

Rates of Rearrangement of Pyrazolylborate Complexes of Molybdenum Which Contain Strong Aliphatic Hydrogen to Molybdenum Interactions. Estimates of the Strength of the Interaction

F. Albert Cotton* and Anna G. Stanislawski

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843. Received March 18, 1974

Abstract: The proton nuclear magnetic resonance spectra of $[\text{Et}_2\text{B}(\text{pz})_2]\text{Mo}(\text{CO})_2(\eta^3\text{-allyl})$, where $\eta^3\text{-allyl} = \text{H}_2\text{CCPhCH}_2$ (**1**) and H_2CCHCH_2 (**2**), have been studied at various temperatures from -75 to $+110^\circ$. These spectra establish, first, that the type of structure found for **1** in the crystal is adopted by both compounds in solution. This is a dissymmetric structure involving a $\text{C-H}\cdots\text{Mo}$ three-center two-electron bond formed by one of the $\alpha\text{-C-H}$ bonds of one ethyl group. It is further shown that the molecules are fluxional in two ways. First, there is a low temperature process, with an Arrhenius activation energy of about 14 kcal mol^{-1} , in which the two hydrogen atoms on the α -carbon atom of the ethyl group which is closest to Mo change places. This is accompanied by an overall rearrangement of the rest of the coordination shell such that the two enantiomorphs of the ground state structure are interconverted. At temperatures above room temperature, another process becomes fast enough to affect line shapes. In this high-temperature process, the $\text{C-H}\cdots\text{Mo}$ bonds are severed completely and the boat conformation of the $\overline{\text{BNNMoNN}}$ ring "flips." Other shifts occur in the ligand arrangement so that the ground state structure is recovered but with the ethyl groups having exchanged structural roles. The activation energy of this higher energy process is $17\text{--}20 \text{ kcal mol}^{-1}$ and this probably approximates to the strength of the $\text{C-H}\cdots\text{Mo}$ interaction.

We recently reported¹ that there is a strong $\text{C-H}\cdots\text{Mo}$ interaction ($\text{H}\cdots\text{Mo}$, $\sim 2.2 \text{ \AA}$) in $[(\text{C}_2\text{H}_5)_2\text{B}(\text{pz})_2]\text{Mo}(\text{CO})_2(\eta^3\text{-2-phenylallyl})$ (**1**). This was formulated as a three-center, two-electron bond and, like the $\text{B-H}\cdots\text{Mo}$ bonds in $[\text{H}_2\text{B}(3,5\text{-dimethylpyrazolyl})_2]\text{Mo}(\text{CO})_2(\eta^3\text{-C}_7\text{H}_7)$ ² and $[\text{H}_2\text{B}(3,5\text{-dimethylpyrazolyl})_2]\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)$,³ serves to give the molybdenum atom an effective 18-electron configuration. The observed $\text{C-H}\cdots\text{Mo}$ interaction is unique in being by far the shortest and thus, presumably, the strongest such interaction of an aliphatic C-H bond with a transition metal atom ever observed in a static system.

We believe that the observation we have made is uniquely important, since the molecule **1** constitutes a model for the interaction of a saturated hydrocarbon with a hypovalent metal atom, a process which must be involved in the initial stage of any catalytic process which involves activation of saturated hydrocarbons for reaction or rearrangement. The nature of this model is such that the process can proceed no farther than the stage at which the interaction of the hydrocarbon with the metal has become well advanced. We are thus afforded the opportunity of examining this intermediate structure.

The energy involved in the $\text{C-H}\cdots\text{Mo}$ interaction is naturally of interest. In this paper we describe nmr studies of dynamical processes in which the $\text{C-H}\cdots\text{Mo}$ bond is broken and re-formed. These studies were prompted by the thought that the activation energies of

such processes would give an approximate idea of, or at least place some limits upon, the energy required to rupture the bond. The first indication that at least one dynamical process involving the making and breaking of the $\text{C-H}\cdots\text{Mo}$ bond must occur was obtained by comparing the molecular structure in the crystal with Trofimenko's observation⁴ that the molecule has a plane of symmetry in the molecule. Since the structure¹ observed in the crystal has no such plane, we suspected that the molecule must be stereochemically nonrigid and that the rearrangement process, or processes, that it undergoes would involve, *inter alia*, making and breaking of the $\text{C-H}\cdots\text{Mo}$ bond. Stereochemical nonrigidity in other related polypyrazolylborate complexes had previously been well established by nmr studies.⁵

Our investigation has shown that two independent intramolecular rearrangements occur, each involving a different degree of $\text{C-H}\cdots\text{Mo}$ bond breaking. The results and their interpretation are fully reported here. Although we were not successful in an attempt⁶ to determine the crystal structure of $[(\text{C}_2\text{H}_5)_2\text{B}(\text{pz})_2]\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)$ (**2**), we thought it highly probable that its molecular structure is similar to that of **1**. We have also studied its proton nmr spectra as a function of temperature, with results that confirm the similarity of the two structures.

The structures can be approximately described in terms of an octahedral arrangement about the molybdenum atom. The bound H atom and one CO group

(1) F. A. Cotton, T. LaCour, and A. G. Stanislawski, *J. Amer. Chem. Soc.*, **96**, 754 (1974).

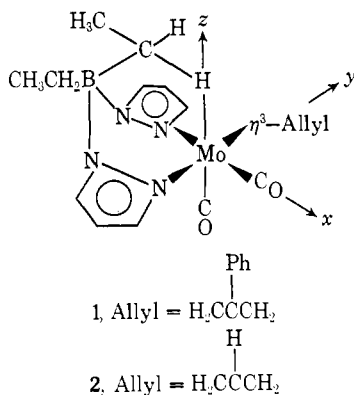
(2) F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, **6**, 543 (1972).

(3) C. A. Kosky, P. Ganis, and G. Avitabile, *Acta Crystallogr., Sect. B*, **27**, 1859 (1971).

(4) S. Trofimenko, *Inorg. Chem.*, **9**, 2493 (1970).

(5) J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometal. Chem.*, **37**, 127 (1972); **38**, 105 (1972); **42**, 419 (1972).

(6) F. A. Cotton, B. A. Frenz, and A. G. Stanislawski, *Inorg. Chim. Acta*, **7**, 503 (1973).



lie along the $+z$ and $-z$ directions, respectively, the other CO group and one pyrazolyl nitrogen atom lie along the $+x$ and $-x$ directions, and the η^3 -allyl group and the other pyrazolyl nitrogen atom lie along the $+y$ and $-y$ directions, as indicated in the diagram. We shall refer to the ethyl group which lies close to the molybdenum atom as the axial ethyl group and the other one as the equatorial ethyl group, the designations "axial" and "equatorial" referring, approximately, to their relationship to the six-membered BNNMoNN chelate ring.

Experimental Section

Samples of (diethyldipyrazolylborato)(dicarbonyl)(η^3 -2-phenylallyl)molybdenum, $[\text{Et}_2\text{B}(\text{pz})_2](\text{CO})_2(\eta^3\text{-H}_2\text{CCPhCH}_2)\text{Mo}$ (1), and (diethyldipyrazolylborato)(dicarbonyl)(η^3 -allyl)molybdenum, $[\text{Et}_2\text{B}(\text{pz})_2](\text{CO})_2(\eta^3\text{-H}_2\text{CCHCH}_2)\text{Mo}$ (2), were supplied by Dr. S. Trofimenko and Dr. A. G. Shaver, respectively.

All nmr spectra were run on a Varian HA-100D spectrometer equipped with a V-4060 variable temperature unit. A copper-constantan thermocouple placed in the nitrogen stream, directly below the sample, and attached to a Leeds and Northrup Model 713 digital thermometer was used to measure the temperatures of the sample and of the probe. The thermocouple was calibrated with ethylene glycol and methanol. Chemical shifts were measured from an internal reference with a Varian V-4315 frequency counter and are accurate to ± 1.0 Hz. When the internal reference was other than tetramethylsilane (TMS), the chemical shift of the lock solvent was later measured in a similar solvent mixture with respect to TMS, so that all chemical shifts in this paper are in τ units (where τ 10 is assigned to TMS).

Samples were prepared under a nitrogen atmosphere in serum-stoppered nmr tubes. The chloroform solvent was pretreated by shaking three times with 50 ml/l. of concentrated sulfuric acid and then washed with distilled water. The wet chloroform was then dried overnight over CaCl_2 and finally distilled. It was stored in a dark vessel over molecular sieve. 1,1,2,2-Tetrachloroethane was distilled before use. All other nondeuterated solvents were dried over molecular sieve and were of spectroscopic quality. All solvents were degassed by three freeze-thaw cycles and admitted to the sample from a syringe.

Line-shape calculations were carried out using the DNMR3 program written by G. Binsch and D. A. Kleier and modified by L. J. Kruczynski and A. G. Stanislawski. The activation parameters were obtained using Krieger's EXEN.⁷

Results

The proton nmr spectra of both 1 and 2 at about 25° were first reported and tentatively assigned by Trofimenko.^{4,8} Our observations and assignments agree well with his and are listed in Table I. The nuclei are identified according to the sketch which forms a part of

(7) J. K. Krieger, Ph.D. Thesis, Massachusetts Institute of Technology, 1971.

(8) S. Trofimenko, *J. Amer. Chem. Soc.*, **90**, 4754 (1968).

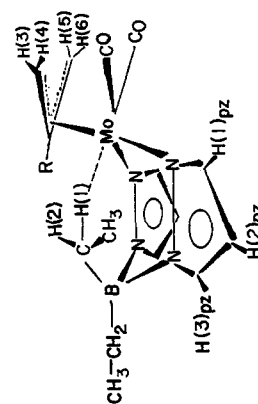


Table I. The Nmr Spectra of 1 and 2 at Room Temperature

Compound	Chemical shift ^a Chemical shift ^b Assignment	Chemical shift ^a Chemical shift ^b Assignment	Chemical shift ^a Chemical shift ^b Assignment	Chemical shift ^a Chemical shift ^b Assignment	Chemical shift ^a Chemical shift ^b Assignment	Chemical shift ^a Chemical shift ^b Assignment	Chemical shift ^a Chemical shift ^b Assignment
R = C ₆ H ₅	d (2.1) 1.8 1.96 ^c H(1)pz or H(3)pz	d (2.1) 1.85 1.90 ^f H(1)pz or H(3)pz	d (2.3) 2.66 2.80 ^e H(3)pz or H(1)pz	d (2.2) 3.78 3.86 ^c H(2)pz	t (2.2) 3.78 3.79 ^f H(2)pz	t (2.2) 3.78 3.79 ^f H(2)pz	t (2.2) 3.78 3.86 ^c H(2)pz
R = H	d (2.1) 1.85 1.90 ^f H(1)pz or H(3)pz	d (2.1) 1.85 1.90 ^f H(1)pz or H(3)pz	d (2.3) 2.57 2.59 ^e H(3)pz or H(1)pz	d (6.8) 6.36 ^g H(3), H(6)	d (9.8) 8.51 ^h H(4), H(5)	d (9.8) 8.51 ^h H(4), H(5)	d (9.8) 8.51 ^h H(4), H(5)
R = C ₆ H ₅	m 2.85 2.96 ^c C ₆ H ₅	m 2.85 2.96 ^c C ₆ H ₅	m 2.85 2.96 ^c C ₆ H ₅	s 5.82 5.90 ^d H(3), H(6)	s 5.82 5.90 ^d H(3), H(6)	s 5.82 5.90 ^d H(3), H(6)	s 5.82 5.90 ^d H(3), H(6)
R = C ₆ H ₅	s 8.31 8.37 ^d H(4), H(5)	s 8.31 8.37 ^d H(4), H(5)	s 8.31 8.37 ^d H(4), H(5)	s 9.34 9.46 ^e C ₆ H ₅ (eq)	s 9.34 9.46 ^e C ₆ H ₅ (ax)	s 9.34 9.46 ^e C ₆ H ₅ (ax)	s 9.34 9.46 ^e C ₆ H ₅ (ax)
R = C ₆ H ₅	q (7.0) 13.8 13.8 ^e H(1), H(2)	q (7.0) 13.8 13.8 ^e H(1), H(2)	q (7.0) 13.8 13.8 ^e H(1), H(2)	m 9.16 br, 9.26 ^h C ₆ H ₅ (eq) and CH ₃ (ax)	m 9.16 br, 9.26 ^h C ₆ H ₅ (eq) and CH ₃ (ax)	m 9.16 br, 9.26 ^h C ₆ H ₅ (eq) and CH ₃ (ax)	m 9.16 br, 9.26 ^h C ₆ H ₅ (eq) and CH ₃ (ax)

^a Multiplicity (*J* in hertz) τ . Chemical shifts from ref 4. ^b This work. ^c Solvent: CS₂ + CF₂Cl₂ (1:1). ^d Solvent: CS₂ + CHCl₃ (3:2). ^e Solvent: CS₂ + CH₂ClCH₂Cl (8:3). ^f Solvent: CD₂Cl₂ + CF₂Cl₂ (1:1). ^g Solvent: CHCl₃ + CD₂Cl₂ (1:1). ^h Solvent: toluene-d₆ + CS₂ + CH₂Cl₂ (5:5:2).

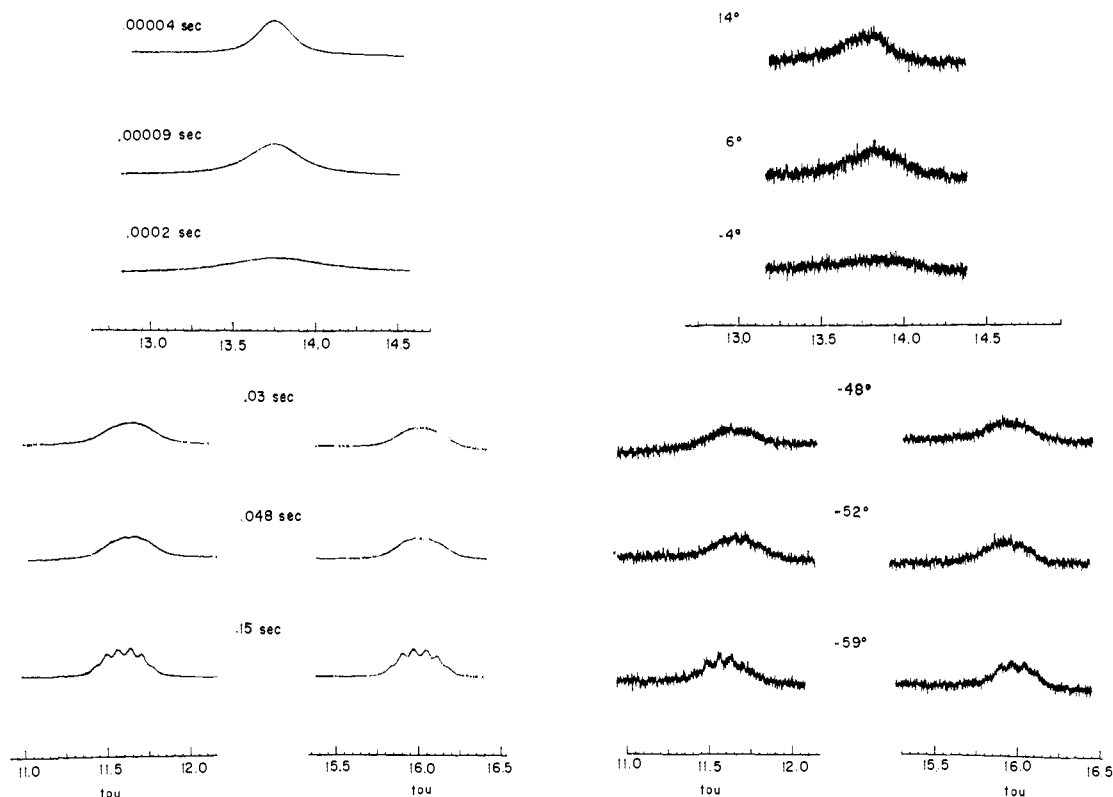


Figure 1. The 100-MHz pmr spectra at several temperatures of the upfield methylene region of $[\text{Et}_2\text{B}(\text{pz})][\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2](\text{CO})_2\text{Mo}$ dissolved in $\text{CF}_2\text{Cl}_2 + \text{CDCl}_3 + \text{CH}_2\text{Cl}_2$ (5:5:2).

Table I. Descriptive terms to be used in reporting and discussing the results will include, in addition to the designations axial and equatorial for the ethyl groups (as already explained), the designation of allyl protons 4 and 5 as anti and allyl protons 3 and 6 as syn.

Compound 1. The assignment of the peaks at τ 5.90 and 8.37 in **1** to the syn and anti π -allyl protons, respectively, is based on numerous examples in the literature.^{9,10} Other assignments are straightforward. A distinction between H(1)pz and H(3)pz might be based on the idea that the former would be expected to show the greater chemical shift difference from one ring to the other in the slow-exchange region due to their closer proximity to the other ligands. This would place the H(1)pz signals at lower field. However, the explicit assignment of the H(1)pz and H(3)pz signals is not necessary to the analysis.

Because of the complexity of the spectra of both **1** and **2**, different portions of the spectra were run in different solvent mixtures. Small changes in chemical shifts were observed for certain peaks when solvents were changed.

The behavior of the axial methylene resonance of **1** at room temperature and below is shown in Figure 1. At room temperature there is only one broad signal at τ 13.8, which collapses at about -4° and reappears at about -48° as two signals at τ 11.56 and 16.07. These signals sharpen until at about -60° they have

the appearance of 1-4-6-6-4-1 sextets. This multiplet structure is presumably due to the fact that each is coupled with the methyl protons to produce a quartet, while coupling to each other causes the two quartets to overlap so as to give a sextet. The simulated spectra were so calculated.

The low-temperature behavior of the signals assigned to the syn protons of the $\eta^3\text{-CH}_2\text{CPhCH}_2$ ligand of **1** is shown in Figure 2. These protons give a sharp singlet at $+5^\circ$ and above. With cooling, this singlet collapses and between -33 and -43° re-forms as two broad, equally intense signals at τ 5.64 and 6.16, which sharpen at lower temperatures. The resonance assigned to the anti protons of $\eta^3\text{-CH}_2\text{CPhCH}_2$ is a singlet at 5° and it collapses and re-forms as two singlets (τ 7.88 and 8.85) in much the same way.

In the pyrazolyl region, all signals for compound **1** change markedly at lower temperatures, as shown in Figure 3. Each of the doublets seen at -6° at τ 1.96 and 2.80 broadens and between -45 and -55° re-forms as two signals, each of which sharpens and becomes a doublet at temperatures below about -65° . These four doublets are located at τ 1.76, 2.04, 2.72, and 2.82. The splitting in each one is 2.2 ± 0.3 Hz, which is the same as that observed in each of the two doublets at -6° . The phenyl multiplet at about τ 2.9 and the pyrazolyl triplet at τ 3.86 also change considerably from -6 to -74° , but the changes do not lend themselves to line-shape analysis. The region from τ 1.7 to 2.1 is very suitable for analysis to determine exchange rates, and computer-simulated spectra for this region are shown at the left in Figure 3.

The four, small, broad signals at -74° at τ 2.3, 2.5,

(9) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).

(10) This assignment is also favored by the fact that the dihedral angle between the plane of the allyl group and the plane of the phenyl ring is 170° so that the syn protons are in a position to be measurably deshielded by the phenyl ring.

3.6, and 4.0 are of uncertain origin. They may belong to a minor conformational isomer of **1** or they may be due to an impurity. There is also a small peak at about τ 8.6 which obscures somewhat the low-temperature line-shape changes of the allyl proton signal at τ 8.85. Several investigators have commented previously on the frequent presence of impurities in η^3 -allyl complexes.^{11,12}

The low-temperature (slow-exchange) results just presented can be fully understood in terms of the dissymmetric structure which was found for **1** in the crystal. To give the reader an adequate appreciation of the spatial relationships that exist in one enantiomorph of this structure, it is presented as a stereo pair in Figure 4. The six pyrazolyl protons should give rise to six separate resonances; this is observed except for the lack of resolution of the signals at τ 3.86. The two protons of the methylene group of the axial C_2H_5 are nonequivalent, one being bound to Mo and the other not. The former occurs at a very high τ value while the other is close to the normal range for an aliphatic hydrogen atom. The 2-phenyl allyl group also shows separate signals for each of its four syn and anti protons.

The collapse of this spectrum to give, near room temperature, a spectrum consistent with there being a plane of symmetry relating the two pyrazolyl rings, the two halves of the η^3 -allyl group, and the two methylene protons of the axial ethyl group is the important qualitative observation thus far reported. It is explicable in terms of increasingly rapid interconversion of the two enantiomorphs of the molecular structure. The transformation of one enantiomorph to the other necessitates a rotation of the axial C_2H_5 group about the B-C bond so that one $C-H \cdots Mo$ interaction is replaced by the other one while essentially simultaneously the configuration of the ligand set made up of the two CO groups and the η^3 -allyl group shift to the opposite chirality. We think it likely that they do this by a rotation relative to the rest of the molecule such that the CO groups change roles. This could be checked by ^{13}C nmr study of the CO groups, but we have not carried out that experiment.

We turn now to the remaining signals of the ethyl groups and their behavior at higher temperatures. Figure 5 shows this behavior for both of the compounds. For **1** we see at 36° a singlet at τ 9.45 and a triplet ($J = 6.5$ Hz) at τ 9.85. As the temperature is raised they broaden and coalesce; eventually at about 107° a single triplet at τ 9.54 is seen. As these changes are occurring, the methylene resonance at τ 13.5 also broadens and essentially disappears above $\sim 70^\circ$. Above about 110° decomposition of **1** becomes rapid and peaks grow in at τ 9.10 and 9.42 due to the decomposition product or products. These remain sharp when the sample is cooled.

The assignment of the signals at $\sim \tau$ 9.5, ~ 9.9 , and ~ 13.5 was investigated by spin decoupling at 7° . As shown in Figure 6a, irradiation of the signal at $\sim \tau$ 13.5 causes the triplet at $\sim \tau$ 9.9 to become a singlet while the singlet at $\sim \tau$ 9.5 is unaffected. At -52° irradiation of the triplet at $\sim \tau$ 9.9 changes each of the broad peaks at $\sim \tau$ 11.56 and ~ 16.07 into doublets ($J = 15.0$ Hz).

(11) C. A. Reilly and H. Thyret, *J. Amer. Chem. Soc.*, **89**, 5144 (1967).

(12) J. W. Faller and M. J. Inorvia, *Inorg. Chem.*, **7**, 840 (1968).

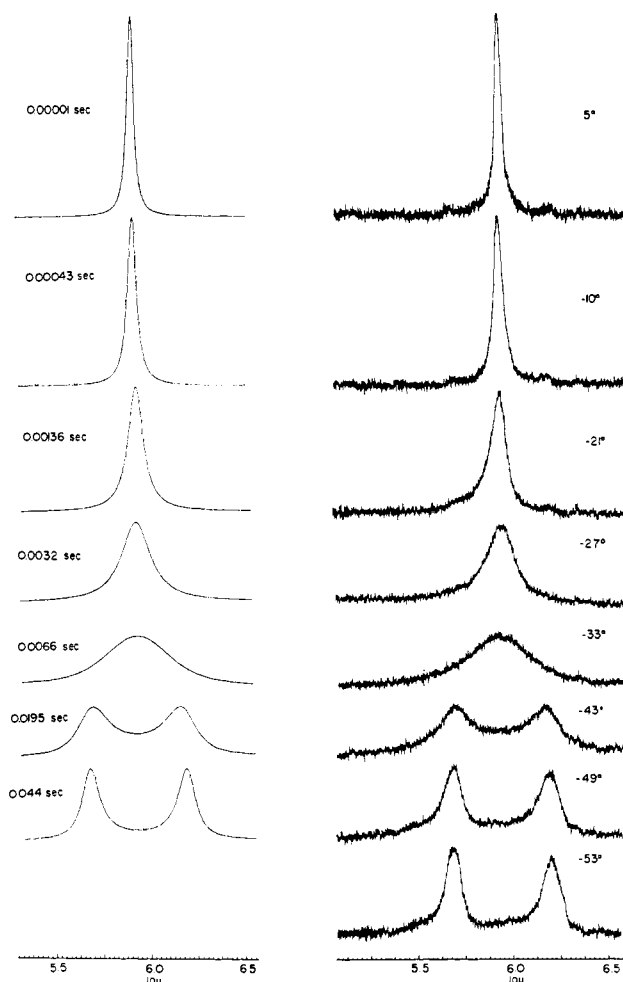


Figure 2. The pmr spectrum of the syn- π -allyl protons of $[Et_2B(pz)_2][\eta^3-CH_2C(Ph)CH_2](CO)_2Mo$ in $CS_2 + CHCl_3$ (3:2) at various temperatures.

We conclude from these results that in the spectra shown at 36° in Figure 5a and at 7° in Figure 6a, the singlet of relative intensity 5 at $\sim \tau$ 9.5 must be due to all five protons of the equatorial ethyl group; the methyl and methylene protons have accidentally virtually identical chemical shifts. The triplet at $\sim \tau$ 9.9 is due to the methyl protons of the axial ethyl group. The process which causes the line-shape changes observed in Figure 5a is site exchange of the two ethyl groups. Thus at the highest temperature the two CH_3 groups are nmr equivalent, giving rise to a triplet as a result of splitting of each CH_3 by one of the two nmr equivalent CH_2 groups. The nonobservance of a signal for the latter below the decomposition temperature is attributable to the large chemical shift difference between three of the methylene protons ($\sim \tau$ 9.45, ~ 9.45 , ~ 11.56) and the other one (τ 16.07).

Compound 2. The spectra of this compound behave similarly as a function of temperature to those of compound **1**. The resonances in the pyrazolyl region are shown in Figure 7. It can be seen that the spectrum at -70° is consistent with the dissymmetric structure, with doublets at τ 1.52 ($J = 2.0$ Hz) and τ 2.14 ($J = 1.9$ Hz) which can be assigned to the H(1)pz protons of each ring, a nearly superposed pair of doublets at τ 2.52 and 2.57, each with $J \approx 2.0$ Hz and two triplets at

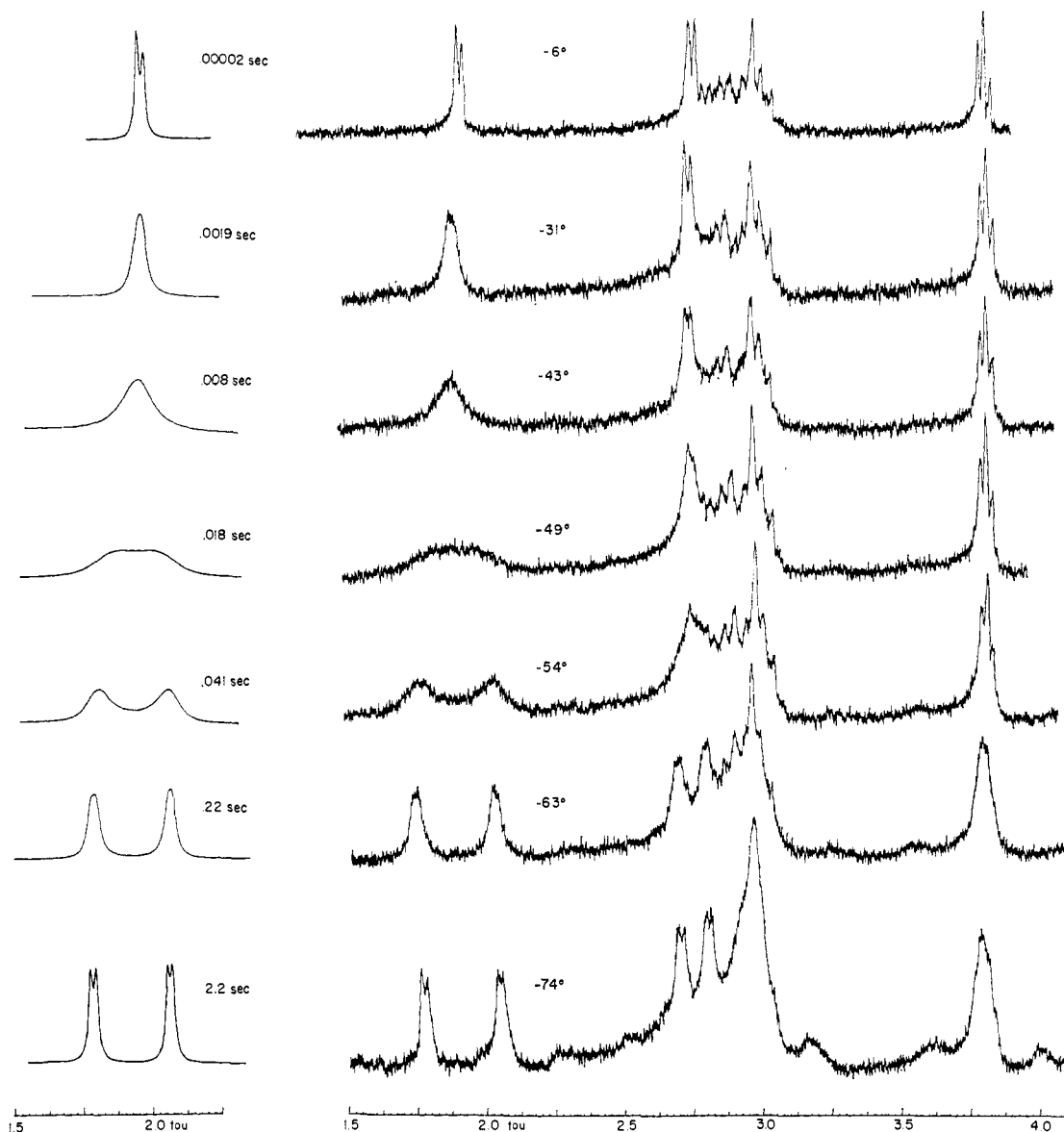


Figure 3. The pmr spectra of the pyrazolyl region of $[\text{Et}_2\text{B}(\text{pz})_2][\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2](\text{CO})_2\text{Mo}$ in CS_2 , at various temperatures.

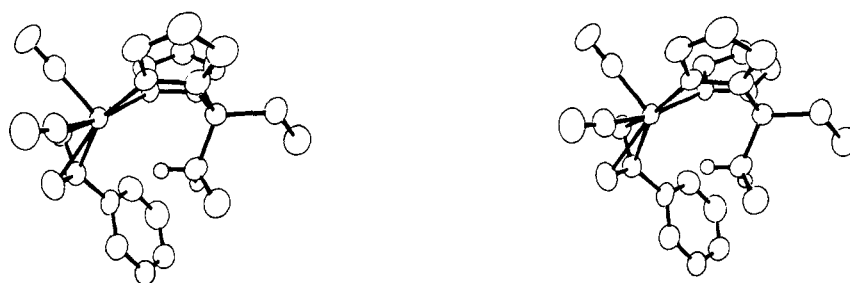


Figure 4. Stereoview of $[\text{Et}_2\text{B}(\text{pz})_2][\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2](\text{CO})_2\text{Mo}$.

τ 3.65 ($J = 2.1$ Hz) and 3.80 ($J = 1.9$ Hz), the latter arising from the two H(2)pz protons. A number of very small, broad impurity peaks can also be seen. As the temperature is raised, the spectrum collapses and coalesces exactly as would be expected if a process which gives the two pyrazolyl rings time-average equivalence were becoming rapid on the nmr time scale.

Computer simulation of a portion of these spectra appears at the left in Figure 7.

The allyl resonances for **2** are not shown, but behave as expected on the basis of the behavior of those in **1**. The peaks are not as well separated as in the case of **1** and thus do not lend themselves to line shape analysis. At room temperature, there is a broad multiplet at τ

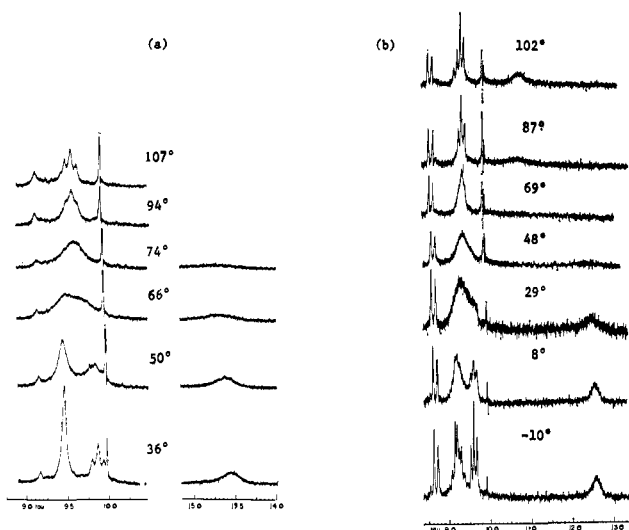


Figure 5. (a) The high temperature pmr of $[\text{Et}_2\text{B}(\text{pz})_2][\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2](\text{CO})_2\text{Mo}$ in the ethyl region. 1,1,2,2-Tetrachloroethane was used as a solvent. The sharp line at τ 10.0 is due to silicone grease impurity. (b) The spectra of the ethyl portion of $[\text{Et}_2\text{B}(\text{pz})_2](\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}$. Toluene- d_6 and 1,1,2,2-tetrachloroethane (5:1) mixture was used as a solvent, from -10 to 102° .

6.2, of relative intensity 1 and two doublets, each of relative intensity 2 at τ 6.36 ($J = 6.8$ Hz) and τ 8.51 ($J = 10.0$ Hz). The upfield doublet collapses as the temperature is lowered and at -70° reappears as two doublets at τ 8.20 ($J = 10.0$ Hz) and 8.66 ($J = 10.0$ Hz), but these signals were not sharp at -70° . The remainder of the allyl spectrum at -70° was complex due to the closeness of the chemical shifts and could not be described quantitatively.

The axial methylene protons are shown in Figure 8. At $+9^\circ$ there is one broad peak at τ 12.41 which collapses at -21° and reappears below -53° as two broad peaks at τ 10.83 and 14.30. The results of a decoupling experiment, at -69° , employing the broad signal at τ 14.30 are shown in Figure 6b. The triplet at τ 9.53 becomes a doublet, and the resonance at τ 10.83 becomes less broad. This indicates that the former is the axial methyl resonance coupled about equally to both methylene protons, while the latter are also coupled to each other.

Thus the spectra of **2** in the low temperature region strongly support the idea that both the instantaneous structure of this molecule and the dynamical process it undergoes in this temperature range are analogous to the structure and rearrangement of **1** in the low temperature range. The behavior of the allyl resonances is such as to leave open the possibility that the allyl groups in **1** and **2** might be oppositely oriented, but we do not see any positive reason to suppose that this is actually the case.

Changes in the spectra of **2** at higher temperatures are shown in Figure 5b. At -10° , the equatorial ethyl group gives a multiplet at τ 9.22, while the axial methyl group gives a well-formed 1-2-1 triplet at τ 9.62. The time-averaged methylene protons of the axial ethyl group give the broad peak seen at τ 12.65. As the temperature rises all signals collapse and by room temperature both methyl groups are included in the broad signal at $\sim\tau$ 9.3. This resonance then continues

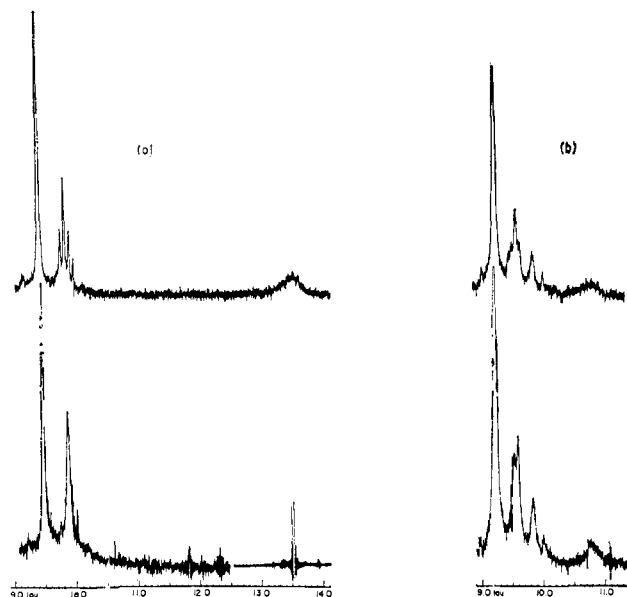


Figure 6. (a) The pmr spectra of $[\text{Et}_2\text{B}(\text{pz})_2][\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2](\text{CO})_2\text{Mo}$ in the region of the ethyl protons. The bottom spectrum shows the effect of irradiation at the broad peak at τ 13.5. Both spectra were taken at $+7^\circ$ with CS_2 and $\text{CH}_2\text{ClCH}_2\text{Cl}$ (8:3) used as a solvent. (b) The -69° spectra of $[\text{Et}_2\text{B}(\text{pz})_2](\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}$ in the ethyl region. The top trace represents the spectrum without, and the bottom one with, irradiation at τ 14.20. A mixture of CD_2Cl_2 and CH_2Cl_2 (2:1) was used as a solvent.

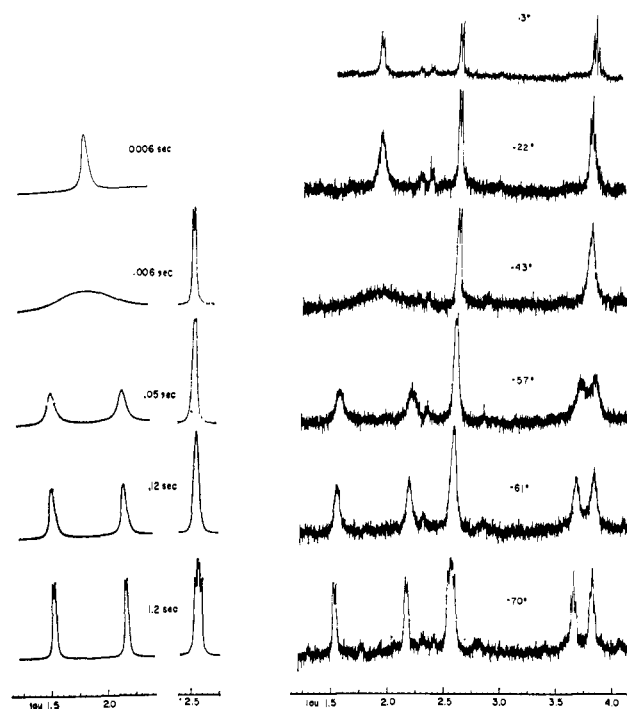


Figure 7. The pmr spectra in the pyrazolyl region of $[\text{Et}_2\text{B}(\text{pz})_2](\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}$, at various temperatures (solvent, $\text{CS}_2 + \text{CF}_2\text{Cl}_2$, 1:1).

to sharpen and by 87° appears as a clean 1-2-1 triplet. Also at 87° we can see the emergence of a broad signal at $\sim\tau$ 10.8 which is the time-averaged resonance for the four methylene protons. This sharpens as the temperature is raised to 102° , but, at this temperature

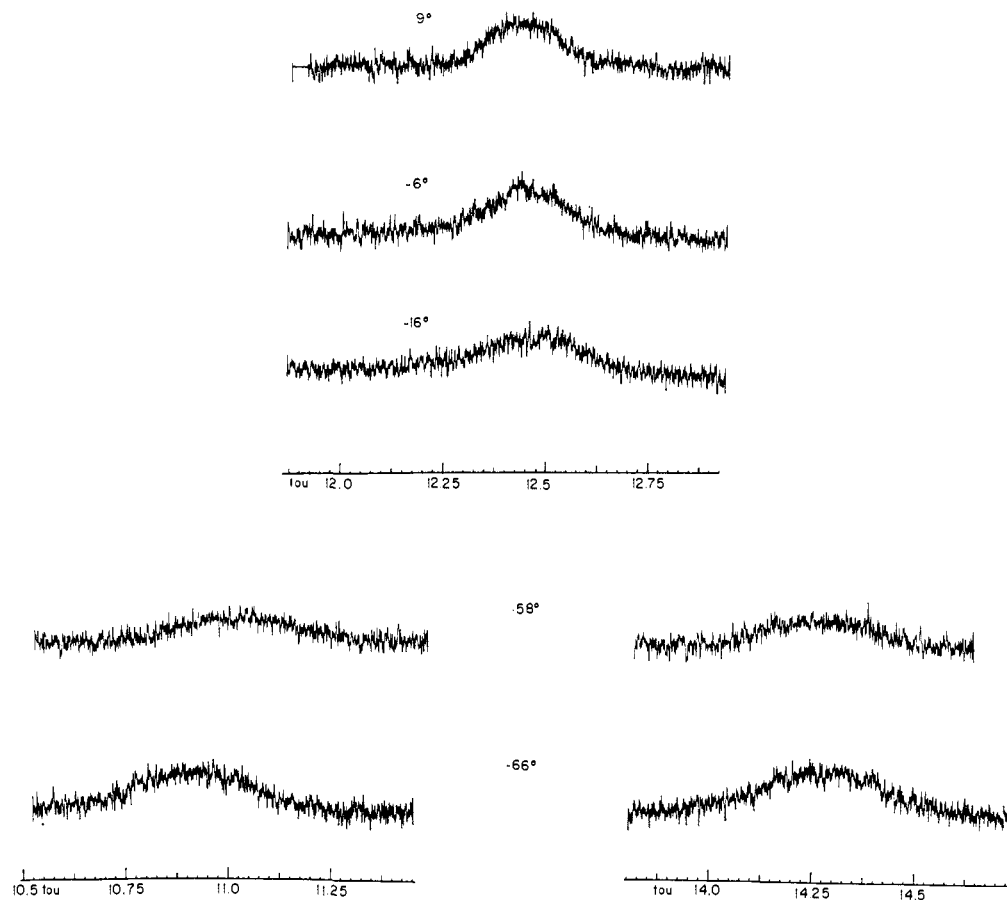


Figure 8. The pmr spectra of the axial methylene of $[\text{Et}_2\text{B}(\text{pz})_2](\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}$ in $\text{CD}_2\text{Cl}_2 + \text{CH}_2\text{Cl}_2$ (2:1) at various temperatures.

Table II. Some Activation Parameters Derived by Line Shape Analysis

Molecule	No. of points ^a	Signals used	E_a , ^b kcal mol ⁻¹	Log A ^c	ΔH^\ddagger , ^b kcal mol ⁻¹	ΔS^\ddagger , ^d cal deg ⁻¹	ΔG_{298}^\ddagger , ^e kcal mol ⁻¹
Low-Temperature Process							
1	15	Low-field allyl	16.6	17.3	16.1	19	10.4
	11	Axial CH_2	13.8	15.0	13.3	8	10.9
	12	Low-field pyrazolyl	15.6	16.9	15.1	17	10.0
	15	Upfield allyl	14.6	15.6	14.1	13	10.7
	53	All of the above	14.2	15.3	13.7	10	10.7
2	12	Low-field pyrazolyl	14.1	15.5	13.6	11	10.4
High-Temperature Process							
1	10	Ethyl	19.6	14.6	19.0	6	17.1
2	8	Ethyl	17.4	14.1	16.7	4	15.6

^a Each point is a measurement of temperature at a rate at which the computed spectrum matches. ^b For the low-temperature process (LTP), ± 1 kcal mol⁻¹; for the high-temperature process (HTP), ± 2 kcal mol⁻¹. ^c For the LTP, ± 1 kcal mol⁻¹; for the HTP, ± 1 kcal mol⁻¹. ^d All uncertainties about ± 4 cal deg⁻¹. ^e For the LTP, ± 2 kcal mol⁻¹; for the HTP, ± 3 kcal mol⁻¹.

decomposition is becoming rapid, as the appearance of a new signal just to the low-field side of the methyl triplet shows, and it was not possible to continue sharpening the methylene signal.

It should be noted that when toluene- d_8 is used as a solvent, Figure 6b, the equatorial ethyl group in **2** gives rise to a singlet, as in **1**. The chemical shift separation of the CH_3 and CH_2 signals of the equatorial C_2H_5 group is observably solvent sensitive.

Activation Parameters. Using a number of the lines in the spectra of **1** and **2**, activation parameters for both the high- and low-temperature processes were evaluated. These results are collected in Table II.

Discussion

We show in Figure 9 a systematic array of possible structures for the type of molecule under study. Each conformer is represented as a projection along that quasi-threefold axis of the essentially octahedral array of ligands which relates the allyl and two CO ligands to each other in the foreground and the two coordinated nitrogen atoms and the bridging hydrogen atom in the background. Only the axial ethyl group is included; the equatorial ethyl group and the pyrazolyl rings are omitted in the interest of clarity, but their positions can be easily inferred from that portion of the molecule which is shown.

The nmr results clearly show that the majority of these conformations and/or isomers are not significantly populated, if at all. All eight structures in rows C and D are related to those above by a 180° rotation of the allyl ligand about an axis from the molybdenum atom to the centroid of the allyl group and essentially perpendicular to the mean plane of the allyl group. Although there are cases known¹³ in which this sort of isomerism is important, we find no definite evidence for it here. The possibility that some of the very weak peaks seen in the low-temperature spectra may be due to such isomers cannot be definitely excluded, as noted earlier, but, even if this is the case, these isomers are very minor and not intimately involved in the dynamical processes of direct interest.

Interchange between the molecules in row A and row B ($1A \rightleftharpoons 1B$, $2A \rightleftharpoons 2B$, etc.) involves a rotation of the axial ethyl group about the CH_2-B axis and would be expected to give two separate signals for the axial methyl group along with four separate signals for the axial methylene protons.

Our low temperature pmr spectra nowhere showed any change in the axial methyl signal; neither did we observe more than two signals for the axial methylene protons. We consider this evidence that structures with configuration B are also of no importance for the molecules in question. This is especially reasonable when one looks at a model of compound 1. Configuration B has the axial methyl group pointing at the phenyl group and thus causing a certain amount of unfavorable steric interaction. We conclude that only structures of type A need be considered henceforth in discussing these molecules in solution.

The isomers $2A$ and $3A$ are mirror images of each other. Their interconversion involves simply a 60° rotation of the two carbonyls and of the allyl group, as well as a rotation by 60° of the axial ethyl group about the C-B bond. This process interconverts the two halves of the molecule so that when it is very fast on the pmr time scale the averaged spectrum has the appearance of resulting from a molecule with a plane of symmetry, such as the one in column 4.

Our low-temperature spectra of both 1 and 2 show six signals for the pyrazolyl protons, four separate signals for the syn and anti η^3 -allyl protons and two signals for the axial methylene protons while the fast exchange spectra have only six signals in addition to the equatorial ethyl and axial methyl peaks. Some small peaks scattered in the pyrazolyl and the allyl portions of the spectra at low temperature suggest that $4A$ may possibly be a minor isomer (its existence would add three peaks in the pyrazolyl region and two peaks in the allyl region) but the data at hand preclude any conclusion on this.

The observations are consistent, however, with the $2A \rightleftharpoons 3A$ process. Evidence of this type of an interconversion was found earlier⁵ for the $[H_2B(3,5-Me_2-pz)_2](\eta^3-C_7H_7)(CO)_2Mo$ molecule. This compound was shown by an X-ray study¹⁴ to exhibit a strong interaction between the molybdenum atom and one of the

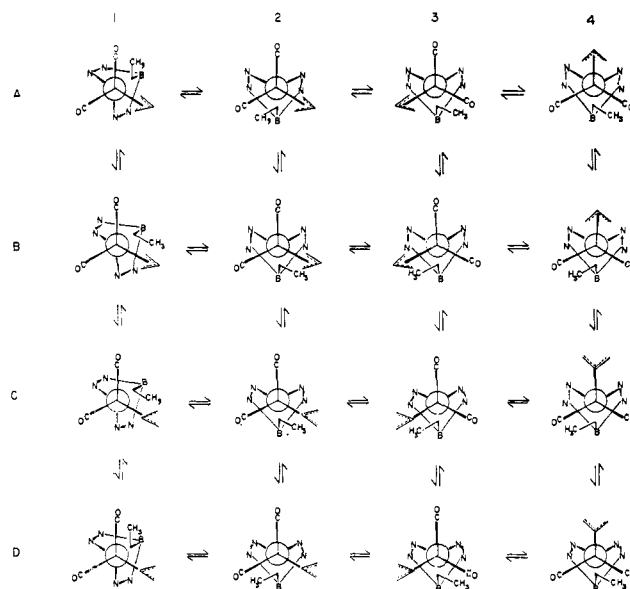


Figure 9. The schematic representation of the possible conformational isomers of 1 and 2 in solution. The equatorial ethyl group is omitted for simplicity.

hydrogen atoms bonded to the boron atom. The $2A \rightleftharpoons 3A$ interconversion is a process with an energy of activation equal to ~ 14 kcal mol⁻¹ for both compounds 1 and 2. At room temperature it has already reached its fast exchange limit. By comparison, the $[H_2B(3,5-Me_2pz)_2](\eta^3-C_7H_7)(CO)_2Mo$ is at 29° in the slow exchange region and the two enantiomers give rise to an averaged spectrum only at 113° , suggesting that for this molecule it is a process of much higher energy. This is further support for an observation we made earlier¹ about the relative strength of the two types of interaction, $B-H \cdots Mo$ and $C-H \cdots Mo$, the first one being stronger than the latter.

The high temperature process is of much interest in relation to this. At high temperature, both 1 and 2 exchange their ethyl groups in a process consistent with $1A \rightleftharpoons 2A$ interconversion in Figure 9. The energies of activation are ~ 20 kcal mol⁻¹ for 1 and ~ 17 kcal mol⁻¹ for 2. This interconversion involves a complete breaking of the $C-H \cdots Mo$ bond and a subsequent ring flip with a concurrent rearrangement of the remaining ligands. A similar ring flip was observed⁵ in $[B(pz)_4](\eta^5-C_5H_5)(CO)_2Mo$, $[HB(pz)_3](\eta^5-C_5H_5)(CO)_2Mo$, and in $[Et_2B(pz)_2](\eta^5-C_5H_5)(CO)_2Mo$ all of which contain a coordinatively saturated molybdenum atom. For the tetrakis(pyrazolyl)borate compound the ring flip interconversion is observed between -110° and room temperature; for the $[HB(pz)_3](\eta^5-C_5H_5)(CO)_2Mo$ it is observed between -49° and 114° , while for $[Et_2B(pz)_2](\eta^5-C_5H_5)(CO)_2Mo$ the two isomers could not be "frozen out."⁵ The energy of activation for the tetrakis(pyrazolyl)borate was estimated to be of the order of 10 kcal/mol and it must be within several kilocalories per mole for the other two compounds in ref 5, significantly lower than for either 1 or 2, both of which have to break the $C-H \cdots Mo$ bond first. Furthermore, for $[H_2B(3,5-Me_2pz)_2](\eta^3-C_7H_7)(CO)_2Mo$ this process would involve a breaking of the $B-H \cdots Mo$ bond which is stronger than the $C-H \cdots Mo$ bond. For this com-

(13) A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967); J. W. Faller, *ibid.*, **8**, 767 (1969).

(14) (a) F. A. Cotton, J. L. Calderon, M. Jeremic, and A. Shaver, *J. Chem. Soc., Chem. Commun.*, 777 (1972); (b) F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, **6**, 543 (1972).

pound, the ring flip would, therefore, require still more energy than for either 1 or 2 and this is evidenced in the fact that the ring flip of the dihydrobis(pyrazolyl)borate is not observed by pmr.

One of the major goals of this investigation was to obtain some estimate of the strength of the C-H...Mo interaction. Using the results presented in Table II, we proceed as follows. From the low-temperature process, with $E_a \approx \Delta H^\ddagger \approx 14 \text{ kcal mol}^{-1}$, we do not believe that much can be learned. The breaking of one C-H...Mo bond is probably compensated by the formation of the new one as the rotation about the B-C bond proceeds. There is probably some partial loss of bond energy in the transition state, but the shift of the other ligands probably also contributes significantly to the total activation energy. There does not appear to be any way to sort out the two contributions nor to determine the degree of C-H...Mo bond breaking which has occurred in the transition state.

The high-temperature process does, however, provide some estimate of the C-H...Mo interaction energy. The activation energy for this process, which is about

19 kcal mol⁻¹ for 1 and about 17 kcal mol⁻¹ for 2, has three main components: (1) the energy of breaking the C-H...Mo bond, A, (2) the energy of relaxing the very puckered boat conformation of the chelate ring to a flatter boat, like that found in [Et₂B(pz)₂]Mo(CO)₂-(η^3 -C₃H₅)(pyrazole),⁶ B, (3) the activation energy for the ring flip (and associated ligand rearrangements), C. The quantities A, B, and C are +, - and +, respectively. The magnitude of C is probably similar to that for the ring inversion in cyclohexane, *viz.*, about 6 kcal/mol. If it is assumed that B also has a magnitude of about 6 kcal mol⁻¹, C and B cancel each other, leaving A equal to the measured ΔH^\ddagger , namely 17-19 kcal mol⁻¹. This is admittedly a very rough estimate, but it seems a reasonable one.

Acknowledgments. We thank Dr. S. Trofimenko and Dr. A. G. Shaver for providing samples, and Mr. Alan J. White for assistance in operating and maintaining the nmr spectrometer. This research was supported by The Robert A. Welch Foundation under Grant No. A494.

Kinetics of Reaction of Copper(II) Ion with a Variety of Ligands

Thomas S. Roche and Ralph G. Wilkins*¹

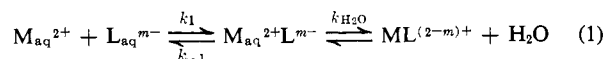
Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received November 17, 1973

Abstract: The activation parameters for the formation of the monocomplex of copper(II) with ten different ligands have been determined. The ligands studied included 2-substituted pyridyl derivatives, tri- and tetraamines, and aminodicarboxylates. The results are compared with complexing of these ligands by nickel(II), and conclusions are drawn as to the mechanisms of complex formation.

There has been an increasing number of studies of the kinetics of complexing of copper(II). Recent work has centered on the ligands ammonia,² ethylenediamine,^{3,4} and tetraethylenepentaamine,⁵ amino acids and derivatives,⁶⁻¹² β -diketones,^{13,14} and the dye

pyridine-2-azo-*p*-dimethylaniline^{15,16} in their reactivity toward the aquated copper ion, as well as toward complexed copper(II), forming ternary complexes.¹⁷

Disagreement exists as to the detailed mechanism of complex formation, particularly in the formation of ternary complexes. Toward Cu²⁺, the reactions of a large number of ligands can be interpreted in terms of the generally accepted mechanism for complexation by bivalent metal ions in aqueous solution. In this, ligand-water interchange occurs within the outer-sphere complex, leading to the inner-sphere complex



(1) Address correspondence to this author at the Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003.

(2) H. Diebler and P. Rosen, *Ber. Bunsenges. Phys. Chem.*, **76**, 1031 (1972).

(3) L. J. Kirschenbaum and K. Kustin, *J. Chem. Soc. A*, 684 (1970).

(4) V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, **11**, 138 (1972).

(5) R. E. Shepherd, G. M. Hodgson, and D. W. Margerum, *Inorg. Chem.*, **10**, 989 (1971).

(6) A. F. Pearlmutter and J. Stuehr, *J. Amer. Chem. Soc.*, **90**, 858 (1968).

(7) R. F. Pasternack and K. Kustin, *J. Amer. Chem. Soc.*, **90**, 2995 (1968).

(8) W. B. Makinen, A. F. Pearlmutter, and J. E. Stuehr, *J. Amer. Chem. Soc.*, **91**, 4083 (1969).

(9) R. F. Pasternack, K. Kustin, L. A. Hughes, and E. Gibbs, *J. Amer. Chem. Soc.*, **91**, 4401 (1969).

(10) R. F. Pasternack, E. Gibbs, and J. C. Cassatt, *J. Phys. Chem.*, **73**, 3814 (1969).

(11) R. L. Karpel, K. Kustin, A. Kowalak, and R. F. Pasternack, *J. Amer. Chem. Soc.*, **93**, 1085 (1971).

(12) R. F. Pasternack, M. Angwin, and E. Gibbs, *J. Amer. Chem. Soc.*, **92**, 5878 (1970).

(13) R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, **9**, 39 (1970).

(14) M. R. Jaffe, D. P. Fay, M. Cefola, and N. Sutin, *J. Amer. Chem. Soc.*, **93**, 2878 (1971).

(15) R. G. Wilkins, *Inorg. Chem.*, **3**, 520 (1964).

(16) M. A. Cobb and D. N. Hague, *Chem. Commun.*, 192 (1971).

(17) R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Siegel, *Inorg. Chem.*, **11**, 276 (1972).