Contribution No. 2343 from the Central Research and Development Department,
Experimental Station, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898

Stereochemically Nonrigid Five-Coordinate Methylplatinum(II) Complexes Containing the Hydrotris(1-pyrazolyl)borate Ligand

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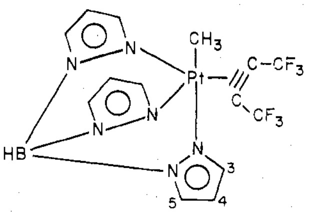
Received June 17, 1976

AIC60444D

The preparation and variable-temperature NMR spectra (^{13}C and ^{1}H) for a series of compounds $Pt(CH_3)[HB(pz)_3]L$ ($HB(pz)_3$ = hydrotris(1-pyrazolyl)borate; L = CO, $CNC(CH_3)_3$, CNC_6H_{11}, or $P(OCH_3)_3$) are reported. Line shape analyses of the temperature-dependent spectra are reported. The spectra in the slow-exchange limit indicate that the complexes are five-coordinate. The intramolecular exchange probably involves a rotation of the $HB(pz)_3$ ligand about the Pt–B axis. The temperature-dependent $^{13}C\{^1H\}$ NMR spectrum for the complex $Pt(CH_3)[B(pz)_4]CO$ has also been recorded and analyzed. In this case three different exchange processes are observed.

Introduction

Recently we described the preparation of several five-coordinate olefin, acetylene, and allene complexes of platinum,[1,2] $Pt(CH_3)[HB(pz)_3](un)$ (where $HB(pz)_3$ is the hydrotris(1-pyrazolyl)borate ligand and un = an olefin, acetylene, or allene ligand). The structures of the hexafluorobut-2-yne[3] **1** and tetrafluoroethylene[4] **2** complexes were determined by x-ray diffraction and the five-coordination was confirmed. The compounds in solution were nonfluxional on the NMR time scale even in boiling toluene. A carbonyl complex[2] $Pt(CH_3)[HB(pz)_3]CO$ was also prepared but unlike the acetylene and olefin complexes this compound in solution was stereochemically nonrigid on the NMR time scale. The low-temperature spectra indicated that the molecule was five-coordinate; however, an x-ray structural analysis of the molecule[5] showed that the geometry was square planar about platinum and that the third pyrazolyl ring was uncoordinated. This apparent anomaly of the structure in the solid state and in solution warranted further investigation. In this paper we describe the preparation and variable-temperature ^{13}C and ^{1}H NMR spectra and line shape analyses for several complexes of the type $Pt(CH_3)[HB(pz)_3]L$. The temperature-dependent $^{13}C\{^1H\}$ NMR spectrum of $Pt(CH_3)[B(pz)_4]CO$ was also recorded and analyzed.



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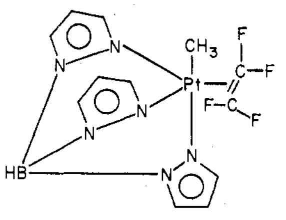

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Experimental Section

All of the complexes were prepared from $Pt(CH_3)[HB(pz)_3]$.[1] Microanalyses were performed in this department.

^{1}H NMR spectra were recorded on a Varian HR-220 spectrometer operating at 220 MHz using CD_2Cl_2 solutions. The ^{13}C NMR spectra were recorded on a Bruker WH-90 spectrometer operating at 22.63 MHz using CD_2Cl_2 as solvent and internal reference. The $^{13}C\{^1H\}$ NMR spectrum for $Pt(CH_3)[B(pz)_4]CO$[2] was recorded in a variety of solvents (toluene-d_8, CD_2Cl_2, DMSO-d_6, and CD_3CN) between −100 and +100 °C at 22.63 MHz. Chemical shifts are reported in ppm relative to TMS and coupling constants are in hertz.

Preparation of $Pt(CH_3)[HB(pz)_3][P(OCH_3)_3]$. To a solution of $Pt(CH_3)[HB(pz)_3]$ (0.291 g, 0.688 mmol) in CH_2Cl_2 was added $P(OCH_3)_3$ (0.069 g). When all of the solid had dissolved, the solution was filtered through a fine sintered-glass frit to give a clear colorless solution. The solvent was removed by rotary evaporation to give a clear oil. Hexane was added and the solution was warmed slightly and then cooled to −15 °C overnight. Large crystals separated. They were filtered off and dried under vacuum; yield 0.253 g; mp 111–112 °C.

Anal. Calcd for $C_{13}H_{22}B_1N_6O_3PtP$: C, 29.84; H, 4.24; N, 16.06. Found: C, 28.61; H, 4.11; N, 15.42. ^{1}H NMR (35 °C) δ(Pt–CH$_3$) 0.64, J(P–H) = 2.2 Hz, J(Pt–H) = 70.0 Hz, δ(O–CH$_3$) 3.54, J(P–H) = 2.4 Hz, J(Pt–H) = 12.6 Hz, δ(4-H) 6.24, J(H–H) = 2.2 Hz, J(Pt–H) = 4.0 Hz; ^{13}C NMR (35 °C) δ(Pt–CH$_3$) −20.44, J(Pt–C) = 610; J(P–C) = 12.0 Hz; equatorial pyrazolyl carbons δ(C) 104.88, 135.42, 140.21 (J(Pt–C) = 11.5 Hz); axial pyrazolyl carbons δ(C) 105.26, 136.72, 143.10 (J(Pt–C) = 34.4 Hz).

Preparation of $Pt(CH_3)[HB(pz)_3](CNC(CH_3)_3)$. To a solution of $Pt(CH_3)[HB(pz)_3]$ (0.250 g, 0.591 mmol) in 5 ml of CH_2Cl_2 was added $CNC(CH_3)_3$ (0.051 ml). When the solid had dissolved, the solution was filtered through a fine frit to give a clear colorless solution. The solvent was removed by rotary evaporation to give an oil. Hexane was added and the flask was cooled overnight. The crystals that separated were filtered off and dried under vacuum; yield 0.165 g; mp 141–145 °C.

Anal. Calcd for $C_{15}H_{22}BN_7Pt$: C, 35.61; H, 4.34; N, 19.39. Found: C, 36.06; H, 4.54; N, 18.93. ^{1}H NMR δ(PtCH$_3$) 0.83, J(Pt–H) = 74 Hz, δ(C(CH$_3$)$_3$) 1.51, δ(4-H) 6.22, J(Pt–H) = 4.0 Hz, J(H–H) = 2.0 Hz, δ(5-H) 7.52, δ(3-H) 7.68, J(Pt–H) = 9 Hz; ^{13}C NMR δ(Pt–CH$_3$) −22.18, J(Pt–C) = 606 Hz, δ(C–CH$_3$) 30.20, δ(N–C–C$_3$) 50.60; equatorial carbons δ(C$_5$) 135.68, J(Pt–C) = 11.8 Hz, δ(C$_4$) 104.88, J(Pt–C) = 20.6 Hz, δ(C$_3$) 140.56, J(Pt–C) = 32.4 Hz; axial carbons δ(C$_4$) 105.85, J(Pt–C) = 20.6 Hz, δ(C$_3$) 141.73, J(Pt–C) = 38.2 Hz, δ(C$_5$) 136.07.

Preparation of $Pt(CH_3)[HB(pz)_3](CNC_6H_{11})$. A mixture of $Pt(CH_3)[HB(pz)_3]$ (1.0 g, 2.36 mmol) and cyclohexyl isocyanide (0.25 g) in CH_2Cl_2 was stirred for 15 min and worked up as in the previous experiments; yield 0.75 g.

Anal. Calcd for $C_{17}H_{24}B_1N_7Pt$: C, 38.35; H, 4.54; N, 18.42. Found: C, 37.98; H, 4.49; N, 18.41.

NMR Line Shape Analysis. Although the exchange processes reported in this paper are of the mutual exchange type, the temperature-dependent NMR spectra are most conveniently analyzed as an intramolecular exchange between two or more sites. The spectra are essentially first order and consequently the density matrix equations of Kaplan[6] and Alexander[7] reduce to the equations given by Sack[8] and the calculation of NMR line shapes is considerably simplified. Details of the numerical techniques used in the line shape calculations are given in ref 9. In order to calculate accurate exchange rates the chemical shift separations must be known at all temperatures. The chemical shift separations near the low-temperature limit were observed to be significantly temperature dependent. Consequently chemical shift separations in the intermediate- and fast-exchange spectra were calculated assuming a linear temperature dependence. Although we do not necessarily expect a linear temperature dependence, the range of temperatures over which the slow-exchange limit spectra can be observed is too small to justify any other type of extrapolation. The linear extrapolation is expected to be quite satisfactory provided it is not applied over too wide a temperature range. The use of this extrapolation is justified to some extent by the observation that a better fit can be obtained between the experimental and calculated spectra if the extrapolation is carried out.

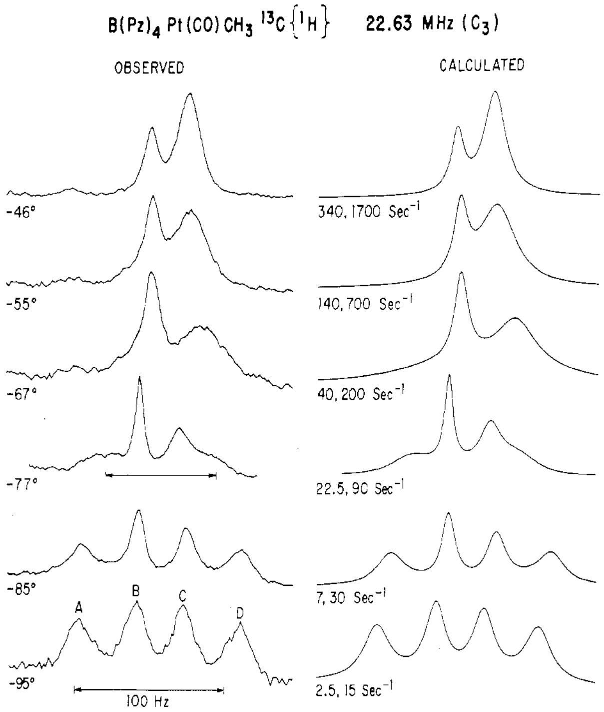

Figure 1. Observed and calculated $^{13}C\{^1H\}$ NMR spectra for a solution of $Pt(CH_3)[B(pz)_4]CO$ in CD_2Cl_2. It should be noted that the −77 °C spectrum (observed and calculated) has a frequency scale different from that for the other spectra (scale given at bottom). The two exchange rates are for the processes A ↔ C and A ↔ D, respectively.

$$\begin{tikzcd}[column sep=small] {} \arrow[dr, leftrightarrow] & & {} \arrow[dl, leftrightarrow] \\ & D & \end{tikzcd}$$

Results

A. $Pt(CH_3)[B(pz)_4]CO$. The portion of the $^{13}C\{^1H\}$ NMR spectrum for a solution of $Pt(CH_3)[B(pz)_4]CO$ in CD_2Cl_2 assigned to the ^{13}C nuclei at the three positions (see **1** for the numbering scheme) in the pyrazolyl rings is shown in Figure 1 as a function of temperature between −95 and −46 °C. At the low-temperature limit four ^{13}C resonances (with unresolved ^{195}Pt satellites) of equal intensity are observed indicating that all four of the pyrazolyl rings in the $B(pz)_4$ ligand are inequivalent on the NMR time scale. The slow-exchange limit spectra are consistent with the essentially trigonal-bipyramidal structure **3** in which internal rotation of the uncoordinated pyrazolyl ring about the B–N bond is slow on the NMR time scale. As the temperature is raised from −98 °C, the two outer resonances begin to broaden approximately equally indicating that two of the pyrazolyl groups are exchanging. The process responsible for this contribution to the NMR line shape effect is assumed to be internal rotation of the uncoordinated pyrazolyl group about the B–N bond. This process will exchange pyrazolyl groups A and D in **3** corresponding to resonances A and D in Figure 1. As the temperature is raised, a further resonance C begins to broaden and eventually coalesces with A and D. This second process is attributed to exchange of the three coordinated pyrazolyl groups. Resonance B remains sharp up to about 60 °C. Above 60 °C resonance B also begins to broaden and eventually all four slow-exchange limit resonances coalesce; we attribute this "high-temperature" line shape effect to exchange of the coordinated pyrazolyl groups with the uncoordinated pyrazolyl—an intramolecular bond-breaking process.

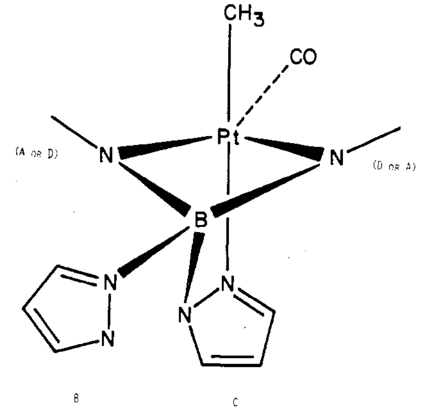

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Figure 1 shows a comparison between the observed $^{13}C\{^1H\}$ NMR spectra and those calculated assuming that two exchange processes are taking place independently. The good

A ↔ B

$$\begin{tikzcd}[column sep=small] A \arrow[rr, leftrightarrow] \arrow[dr, leftrightarrow] & & B \arrow[dl, leftrightarrow] \\ & C & \end{tikzcd}$$

agreement between the observed and calculated spectra confirms this assumption. In this case the ^{195}Pt satellite resonances were not included in the calculation since they could not be resolved in the low-temperature-limit spectrum. The temperature dependence of the exchange rates was analyzed in terms of the Eyring equation

$$R(T) = K(kT/h)e^{-\Delta G^{\ddagger}/RT}\ \mathrm{s}^{-1} \tag{1}$$

and the Arrhenius equation[13]

$$R(T) = Ae^{-E_a/RT}\ \mathrm{s}^{-1} \tag{2}$$

From the spectra shown in Figure 1 and others not shown we find for the internal rotation of the uncoordinated pyrazolyl ring that $\Delta G^{\ddagger}_{198} = 9.9$ kcal mol^{-1}, $\Delta H^{\ddagger} = 9.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = 0$, $E_{a_{198}} = 10.2$ kcal mol^{-1}, and $\log A_{198} = 13.0$. For exchange of the three coordinated pyrazolyl rings we find $\Delta G^{\ddagger}_{198} = 10.5$ kcal mol^{-1}, $\Delta H^{\ddagger} = 9.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = -7$ cal mol^{-1} deg^{-1}, $E_{a_{198}} = 9.4$ kcal mol^{-1}, and $\log A_{198} = 11.4$. For the third process (exchange of coordinated and uncoordinated pyrazolyls) spectra could not be measured over a wide enough temperature range to warrant calculation of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, E_a, and A. However, a $\Delta G^{\ddagger}$ of 18.1 kcal mol^{-1} was calculated at 85 °C.

It is difficult but not impossible to rationalize the temperature-dependent NMR spectra for $Pt(CH_3)[B(pz)_4]CO$ on the basis of a four-coordinate structure of the type determined by Rush and Oliver[5] for $Pt(CH_3)[HB(pz)_3]CO$ in the solid phase. Since all four pyrazolyl groups become equivalent on the NMR time scale at sufficiently high temperatures, bond-breaking processes are suggested and it is possible that a four-coordinate complex of the type found by Rush and Oliver acts as an intermediate in the "high-temperature" exchange process. It is also clear that bond-breaking processes must be considered in interpreting the temperature-dependent NMR spectra for the $Pt(CH_3)[HB(pz)_3]L$ complexes.

Spectra similar to those discussed above and shown in Figure 1 were also obtained for the ^{13}C nuclei assigned to the 4 and 5 positions. However, these spectra were not analyzed in detail since their low-temperature limits are not as well resolved as those of the −95 °C spectrum shown in Figure 1.

B. $Pt(CH_3)[HB(pz)_3]L$ Complexes. The polymeric compound[1] $Pt(CH_3)[HB(pz)_3]$ reacts rapidly, in CH_2Cl_2, with a variety of neutral ligands L (L = $CNC(CH_3)_3$, CO, CNC_6H_{11}, $P(OCH_3)_3$) to form 1:1 adducts which can be isolated as air-stable white crystalline solids. Part of the observed and calculated $^{13}C\{^1H\}$ NMR spectra for a solution

Table I. Activation Parameters for Exchange in Complexes of the Type $Pt(CH_3)[HB(pz)_3]L$

	$\Delta G^{\ddagger}_{298}$, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	$E_{a_{298}}$, kcal mol^{-1}	log A_{298}
L = CO ($^{13}C\{^1H\}$)	14.2	13.6	−2	14.1	12.7
L = $(CH_3)_3CNC$ ($^{13}C\{^1H\}$)	16.8	16.7	0	17.3	13.1
L = $(CH_3)_3CNC$ (^1H)	17.0	16.6	−1	17.1	13.0
L = $P(OCH_3)_3$ ($^{13}C\{^1H\}$)	15.6				
L = $P(OCH_3)_3$ (^1H)	16.0	12.9	−10	13.5	11.0
L = $C_6H_{11}NC$ (^1H)	17.0	17.3	1.0	18.0	13.5

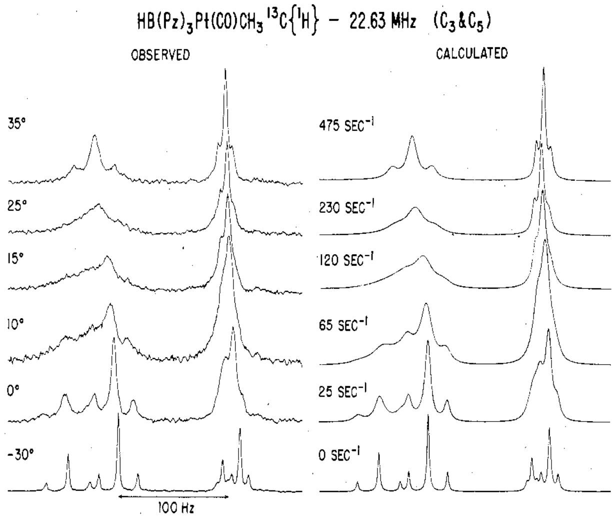


Figure 2. Calculated and observed variable-temperature $^{13}C\{^1H\}$ spectra of $Pt(CH_3)[HB(pz)_3]CO$ showing only the 3-C and 5-C carbon resonances.

of $Pt(CH_3)[HB(pz)_3]CO$ in CD_2Cl_2 are shown at several temperatures and associated exchange rates in Figure 2. These resonances are assigned to carbon atoms at the 3 and 5 positions of the pyrazolyl rings (for numbering see **1**) on the basis of the ^{13}C chemical shifts and the magnitudes of the ^{13}C–^{195}Pt coupling constants. The 2:1 ratio of peak intensities in Figure 2 at −30 °C indicates that the three pyrazolyl rings occupy two equivalent positions and one unique position in the molecule. The temperature-dependent line shapes associated with the resonances assigned to the carbon atoms in the 4 positions were also analyzed in detail. These resonances lie to the high-field side of those shown in Figure 2 and magnitudes of the ^{13}C–^{195}Pt coupling constants are intermediate between those for the 3 and 5 positions. The ^{13}C–^{195}Pt coupling constants are 35.3, 21.3, and 15.4 Hz for the ^{13}C nuclei assigned to the 3, 4, and 5 positions, respectively, of the two equivalent pyrazolyl rings and 39.0, 22.1, and 8.8 Hz for the ^{13}C nuclei assigned to the 3, 4, and 5 positions of the unique pyrazolyl ring. Resonances assigned to the CH_3 and to the CO ^{13}C nuclei were also observed. These resonances are unaffected by the exchange process and their NMR line shapes are essentially temperature independent.

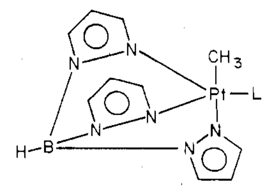
The $^{13}C\{^1H\}$ NMR spectra of the other $Pt(CH_3)[HB(pz)_3]L$ compounds (L = $(CH_3)_3CNC$, $P(OCH_3)_3$, and $C_6H_{11}NC$) are qualitatively similar with resonances assigned to the ^{13}C nuclei in the 3 and 5 positions 140–143 ppm downfield from internal TMS and resonances assigned to carbon nuclei in the 4 position 135–137 ppm downfield.

The ^1H NMR spectra of the $Pt(CH_3)[HB(pz)_3]L$ compounds are similar in many respects to the ^{13}C spectra. In the low-temperature limit the resonances assigned to the protons in the 3 position consist of two doublets with a 2:1 intensity ratio with attendant ^{195}Pt satellite lines. The doublet splitting of about 2.2 Hz is a result of spin–spin coupling between hydrogens on the 3 and 4 positions of a particular pyrazolyl ring. The resonances assigned to the protons in the 5 position are quite similar except that the ^{195}Pt–^1H coupling constant is now small and the ^{195}Pt satellite lines cannot be resolved. The protons in the 4 positions give rise to two triplets ($J_{H_3H_4} \approx J_{H_4H_5} \approx 2.2$ Hz) with a 2:1 intensity ratio corresponding to protons on the two equivalent pyrazolyl rings and one unique ring, respectively. Again the ^{195}Pt satellites cannot be resolved. As in other pyrazolylborates[10] the chemical shifts associated with the protons in the 4 positions lie to the high-field side of those associated with the 3 and 5 positions.

Except for the presence of the ^{195}Pt satellites for protons in the 3 positions of the pyrazolyl rings the temperature-dependent ^1H NMR spectra are very similar to those for systems of the type $R^1B(pz)_3Mo(CO)_2[\pi\text{-}CH_2C(R^2)CH_2]$ which have previously been analyzed.[11] The temperature dependence of that part of the $^{13}C\{^1H\}$ spectrum associated with the carbon nuclei in the 3 and 5 positions is shown in Figure 2. As the temperature is raised, the spectra at first broaden and then coalesce. The high-temperature-limit spectra indicate that the three pyrazolyl rings have become equivalent on the NMR time scale. A quantitative line shape analysis such as that shown on the right-hand side of Figure 2 permits exchange rates to be obtained as a function of temperature. No detailed mechanistic information can be obtained since there is only one basic permutational set[9,12] apart from the identity. The results obtained from the line shape analysis are summarized in Table I.

Discussion

The observation of ^{195}Pt satellite lines associated with all of the $^{13}C\{^1H\}$ resonances assigned to the pyrazolyl carbons in the complexes $Pt(CH_3)[HB(pz)_3]L$ indicates that all three pyrazolyl rings are directly coordinated to the platinum atom and $HB(pz)_3$ is acting as a tridentate ligand.[14] Consequently we can assume that the complexes discussed in this work are *five*-coordinate in the slow-exchange limit. The structures of five-coordinate complexes are commonly discussed in terms of the idealized trigonal-bipyramidal and square-pyramidal geometries. Structures with two equivalent and one unique pyrazolyl ring can be drawn based on either geometry. However the two equivalent ligands would have to occupy trans positions in the basal plane of the square pyramid. A more reasonable structure can be envisioned based on the trigonal-bipyramidal geometry with the unique pyrazolyl ring occupying an axial position and the two equivalent ligands occupying equatorial positions, **4**. X-ray crystal structures of this type have been reported where L = $CF_3C{\equiv}CCF_3$[3] and $CF_2{=}CF_2$.[4] The methyl group occupies an axial position and the olefin or acetylene occupies an equatorial position.



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The x-ray structure of $HB(pz)_3Pt(CO)CH_3$ (one of the complexes studied in this work) has also been determined.[5]

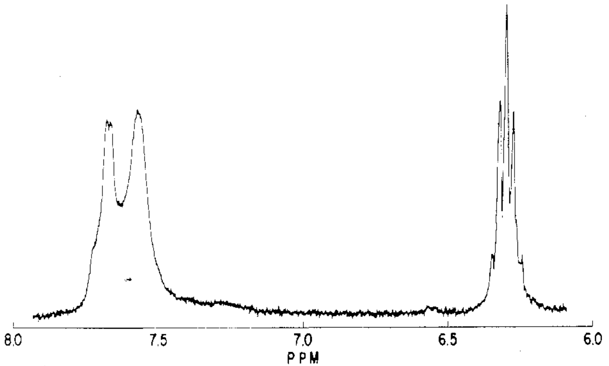

Figure 3. ^{1}H NMR spectrum of $Pt(CH_3)[B(pz)_4]CO$ in CD_2Cl_2 showing pyrazolyl resonances.

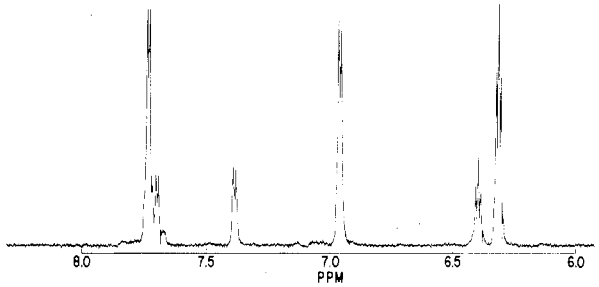

Figure 4. ^{1}H NMR spectrum of $Pt(CH_3)[HB(pz)_3]CO$ in CD_2Cl_2 showing pyrazolyl resonances.

In this case the coordination about platinum consists of a slightly distorted square-planar arrangement with two pyrazolyl nitrogens occupying cis positions. The $HB(pz)_3$ is acting as a bidentate ligand. The change in coordination number on going from the liquid to the solid phase suggests that the exchange process responsible for the NMR line shape behavior may involve breaking of a N–Pt bond. However dissociation and association of the axial pyrazolyl ring will not result in any exchange of pyrazolyl groups, and dissociation of an equatorial pyrazolyl will not result in exchange unless the two pyrazolyl rings which remain coordinated to the platinum can be exchanged. This seems improbable if the four-coordinate intermediate is essentially square planar. In order to determine if N–Pt bond breaking was involved in the exchange process, we ran the spectrum of $Pt(CH_3)[B(pz)_4]CO$ (vide supra). The temperature-dependent $^{13}C\{^1H\}$ NMR spectrum assigned to $Pt(CH_3)[B(pz)_4]CO$ demonstrates that N–Pt bond breaking *does* occur but that (in this complex at least) exchange of the three coordinated pyrazolyl groups occurs more readily (at a lower temperature). Similar results can be obtained from the ^{1}H NMR spectra. Figure 3 shows the room-temperature ^{1}H NMR spectrum of $Pt(CH_3)[B(pz)_4]CO$. The spectrum clearly shows the presence of three equivalent pyrazolyl rings and one unique ring. Therefore the exchange process for the $B(pz)_4$ complex involves a mechanism by which the uncoordinated ring does not exchange with the coordinated rings. It is unlikely that the exchange process responsible for the NMR line shape behavior involves a process involving N–Pt bond breaking.

As can be seen from the spectrum of $Pt(CH_3)[HB(pz)_3]CO$ (Figure 4), at room temperature, three resonances are observed which correspond to the 3-H, 5-H, and 4-H protons on the pyrazolyl rings. Consequently exchange of the three coordinated pyrazolyls in $Pt(CH_3)[HB(pz)_3]CO$ must be considerably slower than in $Pt(CH_3)[B(pz)_4]CO$ (compare also Figures 1 and 2). This raises the possibilities that we are looking at a bond-breaking process in one case and a non-bond-breaking process in the other. However, we believe it is unlikely that the exchange process observed in the $Pt(CH_3)[HB(pz)_3]L$ complexes involves N–Pt bond breaking.

Possible non-bond-breaking processes include Berry[15] type rearrangements with pyrazolyl groups as the pivotal ligands (if the pyrazolyl equatorial ligand acted as the pivot, the $HB(pz)_3$ group would have to span trans positions in the base of the square-pyramidal intermediate). Alternatively, the $HB(pz)_3$ group could rotate about the B–Pt axis. A process of this type was proposed for the six-coordinate complexes $R^1B(pz)_3Mo(CO)_2(\pi\text{-}CH_2C(R^2)CH_2)$.[15] This process is not equivalent to the turnstile process proposed by Ugi et al.[16] For the turnstile process rotation of the $HB(pz)_3$ group **3** by 120° is accompanied by exchange of the two other ligands to give a second isomer. However, two turnstile exchanges are equivalent to a 120° rotation of the $HB(pz)_3$ group.

Under normal conditions the Berry mechanism is the preferred mechanism for intramolecular rearrangement in five-coordinate complexes.[17] However in this case the unique nature of the $HB(pz)_3$ ligand may act in favor of the turnstile process. These two processes are permutationally equivalent and cannot be distinguished on the basis of an NMR line shape analysis. In both cases a second isomer in which the two nonpyrazolyl ligands have exchanged positions is involved. If this second isomer were present in only very small quantities, it would not be necessary to include its resonances in the NMR line shape calculations and the model described above would be adequate.

Registry No. $Pt(CH_3)[HB(pz)_3][P(OCH_3)_3]$, 60498-74-0; $Pt(CH_3)[HB(pz)_3](CNC(CH_3)_3)$, 60498-75-1; $Pt(CH_3)[HB(pz)_3](CNC_6H_{11})$, 60498-76-2; $Pt(CH_3)[HB(pz)_3]CO$, 51703-30-1; $Pt(CH_3)[B(pz)_4]CO$, 51567-36-3; $Pt(CH_3)[HB(pz)_3]$, 39395-33-0; ^{13}C, 14762-74-4.

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