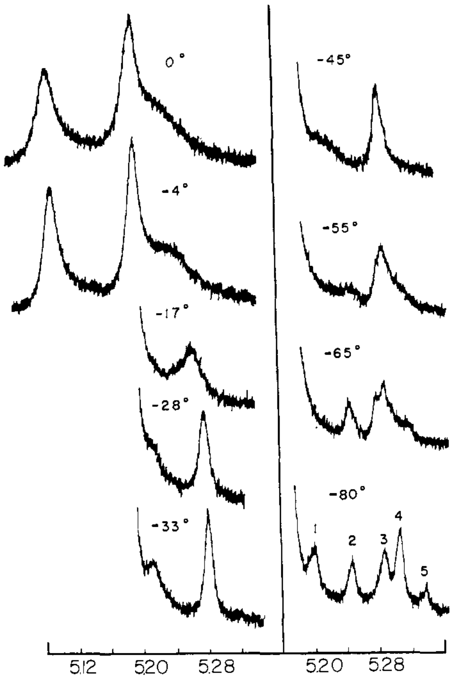

Figure 5. Enlargements of portions of the spectra of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ observed in toluene-d_8 solvent, showing the behavior of the smaller signals at high field.

Finally, there is the lone peak at approximately τ 4.5. This peak does not change in intensity with the age of the sample, but it does decrease in intensity when the acetone solution is diluted with toluene. Furthermore, the peak clearly collapses and averages with the other resonances in the sample. The solvent-dependent behavior might be taken to imply that this peak arises from a gauche rotamer also, but once again, this is not required by the data. The appearance of only one signal for some isomer could be due either to accidental shift equivalence of the two cyclopentadienyl resonances in the isomer or to the fact that this isomer is still rapidly exchanging the methyl isocyanide ligand between the two metal atoms even at $-65°$. For a sample dissolved in acetone-d_6–CF_2Cl_2 (2:1, v/v) solvent, this peak showed no evidence of broadening at temperatures as low as $-110°$. On the other hand when samples in toluene-d_8 (*vide infra*) were diluted progressively with acetone-d_6 two peaks appeared to converge to the position observed in the pure acetone solvent. For these reasons, it is believed that the single resonance may actually be a composite of two resonances.

The room temperature spectrum of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ in pure toluene-d_8 solvent consists of a broad singlet at τ 5.08 from the cyclopentadienyl protons and another broad singlet at 7.57 from methyl protons, with relative intensities of 10:3. The changes in the cyclopentadienyl resonance as a function of temperature are shown in Figure 4. The sharp singlet at $+60°$ collapses on cooling and re-forms as two

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

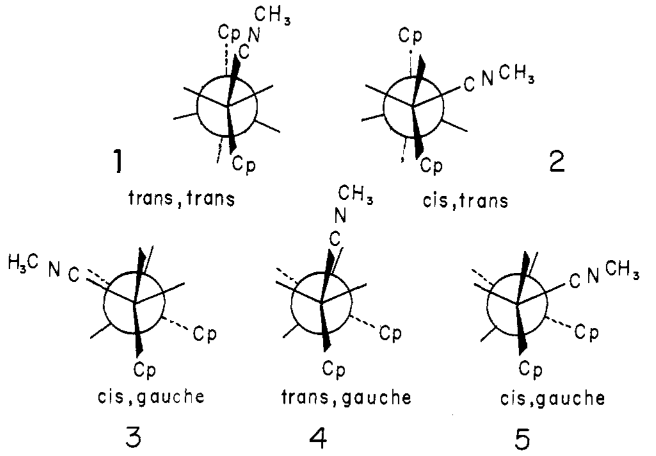

Figure 6. Newman projections of the five geometric isomers of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$. The nomenclature describes, first, the coordination geometry on the isocyanide-substituted molybdenum atom, and, second, the rotational relationship between the two molecular halves. The CO labels have been omitted for clarity (Cp = cyclopentadienyl).

broad singlets of unequal intensity at about 15°. With further cooling, these resonances sharpen, but simultaneously a broad peak emerges from the higher field resonance. At −33° the two large peaks at τ 5.09 and 5.19 are very sharp and of equal intensity. The broad peak has become a relatively sharp singlet at 5.28, and there seems to be a small, broad singlet on the high field side at the base of the large sharp singlet at 5.19. Contrary to what we stated in our preliminary report,[4] the small low field peak at 4.89, which can be seen in the spectra at 15, 3, and −17°, has now been shown to arise from an impurity. This resonance has a temperature-dependent chemical shift. Although the peak does collapse and disappears at the higher temperatures, it grows in intensity over a period of days as the sample decomposes.

At lower temperatures the small singlet at τ 5.28, which is sharp at −33°, broadens, and the small broad resonance at the base of the large peak at τ 5.19 disappears. At −80°, the peak at 5.28 has re-formed as two peaks, and two more small peaks have appeared at 5.22 and 5.27. In addition, the peaks at 5.09 and 5.19 are now of slightly different intensities.

In Figure 5 are shown enlarged spectra in the region of these small peaks. Five resonances are resolved at −80°, and are numbered from 1 to 5 in order of increasing τ value. With an increase in temperature, peak 1 shifts into the large peak at a lower τ value and peak 2 collapses. Peaks 3, 4, and 5 re-form as a broad singlet. At −33°, a broad peak, which seems to be the fast-exchange average of peaks 1 and 2, has formed at a τ value slightly higher than that of the large peak at 5.19. The average of peaks 3, 4, and 5 is sharpening. At higher temperatures, the average of peaks 1 and 2 disappears into the large peak and the average of peaks 3, 4, and 5 collapses and finally merges with the large resonance. In all samples, both fresh and partially decomposed, the relative intensities of these small resonances remained the same, and it is, therefore, believed that they are genuine resonances due to isomers of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$.

When a sample in toluene solvent is diluted with acetone the small resonances shift to lower τ values. When the solvent composition reaches approximately 40% acetone, the spectrum has the same appearance as that in pure acetone-d_6. The large resonances in the toluene-d_6 solvent, τ 5.09 and 5.19, correspond to the largest resonances in the acetone-d_6 solvent. We know, therefore, that in both acetone and toluene solvents, the predominant species is isomer A, the isomer found in the solid state.

The methyl resonance does not provide any helpful information in toluene-d_8 solvent. It is a sharp singlet at +60°. It collapses upon cooling and re-forms, mainly, as one large singlet, as expected. Some very small peaks do appear to form, but, simultaneously, they also shift toward the ever present methyl resonance of impurity toluene-d_7, which completely masks them.

The presence of five cyclopentadienyl resonances, in addition to the two resonances from isomer A, requires the presence of at least three of the remaining four isomers. All of the five possible, nonequivalent isomers are shown in Figure 6. These diagrams are Newman projections along the metal–metal bond. The carbonyl labels have been omitted for clarity. With the aid of a molecular model it is easy to see that this set of isomers is correct and complete. The reader who is attempting to verify this without the aid of a model should begin by recognizing that we are dealing with a case of three against three internal rotation, formally analogous to appropriately substituted ethanes. Careful inspection of Figure 2 will perhaps suffice in place of a model. The ligands trans to the Mo–Mo bond are so oriented that they do not participate in the set of nonbonded repulsions that give rise to the rotational barriers. In the trans isomer, the opposing sets of groups are Cp, CO, and CO and Cp, CO, and CO; the two enantiomeric gauche rotamers are equivalent. In the cis isomer, however, where Cp, CO, and $CNCH_3$ rotates against Cp, CO, and CO, the two gauche rotamers, 3 and 5, are nonequivalent. Two isomers, 3 and 5, are these gauche rotamers which have the isocyanide ligand located cis to the metal–metal bond. The presence of four of the five isomers in solution requires the presence of one of these two gauche rotamers. This is consistent with our inferences from the spectra in acetone solvent. Isomer 1 is the one present in the crystal and is the solution species we have designated as isomer A.

Discussion

Figure 7 presents a schematic representation of the isomers and the basic rearrangement pathways as we presently envision them. The square pyramidal bases consisting of three ligands and the metal–metal bond are drawn as squares. The carbonyl labels have again been omitted, for clarity. The diagram is imperfect in that it does not distinguish between the two gauche rotamers of isomer D and the different rearrangement pathways available to each. Despite this shortcoming, the diagram is helpful in presenting a discussion of the fundamental rearrangement pathways to the extent warranted by the available data. As mentioned before, only ligands located cis to the metal–metal bond are appropriately positioned to participate directly in bridge–terminal shifts. Thus isomer A cannot directly exchange in the isocyanide ligand between the metal atoms; it must first shift the ligand to a cis position. This can be done *via* rearrangements 1 or 2 and 3. Pathway 1 is a polytopal[23] rearrangement of the type thoroughly investigated by Faller.[24-26] Through pathways 2 and 3, two cis positioned carbonyl groups are simultaneously exchanged between the metal atoms *via* the bridged intermediate A′. Concomitantly, the isocyanide ligand gets shifted to a cis position, isomer B. Alternatively, isomer A could rotate around the metal–metal bond, pathway 5, and then engage in similar rearrangements, 1′ or 2′ and 3′, which are available to the gauche rotamers. Transposition of the isocyanide ligand can occur only by pathways 4 or 4′, wherein the isocyanide ligand and one carbonyl group simultaneously shift to form a bridged intermediate, B′ or D′.

The presence of five cyclopentadienyl resonances in the low temperature spectra in acetone solvent requires the presence of at least three isomers, one of which must be a gauche rotamer. The lowest energy exchange process observed in this system first averages a pair of resonances with equal intensities (Figure 3). This rearrangement is probably 4 or 4′, in which the isocyanide ligand is exchanged between the metal atoms. Treating this as a two site uncoupled exchange process, a line shape analysis of the spectral changes has provided the kinetic activation parameters of the rearrangement. An adequate fit to the Arrhenius equation gave $E_a = 12.7 \pm 0.5$ kcal/mol, and $\log A = 12.6 \pm 0.5$. From the Eyring equation we obtain $\Delta H^{\neq} = 12.3 \pm 0.5$ kcal/mol, $\Delta S^{\neq} = -2.6 \pm 1.4$ eu, and $\Delta G^{\neq}_{298} = 13.0 \pm 0.5$ kcal/mol. These results are very similar to those for bridge–terminal rearrangement barriers involving one isocyanide and one carbonyl ligand in the dinuclear iron compounds.[7]

At about 0° (Figure 3) all four resonances are beginning to broaden. No single exchange process can interconvert all three isomers. The observation indicates, therefore, that two rearrangement processes have barriers of nearly equal magnitude.

One of the rearrangements must be a rotation around the metal–metal bond, *i.e.*, pathway 5 or 6, which exchanges the gauche rotamer(s) with the trans rotamer(s). Since these isomers will be nearly identical sterically with those of $[\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$, the rotational barriers should be very similar in the two cases. Now it is known[22] that exchange between the gauche and trans rotamers in $[\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$ becomes rapid on the nmr time scale only when the temperature rises to about 0°. The other process starting at this temperature in the present case must be a rearrangement which exchanges the isonitrile ligand between cis and trans positions (*i.e.*, either pathways 1 or 1′ or pathways 2 and 3 or 2′ and 3′). Of the two different types of pathways by which this can occur, rearrangement *via* the bis-carbonyl bridged intermediate seems preferable for two reasons. (1) Rearrangement through the intermediate with two carbonyl bridges should not require significantly higher energy than the corresponding rearrangement involving one carbonyl and one isocyanide ligand. (2) In the molecules studied by Faller,[24] which undergo rearrangements similar to pathway 1, all, except for the hydrides, had substantially higher activation energies than that for the rearrangement under consideration here.

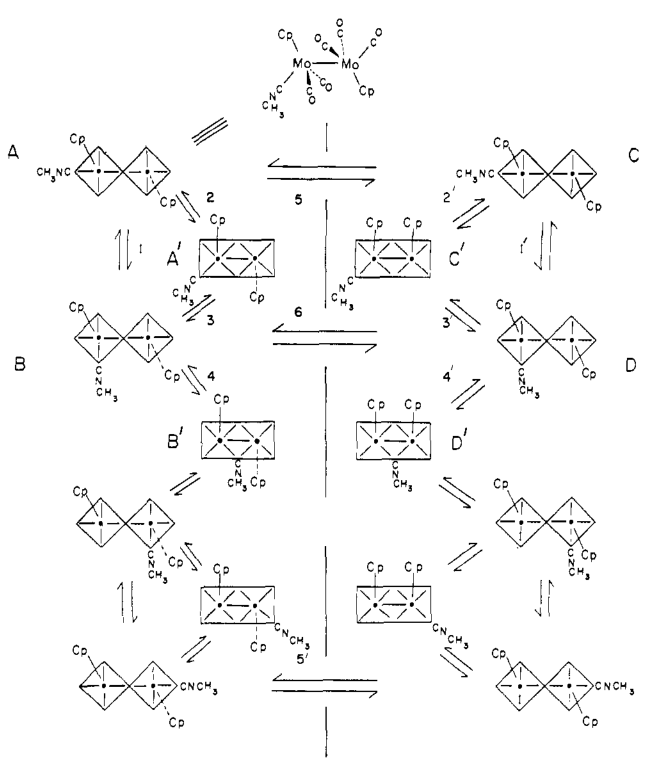

Figure 7. A schematic representation of some of the rearrangement processes which can occur in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_5\text{CNCH}_3$. The square pyramidal base consisting of three ligands and the second metal atom have been drawn as a square. The carbonyl labels have been omitted for clarity. Many of the structures shown have enantiomers, which are accessible by rotating the isocyanide to and from the other bridging site. The scheme does not show all enantiomers nor all possible rearrangements but is adequate to discuss the available data.

Since all the molecules studied by Faller contained phosphine ligands, and it was not certain how substitution of an isonitrile ligand for the phosphine might affect that rearrangement barrier, we have investigated the cis–trans isomerization of $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\text{(CNCH}_3)\text{I}$, which can only rearrange by a polytopal mechanism similar to 1.

At room temperature in *o*-dichlorobenzene solvent the pmr spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{(CNCH}_3)\text{I}$ consists of two sharp cyclopentadienyl resonances at τ 4.70 and 4.84, and two sharp methyl resonances at 6.87 and 6.94. These resonances result from the presence of cis and trans isomers. It was established from the infrared spectra[27] of freshly dissolved samples that the compound crystallizes in the trans form and only slowly rearranges to the cis form. From pmr spectra of freshly dissolved samples the resonances of the cis isomer have been identified as those at τ 4.70 and 6.94. The resonances of the trans isomer are at τ 4.84 and 6.87. The equilibrium cis/trans ratio at 26° is 2.0. From the temperature dependence of this equilibrium ratio the thermodynamic parameters of the trans to cis rearrangement have been determined:

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$\Delta H^\circ = +1.04 \pm 0.10$ 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.

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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-$P2_1/c$ 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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