$$CuA_2{}^{2+} + CuB_2{}^{2-} \rightleftharpoons 2CuAB \qquad (11)$$

This means, the driving "forces" are coulombic attraction and a decrease in the orientation of the outer sphere solvent molecules (hence, enthalpy and entropy effects, respectively).

Finally, it is of interest to note that for all the systems listed in Table III the values for $\Delta \log K$ are negative, *i.e.*, equilibrium 7 is on its left side. This is obviously characteristic for ternary complexes containing an *aliphatic* amine and in contrast to those formed with *aromatic* amines.[10,11] A more detailed comparison can be made based on the data listed in Table IV which are due to ethylenediamine–Cu^{2+}–L systems and the corresponding 2,2'-bipyridyl–Cu^{2+}–L systems. In fact, these results confirm unequivocally the earlier conclusion[10,11] about the stability increasing effect of 2,2'-bipyridyl which was attributed to its π-accepting qualities.[12] As the data of $\Delta \log K$ and $\log X$ show, the mixed-ligand complex in the 2,2'-bipyridyl–Cu^{2+}–L systems is always significantly more stable than the corresponding complex in the ethylenediamine–Cu^{2+}–L system, as long as the second ligand, L, contains at least one oxygen atom as a donor.

Furthermore, the discriminating qualities of the binary Cu^{2+}-2,2'-bipyridyl 1:1 complex are very remarkable; for example, the values of $\Delta \log K$ (*cf.* Table IV) differ for the 2,2'-bipyridyl–Cu^{2+}-oxalate and the 2,2'-bipyridyl–Cu^{2+}-ethylenediamine systems by about 2 log units, *i.e.*, a second ligand with oxygen donors is preferably bound. Compared with this result, the discriminating qualities of the Cu^{2+}-ethylenediamine 1:1 complex are insignificant.

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Infrared Intensity and Nuclear Magnetic Resonance Studies of Steric and Electronic Effects in (Pyrazolylborato)carbonyl Derivatives of Manganese(I)

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Infrared intensity studies of the carbonyl stretching vibrations in $PzB(Pz)_3Mn(CO)_2L$ [Pz = 1-pyrazolyl; L = PCl_3, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(C_6H_{11})_3$] and $HB(CH_3PzCH_3)_3Mn(CO)_2P(OC_6H_5)_3$ [CH_3PzCH_3 = 3,5-dimethyl-1-pyrazolyl] have been carried out. A method is proposed for determining the angles θ between CO vibrators in metal dicarbonyl compounds. Angles calculated for the pyrazolylborate derivatives indicate that the steric properties of the ligands influence the magnitude of the intercarbonyl angles. The electronic nature of the pyrazolylborate ligand is also compared with that of the cyclopentadienyl ligand. Nmr studies were carried out on the compounds $PzB(Pz)_3Mn(CO)_2L$ [L = CO, $P(OCH_3)_3$, $P(CH_3)_3$] and $HB(CH_3PzCH_3)_3Mn(CO)_2L$ [L = CO, $P(OCH_3)_3$, $P(CH_3)_3$, $P(OC_6H_5)_3$]. Whereas free rotation about the B–Mn axis occurred at 5° in the compounds $PzB(Pz)_3Mn(CO)_2L$ and $HB(CH_3PzCH_3)_3Mn(CO)_3$, stereochemical rigidity was observed in $HB(CH_3PzCH_3)_3Mn(CO)_2L$. Results are interpreted in terms of steric and electronic properties of the ligands.

Introduction

A number of substituted phosphine- and phosphite-dicarbonyl derivatives of the type $PzB(Pz)_3Mn(CO)_2L$ [Pz = 1-pyrazolyl] and $HB(CH_3PzCH_3)_3Mn(CO)_2L$ [CH_3PzCH_3 = 3,5-dimethyl-1-pyrazolyl] have been synthesized.[2] Steric properties of the ligand L were found to play an important role in the synthesis. However, no further investigation of the influence of steric effects on the structures of the compounds was reported. Furthermore, the electronic properties of pyrazolylborate ligands are not well understood. Since these tridentate, uninegative ions are analogous to the cyclopentadienide ion, it is of particular interest to compare electronic effects of $PzB(Pz)_3Mn(CO)_2L$ with those of h^5-$C_5H_5Mn(CO)_2L$.[3] A comparison of carbonyl stretching frequencies

for the two series of compounds has been made previously,[2] but other physical measurements have not been reported.

The intensities of the carbonyl stretching vibrations in the infrared spectra of metal carbonyls have been proposed as a probe of electronic effects.[4-8] Results of infrared intensity measurements on a variety of compounds of the type h^5-$C_5H_5Mn(CO)_2L$ have been interpreted in terms of the bonding properties of the cyclopentadienyl ligand.[9] Attempts have also been made to use infrared intensities to determine angles in metal carbonyl derivatives.[10-14] Most of the studies

(1) Taken in part from the Ph.D. thesis of A. R. Schoenberg, University of Delaware, 1973.

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have been carried out on molecules of the type M(CO)₅L in which interpretation of the results is complicated by coupling between the two carbonyl stretching modes having A_1 symmetry. Since coupling between carbonyl stretching vibrations does not occur in cis metal dicarbonyl compounds, analysis of the data should be simpler in principle. Because of the above factors, infrared intensities would seem to be a promising probe of electronic and steric effects in pyrazolylborato-manganese dicarbonyl compounds.

Electronic properties of h^5-C₅H₅Mn(CO)₂L have been investigated by nmr spectroscopy,[15-18] and nmr techniques have also been used as a structural probe in compounds such as RB(Pz)₃Mo(CO)₂L.[19-21] These facts suggest that an nmr analysis of the pyrazolylborate complexes would be fruitful.

In this paper results of infrared intensity and nmr studies of the compounds PzB(Pz)₃Mn(CO)₂L and HB(CH₃PzCH₃)₃-Mn(CO)₂L [L = substituted phosphines and phosphites] are reported and the results related to structural and electronic factors.

Experimental Section

Compounds were prepared by the methods described previously.[2,22]

Samples for infrared intensity studies were weighed on a Cahn RTL electrobalance and placed in volumetric flasks; deoxygenated spectrograde carbon disulfide was added in a nitrogen-filled glove bag.

Infrared intensity measurements were carried out using a Perkin-Elmer Model 180 infrared spectrophotometer and 1.00-mm NaCl cells. Spectra were recorded in linear absorbance mode using a spectral slit width of 1.0-1.5 cm⁻¹, an expanded scale of 2 cm⁻¹/cm of chart paper, and a scanning speed of 5-11 cm⁻¹/min.

The reported integrated absorption intensities were calculated from the expression

$$I_\nu = \frac{2.303}{Cl} \left[\int_{\nu_1}^{\nu_2} \log(I_0/I) \, d\nu \right]$$

where C is the concentration, l is the path length of the cell, and the bracketed expression is the area under the band between frequencies ν_1 and ν_2. Band areas were measured with a planimeter, with integration being carried out over an interval between points which were 24-30 cm⁻¹ on either side of the peak maximum. No wing corrections were made. The reported intensities are the average of four to eight measurements over the concentration range (6-20) × 10⁻⁴ M in CS₂.

Nuclear magnetic resonance spectra were measured by Dr. Walter Freeman on a Varian Model A-60A spectrometer equipped with a V-6040 variable-temperature controller. The probe temperature was measured with Wilmad nmr thermometers. Deoxygenated spectrograde carbon disulfide was used as a solvent with TMS as an internal standard.

Least-squares treatments were carried out on a Burroughs 6700 computer at the University of Delaware Computing Center.

Results and Discussion

Infrared Intensities. The intensities of the symmetric and antisymmetric carbonyl stretching vibrations in cis metal di-

carbonyl compounds are related to electronic and geometric factors through the equations[7]

$$\mu'_s = \frac{\sqrt{I_s}}{0.540 \cos \theta} \tag{1a}$$

$$\mu'_a = \frac{\sqrt{I_a}}{0.540 \sin \theta} \tag{1b}$$

$$\theta = \sin^{-1}\left[\frac{\sqrt{I_a}}{0.540\mu'_a}\right] \approx \cos^{-1}\left[\frac{\sqrt{I_s}}{0.540\mu'_s}\right] \tag{2}$$

In these equations μ'_s and μ'_a are the MCO dipole moment derivatives for the symmetric and antisymmetric vibrations, I_s and I_a are the measured intensities ×10⁻⁴, and 2θ is the angle between M-CO vectors. In general, no simple relationship exists between μ'_s and μ'_a (e.g., $\mu'_s = \mu'_a$).[14,23] Therefore, eq 3 cannot be used in a straightforward fashion to compare

$$\theta = \tan^{-1}\left[\frac{\mu'_s}{\mu'_a}\left(\frac{I_a}{I_s}\right)^{1/2}\right] \tag{3}$$

θ in a series of compounds. However, if the magnitude of μ'_a or μ'_s can be determined in some way, the value of θ can be obtained from the measured intensity through use of eq 2. A method of estimating the value of μ'_a is described below.

The magnitude of μ'_a is generally assumed to be related to the net electron density on the metal.[14] Therefore, a correlation should exist between μ'_a and K_{CO}, the CO stretching force constant.[23] To test this relationship further, values of μ'_a for a number of compounds of the type h^5-C₅H₅Mn-(CO)₂L[9] are plotted (Figure 1) as a function of K_{CO}, determined from reported frequencies using the method of Cotton and Kraihanzel.[24] Based on crystal structure data for h^5-C₅H₅Mn(CO)₃[25] and h^5-C₅H₅Mn(CO)₂(norbornadiene),[26] an angle of 46° was assumed for all compounds. Since steric interactions between the ring and L should be minimal in these compounds, deviations in θ should be small. The least-squares line obtained[27] is given by

$$\mu'_a = -0.489K_{CO} + 15.97 \tag{4}$$

Standard deviation between the values of μ'_a calculated from eq 4 and those obtained from the measured intensities assuming $\theta = 46°$ is 0.13 (1.4%). This is equivalent to an average uncertainty of 0.9° in the value of θ (assuming there is no error in the measured intensities).

It is not known for certain whether the relationship between μ'_a and K_{CO} given in eq 4 is general for all cis metal dicarbonyl compounds or whether the specific relationship between the two parameters is a function of the metal or the ligands trans to CO. Since the ability of the metal to transmit π-electron density to the carbonyls is reflected in the

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(27) Two points (L = P(OC₆H₅)₃ and piperdine) for the manganese system were excluded from the least-squares treatment and from Figure 1 because they had unusually large error associated with the intensity measurements in comparison with other members of the series.
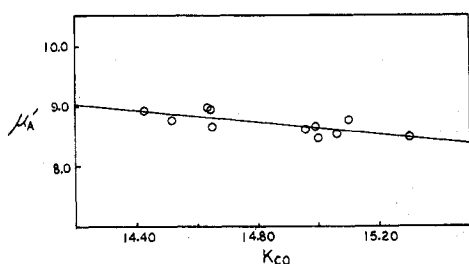
Figure 1. Plot of dipole moment derivatives for antisymmetric carbonyl stretching vibrations as a function of the CO stretching force constant in h^5-$C_5H_5Mn(CO)_2L$. (Data taken from ref 9.)

Table I. Calculated Angles for Iron Dicarbonyl Derivatives

Compd	θ,[a] deg	Compd	θ,[a] deg
h^5-$C_5H_5Fe(CO)_2Cl$	47.7	h^5-$C_5H_5Fe(CO)_2CN$	47.0
h^5-$C_5H_5Fe(CO)_2I$	46.8	h^5-$C_5H_5Fe(CO)_2C(O)$-CH_3	56.5
h^5-$C_5H_5Fe(CO)_2SnCl_3$	45.9	h^4-$C_6H_5CH_2C_5H_5Fe$-$(CO)_2P(C_6H_5)_3$	53.3

[a] Calculated from eq 2 and 4. Data taken from ref 7.

values of μ'_a and K_{CO}, a change in metal might alter the slope and intercept of eq 4. In an attempt to investigate the effect of a change in metal, values of μ'_a were calculated for a series of compounds h^5-$C_5H_5Fe(CO)_2X$ (X = Cl, I, CN, SnCl$_3$, C(O)CH$_3$) using the intensity data of Darensbourg[7] and an angle of 47°.[28,29] Values of the slope (−2.02), intercept (41.57), per cent deviation in μ'_a from the line (2.9%), and average uncertainty in θ (1.8°) were obtained by plotting μ'_a vs. K_{CO}. The per cent deviation in μ'_a and uncertainty in θ are double those found in the manganese series. Furthermore, a drastically different slope (−0.16) and intercept (10.42) were obtained if h^5-$C_5H_5Fe(CO)_2C(O)CH_3$ was eliminated from the plot, suggesting that the angle θ for this derivative deviates significantly from the assumed value of 47°. Since the four remaining points lie within a narrow range of K_{CO}, considerable error in the slope and intercept could be introduced by a small error in the intensity measurements. Because of the problems encountered in our attempts to determine the relationship between μ'_a and K_{CO} from the iron data, an alternative procedure was used to examine the effect of a change in metal. Values of θ were calculated from the reported intensities of the iron derivatives assuming that eq 4 is valid. Results are given in Table I. Angles calculated for h^5-$C_5H_5Fe(CO)_2X$ (X = Cl, I, CN, SnCl$_3$) are in good agreement with the values of 47–48° found in crystal structures of a number of cyclopentadienyliron dicarbonyl compounds.[29] The calculated angle (56.5°) for h^5-C_5H_5Fe-$(CO)_2C(O)CH_3$ is considerably larger, in agreement with the earlier conclusion. Therefore, we believe that eq 4 can be used to obtain reasonable estimates of intercarbonyl angles (2θ) in dicarbonyl compounds other than h^5-$C_5H_5Mn(CO)_2L$. Even if the specific relationship between μ'_a and K_{CO} differs somewhat from eq 4, thereby introducing small errors in the absolute values of θ calculated, trends within a series of similar compounds should be correctly reflected by its use. Of course, final justification must await crystal structure data on h^5-$C_5H_5Fe(CO)_2C(O)CH_3$ or h^4-$C_6H_5CH_2C_5H_5Fe(CO)_2P$-$(C_6H_5)_3$.

Given the above considerations, it seems reasonable to assume that a change in ligands about manganese will not so alter the relationship between μ'_a and K_{CO} that invalid trends in the calculated angles are obtained. Therefore, we have used the measured intensities (Table II), values of K_{CO}, and eq 4 to calculate values of θ for the pyrazolylborate derivatives. Results are given in Table III. Three compounds,

PzB(Pz)$_3$Mn(CO)$_2$P(C$_6$H$_5$)$_3$, PzB(Pz)$_3$Mn(CO)$_2$P(C$_6$H$_{11}$)$_3$, and HB(CH$_3$PzCH$_3$)$_3$Mn(CO)$_2$P(OC$_6$H$_5$)$_3$, have calculated angles which are more than 2° smaller than 46° value used to generate eq 4. It is significant that P(C$_6$H$_5$)$_3$ and P(C$_6$H$_{11}$)$_3$ have the largest cone angles[30] of the ligands L used. Thus, appreciable steric interactions between the pyrazolylborate ligand and L occur in PzB(Pz)$_3$Mn(CO)$_2$L when L is a bulky ligand leading to a decrease in the intercarbonyl angle. The same conclusion is reached if one examines the trend in θ within the series PzB(Pz)$_3$Mn(CO)$_2$L. The P(C$_6$H$_{11}$)$_3$ derivative has a significantly smaller angle than the P(OC$_6$H$_5$)$_3$ and P(C$_4$H$_9$)$_3$ derivatives.[31] The compound HB(CH$_3$PzCH$_3$)$_3$Mn-(CO)$_2$P(OC$_6$H$_5$)$_3$ has a significantly smaller angle than PzB-(Pz)$_3$Mn(CO)$_2$P(OC$_6$H$_5$)$_3$. Therefore, increased steric requirements of the substituted pyrazolylborate ligand also lead to a decrease in θ.

Values of μ'_s/μ'_a for the pyrazolylborate compounds are also given in Table III. These values are only slightly lower than those determined previously for phosphine and phosphite derivatives of the type h^5-$C_5H_5Mn(CO)_2L$. This indicates that vibronic contributions[14] to μ'_s are similar in the two series. Since vibronic contributions to μ'_s are generally attributed primarily to the π-acceptor ability of the ligands trans to the carbonyl groups,[7,14] our results suggest that the C$_5$H$_5^-$ is only a slightly better π acceptor than PzB(Pz)$_3^-$.

Nuclear Magnetic Resonance Spectra. The nmr spectra of the compounds PzB(Pz)$_3$Mn(CO)$_2$L (L = CO, P(OCH$_3$)$_3$) and HB(CH$_3$PzCH$_3$)$_3$Mn(CO)$_2$L (L = CO, P(OCH$_3$)$_3$, P(OC$_6$H$_5$)$_3$) in CS$_2$ are shown in Figures 2 and 3. Although low solubility in solvents hindered nmr studies, some informative results were obtained.

Spectra for the two tricarbonyl compounds are independent of temperature over the range −20 to +120° and are in agreement with the results in CDCl$_3$ reported by Trofimenko.[19] The spectrum of PzB(Pz)$_3$Mn(CO)$_3$ consists of a multiplet at τ 2.2–2.3 corresponding to the 3-H and 5-H of coordinated and uncoordinated pyrazolyl groups and peaks at τ 3.45 and 3.82, having a ratio of 1:3, corresponding to the 4-H of the uncoordinated and coordinated pyrazolyl groups. In the spectrum of HB(CH$_3$PzCH$_3$)$_3$Mn(CO)$_3$ peaks at τ 4.29, 7.56, and 7.70 having a ratio 1:3:3 correspond to the 4-H, 3-CH$_3$, and 5-CH$_3$ of the coordinated pyrazolyls.

If one carbonyl group is replaced by a ligand L, the observed spectrum depends on whether or not there is free rotation of the pyrazolylborate ligand about the manganese. If free rotation occurs, only one kind of coordinated pyrazolyl will be observed. On the other hand, if the pyrazolylborate

(28) This value was chosen on the basis of angles determined for a number of compounds of the type h^5-$C_5H_5Fe(CO)_2L$.[29]

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(31) Data for PzB(Pz)$_3$Mn(CO)$_2$L (L = PCl$_3$, P(OC$_6$H$_5$)$_3$, P(C$_4$H$_9$)$_3$) were also used to determine the relationship between μ'_a and K_{CO} assuming θ = 45° and the resulting equation was used to calculate θ for PzB(Pz)$_3$Mn(CO)$_2$P(C$_6$H$_5$)$_3$, PzB(Pz)$_3$Mn(CO)$_2$P-(C$_6$H$_{11}$)$_3$, and HB(CH$_3$PzCH$_3$)$_3$Mn(CO)$_2$P(OC$_6$H$_5$)$_3$. Values obtained were 42.3, 40.9, and 42.0°, respectively. Therefore, in spite of the extremely limited data used to determine the line, conclusions identical with those resulting from the use of eq 4 were obtained.

Table II. Infrared Intensities of the Carbonyl Stretching Vibrations in the Compounds
$PzB(Pz)_3Mn(CO)_2L$ and $HB(CH_3PzCH_3)_3Mn(CO)_2P(OC_6H_5)_3$

Compd	$\nu_s{}^a$	$\nu_a{}^a$	$I_s{}^b$	$I_a{}^b$	K_{CO}
$PzB(Pz)_3Mn(CO)_2PCl_3$	1993	1930	7.73 (0.05)	9.99 (0.04)	15.54
$PzB(Pz)_3Mn(CO)_2P(OC_6H_5)_3$	1968	1893	7.7 (0.1)	11.04 (0.07)	15.06
$PzB(Pz)_3Mn(CO)_2P(C_6H_5)_3$	1940	1862	9.30 (0.08)	10.9 (0.2)	14.60
$PzB(Pz)_3Mn(CO)_2P(C_4H_9)_3$	1931	1853	8.9 (0.10)	12.3 (0.2)	14.46
$PzB(Pz)_3Mn(CO)_2P(C_6H_{11})_3$	1928	1848	8.4 (0.2)	10.7 (0.2)	14.40
$HB(CH_3PzCH_3)_3Mn(CO)_2P(OC_6H_5)_3$	1956	1877	8.96 (0.05)	10.30 (0.05)	14.84

a In cm^{-1}. *b* In units of 10^4 l. mol^{-1} cm^{-2}. Numbers in parentheses are standard deviations from the mean.

Table III. Calculated Angles and Dipole Moment Derivatives for the
Compounds $PzB(Pz)_3Mn(CO)_2L$ and
$HB(CH_3PzCH_3)_3Mn(CO)_2P(OC_6H_5)_3$

Compd	$\theta,{}^a$ deg	$\mu'_s{}^b$	$\mu'_a{}^b$	$\mu'_s/\mu'_a{}^b$	Ligand cone angles,^{c} deg
$PzB(Pz)_3Mn(CO)_2PCl_3$	44.4	7.20	8.37	0.86	125
$PzB(Pz)_3Mn(CO)_2P(OC_6H_5)_3$	45.6	7.35	8.61	0.85	121
$PzB(Pz)_3Mn(CO)_2P(C_6H_5)_3$	43.8	7.82	8.83	0.89	145
$PzB(Pz)_3Mn(CO)_2P(C_4H_9)_3$	46.9	8.10	8.90	0.91	130
$PzB(Pz)_3Mn(CO)_2P(C_6H_{11})_3$	42.7	7.30	8.93	0.82	179
$HB(CH_3PzCH_3)_3Mn(CO)_2P-(OC_6H_5)_3$	43.0	7.58	8.72	0.87	121

a Calculated from eq 2 and 4. Estimated uncertainty ±1°. *b* Based
on the angle θ determined from eq 2 and 4. *c* See ref 30.
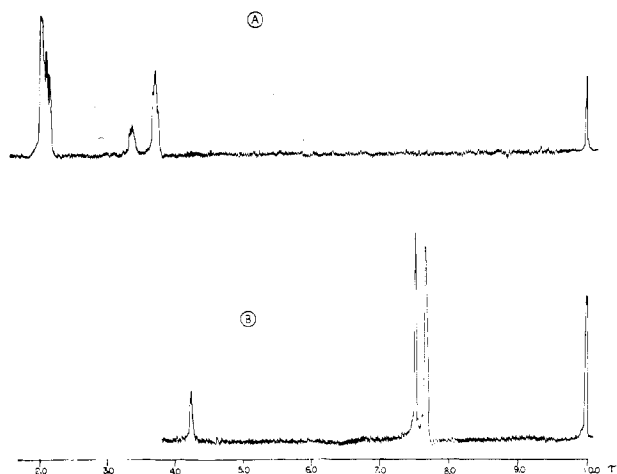
Figure 2. Nmr spectra of $PzB(Pz)_3Mn(CO)_3$ (A) and $HB(CH_3PzCH_3)_3$-$Mn(CO)_3$ (B). TMS reference peak is also shown.

Figure 3. Nmr spectra of $PzB(Pz)_3Mn(CO)_2P(OCH_3)_3$ (A),
$HB(CH_3PzCH_3)_3Mn(CO)_2P(OCH_3)_3$ (B), and $HB(CH_3PzCH_3)_3Mn$-
$(CO)_2P(OC_6H_5)_3$ (C) at 5°. TMS reference peak is also shown.

ligand is locked into position, two coordinated pyrazolyls
are of one type (trans to CO) and the third is unique (trans
to L) (see Figure 4). Further splittings can be observed if
the uncoordinated pyrazolyl group of the $PzB(Pz)_3{}^-$ ligand
is not freely rotating. The temperature-dependent nmr spec-
trum of $PzB(Pz)_3Mo(CO)_2$-h^3-$CH_2C(CH_3)CH_2$ reported by
Trofimenko[19] is a good example of the kinds of changes
which occur as the pyrazolylborate ligand proceeds from free
rotation to a sterically rigid condition.

The nmr spectrum of $PzB(Pz)_3Mn(CO)_2P(OCH_3)_3$ at 5° is
almost identical in the pyrazolyl region to the room-tempera-
ture spectrum of $PzB(Pz)_3Mo(CO)_2$-h^3-$CH_2C(CH_3)CH_2$.[19]
Peaks at τ 1.96, 2.21, and 2.38 are a result of an overlap of
peaks corresponding to the 3- and 5-H's of the pyrazolyl
groups (both coordinated and uncoordinated). Separate
peaks, having a ratio 1:3 are observed at τ 3.49 and 3.90,
respectively, for the uncoordinated and coordinated pyrazolyl
4 protons. Finally, a sharp doublet (τ 6.68, 6.84) results
from coordinated $P(OCH_3)_3$. Since all three coordinated
pyrazolyl groups are equivalent in this molecule, rotation of

Figure 4. Geometrical arrangement of ligands in $PzB(Pz)_3Mn(CO)_2L$.

the tridentate ligand about the B–Mn axis is occurring. Be-
cause of solubility problems, the spectrum was not recorded
at lower temperatures. In contrast to these results, the spec-
trum of $HB(CH_3PzCH_3)_3Mn(CO)_2P(OCH_3)_3$ at 5° shows
nonequivalency of the three coordinated pyrazolyl groups.
Peaks at τ 4.34 and 4.48, having a relative area 2:1, are ob-
served for the 4 protons of the coordinated pyrazolyls. The

methyl protons appear as a broad multiplet at τ 7.58–7.89. Peaks at τ 6.79 and 6.98 correspond to the coordinated $P(OCH_3)_3$ doublet. These results imply that increased steric hindrance in $HB(CH_3PzCH_3)_3Mn(CO)_2P(OCH_3)_3$ resulting from the presence of methyl groups on the pyrazole rings inhibits free rotation of the tridentate ligand about the B–Mn axis. Nmr spectra of $PzB(Pz)_3Mn(CO)_2P(CH_3)_3$ and HB-$(CH_3PzCH_3)_3Mn(CO)_2P(CH_3)_3$ at 5° are similar to those shown for the corresponding trimethyl phosphite derivatives. The spectrum of $PzB(Pz)_3Mn(CO)_2P(CH_3)_3$ consists of a multiplet (τ 2.19, 2.27, 2.46) corresponding to 3 and 5 protons (coordinated and uncoordinated), singlets at τ 3.51 and 3.84 corresponding to uncoordinated and coordinated 4 protons, and a doublet (τ 8.70, 8.83) corresponding to the coordinated $P(CH_3)_3$. The spectrum of $HB(CH_3PzCH_3)_3Mn$-$(CO)_2P(CH_3)_3$ shows singlets at τ 4.26 and 4.55 (2:1) for coordinated pyrazolyls, a multiplet (τ 7.50, 7.63, 7.88) assigned to 3 and 5 methyl protons, and a doublet (τ 8.81, 8.94) corresponding to coordinated $P(CH_3)_3$. Therefore, the steric effect of the ring methyl groups on the stereochemical rigidity of the molecule can again be seen.

The nmr spectrum of $HB(CH_3PzCH_3)_3Mn(CO)_2P(OC_6H_5)_3$ shows the effect of steric factors more clearly. Peaks corresponding to coordinated pyrazolyl 4-H's are observed at τ 4.40 and 4.50 (2:1 ratio). Furthermore, peaks due to the 3 and 5 methyl groups on nonequivalent pyrazolyls can be clearly distinguished, one set occurring at τ 7.44 and 7.80 (relative intensity 2) and the other set occurring at τ 7.68 and 7.95 (relative intensity 1). Thus, the pyrazolylborate ligand is more tightly locked into position in the $P(OC_6H_5)_3$ derivative than in the $P(OCH_3)_3$ derivative.

The above results are consistent with those obtained from infrared intensities. Steric interactions in $HB(CH_3PzCH_3)_3$-$Mn(CO)_2L$ (sterically rigid) are greater than those in $PzB(Pz)_3$-$Mn(CO)_2L$ (free rotation). This causes the OC–M–CO angle to be smaller in $HB(CH_3PzCH_3)_3Mn(CO)_2P(OC_6H_5)_3$ than in $PzB(Pz)_3Mn(CO)_2P(OC_6H_5)_3$.

In an attempt to induce free rotation of the $HB(CH_3PzCH_3)_3$-ligand samples of the $P(OCH_3)_3$ and $P(OC_6H_5)_3$ derivatives were heated over the range 30–120°. Although some changes in the spectra occurred, interpretation was complicated by partial decomposition of the samples in solution. Free rota-

tion was not observed in either case. If solutions of PzB-$(Pz)_3Mn(CO)_2P(CH_3)_3$ or $HB(CH_3PzCH_3)_3Mn(CO)_2P(CH_3)_3$ in CS_2 were heated, a deep red coloration appeared, probably as a result of reaction of $P(CH_3)_3$ formed by partial decomposition of the samples with carbon disulfide.

Although considerable caution must be exercised in drawing conclusions about electronic factors from nmr chemical shift data, one feature seems to stand out in the above results. The value of τ for the 4 protons of coordinated pyrazolyl groups is larger than that for uncoordinated pyrazolyls regardless of the nature of L. Furthermore, the τ value of the 4 proton of the coordinated pyrazolyl group which is trans to L is larger than that for coordinated pyrazolyls which are trans to CO. These results suggest that the electron density on the pyrazolyls decreases in the order (coordinated–trans L) > (coordinated–trans CO) > (uncoordinated). This conclusion is consistent with the usual concepts that ligands of the type PR_3 and $P(OR)_3$ are better σ donors and/or poorer π acceptors than CO,[32-34] and the strongest interaction occurs between ligands which are trans rather than cis to one another.[24,35,36]

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