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Polypyrazolylborate–Phosphine Complexes of Platinum(II). X-ray Crystal Structure of the Unusual Dimer $Br(PEt_3)Pt\{\mu\text{-}[(pz)_2BH(pz)]\}Pt(PEt_3)Br_2$

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Abstract

Reaction of $[Pt(PEt_3)X_2]_2$ (X = Cl, Br) with two equivalents of $K[H_2B(pz)_2]$ (pz = pyrazolyl ring) yields $[\eta^2\text{-}H_2B(pz)_2]Pt(PEt_3)X$ contaminated with an impurity from which it could not be separated. A similar reaction with $K[B(pz)_4]$ (X = Br) yields the five-coördinate complex $[\eta^3\text{-}B(pz)_4]Pt(PEt_3)Br$. In contrast, the $K[HB(pz)_3]$ ligand produces the unusual bridged dimer $Br(PEt_3)Pt\{\mu\text{-}[(pz)_2BH(pz)]\}Pt(PEt_3)Br_2$. This complex forms in better yield in the stoichiometric reaction of one equivalent of the ligand per dimer. It has been characterized in the solid state by X-ray crystallography: orthorhombic, in the space group $P2_12_12_1$ with $a = 12.462(3)$, $b = 30.985(5)$, $c = 8.383(2)$ Å, $V = 3237$ Å^3 and $Z = 4$. The complexes $[MeC(O)CHC(O)Me]Pt(PEt_3)Cl$ and $[EtOCS_2]Pt(PEt_3)Cl$ have also been prepared from the reaction of $[Pt(PEt_3)Cl_2]_2$ and the respective ligand salt.

Introduction

As part of a study to synthesize new organometallic complexes of the general formula [A-A]PtL(alkyl), where A-A = bidentate, monoanionic ligand and L = a neutral, two-electron donor ligand, we have investigated the preparation of [polypyrazolylborate]$Pt(PEt_3)X$ [X = Cl, Br) complexes as potentially useful starting materials. We report here that the reactions of $Pt_2(PEt_3)_2X_4$ with the three ligands $[H_nB(pz)_{4-n}]^-$ (pz = pyrazolyl ring, $n = 0, 1, 2$) yield a different product in each case. Of particular interest is the unusual trispyrazolylborate bridged dimer, $Br(PEt_3)Pt\{\mu\text{-}[(pz)_2BH(pz)]\}Pt(PEt_3)Br_2$, characterized in the solid state by X-ray crystallography.

Experimental

General Procedure

All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. The ^1H, ^{11}B and ^{31}P NMR spectra were recorded on a Bruker AM300 spectrometer using a 5 mm broad band probe. ^1H and ^{31}P NMR chemical shifts are reported in ppm versus TMS and H_3PO_4, respectively. The triethylphosphine proton resonances are seen as a doublet of quartets for the CH_2 resonance ($J_{HP} = 10$ Hz, $J_{HH} = 8$ Hz) and a doublet of triplets for the CH_3 resonance ($J_{HP} = 17$ Hz, $J_{HH} = 8$ Hz). These coupling constants are not reported separately for each compound. Boron-11 chemical shifts are reported in ppm versus an external standard of $BF_3\cdot OEt_2$. Phosphorus-31 spectra were run with proton decoupling, all signals are singlets except where specified. An IBM NR-80 spectrometer was used to obtain ^{13}C NMR spectra. Carbon-13 NMR chemical shifts are reported versus TMS with $CDCl_3$ as the internal standard ($CDCl_3$ resonance at 77.00 ppm). High resolution mass spectra were run as solids on a VG 70SQ spectrometer, low resolution spectra were recorded on a Finnigan 4521 GC-mass spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by Robertson Laboratory, Inc. $Pt_2Cl_4(PEt_3)_2$ [1], $\{Pt[Me_2NCS_2]Cl\}_2$ [2], $K[H_2B(pz)_2]$, $Na[HB(pz)_3]$ and $Na[B(pz)_4]$ [3] were prepared by the published methods. $Pt_2Br_4(PEt_3)_2$ was prepared by the reaction of $Pt_2Cl_4(PEt_3)_2$ with an excess of KBr in refluxing acetone [4].

Dihydrobis(pyrazolyl)boratochlorotriethylphosphineplatinum(II) $[H_2B(pz)_2]Pt(PEt_3)Cl$ (1)

$Pt_2Cl_4(PEt_3)_2$ (0.100 g, 0.13 mmol) and $K[H_2B(pz)_2]$ (0.046 g, 0.26 mmol) were combined in a 50 ml round bottomed flask. THF (5 ml) was added to the solids. The reaction mixture was stirred at room temperature for 5 h. The solvent was removed under vacuum and the solid extracted with benzene. The product was an oily white solid (0.12 g). The spectra for this product indicate that two compounds are present in a c. 4/1 ratio. These two compounds could not be separated by chromatography or fractional

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crystallization. The spectral data for the major product, $[H_2B(pz)_2]Pt(PEt_3)Cl$, follow. ^1H NMR ($CDCl_3$): δ 7.76, 7.57, 7.48, 7.37 (d, d, m, d; all 1; $J = 2$ Hz; 3-H, 5-H (pz)); 6.16 (m, 2, 4-H (pz)); 1.85 (6, $PC\underline{H}_2CH_3$); 1.16 (9, $PCH_2C\underline{H}_3$). ^{31}P NMR ($CDCl_3$): δ 0.98 ($J_{PPt} = 3420$ Hz). ^{13}C NMR ($CDCl_3$): δ 141.2, 139.0, 136.2, 135.2 (s, d, s, d; $J_{CP} = 4$ Hz; 3-C, 5-C (pz)); 106.0, 104.3 (s, d; $J_{CP} = 4$ Hz; 4-C (pz)); 14.8 (d, $J_{CP} = 39$ Hz, $P\mathit{C}H_2CH_3$); 7.7 (d, $J_{CP} = 3$ Hz, $PCH_2\mathit{C}H_3$). ^{11}B NMR ($CDCl_3$): δ −7.7 (t, $J_{BH} = 104$ Hz). IR spectrum (neat), cm^{-1}: 2420 (BH). The mass spectrum shows clusters at *m/e* 494 (M^+) and 459 ($M^+ - Cl$).

Hydrotris(pyrazolyl)boratotribromobis(triethylphosphine)diplatinum(II) $Br(PEt_3)Pt\{\mu\text{-}[(pz)_2BH(pz)]\}Pt(PEt_3)Br_2$ (2)

$Pt_2Br_4(PEt_3)_2$ (0.100 g, 0.11 mmol) and $Na[HB(pz)_3]$ (0.026 g, 0.11 mmol) were combined in a 50 ml round bottomed flask. THF (5 ml) was added to the solids. The reaction mixture was stirred at room temperature for 3.5 h. The solution was filtered and the solvent removed under vacuum. The product was a yellow–orange solid (0.10 g, 0.09 mmol, 84%). Yellow crystals were obtained from 5 ml hot/cold hexane–CH_2Cl_2 (90:10). ^1H NMR ($CDCl_3$): δ 8.41, 8.16, 7.82, 7.67, 7.57, 7.44 (d, d, m, d, m, d; all 1; $J = 2$ Hz; 3-H, 5-H (pz)); 6.34, 6.26 (m, m; 1, 2; $J = 2$ Hz; 4-H (pz)); 2.02, 1.84 (6, 6; $PC\mathit{H}_2CH_3$); 1.22, 0.97 (9, 9; $PCH_2C\mathit{H}_3$). ^{31}P NMR ($CDCl_3$): δ −1.53 ($J_{PPt} = 3387$ Hz), −6.48 ($J_{PPt} = 3328$ Hz).

Tetrakis(pyrazolyl)boratobromotriethylphosphineplatinum(II) $[\eta^3\text{-}B(pz)_4]Pt(PEt_3)Br$ (3)

$Pt_2Br_4(PEt_3)_2$ (0.100 g, 0.11 mmol) and $Na[B(pz)_4]$ (0.068 g, 0.22 mmol) were combined in a 50 ml round bottomed flask. Acetone (10 ml) was added to the solids. The reaction mixture was stirred at room temperature for 1 h. The solution was filtered and the solvent removed under vacuum. The product was a pale yellow solid (0.12 g, 0.18 mmol, 69%). ^1H NMR ($CDCl_3$): δ 8.15, 7.76, 7.70, 7.50, 7.46, 7.23, 7.08, 6.80 (d, m, m, d, d, m, m, m; all 1; $J = 2$ Hz; 3-H, 5-H (pz)); 6.31, 6.26, 6.22 (m, t, m; 2, 1, 1; $J = 2$ Hz; 4-H (pz)); 1.73 (6, $PC\mathit{H}_2CH_3$); 0.95 (9, $PCH_2C\mathit{H}_3$). ^{31}P NMR ($CDCl_3$): δ −1.17 ($J_{PPt} = 3414$ Hz). The mass spectrum shows clusters at 672 (M^+) and 605 ($M^+ - pz$). *Anal.* Calc. for $C_{18}H_{27}BBrN_8PPt$: C, 32.14; H, 4.02. Found: C, 31.85; H, 4.11%.

Acetylacetonatochlorotriethylphosphineplatinum(II) $[MeC(O)CHC(O)Me]Pt(PEt_3)Cl$

$Pt_2Cl_4(PEt_3)_2$ (0.10 g, 0.13 mmol), $Na[MeC(O)CHC(O)Me]$ (0.063 g, 0.26 mmol) and KPF_6 (0.096 g, 0.52 mmol) were combined in a 50 ml round bottomed flask. Acetone (10 ml) was added to the solids. The reaction mixture was stirred at room temperature for 3 h. The solution was filtered and the solvent removed under vacuum. The ^{31}P NMR spectrum of this crude product shows the presence of two new compounds in a 4:1 ratio. The solid was dissolved in CH_2Cl_2 and chromatographed on silica. The major product was eluted with CH_2Cl_2. The yield of the yellow–orange solid was 0.067 g, 0.15 mmol, 57%. The ^1H NMR spectrum matches that reported in the literature [5]. ^{31}P NMR ($CDCl_3$): δ 0.905 ($J_{PPt} = 3919$ Hz). The mass spectrum shows clusters at *m/e* 448 (M^+) and 412 ($M^+ - Cl$).

Chlorotriethylphosphine(O-ethylxanthato)platinum(II) $[EtOCS_2]Pt(PEt_3)Cl$

$Pt_2Cl_4(PEt_3)_2$ (0.10 g, 0.13 mmol) and $K[EtOCS_2]$ (0.042 g, 0.26 mmol) were combined in a 50 ml round bottomed flask. CH_2Cl_2 (10 ml) was added to the solids. The reaction mixture was stirred at room temperature for 18 h. The solution was filtered and the solvent removed under vacuum. The product was a yellow solid (0.10 g, 0.21 mmol, 81%). ^1H NMR ($CDCl_3$): δ 4.62 (q, 2, $J = 7$ Hz, $OC\mathit{H}_2CH_3$); 1.84 (6, $PC\mathit{H}_2CH_3$); 1.48 (t, 3, $J = 7$ Hz, $OCH_2C\mathit{H}_3$); 1.15 (9, $PCH_2C\mathit{H}_3$). ^{31}P NMR ($CDCl_3$): δ 8.28 ($J_{PPt} = 3594$ Hz). The mass spectrum shows clusters at *m/e* 469 (M^+) and 405 ($M^+ - Cl - Et$).

Crystallographic Analysis of $Br(PEt_3)Pt\{\mu\text{-}[(pz)_2BH(pz)]\}Pt(PEt_3)Br_2$

Transparent prisms of 2 were mounted in thin-walled capillaries on a CAD-4 diffractometer. The unit cell parameters were determined and refined from 25 general reflections. Crystal data, data collection parameters and results of the analysis are listed in Table 1. The structure was solved by the heavy atom

TABLE 1. Crystallographic data for the structural analysis of $Br(PEt_3)Pt\{\mu\text{-}[(pz)_2BH(pz)]\}Pt(PEt_3)Br_2$ (2)

Formula	$C_{21}H_{40}BBr_3N_6P_2Pt_2$
Space group	$P2_12_12_1$
Crystal dimensions (nm)	0.30 × 0.10 × 0.08
a (Å)	12.462(3)
b (Å)	30.985(5)
c (Å)	8.383(2)
V (Å^3)	3237
Z	4
Radiation	Mo Kα (0.71073 Å)
Temperature (°C)	ambient
No. reflections	3260
2θ range (°)	2–50
Linear absorption coefficient (cm^{-1})	113
Transmission factors	
min.	0.801
max.	1.261
average	1.017
R_F	0.026
R_{WF}	0.031

TABLE 2. Positional parameters and their e.s.d.s for **2**

Pt(1)	0.14331(4)	0.08181(2)	0.06362(8)	3.66(1)
Pt(2)	−0.19780(4)	0.16642(2)	0.36767(9)	4.02(1)
Br(1)	0.1541(1)	0.15963(5)	0.0388(3)	5.76(4)
Br(2)	0.1218(1)	0.00467(5)	0.0810(4)	7.50(6)
Br(3)	−0.3800(1)	0.18705(6)	0.3014(3)	7.13(5)
P(1)	0.3216(3)	0.0781(1)	0.0703(7)	5.0(1)
P(2)	−0.1453(3)	0.2315(1)	0.2783(6)	4.9(1)
N(11)	−0.1036(8)	0.0840(4)	0.137(2)	4.2(3)
N(12)	−0.0240(9)	0.0872(3)	0.029(1)	4.3(3)
N(21)	−0.1917(8)	0.0695(4)	0.401(2)	4.7(3)
N(22)	−0.2488(8)	0.1046(4)	0.436(2)	4.4(3)
N(31)	−0.0143(8)	0.1053(3)	0.403(2)	3.8(3)
N(32)	−0.0532(7)	0.1451(3)	0.439(2)	3.4(2)
C(1)	0.367(1)	0.0957(7)	−0.136(4)	10.7(7)
C(2)	0.467(2)	0.0952(9)	−0.174(4)	15(1)
C(3)	0.385(1)	0.1164(5)	0.211(4)	10.8(7)
C(4)	0.362(1)	0.1105(7)	0.372(3)	9.2(6)
C(5)	0.376(1)	0.0272(6)	0.102(3)	8.0(6)
C(6)	0.502(1)	0.0229(7)	0.142(4)	9.6(7)
C(7)	−0.001(1)	0.2432(6)	0.299(3)	6.7(5)
C(8)	0.037(1)	0.2831(6)	0.210(4)	9.2(6)
C(9)	−0.184(1)	0.2376(6)	0.072(3)	7.1(5)
C(10)	−0.137(2)	0.2065(6)	−0.047(3)	9.6(6)
C(11)	−0.208(1)	0.2747(5)	0.383(3)	6.8(5)
C(12)	−0.197(1)	0.2729(5)	0.562(3)	7.5(5)
C(13)	−0.069(1)	0.0891(5)	−0.114(2)	5.4(4)
C(14)	−0.179(1)	0.0881(5)	−0.106(2)	5.5(4)
C(15)	−0.195(1)	0.0840(5)	0.058(2)	4.9(3)
C(23)	−0.339(1)	0.0923(5)	0.500(2)	5.6(4)
C(24)	−0.342(1)	0.0473(5)	0.514(2)	6.2(4)
C(25)	−0.246(1)	0.0340(4)	0.447(2)	5.4(4)
C(33)	0.015(1)	0.1627(4)	0.548(2)	3.7(3)
C(34)	0.100(1)	0.1345(5)	0.571(2)	5.0(4)
C(35)	0.0768(9)	0.0996(5)	0.483(2)	4.0(3)
B(1)	−0.084(1)	0.0726(5)	0.317(2)	3.2(3)

method and refined using SDP [6]. Hydrogen atoms were placed in calculated positions and not refined. Full-matrix least-squares refinements were carried out with weights $w = (\sigma^2(F) + 0.0004F^2)^{-1}$ for reflections with $I > 3\sigma(I)$. Table 2 shows positional parameters for 2.

Results and Discussion

Reaction of the platinum(II) dimer, $Pt_2(PEt_3)_2X_4$ (X = Cl, Br), with $K[H_2B(pz)_2]$ (pz = pyrazolyl ring) proceeds as in eqn. (1) but the desired product is contaminated by a second unidentified compound from which it has not been completely separated.

$$Pt_2(PEt_3)_2X_4 + 2\,[H_2B(pz)_2]^- \longrightarrow 2\,[H_2B(pz)_2]Pt(PEt_3)X + 2X^- \qquad (1)$$

Column chromatography of this mixture leads to decomposition and repeated attempts at fractional crystallization have not yielded the pure product. Identification of the major product for X = Cl by ^1H, ^{11}B, ^{13}C, and ^{31}P NMR as well as infrared and mass spectroscopy clearly indicates that this compound is $[\eta^2\text{-}H_2B(pz)_2]Pt(PEt_3)Cl$ (**1**) with the expected square planar structure. The infrared spectrum shows only a terminal B–H stretch at 2420 cm^{-1} and the coupled ^{11}B NMR spectrum shows that the two hydrogen atoms on boron are equivalent. These measurements demonstrate that no agostic B–H···Pt interactions are present. It is important to consider this interaction because a number of complexes have now been characterized with this type of bonding [7]. Also, the five-coordinate complexes that would be produced by such an interaction are reasonable because the analogous five-coordinate complex $[\eta^3\text{-}B(pz)_4]Pt(PEt_3)Cl$ has been prepared in this work (*vide infra*) and a variety of $[\eta^3\text{-}HB(pz)_3]PtMeL$ complexes (L = RC≡CR, $R_2C{=}CR_2$, and PR_3) have been reported by Clark and Manzer [8]. The five-coordinate structure of $[\eta^3\text{-}HB(pz)_3]PtMe(CF_3C{\equiv}CCF_3)$, showing that all three pyrazolyl rings are bonded to the platinum, has been confirmed crystallographically [9]. Not all of these types of complexes are five-coordinate as shown by the crystal structure of four-coordinate $[\eta^2\text{-}HB(pz)_3]PtMe(CNBu^t)$, where only two of the pyrazolyl rings are attached to the platinum in the solid state [10]. An attempted preparation of $[H_2B(pz)_2]Pt(PPh_3)Cl$ by the method outlined in eqn. (1) also led to two products.

The reaction of $Pt_2(PEt_3)_2Br_4$ with $Na[HB(pz)_3]$ in the stoichiometry of eqn. (1) also yields a mixture (*c.* 3/1 ratio) of two products. The two products were separated on a silica column, the major product eluting with CH_2Cl_2 and the minor product with THF, but only small amounts of each product were isolated using this method. The reaction of $Pt_2(PEt_3)_2Br_4$ with one equivalent of $Na[HB(pz)_3]$ leads to the exclusive formation of the major product described above in good yield. This complex does not have the spectral properties expected for either a four- or five-coordinate $[HB(pz)_3]Pt(PEt_3)Br$ complex. The ^{31}P NMR spectrum shows two equal intensity phosphorus resonances and the ^1H NMR spectrum shows that the pyrazolyl rings are all nonequivalent.

In order to characterize this complex definitively, the solid state structure was determined by X-ray crystallography. An ORTEP drawing of the molecule is shown in Fig. 1 and bond distances and angles are in Table 3.

As suggested by the two platinum to one trispyrazolylborate stoichiometry in the more successful preparation, the species is a dimer, $Br(PEt_3)Pt\{\mu\text{-}[(pz)_2BH(pz)]\}Pt(PEt_3)Br_2$ (**2**), with the trispyrazolylborate ligand bridging $Pt(PEt_3)Br$ and *trans*-$Pt(PEt_3)Br_2$ units with bidentate coordination to the former and monodentate coordination to the latter.

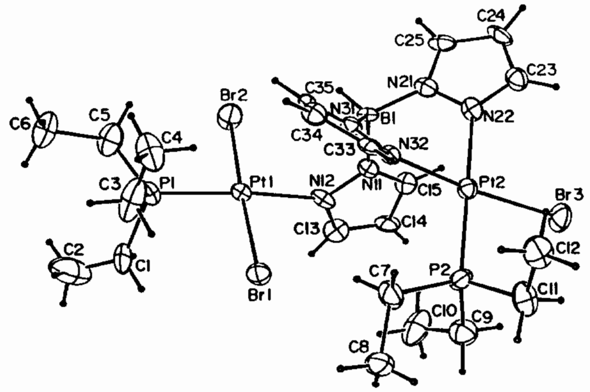

Fig. 1. ORTEP drawing of Br(PEt$_3$)Pt{μ-[(pz)$_2$BH(pz)]}Pt(PEt$_3$)Br$_2$.

TABLE 3. Selected bond distances (A) and bond angles (°) for Br(PEt$_3$)Pt{μ-[(pz)$_2$BH(pz)]}Pt(PEt$_3$)Br$_2$ (2) with e.s.d.s in parentheses

Bond distances			
Pt1–Br1	2.424(2)	P2–C9	1.81(3)
Pt1–Br2	2.409(2)	P2–C11	1.78(2)
Pt1–P1	2.225(4)	N11–B1	1.56(3)
Pt1–N12	2.12(1)	N21–B1	1.53(2)
Pt2–Br3	2.424(2)	N31–B1	1.52(2)
Pt2–P2	2.249(5)	C1–C2	1.29(4)
Pt2–N22	2.10(1)	C3–C4	1.39(5)
Pt2–N32	2.01(1)	C5–C6	1.61(3)
P1–C1	1.90(4)	C7–C8	1.52(3)
P1–C3	1.85(3)	C9–C10	1.50(3)
P1–C5	1.74(3)	C11–C12	1.52(4)
P2–C7	1.84(2)		
Bond angles			
P1–Pt1–N12	173.4(4)	Pt2–P2–C11	112.5(8)
P2–Pt2–N22	176.4(6)	C7–P2–C9	109(1)
P2–Pt2–N32	97.6(4)	C7–P2–C11	104(1)
N22–Pt2–N32	83.7(5)	C9–P2–C11	106(1)
Br1–Pt1–Br2	176.5(1)	Pt1–N12–N11	130(1)
Br1–Pt1–P1	89.9(1)	Pt1–N12–C13	123(1)
Br1–Pt1–N12	88.0(4)	Pt2–N22–N21	121(2)
Br2–Pt1–P1	93.4(1)	Pt2–N22–C23	130(1)
Br2–Pt1–N12	88.6(4)	Pt2–N32–N31	124(2)
Br3–Pt2–P2	87.7(1)	Pt2–N32–C33	129(2)
Br3–Pt2–N22	91.1(4)	P1–C1–C2	121(3)
Br3–Pt2–N32	174.2(4)	P1–C3–C4	117(3)
Pt1–P1–C1	105.2(8)	P1–C5–C6	119(2)
Pt–P1–C3	114.1(9)	P2–C7–C8	115(2)
Pt1–P1–C5	116.0(7)	P2–C9–C10	117(2)
C1–P1–C3	106(2)	P2–C11–C12	115(2)
C1–P1–C5	106(1)	N11–B1–N21	109(1)
C3–P1–C5	109(1)	N11–B1–N31	113(1)
Pt2–P2–C7	115.4(7)	N21–B1–N31	110(1)
Pt2–P2–C9	109.7(7)		

Each of the platinum atoms has essentially square planar geometry. Pt1 is 0.0720(7) Å and Pt2 is only 0.0075(7) Å out of the ligand donor atom planes. The planes of each square unit form an angle of 17.1(3)°. The bridging trispyrazolylborate ligand is in a shallow boat configuration as is observed for bidentate polypyrazolylborate ligands [8, 9]. The N22–Pt2–N32 angle in the chelate ring of 83.7(5)° is considerably less than expected for square planar geometry. The analogous angle in three [η^2-polypyrazolylborate]Pt(Me)L structures ranges from 87.4(3)° to 89.0(5)° [10, 11]. The adjacent N32–Pt2–P2 angle is correspondingly large at 97.6(4)°. The distortions in these two angles likely arise from steric repulsions between the triethylphosphine ligand and the two adjacent pyrazolyl rings, one coordinated to each platinum. Bond distances in both halves of the molecule are as expected [9, 12]. The Pt–N length *trans* to bromine is *c.* 0.1 Å shorter than the two *trans* to triethylphosphine reflecting the greater *trans* influence expected for phosphine ligands.

The formation of this dimer in the presence of excess trispyrazolylborate ligand in preference to either a four- or five-coordinate [HB(pz)$_3$]Pt(PEt$_3$)-Br complex, both of which have precedence as outlined above [8], is surprising. This complex is extremely stable and does not react with additional trispyrazolylborate ligand or even triethylphosphine. In two other examples where the [HB(pz)$_3$] ligand acts as a bridge between two metals, {[HB(pz)$_3$]-PtMe}$_n$ [8b] and Cu$_2$[HB(pz)$_3$]$_2$ [13], the bridging interaction is broken easily by donor ligands. The reaction of the dimeric chloride, Pt$_2$(PEt$_3$)$_2$Cl$_4$, with the trispyrazolylborate ligand also produces an analogous dimeric material as characterized by ^{1}H and ^{31}P NMR.

The formation of this dimeric complex is even more surprising given that the Na[B(pz)$_4$] reacts with Pt$_2$(PEt$_3$)$_2$Br$_4$ to form the expected product, [η^3-B(pz)$_4$]Pt(PEt$_3$)Br (**3**). Analogous to the majority of the complexes of similar formula prepared by Clark and Manzer with both the tris- and tetrakis-pyrazolylborate ligands [8], this is a five-coordinate complex in which three of the pyrazolyl rings are attached to the platinum while the other is not coordinated. This is evidenced by the ^{1}H NMR spectrum which shows four distinct sets of pyrazolyl peaks. In a four-coordinate structure, the two non-coordinated pyrazolyl rings would be equivalent because of the known low barrier to flipping of the two boat conformers formed by the BN$_4$Pt ring [14].

Two other ligands have been investigated for the preparation of [A-A]PtLX type complexes. [MeC(O)CHC(O)Me]Pt(PEt$_3$)Cl (prepared previously by an indirect route) [5] forms in the reaction of Pt$_2$Cl$_4$(PEt$_3$)$_2$ and Na[MeC(O)CHC(O)Me]. The yield of the desired compound is improved greatly by the addition of KPF$_6$ to the reaction [15]. The *O*-ethylxanthate complex, [EtOCS$_2$]Pt(PEt$_3$)Cl, also forms in good yield (81%) in a similar reaction using K[EtOCS$_2$]. Reaction of the platinum halide complexes prepared in this work with alkyllithium and Grignard reagents to prepare platinum–alkyl products gave mixtures of products that have not been characterized.

Supplementary Material

Thermal parameters, positional parameters of H atoms, torsion angles and calculated and observed structure factors are available from the authors on request.

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