Stereochemical Nonrigidity in Some Transition Metal Complexes Containing Tris(1-pyrazolyl)borate Ligands

S. Trofimenko

Contribution No. 1531 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898. *Received December 26, 1968*

Abstract: The temperature dependence of the proton nmr spectra of some transition metal complexes containing tris(1-pyrazolyl)borate ligands has been studied with emphasis on compounds having structure $RB(pz)_3M(CO)_2$-π-allyl as well as substituted analogs (pz stands for 1-pyrazolyl; M is Mo or W). Three types of fluxional behavior were observed: (1) "tumbling" or rapid intramolecular exchange of the coordinated pyrazolyl group which makes all pyrazolyl groups in, *e.g.*, $Ba[B(pz)_4]_2$ or $B(pz)_4Pd$-π-C_3H_5, spectroscopically equivalent; (2) rotation of the tridentate $RB(pz)_3$ ligand around the B–M axis; (3) rotation of substituent R, when it is 1-pyrazolyl, around the N–B bond. Well-defined limiting spectra were obtained for processes 2 and 3. There is no evidence for rotation of the π-allyl moiety. Introduction of methyl groups at the 3,5 positions raises the rotational energy barrier, as does substitution on the π-allyl group. Surprisingly, the barrier to rotation is lowest with π-CH_2CMeCH_2 rather than with an unsubstituted π-allyl group.

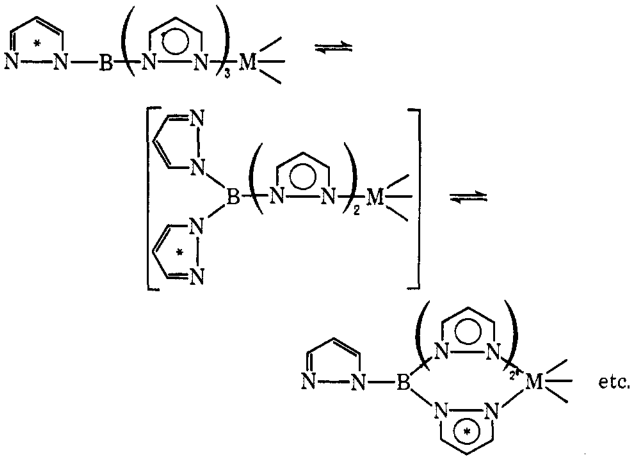
Stereochemical nonrigidity in organometallic compounds has received considerable attention in the past decade. The principal ligands exhibiting fluxional behavior in a temperature range suitable for nmr study include C_nH_n systems such as the cyclopentadienyl, cycloheptatrienyl, and cyclooctatetraene rings (the latter with or without substitution) as well as diverse types of allyl groups,[1] most commonly bonded to a metal carbonyl moiety.

It was of interest to examine in this context transition metal complexes containing the trispyrazolylborate ligand and, in particular, group VIb derivatives of general structure $RB(pz)_3M(CO)_2$-π-allyl where behavior similar to that found in $C_5H_5Mo(CO)_2$-π-C_3H_5[2] and the methallyl analog[3] might be expected. Surprisingly, a different type of stereochemical nonrigidity was observed. This paper examines the temperature dependence of the nmr spectra of selected transition metal polypyrazolylborates with reference to the different ways in which their stereochemical nonrigidity can be manifested.

Transition metal polypyrazolylborates are particularly convenient to study since both the parent ligands[4] and substituted analogs[5] are readily available, and a wide variety of half-sandwich compounds may be synthesized.[6]

The nmr spectra of polypyrazolylborates containing no substituents on the pyrazole nucleus show three types of protons: two doublets in the τ 1.0–2.5 range derived from the 3- and 5-H's and a triplet, usually around τ 3.5–4, derived from the 4-H. In tetrapyrazolylborate salts (*e.g.*, $KB(pz)_4$, $Ba[B(pz)_4]_2$), all pyrazolyl groups are spectroscopically identical and only three signals are observed. In transition metal complexes, where $B(pz)_4$ acts as a tridentate ligand of local C_{3v} symmetry as, for instance, in $Co[B(pz)_4]_2$,[7] $Ni[B(pz)_4]_2$, $Fe[B(pz)_4]_2$, $B(pz)_4Mo(CO)_3^-$, or $B(pz)_4Mn(CO)_3$, the signals observed correspond to three coordinated and one uncoordinated pyrazolyl groups. In $Co[B(pz)_4]_2$ and $Ni[B(pz)_4]_2$ the signals are widely separated because of contact shift interactions. In the latter compounds the chemical shift differences are more modest but still readily distinguishable. It was surprising, therefore, that the nmr spectrum of $Zn[B(pz)_4]_2$, which is isomorphous with $Co[B(pz)_4]_2$, showed only three signals, implying spectroscopic identity of all four pyrazolyl groups. Even when the spectrum was recorded on a higher resolution 220-MHz nmr spectrometer, only one type of pyrazolyl group was observed.

Since $B(pz)_4^-$ cannot act as a tetradentate ligand of C_{4v} symmetry, the identity of all the pyrazolyl groups is ascribed to an exchange process which is fast on the nmr time scale, akin to that found in the ionic $B(pz)_4$ compounds (*e.g.*, $Ba[B(pz)_4]_2$). Mechanistically, the process could involve random dissociation of one coordinated pyrazolyl group followed by inversion and coordination of the previously unattached group ("tumbling").



Attempts to observe slowing of this process by recording the 220-MHz spectrum at −40° were unsuccessful.

---

[1] Pertinent references are cited in the following recent publications: F. A. Cotton, J. W. Faller, and A. Musco, *J. Am. Chem. Soc.*, **90**, 1438 (1968) (C_nH_n systems); and K. Vrieze, P. Cossee, A. P. Praat, and C. W. Hilbers, *J. Organometal. Chem.*, **11**, 353 (1968) (allyl groups); see also F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

(2) A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967).

(3) J. W. Faller and M. J. Incorvia, *ibid.*, **7**, 840 (1968).

(4) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).

(5) S. Trofimenko, *ibid.*, **89**, 6288 (1967).

(6) S. Trofimenko, *ibid.*, **89**, 3904 (1967); **91**, 588 (1969).

(7) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, **89**, 3148 (1967).

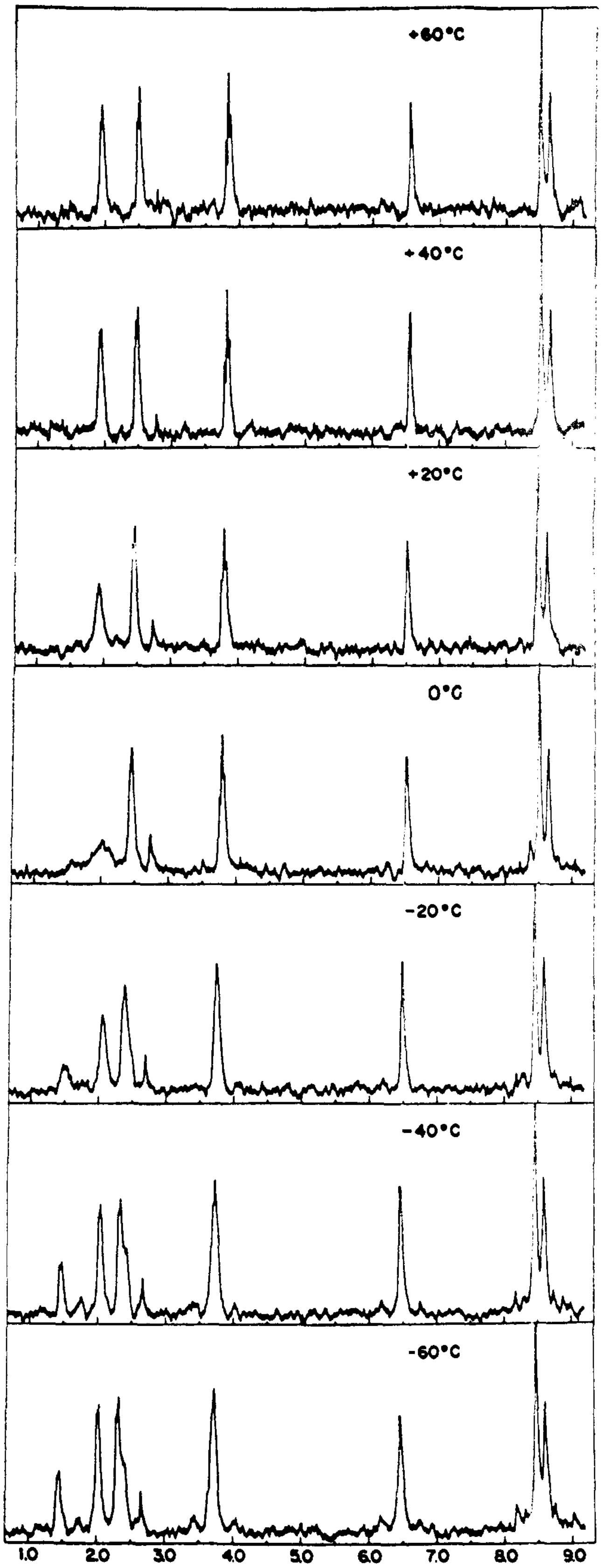


Figure 1. The temperature-dependent nmr spectrum of HB(pz)$_3$-Mo(CO$_2$)-π-CH$_2$CMeCH$_2$ at 60 MHz (in CDCl$_3$).

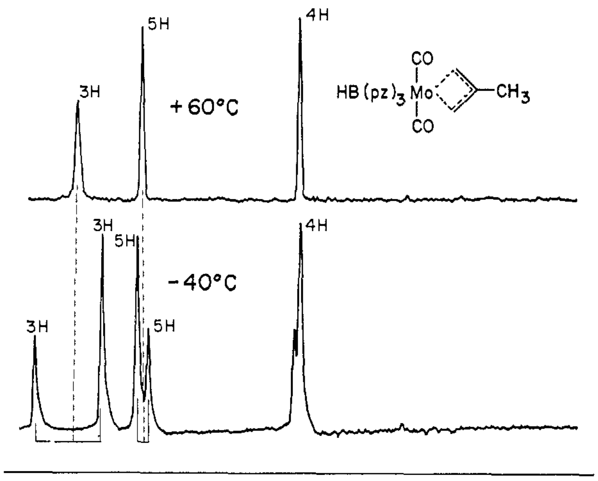


Figure 2. The temperature-dependent nmr spectrum of HB(pz)$_3$-Mo(CO)$_2$-π-CH$_2$CMeCH$_2$ at 220 MHz in CDCl$_3$ (HB(pz)$_3$ portion only).

However, the nmr spectrum of B(pz)$_4$Pd-π-C$_3$H$_5$, which from room temperature to −20° shows only three sharp peaks in the pyrazole region and thus indicates spectroscopic identity of all four pyrazolyl groups, changed to a 4:2:2:4 pattern at −60°. Although this was not a limiting spectrum, it indicated slowing of the exchange rate and fixation of the two coordinated and two uncoordinated pyrazolyl groups. Throughout this temperature range the π-allyl pattern remained unaltered. We have thus one type of fluxional behavior which averages the environments of all pyrazolyl groups through a "tumbling" process.

Another kind of fluxional behavior is indicated by the well-defined temperature-dependent spectra obtained from compounds of the type RB(pz)$_3$M(CO)$_2$-π-allyl (M = Mo, W). The thermally unstable chromium analog B(pz)$_4$Cr(CO)$_2$-π-allyl could not be studied, although the 25° spectrum indicated stereochemical nonrigidity.[6]

The temperature-dependent spectrum of HB(pz)$_3$-Mo(CO)$_2$-π-CH$_2$CMeCH$_2$ is shown in detail in Figure 1. The limiting high- and low-temperature spectra[8] were obtained at +50 and −40°, respectively. Several features of these spectra are noteworthy. (1) The 2-methallyl part of the spectrum does not change significantly in contrast to findings in the corresponding C$_5$H$_5$ system; all the changes occur in the pyrazolylborate part of the spectrum. (2) The high-temperature limiting spectrum indicates equivalence of all three pyrazolyl groups. (3) The low-temperature limiting spectrum indicates two identical and one different pyrazolyl groups. This is more obvious in Figure 2 where the pyrazolyl portion of the limiting spectrum was recorded on the 220-MHz spectrometer. Here, even the 4-H signal is resolved into a 2:1 pattern. The same behavior is observed with HB(pz)$_3$Mo(CO)$_2$-π-C$_3$H$_5$.

These data are interpreted as follows. The absence of significant changes in the nmr spectrum of the π-methallyl group, as well as the presence of only two carbonyl peaks in the high-resolution infrared spectrum, points to a "static" π-methallyl group, presumably in the least sterically hindered conformation. The limiting low-temperature spectrum follows readily from a molecular model, similar to that of C$_5$H$_5$Mo(CO)$_2$-π-C$_3$H$_5$, as shown in Figure 3. Regardless whether the molecule exists in conformation A or B, one pyrazolyl

---

[8] No further changes were observed upon heating, or cooling by ~20°. Fine structure was also discernible.

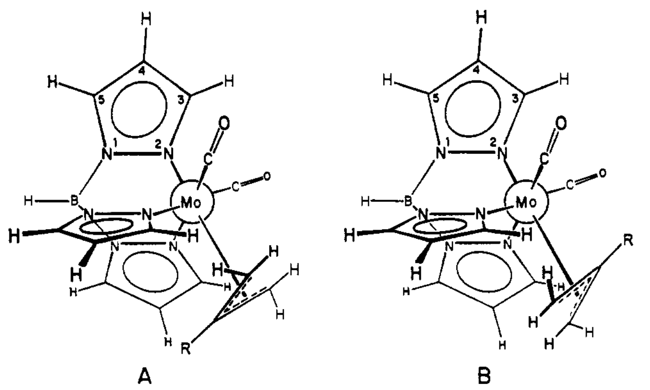


Figure 3. Structures of the two rotamers of HB(pz)$_3$Mo(CO)$_2$-π-CH$_2$CRCH$_2$ also showing the numbering system used in RB(pz)$_3$ ligands.

group (the top one) would be unique and the other two identical. Furthermore, the low-field pair of peaks showing the greatest chemical shift difference can safely be assigned to the 3-H's, two of which should obviously exist in a much more disparate environment than the third one. By comparison, the environments and chemical shifts of the three 5-H's should be more similar.

The +60° spectrum can be explained by postulating a rotation of the tridentate ligand around the B–Mo axis. This should average the environments of the three pyrazolyl groups and would be consistent with the spectroscopic identity of the 3-H's. A dissociation–recombination process would be rather unlikely. Additional support for the rotational mechanism was elicited from the temperature-dependent nmr spectrum of B(pz)$_4$Mo(CO)$_2$-π-CH$_2$CMeCH$_2$.

As seen from Figure 4, the methallyl portion of the spectrum is again temperature independent, changes occurring only in the pyrazolylborate region. The limiting high-temperature spectrum shows two types of pyrazolyl groups in 3:1 ratio and thus resembles the spectrum of B(pz)$_4$Mo(CO)$_3^-$. On cooling, the low-field peak which had been assigned to the 3-H's of the coordinated pyrazolyl rings begins to broaden at +20° and eventually transforms into a 2:1 pattern corresponding to that found in HB(pz)$_3$Mo(CO)$_2$-π-CH$_2$CMeCH$_2$. However, the high-field peak assigned to the three 5-H's starts collapsing even at +40° and almost disappears at +20°. In the limiting low-temperature spectrum it reappears as a 2:1 pattern with a separation of 85 cps, thus considerably larger than that of the 3-H's (36 cps). Throughout these changes, the peaks of the 3- and 5-hydrogens belonging to the uncoordinated pyrazolyl group remain virtually unchanged. This, again, is clearly demonstrated in the limiting spectra recorded on the 220-MHz spectrometer (Figure 5).

These findings lead to the following conclusions.

1. The methallyl moiety shows no evidence of rotation and is presumed to be stereochemically rigid on the nmr time scale.

2. The dissociation–recombination or "tumbling" mechanism may be discounted, since it would lead to the equivalence of *all four* pyrazolyl groups at high temperature. Thus, the uncoordinated pyrazolyl group maintains its separate identity.

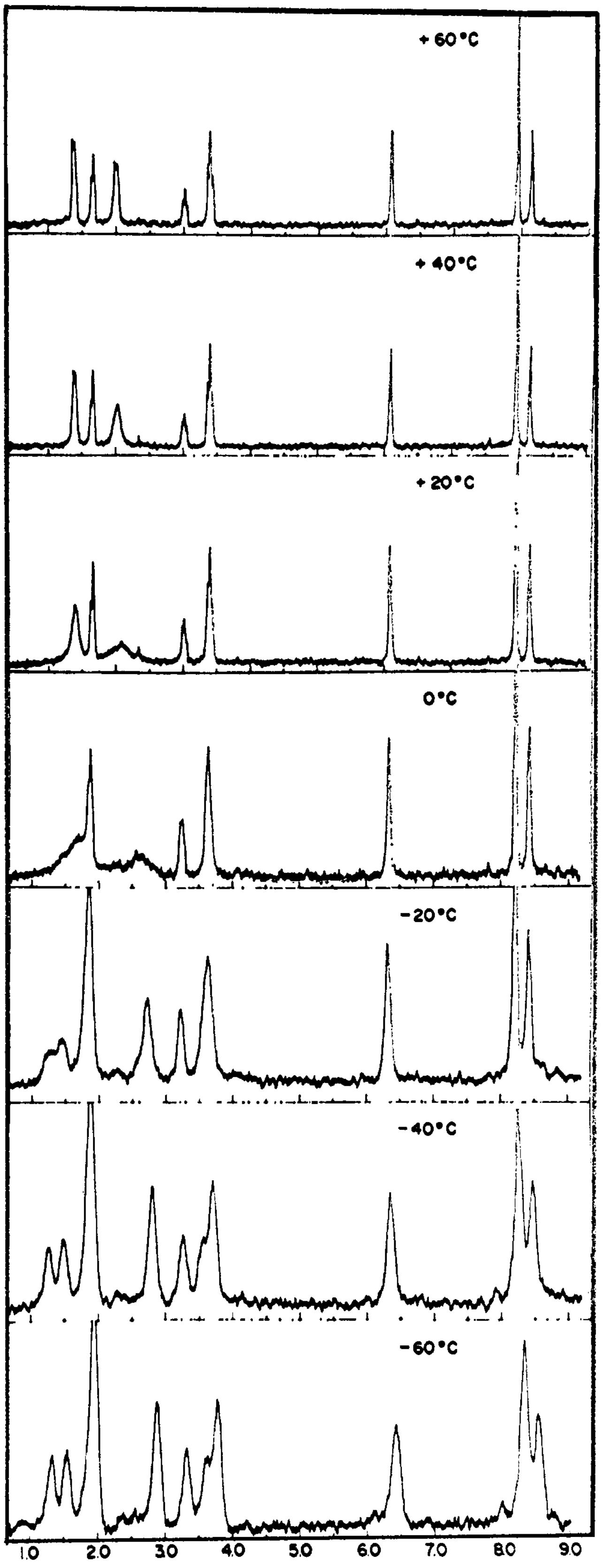


Figure 4. The temperature-dependent nmr spectrum of B(pz)$_4$-Mo(CO)$_2$-π-CH$_2$CMeCH$_2$ at 60 MHz in CDCl$_3$.

3. The process by which the 3-H's of coordinated pyrazolyl groups become equivalent is most likely a rotation of the tridentate ligand around the B–Mo axis.

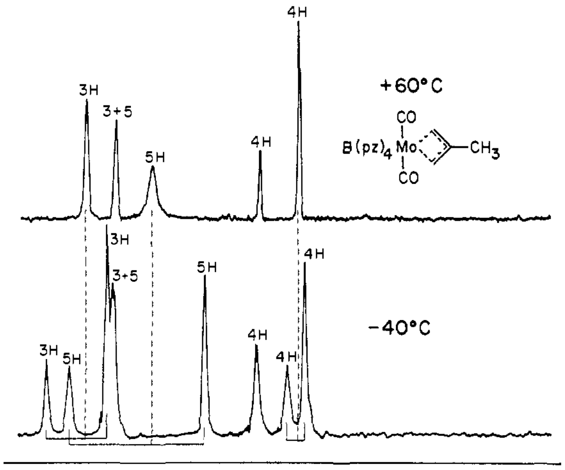


Figure 5. The temperature-dependent nmr spectrum of $B(pz)_4$-$Mo(CO)_2$-π-CH_2CMeCH_2 at 220 MHz in $CDCl_3$ ($B(pz)_4$ portion only).

4. The reason for nonequivalence of the 5-H's of the coordinated pyrazolyl groups is caused by the loss of C_{3v} symmetry introduced into the $B(pz)_4$ ligand by the presence of the fourth pyrazolyl group. At low temperatures, the pyrazolyl group is probably close to bisecting the C_2 symmetry axis;[9] at high temperatures the fourth pyrazolyl group begins to rotate, thus averaging the environment of the 5-H's.

5. The two processes, *i.e.*, rotation of the ligand around the B–Mo axis and rotation of the fourth pyrazolyl group, are independent of each other.

The data do not lend themselves to accurate calculation of absolute activation energies for these rotational processes. However, it is possible to compare the relative heights of the rotational energy barriers from the temperature at which the signal associated with a particular rotational process broadens. Surprisingly, the barrier for the rotation of the fourth pyrazolyl group (broadening at >40°) is higher than that for the rotation of the ligand as a whole (broadening at ~20°). However, X-ray data[10] indicate that a considerable "pinback" effect bends the three coordinated pyrazolyl groups toward the fourth one and thus restricts rotation through nonbonding interactions between the 5-H's and the uncoordinated pyrazolyl group. When the relatively large and planar pyrazolyl group is replaced by the smaller and more flexible *n*-butyl group as in $BuB(pz)_3Mo(CO)_2$-π-C_3H_5, the 25° nmr spectrum shows a sharp doublet for the 5-H while at the same time the 3-H doublet has collapsed to an indistinct broad hump. It seems, therefore, that a fairly sizable and rigid boron substituent R is required for its rotation around the R–B bond to be observed. We may note at this point that $B(pz)_4Mn(CO)_3$ shows no 2:1 splitting of the 5-H's because of restricted rotation of the uncoordinated pyrazolyl group down to −30°. This is thought to be caused by a decrease in the "pinback" effect because Mn is smaller than Mo. This 2:1 splitting should be observable in, *e.g.*, $B(pz)_4Re(CO)_3$. Furthermore, replacement of a carbonyl group by the larger π-allyl group will possibly distort the $B(pz)_4$ ligand by increasing the N–B–Mo angle and thus raising the barrier to rotation of the uncoordinated pyrazolyl group. Thus no restriction of rotation is observed in $B(pz)_4Mo(CO)_3^-$ at room temperature.

It is difficult to speculate on the finer points of these rotational processes in the absence of precise data on bond distances and angles. Nevertheless, some generalizations may be made from the nmr spectra of many substituted $RB(pz)_3M(CO)_2$-π-C_3H_5 compounds. One would expect, *a priori*, that the main process—rotation of the $RB(pz)_3$ ligand as a whole—would be sensitive to (1) the length of the N–M bond and thus to the atomic radius of M and, possibly, to the presence of electron-donating or -withdrawing substituents on the $RB(pz)_3$ ligand; (2) the size of substituents at the 3 position; and (3) the size and electronegativity of substituents on the π-allyl group.

The temperature-dependent nmr spectra of the corresponding Mo and W compounds were almost superimposable, which is not surprising in view of their rather similar atomic radii. Instability of the Cr analog precluded comparison with this first-row transition metal.

With regard to electronic effects of remote substituents, only those containing electron-withdrawing groups (Cl, Br, CN, NO_2) at all the 4 positions were available for comparison, because convenient synthetic routes to 4-alkoxy- or 4-dialkylaminopyrazoles were lacking. The nmr spectra of the negatively substituted compounds and of parent $HB(pz)_3Mo(CO)_2$-π-C_3H_5 hardly differed, except for increased sharpness of the former as a result of removal of 3,4 and 4,5 spin coupling. One can conclude that electronic effects play a minor role and that the height of the rotational barrier is governed primarily by steric factors. The barrier should, therefore, be sensitive to substitution at the π-allyl group and at the 3 positions. Let us consider the π-allyl group first.

In order to decide whether substitution at the central carbon atom or its *anti* positions[11] hinders rotation more, the nmr spectra of appropriately substituted complexes were examined.

In $HB(pz)_3Mo(CO)_2$-π-$CH_2CC_6H_5CH_2$, the limiting spectra were quite similar to those of the methallyl analog (Figure 6) except that collapse of the 3-H peak was quite pronounced already at +30°. This was to be expected, considering the relative sizes of CH_3 and C_6H_5 groups. Surprisingly, however, the room-temperature nmr spectrum of $HB(pz)_3Mo(CO)_2$-π-C_3H_5 had the 3-H peak collapsed as much or, possibly, more than the π-phenallyl and certainly much more so than the π-methallyl analog. This could be seen particularly well by comparing the room-temperature nmr spectra of $HB(4\text{-}Brpz)_3Mo(CO)_2$-π-$C_3H_5$ and $HB(4\text{-}Brpz)_3Mo$-$(CO)_2$-π-CH_2CMeCH_2 where the 3-H and 5-H peaks

---

[9] It is of interest in this context whether any preference is shown for keeping the 5-H or the nonbonding electron pair in the least sterically hindered position. The relative sizes of a hydrogen *vs.* a nonbonding electron pair have been the subject of some debate. For instance, N. L. Allinger and J. C. Tai (*J. Am. Chem. Soc.*, **87**, 1227 (1965)) conclude that the steric effects of a hydrogen are larger than those of an electron pair, while the opposite conclusion is stated by J. B. Lambert and R. G. Keske (*ibid.*, **88**, 620 (1966)).

[10] As extrapolated from the structure of $[H_2B(pz)_2]_2Co$ determined by Dr. C. T. Prewitt (unpublished work).

[11] Unfortunately, there is no consensus with regard to the numbering of the π-allyl substituents. Thus Fischer and Werner call the central position 3, its *syn* position 2, and *anti* 1 (E. O. Fischer and H. Werner, "Metal π-Complexes," Elsevier Publishing Co., Amsterdam, 1966, p 179), while Green and Nagy call the central position 1, its *syn* position 2, and *anti* 3 (M. L. H. Green and P. L. Nagy, *Advan. Organometal. Chem.*, 2 331 (1964)). In order to avoid confusion the *syn–anti* nomenclature will be followed in this paper.

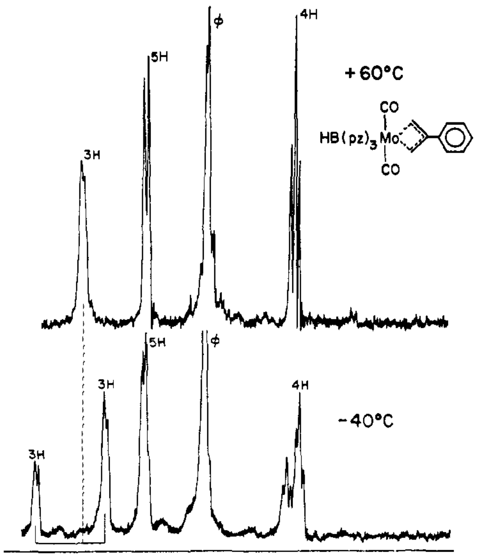


Figure 6. The limiting nmr spectra of $HB(pz)_3Mo(CO)_2$-π-$CH_2CC_6H_5CH_2$ at 60 MHz in $CDCl_3$ ($HB(pz)_3$ portion only).

are singlets. In the former the 3-H was a broad hump (width at half-height ~30 cps) with an indication of resolving into the 2:1 pattern while the 5-H was a sharp (half-height width 1.9 cps) singlet. In the latter the 3-H peak was still fairly sharp as compared with the 5-H singlet (half-height widths 2.5 and 1.5 cps, respectively). It appeared thus that a π-CH_2CMeCH_2 substituent hinders rotation less than an unsubstituted π-allyl group!

To establish this more clearly, it was necessary to magnify the steric hindrance of the $RB(pz)_3$ ligand by replacing the 3-H with a larger group, such as methyl, and, accordingly, compounds $HB(3,5\text{-}Me_2pz)_3Mo(CO)_2$-π-$CH_2CRCH_2$ (R = H, Me, C_6H_5) were synthesized. As noted before,[6] $HB(3,5\text{-}Me_2pz)_3Mo(CO)_3^-$ does not react with allyl bromide to yield the π-allyl derivative. However, the desired compounds could be obtained by preparing $(MeCN)_2Mo(CO)_2Cl$-π-C_3H_5,[12] or the appropriate substituted analogs, and treating them with $HB(3,5\text{-}Me_2pz)_3^-$. The resulting π-allyl compounds were similar in many ways to the unsubstituted ones. It follows, therefore, that while there is no overriding steric bar to the existence of such compounds, there is such a bar for the more crowded transition state in the S_N2-type reaction of the nucleophile $HB(3,5\text{-}Me_2pz)_3Mo(CO)_3^-$. However, when $HB(3,5\text{-}Me_2pz)_3^-$ reacts with $(MeCN)_2Mo(CO)_2Cl$-π-C_3H_5, the reaction may proceed by the less sterically demanding dissociative mechanism.

The compounds $HB(3,5\text{-}Me_2pz)_3Mo(CO)_2$-π-$CH_2CRCH_2$ were yellow, air-stable solids, sublimable *in vacuo* and soluble in common organic solvents. Their infrared spectra contained two strong carbonyl bands displaced by ~13 and ~20 cm^{-1} (the higher and lower ν peaks, respectively) toward lower frequency, as compared with their $HB(pz)_3$ analogs. This, again, is the same type of shift as observed in the anions,[6] and it is consistent with transmittal of the inductive effect from the methyl groups *via* the metal to the carbonyls.

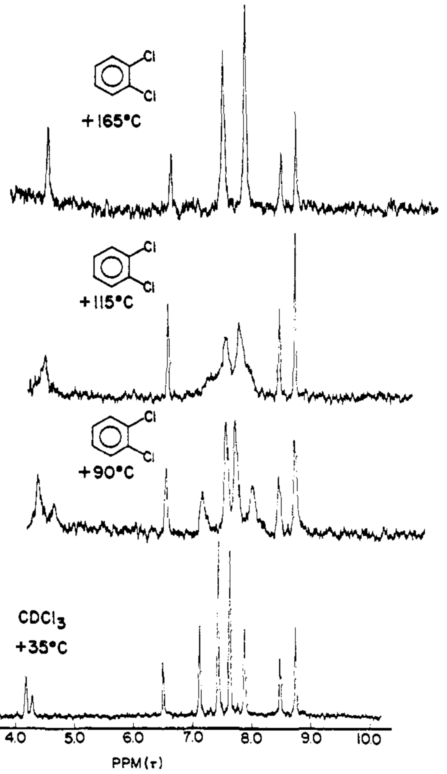


Figure 7. The temperature-dependent nmr spectrum of $HB(3,5\text{-}Me_2pz)Mo(CO)_2$-π-$CH_2CMeCH_2$ at 60 MHz in $CDCl_3$ and in *o*-dichlorobenzene.

The nmr spectra of these compounds were all "static" at room temperature, *i.e.*, the 3- and 5-methyls and the 4-H of the pyrazolyl groups fell into 2:1 patterns. However, rotation of the ligand could be effected by heating, although much higher temperatures were required than for the unsubstituted $HB(pz)_3$ systems. Figure 7 shows the temperature-dependent nmr spectrum of $HB(3,5\text{-}Me_2pz)_3Mo(CO)_2$-π-$CH_2CMeCH_2$. No significant rotation is noted up to 115° but at 165° all three pyrazolyl groups are equivalent as can be seen from the collapse of the 2:1 pattern for the methyls and the 4-H into sharp singlets. By contrast, the π-C_3H_5 and π-$CH_2CC_6H_5CH_2$ analogs even at 165° show only partial collapse of the 2:1 peak patterns and their 165° spectra resembled the 115° spectrum of $HB(3,5\text{-}Me_2pz)_3Mo(CO)_2$-π-$CH_2CMeCH_2$. In all these compounds the π-allyl peaks remain temperature independent. This strikingly demonstrates that a methallyl group interferes least with ligand rotation.

It is unclear why the presence of a methyl group instead of a hydrogen should reduce the steric hindrance (and the effect is undoubtedly steric in nature) to the rotation of an $RB(pz)_3$ ligand. One might suspect a clue in the fact that the nmr spectrum of a π-allyl group in $RB(pz)_3M(CO)_2$-π-C_3H_5 is not typical (where one sees the multiplet and the *syn* and *anti* doublets at progressively higher fields and well separated) in having the multiplet and the *syn* signals overlap to give a multiplet with one sharp, prominent peak. This, however, might only indicate a coincidence of the appropriate chemical shifts, since the unsubstituted π-allyl group in a compound such as $HB(3,5\text{-}Me_2pz)_3Mo(CO)_2$-π-$C_3H_5$ has a normal nmr spectrum but gives rise to a higher rotational energy barrier than the

---

(12) R. G. Hayter, *J. Organometal. Chem.*, **13**, P1 (1968).

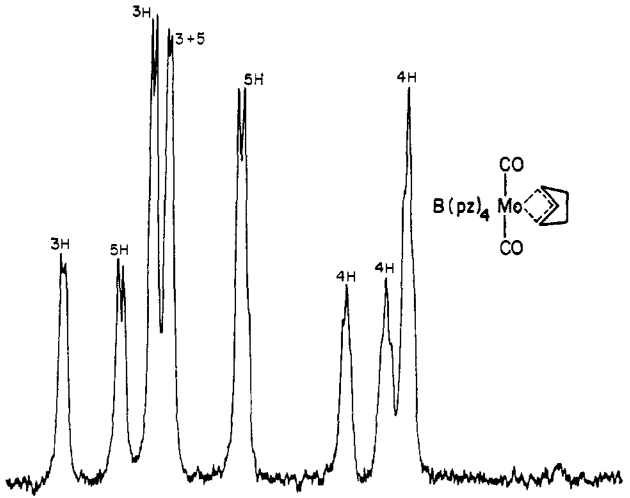


Figure 8. The nmr spectrum of B(pz)$_4$Mo(CO)$_2$-π-cyclopentenyl at 60 MHz in CDCl$_3$ (B(pz)$_4$ portion only).

methylated analog. An interpretation based on the π-allyl group being midway between conformations A and B (Figure 3) is untenable because then the limiting low-temperature nmr spectrum should exhibit a 1:1:1 pattern as all three pyrazolyl groups would be different. A rationalization based on a fast σ–π equilibration of the unsubstituted allyl group, which would increase its effective bulk, is not particularly attractive either.

One could argue that the least sterically hindered conformation of the π-allyl group (A or B), *i.e.*, the one which this group will assume, may impart a higher degree of steric interference to rotation of the RB(pz)$_3$ ligand than the more hindered conformation. In this sense the RB(pz)$_3$Mo(CO)$_3$-π-CH$_2$CRCH$_2$ system is different from C$_5$H$_5$Mo(CO)$_2$-π-CH$_2$CRCH$_2$. In the latter nonbonded interaction of the ring hydrogen with a methyl group was clearly greater than with the *anti* hydrogens, and consequently opposing conformations were adopted by the allyl and methallyl groups. Of course, regardless of the π-allyl conformation, rotation of the C$_5$H$_5$ ring was unaffected (*i.e.*, its local C$_{5v}$ symmetry remained undisturbed) at the temperatures studied. In the RB(pz)$_3$ ligand there is a fair amount of space between the pyrazolyl groups, and molecular models[13] indicate that a methyl group could be accommodated with relative ease. Perhaps the fact that the 4-H in HB(3,5-Me$_2$pz)$_3$Mo(CO)$_2$-π-C$_3$H$_5$ is a singlet but splits into a 2:1 pattern for the π-CH$_2$CMeCH$_2$ and π-CH$_2$CC$_6$H$_5$CH$_2$ analogs could be interpreted as implying the former to exist in conformation B (Figure 3) and the latter two in conformation A which would maximize the interaction of the methyl or phenyl group with the 4-H. This, however, fails to explain why rotation is least impeded by the π-methallyl group.

While the phenyl substituent on the central carbon of the π-allyl group slowed the rotational process somewhat, disubstitution at the *anti* positions had a much more pronounced effect. Thus, the 25° nmr spectrum of B(pz)$_4$Mo(CO)$_2$-π-cyclopentenyl (Figure 8) was characteristic of the limiting low-temperature spectrum (like B(pz)$_4$Mo(CO)$_2$-π-C$_3$H$_5$ at $-60°$), and it remained unchanged to $+130°$. Some broadening of the peaks was observed at $+160°$ (in dimethylacetamide), but no spectrum of a freely rotating RB(pz)$_3$ ligand was observed and decomposition began at higher temperatures. The high barrier to rotation in this system might indicate conformation B, but this conclusion is tentative.

Of the three types of dynamic behavior manifested in transition metal polypyrazolylborates, *viz.*, "tumbling," rotation of the planar boron substituent, and rotation of the tridentate ligand around the B–M axis, the former two have ample analogy in other systems. For instance, tumbling is evident in Zr(BH$_4$)$_4$ where all protons are equivalent[14] in the nmr spectrum and yet on the faster time scale of infrared spectroscopy two types of hydrogens are discernible. Hindered rotation of a substituent which can be observed by nmr as reversible splitting of a single peak into a 2:1 pattern has been reported, for instance, for the adduct of tetrafluorobenzyne to *t*-butylbenzene.[15]

It is more difficult to find a direct analogy to rotation of an RB(pz)$_3$ ligand. The numerous systems containing dynamic *monohapto*-[16] or *trihapto*-C$_5$H$_5$[17] or the dynamic cyclooctatetraene complexes are not centrosymmetric in their instantaneous structure, and dynamic equivalence of the C$_n$H$_n$ protons is achieved not by rotation around the center-of-gravity axis of the polycycle, but rather by a precessional movement of the metal, along with its other ligands, around a suitable orbit within the C$_n$H$_n$ perimeter.

The closest analogy would be, probably, π-C$_5$H$_5$ in half-sandwich complexes, where an instantaneous structure would have the C$_5$H$_5$ hydrogens in several types of environment with regard to the other metal ligands. However, an nmr spectrum corresponding to the instantaneous structure has never been observed because of the very low activation energy for moving from one instantaneous structure to a succession of equivalent but nonidentical structures, *i.e.*, for rotation of the C$_5$H$_5$ ligand. Other substituents on the metal, while sterically interacting with the cyclopentadienyl hydrogens, *e.g.*, in C$_5$H$_5$Mo(CO)$_2$-π-CH$_2$CMeCH$_2$,[13] do not raise that barrier sufficiently to be manifested by broadening of the C$_5$H$_5$ peak, much less by observation of a limiting spectrum. This ought to be possible in cyclopentadienyl systems containing bulky substituents, *e.g.*, in pentakis(isopropyl)cyclopentadienyl half-sandwiches. Thus far, however, RB(pz)$_3^-$ is the only ligand whose rotation around a transition metal lends itself to convenient study by nmr.

Experimental Section

The polypyrazolylborate ligands[4,5] and the various π-allyl complexes[6] were prepared according to published procedures. Since these compounds are not air sensitive, no special precautions in their handling were necessary.

The nmr spectra were recorded on a Varian A-60T spectrometer as well as on a Varian HR-220, both equipped with a variable-

---

(13) The Stuart–Briegleb models offer some help in deciding on the relative extent of steric interference in RB(pz)$_3$Mo(CO)$_3$-π-allyl compounds. However, in the absence of X-ray structural data on these systems, any conclusions must be treated with extreme caution.

(14) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *J. Chem. Soc.*, 182 (1966).

(15) J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 28 (1967).

(16) F. A. Cotton, A. Musco, and G. Yagupsky, *J. Am. Chem. Soc.*, **89**, 6136 (1967); for the *hapto* nomenclature, see F. A. Cotton, *ibid.*, **90**, 6230 (1968).

(17) R. B. King, *Inorg. Chem.*, 7, 90 (1968).

temperature probe. The solvents employed were of the best commercial grade available and were used without further purification.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratedicarbonylmolybdenum-π-allyl. To a suspension of 26.4 g (0.1 mole) of molybdenum hexacarbonyl in 200 ml of acetonitrile was added 15 ml (excess) of allyl bromide. The reaction mixture was stirred and heated until 10 l. of gas, as measured by a wet-test meter, was evolved. About 50 ml of liquid was then distilled out under nitrogen, and after the mixture was cooled, a suspension of 35 g (0.11 mole) of $KHB(3,5\text{-}Me_2pz)_3$ was added. The reaction mixture was stirred at 45° for 20 min and was then drowned in 1.5 l. of cold water containing 10 ml of concentrated hydrochloric acid. The product was filtered off and obtained in 31.6 g (64.6%) yield after chromatography on alumina. It was purified further by recrystallization from toluene; the yellow crystals turn red on heating and gradually decompose from about 250°. This compound is reversibly thermochromic (yellow $\rightleftharpoons$ red).

When previously isolated $(MeCN)_2Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ was used in the above reaction, the yield rose to 70.4%.

Anal. Calcd for $C_{20}H_{27}BMoN_6O_2$: C, 49.0; H, 5.52; N, 17.1. Found: C, 49.0; H, 5.71; N, 17.1. Ir (cyclohexane): CO at 1944 and 1850 cm^{-1}. Uv (cyclohexane): 380 mμ (ε 1320); sh 260 (13,900); 218 (36,600). Nmr ($CDCl_3$): τ s 4.23, m ~5.9, d (J = 7 cps) 6.34; s, 7.15, s, 7.57, s 7.67, s 7.82, d (J = 10 cps) 8.07 in 3:1:2:3:6:6:3:2 ratio. These peaks were assigned,[18] respectively, to the 4-H, π-allyl central H, *syn*-H's, 3-methyls (1 + 2), 5-methyls (2 + 1), and *anti*-H's.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratedicarbonylmolybdenum-π-2-phenylallyl. This compound was obtained as yellow crystals in 18% yield by the above procedure. After recrystallization from toluene–heptane mixture, it decomposed gradually from ~240°.

Anal. Calcd for $C_{26}H_{31}BMoN_6O_2$: C, 55.1; H, 5.48; N, 14.8. Found: C, 55.1; H, 5.97; N, 14.8. Ir (cyclohexane) CO at 1947, 1861 cm^{-1}. Nmr (CDCl): τ m 3.1–3.5, s 4.31, s 4.38, s 5.95, s. 7.15, s 7.43, s 7.90, s 8.03, s 8.46 in 5:2:1:2:3:6:6:3:2 ratio assigned, respectively, to phenyl, 4-H's (2 + 1), 3-Me (1 + 2), 5-Me (2 + 1), and *anti*-H's.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratedicarbonylmolybdenum-π-2-methylallyl. This compound was obtained as yellow crystals in 23% yield by the above procedure. After recrystallization from toluene it melts at 264–266° dec when placed in the apparatus at 250°. When heated gradually from room temperature, it slowly decomposes from 255°.

Anal. Calcd for $C_{21}H_{29}BMoN_6O_2$: C, 50.0; H, 5.75; N, 16.7. Found: C, 50.5; H, 5.68; N, 16.7. Ir (cyclohexane): 1945, 1853 cm^{-1}. Nmr ($CDCl_3$): singlets at τ 4.17, 4.28, 6.51, 7.13, 7.44, 7.65, 7.89, 8.50, and 8.75 in 2:1:2:3:6:6:3:2:3 ratio assigned, respectively, to 4-H (2 + 1), *syn*-H's, 3-Me (1 + 2), 5-Me (2 + 1), *anti*-H's, and 2-Me.

Hydrotris(4-bromo-1-pyrazolyl)boratedicarbonylmolybdenum-π-allyl. This compound was obtained as yellow crystals in 36% overall yield by the three-step sequence published earlier.[6] It was recrystallized from toluene; decomposes gradually from 260°.

Anal. Calcd for $C_{14}H_{12}BBr_3MoN_6O_2$: C, 26.1; H, 1.87; Br, 37.3; N, 13.15. Found: C, 26.7; H, 2.00; Br, 37.3; N, 13.1 Ir (cyclohexane): 1964, 1883 cm^{-1}. Nmr ($CDCl_3$): broad (~30 cps) hump τ ~1.8, s 2.24, m with sharp peak at 6.22, d (J = 9.0 cps) 8.30 in 3:3:3:2 ratio, assigned to 3-H's, 5-H's, central π-allyl H, *syn*-H's, and *anti*-H's.

Hydrotris(4-bromo-1-pyrazolyl)boratedicarbonylmolybdenum-π-2-methylallyl. This compound was prepared by the above procedure and was obtained as yellow crystals in 36% yield. It was recrystallized from toluene, mp 242–244°.

Anal. Calcd for $C_{15}H_{14}BBr_3MoN_6O_2$: C, 27.4; H, 2.13; N, 12.8. Found: C, 27.8; H, 2.19; N, 12.7. Ir (cyclohexane): 1965, 1884 cm^{-1}. Nmr ($CDCl_3$): singlets at τ 1.68, 2.21, 6.34, 8.22, and 8.34 in 3:3:2:3:2 assigned to 3-H's, 5-H's, *syn*-H's, methyl, and *anti*-H's.

---

[18] The assignment of the 3-Me and 5-Me rests on (a) greater difference in chemical shifts expected for the nonidentical 3-methyls than for 5-methyls and (b) faster collapse of the 5-methyls than for the 3-methyls as observed in the limiting high-temperature spectrum for $HB(3,5\text{-}Me_2pz)_3Mo(CO)_2\text{-}\pi\text{-}CH_2CMeCH_2$ and partially collapsed high-temperature spectra of the π-allyl and $\pi\text{-}CH_2C(C_6H_5)CH_2$ analogs.

Kinetics and Mechanisms of the Reduction of Chromium(VI) by Substitution-Inert Iron(II) Complexes in Acidic Aqueous Solution

James P. Birk

*Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania,
Philadelphia, Pennsylvania 19104.* *Received November 25, 1968*

Abstract: The kinetics of the reaction of chromium(VI) with $Fe(CN)_6{}^{4-}$, $Fe(bip)(CN)_4{}^{2-}$ (bip = 2,2′-bipyridine), $Fe(bip)_2(CN)_2$, and $Fe(bip)_3{}^{2+}$ have been examined over wide ranges of initial concentrations at 25.0° in perchlorate solutions of 0.50 M ionic strength. Each reaction follows the rate equation, $-d[HCrO_4{}^-]/dt = k_2[HCrO_4{}^-]\cdot[Fe(II)]$, where k_2 is a complex function of $[H^+]$. A major product of the reactions of the cyanoiron(II) complexes is in each case apparently a Cr(III)–Fe(III) binuclear complex. A comparison of these results with those of previous studies on related systems indicates that the form of the rate equation can be correlated quite well with the relative substitution-inertness of one-equivalent reducing agents.

The reduction of chromium(VI) by one-equivalent reducing agents and oxidation of chromium(III) by one-equivalent oxidizing agents has been interpreted in terms of three successive one-electron transfer steps.[1–5]

$$Cr^{VI} + Red \underset{k_{56}}{\overset{k_{65}}{\rightleftharpoons}} Cr^{V} + Ox \quad (1)$$

$$Cr^{V} + Red \underset{k_{45}}{\overset{k_{54}}{\rightleftharpoons}} Cr^{IV} + Ox \quad (2)$$

$$Cr^{IV} + Red \underset{k_{34}}{\overset{k_{43}}{\rightleftharpoons}} Cr^{III} + Ox \quad (3)$$

For most such reactions studied (oxidation of Cr(III)

---

[1] J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, 82, 3805 (1960).