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Palladium(II) Tetrakis(1-pyrazolyl)borate and some Related Species

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Abstract

The structure of the complex Pd[B(pz)$_4$]$_2$ (Hpz = pyrazole) has been explained on the basis of variable-temperature ^{1}H NMR studies. Reactions of M[B(pz)$_4$]$_2$ (M = Pd, Zn, Pb) with metal dichlorides have been studied and the complexes Pd[B(pz)$_4$]$_2$·2PdCl$_2$ and Pd[B(pz)$_4$]$_2$·2ZnCl$_2$ have been isolated.

Introduction

Several chain-type polynuclear spiro species containing boron [1] as well as boron and metal [2] centers have been described recently. The general building principle for these materials involved the conversion of a terminal B(pz)$_2$ unit (Hpz = pyrazole) into bridging moieties of the type B(μ-pz)$_2$M (M = boron or metal). The complexing B(pz)$_2$ unit originated either from poly(1-pyrazolyl)pyrazaboles or from the [B(pz)$_4$]$^-$ ion. The latter was normally employed as the potassium salt, but Zn[B(pz)$_4$]$_2$ was used in one instance, where the reaction with ZnCl$_2$ was found to give a complex Zn[B(pz)$_4$]$_2$·2ZnCl$_2$, which was formulated as the chain-type polynuclear species Cl$_2$Zn(μ-pz)$_2$B(μ-pz)$_2$-Zn(μ-pz)$_2$B(μ-pz)$_2$ZnCl$_2$. This result suggested that similar species should exist in which even two different metals are incorporated into the chain. The present report describes data on some metal tetrakis(1-pyrazolyl)borates, M[B(pz)$_4$]$_2$, and their interaction with metal dichlorides, M'Cl$_2$.

Results and Discussion

Starting Materials

The three species M[B(pz)$_4$]$_2$ with M = Zn, Pb, and Pd were selected as starting materials for the present study. The ^{1}H NMR spectra of the Zn [2] and the Pb species are quite similar exhibiting only three sharp signals in a 1:1:1 ratio. Essentially no changes were observed in the spectra over the temperature range from +25 to −50 °C indicating the equivalence of all four pz groups. This is essentially the same fluxional situation as that observed for other metal tetrakis(1-pyrazolyl)borates but is significantly different from the ^{1}H NMR spectrum of Pd[B(pz)$_4$]$_2$. This latter compound has been mentioned in the literature [3] but no experimental data were given. It is, however, easily prepared from M$_2$[PdCl$_4$] (M = Na, K) and M'[B(pz)$_4$] (M' = Li, K), although the purification is somewhat tedious.

In contrast to the zinc and lead salts cited above, the palladium complex exhibits a much more complicated ^{1}H NMR spectrum. At −48 °C the spectrum shows sets of signals for three different pz groups with δ(^{1}H) 7.86/6.93/6.36, 7.79/7.38/6.46, and 7.41/7.09/6.32 in a 1:1:2 intensity ratio, of which the two former are merging into a single set near room temperature (see Fig. 1). A variable-temperature study over the range from −25 to +80 °C (performed in CDCl$_2$CDCl$_2$) showed that the lowest

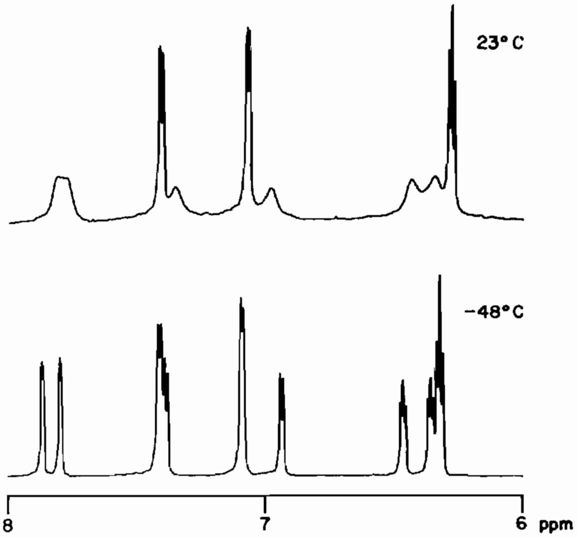

Fig. 1. The ^{1}H NMR spectrum of Pd[B(pz)$_4$]$_2$ in CD$_2$Cl$_2$ at +23 and −48 °C.

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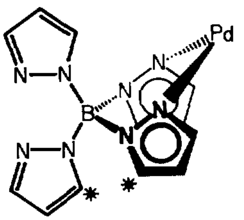
field signals of the two sets of intensity 1 merge near 40 ℃, the highest field signals merge near 60 ℃, but the central set merges only near 70 ℃. The data suggest that the species should be formulated as $(pz)_2B(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2B(pz)_2$. This is based on the following interpretation. In the low-temperature spectrum, the ^1H NMR signals of the presumably puckered $B(\mu\text{-}pz)_2Pd$ rings are assigned to the set $\delta(^1H)$ 7.41/7.09/6.32. This signal set is sharp over the entire temperature range studied and these pz groups remain in the same magnetic environment regardless of the temperature, but they obviously affect the terminal boron-bonded pz groups differently. At low temperatures, the pseudo-axial and -equatorial terminal boron-bonded pz groups give distinctly separate signals until, with raising of the temperature, inversion of the $B(\mu\text{-}pz)_2Pd$ ring becomes rapid on the NMR time scale, and, ultimately, the signals of the terminal pz groups collapse to a single set. Assuming that the 5-H of the bottom terminal pz group in **1** (one half of the molecule) will be in a magnetic environment most similar to those of the 5-H of the bridging pz groups (both marked with an asterisk in **1**), the signal of the former is assigned at 7.38 ppm, those of the latter at 7.41 ppm. This automatically leads to the assignments of all other proton resonance signals in the low-temperature spectrum.



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The foregoing data illustrate that in the Pb and Zn complex all pz groups are equivalent in their bonding to the metal. In contrast, the same two pz groups of each $B(pz)_4$ moiety of the Pd complex are always bonded to the metal. The non-planar $B(\mu\text{-}pz)_2Pd$ rings are static at low temperatures but begin to invert with increasing temperature; only at high temperatures is the inversion sufficiently fast to provide for equivalence of the terminal pz groups, which do not exchange sites with those bridging between the B and the Pd.

The Interaction of $M[B(pz)_4]_2$ *with* $M'Cl_2$

Recently, the preparation of the unusual complex $(pz)_2B(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2PdCl_2\cdot0.5CH_2Cl_2$ has been reported [4]. This compound would be an interesting starting material for chain elongation at the remaining terminal $B(pz)_2$ site. Unfortunately, all attempts to duplicate the reported preparation of this material failed and only $Pd[B(pz)_4]_2$ was isolated when following the original directions. On the other hand, reaction of $Pd[B(pz)_4]_2$ with $PdCl_2$ gave the complex $Pd[B(pz)_4]_2\cdot2PdCl_2$, independent of the stoichiometry of the reagents. In no case was a species of the composition $Pd[B(pz)_4]_2\cdot PdCl_2$ obtained.

The complex $Pd[B(pz)_4]_2\cdot2PdCl_2$ is insoluble in most common solvents but NMR spectra were obtained on a solution in DMSO-d_6. The ^1H NMR spectrum of the material is extremely complex and suggests the presence of several types (at least five!) of pz groups, based on the number of pz 4-H signals. The ^{11}B NMR spectrum exhibits a sharp signal at 0.4 ppm but with a clearly recognizable and intense shoulder at −0.1 ppm. These observations suggest exchange reactions to occur in solution but which could not be specified: A variable-temperature ^1H NMR study was inconclusive.

The reaction of $Zn[B(pz)_4]_2$ with $ZnCl_2$ has previously been reported to give a species which was formulated as $Cl_2Zn(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Zn(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ZnCl_2$ [2]. $Pb[B(pz)_4]_2$ does not react with $PbCl_2$ under similar conditions. However, the reaction of $Pd[B(pz)_4]_2$ with $ZnCl_2$ was found to give the complex $Pd[B(pz)_4]_2\cdot2ZnCl_2$, which probably can also be formulated as $Cl_2Zn(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ZnCl_2$.

Surprisingly, when $Zn[B(pz)_4]_2$ was reacted with $PdCl_2$, the complex $Pd[B(pz)_4]_2\cdot2PdCl_2$ was obtained rather than the desired mixed-metal species. Reaction of $Zn[B(pz)_4]_2$ with MCl_2 (M = Co, Ni; stirring the reagents in a 1:2 molar ratio in ether at room temperature and recrystallizing the insoluble material from toluene) was found to give species of the elemental composition $2Zn[B(pz)_4]_2\cdot3M[B(pz)_4]_2$ (the M = Ni complex is pink, and the one with M = Co is yellow). The ^{11}B NMR spectra exhibited a broad (*ca.* 4000 Hz) base peak (centered near −2 ppm) with a sharp spike at −0.4 ppm, but these species have not yet been investigated further. Reaction of $Pd[B(pz)_4]_2$ with $NiCl_2$ gave $Ni[B(pz)_4]_2$, but no reaction was observed with $CoCl_2$ (mixtures in DMF, 40 h stirring at room temperature).

Experimental

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for ^1H NMR and external $Et_2O\cdot BF_3$ for ^{11}B NMR): s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal.

Coupling constants *J* are given in Hz. Details for 2D NMR experiments have been given elsewhere [5].

$Pd[B(pz)_4]_2$

Solid $K[B(pz)_4]$ [3] (18.44 g, 58 mmol) was added in small portions to a stirred aqueous solution of $Na_2[PdCl_4]$ (10 g of the trihydrate, 28.7 mmol). An immediate precipitate formed and the mixture was stirred at room temperature for 18 h. The precipitate was collected, washed with water and dried in air. The material was purified by repeated dissolution in CH_2Cl_2 and careful (slow) precipitation with diethyl ether to yield 8.5 g (45%) of purified pale yellow material, which begins to decompose near 350 °C. *Anal.* Calc. for $C_{24}H_{24}B_2N_{16}Pd$ (M_r 664.59): C, 43.37; H, 3.64; N, 33.71. Found: C, 43.41; H, 3.81; N, 32.16%.

NMR data (solution in CD_2Cl_2): $\delta(^1H)$ 7.77* (2 H), 7.40 (2 H, d, $J = 2.7$, of d, $J = 0.7$), 7.33* (1 H), 7.05 (2 H, d, $J = 2.1$, of d, $J = 0.7$), 6.96* (1 H), 6.42* (1 H), 6.33* (1 H), 6.27 (2 H, t, $J = 2.4$); $\delta(^{11}B)$ 0.9 ($h_{1/2} = 40$ Hz). At −48 °C: $\delta(^1H)$ 7.86 (1 H, d, $J = 1.6$), 7.79 (1 H, d, $J = 1.5$), 7.41 (2 H, d, $J = 2.6$), 7.38 (1 H, d, $J = 2.3$), 7.09 (2 H, d, $J = 2.2$, of d, $J = 0.7$), 6.93 (1 H, d, $J = 2.4$), 6.46 (1 H, two overlapping d), 6.36 (1 H, two overlapping d), 6.32 (2 H, t, $J = 2.4$). As is based on low-temperature 2D-NMR data, the sets $\delta(^1H)$ 7.86/6.93/6.36, 7.79/7.38/6.46, and 7.41/7.09/6.32, respectively, belong to individual pz groups. Solution in $CDCl_3$ at 25 °C: $\delta(^1H)$ 7.84* (1 H, unresolved), 7.79* (1 H, unresolved), 7.44 (2 H, d, $J = 2.5$), 7.30* (1 H, unresolved), 7.06* (1 H, unresolved), 7.05 (2 H, d, $J = 2.2$, of d, $J = 0.7$), 6.49* (1 H, unresolved), 6.33* (1 H, unresolved), 6.26 (2 H, t, $J = 2.3$); $\delta(^{11}B)$ 0.9 ($h_{1/2} = 40$ Hz). At 40 °C: $\delta(^1H)$ 7.80* (2 H), 7.43 (2 H), 7.28* (1 H), 7.05 (3 H, unresolved with a broad baseline), 6.36* (2 H), 6.25 (2 H, unresolved).

$Pd[B(pz)_4]_2 \cdot 2ZnCl_2$

A solution of 1.25 g (1.9 mmol) of $Pd[B(pz)_4]_2$ in 50 ml of CH_2Cl_2 was added dropwise with stirring to a solution of 3.8 mmol of $ZnCl_2$ in diethyl ether. The mixture was stirred at ambient temperature for 48 h. The insoluble material was collected, washed with ether and air-dried to yield 1.20 g (68%) of pale yellow crystals, melting point (m.p.) 326–330 °C decomposition. *Anal.* Calc. for $C_{24}H_{24}B_2Cl_4N_{16}PdZn_2$ (M_r 937.2): C, 30.8; H, 2.6; B, 2.3; Cl, 15.1; N, 23.9; Pd, 11.3; Zn, 13.9. Found: C, 30.50; H, 2.72; B, 2.07; Cl, 14.75; N, 23.28; Pd, 10.92; Zn, 13.5%.

NMR data (solution in DMF-d_6): $\delta(^1H)$ 7.84* (1 H), 7.76* (2 H), 7.43 (2 H, d, $J = 2.5$, of d, $J = 0.6$), 7.26 (2 H, d, $J = 2.1$, of d, $J = 0.6$), 6.92* (1 H), 6.46 (2 H, t, $J = 2.4$), 6.40* (2 H); $\delta(^{11}B)$: 1.3 ($h_{1/2} = 65$ Hz). At −25 °C: $\delta(^1H)$ 7.94 (1 H, d, $J = 1.1$), 7.92 (1 H, d, $J = 2.3$), 7.83 (1 H, d, $J = 1.3$), 7.45 (2 H, d, $J = 2.5$), 7.33 (2 H, d, $J = 1.6$), 6.90 (1 H, d, $J = 2.0$), 6.53 (2 H, t, $J = 2.4$), 6.50 (1 H, unsym t = two overlapping d, *J ca.* 1.6), 6.44 (1 H, unsym t = two overlapping d, *J ca.* 1.6). As based on selective decoupling experiments, the sets $\delta(^1H)$ 7.94/6.90/6.44, 7.92/7.83/6.50, and 7.45/7.33/6.53 (1:1:2 area ratio) belong to individual pz groups. At 75 °C: $\delta(^1H)$ 7.78 (2 H, unresolved), 7.44 (2 H, unresolved), 7.3* (2 H), 7.22 (2 H, unresolved), 6.41 (4 H, unresolved).

$Pd[B(pz)_4]_2 \cdot 2PdCl_2$

Solid $PdCl_2$ (0.54 g, 3.0 mmol) was added in small portions to a stirred solution of 1.0 g (1.5 mmol) of $Pd[B(pz)_4]_2$ in 25 ml of CH_2Cl_2. The mixture was stirred at room temperature for 48 h. The yellow–brown precipitate was collected, washed with CH_2Cl_2 and dried under vacuum. After recrystallization from dimethylformamide an apricot-colored material (64.5% yield based on $Pd[B(pz)_4]_2$) was obtained, which begins to decompose near 320 °C. *Anal.* Calc. for $C_{24}H_{24}B_2Cl_4N_{16}Pd_3$ (M_r 1019.2): C, 28.29; H, 2.37; B, 2.12; Cl, 13.91; N, 21.99; Pd, 31.32. Found: C, 28.41; H, 2.45; B, 2.10; Cl, 13.68; N, 22.20; Pd, 31.13%.

NMR data (solution in DMSO-d_6): $\delta(^1H)$ see text; $\delta(^{11}B)$ 0.4 (s, $h_{1/2} = 50$ Hz with a sharp shoulder at −0.1).

$Pb[B(pz)_4]_2$ [3]

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.62 (1 H, d, $J = 1.9$, of d, $J = 0.6$), 7.39 (1 H, d, $J = 2.4$, of d, $J = 0.5$), 6.33 (1 H, unsymmetrical t = 2 overlapping d); $\delta(^{11}B)$ 2.0 (s, $h_{1/2} = 30$ Hz). At −50 °C a slight broadening of the two low-field ^1H NMR signals is observed but the high-field signal remains undisturbed.

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