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**Supplementary Material Available:** Figures showing the Curie-Weiss magnetic susceptibility behavior and the unit cell packing and tables listing X-ray crystal structure parameters, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters (6 pages); a table listing observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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### Preparation and Structure of Mononuclear Iron(III) Complexes $[\text{LFeCl}_3]^-$ and $[\text{LFe}(\text{N}_3)_3]^-$ (L = Hydrotris(1-pyrazolyl)borate and Hydrotris(3,5-dimethyl-1-pyrazolyl)borate)

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The utility of tripod nitrogen ligands  $(\text{HB}(\text{pz})_3)^-$  and  $(\text{HB}(3,5\text{-Me}_2\text{pz})_3)^-$  in synthesizing a variety of transition-metal complexes has been demonstrated in recent years.<sup>1</sup> The iron complexes ligated by these ligands are of interest especially from the bioinorganic point of view, because the rigid  $\text{N}_3$  ligand coordination mimics the multiimidazole coordination found often in the active site of non-heme iron proteins. The synthesis and characterization of a binuclear iron complex  $(\text{HB}(\text{pz})_3)_2\text{FeO}(\text{OAc})_2\text{Fe}(\text{HB}(\text{pz})_3)$  as a synthetic analogue for methemerythrin achieved by Lippard et al.<sup>2</sup> is a good example. However, the marked tendency to form a stable full-sandwich  $\text{FeL}_2$  is a serious problem of these ligands. Therefore, to date, a half-sandwich complex  $\text{LFeX}_n$  is not known, whereas the corresponding iron complex  $\text{LFeCl}_3$  with a similar tripod nitrogen ligand 1,4,7-triazacyclononane or 1,4,7-trimethyl-1,4,7-triazacyclononane was reported to be a good reactant for syntheses of a series of iron complexes.<sup>3</sup> We now found that the reaction of a binuclear iron(III) complex  $(\text{Et}_4\text{N})_2(\text{Fe}_2\text{OCl}_6)$  with  $\text{KHB}(\text{pz})_3$  or  $\text{KHB}(3,5\text{-Me}_2\text{pz})_3$  gives the mononuclear iron complex  $[\text{LFeCl}_3]^-$ . The syntheses and structures of the complexes and the azide derivative are described here.

### Experimental Section

**General Data.** Unless otherwise stated, reactions were performed under argon. All reagents were used as received. MeCN was dried over  $\text{CaH}_2$  and distilled under an argon atmosphere.  $(\text{Et}_4\text{N})_2(\text{Fe}_2\text{OCl}_6)$  (**1**) was prepared by the recently improved synthetic method.<sup>4</sup>  $\text{KHB}(\text{pz})_3$  and  $\text{KHB}(3,5\text{-Me}_2\text{pz})_3$  were synthesized by the literature methods.<sup>3</sup> UV-vis and IR spectra were recorded on a Shimadzu UV-260 instrument

**Table I.** Crystallographic Data for  $(\text{Et}_4\text{N})[(\text{HB}(\text{pz})_3)\text{FeCl}_3]$  (**2**) and  $(\text{Et}_4\text{N})[(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Fe}(\text{N}_3)_3]$  (**4**)

Compound 2	
$\text{C}_{17}\text{H}_{30}\text{N}_7\text{Fe}_1\text{Cl}_3\text{B}_1$	orthorhombic, <i>Pcab</i>
$a = 16.993$ (3) Å	$\lambda = 0.71068$ Å
$b = 17.547$ (2) Å	$\mu(\text{Mo K}\alpha) = 9.12$ cm <sup>-1</sup>
$c = 16.166$ (5) Å	$2^\circ < 2\theta < 60^\circ$
$V = 4820$ (2) Å <sup>3</sup>	no. of measd reflns = 7963
$Z = 8$	no. of obsd reflns ( $F_o > 3\sigma(F_o)$ ) = 2166
$fw = 505.5$	$R = 0.0398$
$D_{\text{calcd}} = 1.40$ g cm <sup>-3</sup>	$R_w = 0.0402$
Compound 4	
$\text{C}_{23}\text{H}_{42}\text{N}_{15}\text{Fe}_1\text{B}_1$	monoclinic, <i>Cm</i>
$a = 15.443$ (5) Å	$\lambda = 0.71068$ Å
$b = 12.399$ (3) Å	$\mu(\text{Mo K}\alpha) = 4.78$ cm <sup>-1</sup>
$c = 10.183$ (2) Å	$2^\circ < 2\theta < 60^\circ$
$\beta = 126.37$ (1)°	no. of measd reflns = 2595
$V = 1569.8$ (7) Å <sup>3</sup>	no. of obsd reflns ( $F_o > 3\sigma(F_o)$ ) = 1975
$Z = 2$	$R = 0.0547$
$fw = 609.4$	$R_w = 0.0576$
$D_{\text{calcd}} = 1.29$ g cm <sup>-3</sup>	

and a Hitachi 250-50 instrument, respectively. Elemental analyses were performed in the service department in the Tokyo Institute of Technology.

**(Et<sub>4</sub>N)[(HB(pz)<sub>3</sub>)FeCl<sub>3</sub>] (2).** A 0.603-g (1.00-mmol) sample of **1** and 0.448 g (2.00 mmol) of  $\text{KHB}(\text{pz})_3$  were stirred in 20 mL of MeCN for 20 min. The mixture was filtered over Celite, and the volume of the filtrate was reduced to half under vacuum. Cooling the solution at -20 °C afforded 0.231 g of orange microcrystalline solids (yield 23%). IR (KBr):  $\nu(\text{BH})$  2500 cm<sup>-1</sup>. UV-vis (MeCN): 305 ( $\epsilon = 7600$  M<sup>-1</sup> cm<sup>-1</sup>), 350 nm (5200). Anal. Calcd for  $\text{C}_{17}\text{H}_{30}\text{N}_7\text{BCl}_3\text{Fe}$ : C, 40.39; H, 5.98; N, 19.40; Cl, 21.04. Found: C, 40.40; H, 6.10; N, 19.21; Cl, 21.66.

**(Et<sub>4</sub>N)[(HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>)FeCl<sub>3</sub>] (3).** A 0.602-g (1.00-mmol) sample of **1** and 0.674 g (2.00 mmol) of  $\text{KHB}(3,5\text{-Me}_2\text{pz})_3$  were stirred in 20 mL of MeCN for 1 h. The reaction mixture was filtered, and the volume of the brown filtrate was reduced to half under vacuum. Cooling this solution at -20 °C afforded 0.288 g of orange microcrystalline solids (yield 24%). IR (KBr):  $\nu(\text{BH})$  2554 cm<sup>-1</sup>. UV-vis (MeCN): 291 ( $\epsilon = 4800$  M<sup>-1</sup> cm<sup>-1</sup>), 394 nm (6400). Anal. Calcd for  $\text{C}_{23}\text{H}_{42}\text{N}_7\text{BCl}_3\text{Fe}$ : C, 46.85; H, 7.18; N, 16.63; Cl, 18.04. Found: C, 46.80; H, 7.48; N, 16.72; Cl, 18.31.

**(Et<sub>4</sub>N)[(HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>)Fe(N<sub>3</sub>)<sub>3</sub>] (4). Method A.** A 0.602-g (1.00-mmol) sample of **1** and 0.675 g (2.00 mmol) of  $\text{KHB}(3,5\text{-Me}_2\text{pz})_3$  were stirred in the presence of 0.520 g (8.00 mmol) of  $\text{NaN}_3$  in 20 mL of MeCN for 3 h. The reaction mixture was filtered over Celite. The clear reddish brown filtrate was stored at -20 °C to give red microcrystalline solids (0.367 g, yield 30%). IR(KBr):  $\nu(\text{BH})$  2541 cm<sup>-1</sup>;  $\nu(\text{N}_3)$  2073, 2048 cm<sup>-1</sup>. UV-vis (MeCN): 331 ( $\epsilon = 6200$  M<sup>-1</sup> cm<sup>-1</sup>), 441 (6800), 510 nm (5600). Anal. Calcd for  $\text{C}_{23}\text{H}_{42}\text{N}_{16}\text{BF}_e$ : C, 45.34; H, 6.95; N, 36.78. Found: C, 45.30; H, 6.92; N, 36.82.

**Method B.** A 0.659-g (1.12-mmol) sample of **3** and 0.301 g (4.63 mmol) of  $\text{NaN}_3$  were stirred in 30 mL of MeCN for 20 min. The formed precipitate was removed by filtration, and the filtrate was evacuated to dryness to afford **4** as red solids essentially in quantitative yield.

**Structure Determinations.** Crystals of **2** and **4** suitable for an X-ray analysis were grown from acetone and acetonitrile, respectively. The X-ray data were collected on a Rigaku four-circle diffractometer, Model AFC-5. The lattice parameters were determined by a least-square fit to the automatically centered 25 independent reflections with  $2\theta \leq 30^\circ$ . The crystal parameters and additional details of the data collections are given in Table I. The data were corrected for Lorentz and polarization. Secondary decay was not observed during the data collections for both complexes. The positions of the iron atoms were determined by direct methods. In both cases, the other non-hydrogen atoms were easily located by the subsequent weighted Fourier calculations. The difference Fourier map for **2** showed all of the hydrogen atoms, which were included for the refinements. For **4**, all of the hydrogen atoms except the ones on the cation were found in the difference Fourier map and these were included for the calculations. The structures were refined by full-matrix least-squares methods. The weighting scheme was  $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$  ( $p = 0.0$  for **2** and 0.056 for **4**). The calculations were carried out by CRYSTAN on a FACOM A-70 computer. The final positional parameters for all non-hydrogen atoms of **2** and **4** are listed in Tables II and III, respectively.

### Results and Discussion

Despite our expectation at the outset of this work (generation of a novel  $\mu$ -oxo binuclear complex,  $[(\text{HB}(\text{pz})_3)_2\text{FeOFe}]$

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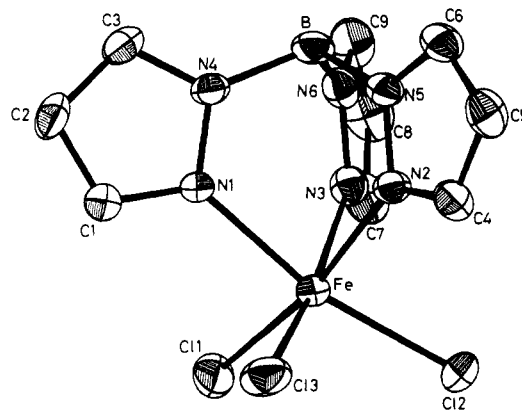
**Table II.** Positional Parameters and Equivalent Isotropic Thermal Parameters,  $B_{eq}$ , for  $(Et_4N)[(HB(pz)_3)FeCl_3]$  (**2**)

atom	$x/a$	$y/b$	$z/c$	$B_{eq}, \text{\AA}^2$
Fe1	0.906 97 (5)	0.307 65 (3)	0.135 95 (3)	2.69 (1)
Cl1	0.859 63 (10)	0.182 77 (7)	0.138 69 (10)	4.73 (4)
Cl2	0.852 97 (10)	0.344 47 (7)	0.010 00 (7)	3.84 (3)
Cl3	1.031 37 (10)	0.278 21 (10)	0.091 59 (10)	4.88 (4)
N1	0.945 47 (25)	0.297 30 (23)	0.262 26 (23)	2.6 (1)
N2	0.941 37 (25)	0.423 87 (25)	0.158 47 (25)	2.8 (1)
N3	0.800 12 (26)	0.345 67 (26)	0.197 49 (28)	3.6 (1)
N4	0.930 08 (26)	0.350 17 (25)	0.322 14 (25)	2.9 (1)
N5	0.922 86 (26)	0.461 80 (23)	0.229 48 (25)	3.0 (1)
N6	0.801 32 (26)	0.390 07 (25)	0.266 63 (28)	3.0 (1)
N1C	0.715 49 (26)	0.089 35 (25)	0.399 26 (28)	3.1 (1)
B1	0.879 87 (41)	0.420 03 (38)	0.299 36 (41)	3.4 (2)
C1	0.987 59 (37)	0.242 81 (35)	0.297 79 (35)	3.3 (2)
C2	0.999 83 (44)	0.258 20 (40)	0.381 44 (35)	3.9 (2)
C3	0.962 50 (38)	0.326 24 (35)	0.393 52 (35)	3.4 (2)
C4	0.982 36 (37)	0.472 08 (35)	0.112 20 (38)	3.5 (2)
C5	0.991 47 (38)	0.541 45 (35)	0.151 90 (43)	4.1 (2)
C6	0.952 91 (40)	0.533 23 (34)	0.225 77 (38)	3.7 (2)
C7	0.725 68 (38)	0.324 02 (38)	0.187 94 (47)	4.4 (2)
C8	0.678 91 (46)	0.352 96 (53)	0.250 30 (63)	5.6 (3)
C9	0.728 23 (43)	0.394 06 (44)	0.297 37 (47)	4.6 (2)
C1C	0.721 20 (41)	0.174 31 (37)	0.418 31 (44)	3.9 (2)
C2C	0.796 17 (59)	0.211 39 (53)	0.390 57 (65)	6.5 (3)
C3C	0.714 86 (49)	0.075 48 (49)	0.306 44 (43)	5.0 (2)
C4C	0.647 57 (65)	0.110 84 (68)	0.259 93 (53)	7.3 (3)
C5C	0.638 84 (41)	0.063 31 (38)	0.438 77 (43)	4.3 (2)
C6C	0.619 95 (68)	-0.019 37 (50)	0.427 41 (65)	7.7 (4)
C7C	0.785 19 (43)	0.046 52 (43)	0.433 36 (46)	4.6 (2)
C8C	0.797 95 (54)	0.056 88 (56)	0.526 06 (59)	6.3 (3)

**Table III.** Positional and Equivalent Isotropic Thermal Parameters,  $B_{eq}$ , for  $(Et_4N)[(HB(3,5-Me_2pz)_3)Fe(N_3)_3]$  (**4**)

atom	$x/a$	$y/b$	$z/c$	$B_{eq}, \text{\AA}^2$
Fe1	0.794 01	0.500 00	0.153 45	3.02 (2)
B1	0.602 94 (54)	0.500 00	-0.240 18 (71)	3.3 (2)
N1A	0.813 77 (47)	0.383 75 (53)	0.307 17 (65)	5.2 (2)
N2A	0.765 44 (59)	0.308 27 (49)	0.295 79 (83)	6.3 (2)
N3A	0.717 88 (114)	0.232 19 (78)	0.284 30 (196)	13.5 (7)
N1B	0.952 38 (53)	0.500 00	0.246 59 (81)	4.4 (2)
N2B	1.021 92 (44)	0.500 00	0.389 27 (83)	3.9 (2)
N3B	1.090 89 (65)	0.500 00	0.522 69 (95)	6.2 (3)
N1	0.551 94 (41)	0.500 00	-0.150 27 (68)	3.2 (2)
N2	0.616 24 (50)	0.500 00	0.017 51 (74)	3.6 (2)
N3	0.673 53 (28)	0.601 64 (28)	-0.191 20 (38)	3.3 (1)
N4	0.760 39 (31)	0.615 82 (34)	-0.030 19 (47)	3.1 (1)
N1C	1.021 51 (68)	0.500 00	0.868 10 (104)	6.0 (3)
C1	0.356 21 (57)	0.500 00	-0.385 55 (111)	5.5 (3)
C2	0.447 20 (56)	0.500 00	-0.208 24 (93)	4.1 (2)
C3	0.443 28 (59)	0.500 00	-0.075 22 (106)	4.7 (2)
C4	0.551 23 (56)	0.500 00	0.063 06 (87)	4.1 (2)
C5	0.590 69 (69)	0.500 00	0.237 63 (109)	5.6 (3)
C6	0.580 18 (59)	0.694 90 (53)	-0.462 39 (65)	5.7 (2)
C7	0.666 47 (40)	0.685 35 (37)	-0.282 55 (52)	3.9 (1)
C8	0.750 96 (44)	0.754 89 (40)	-0.179 98 (59)	4.4 (2)
C9	0.807 55 (40)	0.708 80 (41)	-0.024 23 (59)	3.7 (1)
C10	0.905 21 (47)	0.751 45 (52)	0.128 65 (68)	5.2 (2)
C1C	1.019 24 (93)	0.599 63 (84)	0.769 30 (163)	10.6 (5)
C2C	0.817 47 (133)	0.500 00	0.657 86 (228)	9.0 (7)
C3C	0.903 87 (102)	0.500 00	0.826 49 (157)	7.7 (5)
C4C	1.017 40 (117)	0.705 14 (80)	0.856 56 (239)	13.2 (9)
C5C	1.098 45 (124)	0.500 00	1.035 67 (187)	8.7 (6)
C6C	1.220 62 (166)	0.500 00	1.087 41 (292)	11.8 (9)

$(HBpz_3)]^{2+}$ , the reaction of  $(Et_4N)_2(Fe_2OCl_6)$  (**1**) and  $KHB(pz)_3$  gives a mononuclear half-sandwich complex  $(Et_4N)[(HB(pz)_3)FeCl_3]$  (**2**). The reaction with  $KHB(3,5-Me_2pz)_3$  yields also the corresponding complex  $(Et_4N)[(HB(3,5-Me_2pz)_3)FeCl_3]$  (**3**). In both cases, the yields were not very high, partly because of the significant formation of stable full-sandwich complexes  $FeL_2$  and  $FeL_2^+$ .<sup>6,7</sup> The prolonged reaction in particular causes the for-

**Figure 1.** ORTEP drawing of the crystal structure of the anion in **2**.**Table IV.** Bond Distances ( $\text{\AA}$ ) and Angles (deg) for  $[(HB(pz)_3)FeCl_3]^-$ 

Distances			
Fe-Cl1	2.335 (2)	Fe-Cl2	2.325 (2)
Fe-Cl3	2.291 (2)	Fe-N1	2.152 (4)
Fe-N2	2.152 (4)	Fe-N3	2.175 (5)
N1-N4	1.366 (6)	N2-N5	1.364 (6)
N3-N6	1.363 (6)	B-N4	1.538 (8)
B-N5	1.532 (8)	B-N6	1.529 (8)
N1-C1	1.325 (7)	N2-C4	1.327 (8)
N3-C7	1.330 (8)	N4-C3	1.346 (7)
N5-C6	1.355 (7)	N6-C9	1.340 (9)
Cl1-C2	1.395 (8)	C2-C3	1.366 (10)
C4-C5	1.385 (9)	C5-C6	1.370 (9)
C7-C8	1.380 (12)	C8-C9	1.342 (12)

Angles			
Cl1-Fe-Cl2	98.13 (6)	Cl1-Fe-Cl3	96.44 (7)
Cl2-Fe-Cl3	98.78 (6)	N1-Fe-Cl1	90.4 (1)
N1-Fe-Cl2	167.0 (1)	N1-Fe-Cl3	89.9 (1)
N1-Fe-N2	80.6 (2)	N1-Fe-N3	81.1 (2)
N2-Fe-Cl1	168.4 (1)	N2-Fe-Cl2	89.6 (1)
N2-Fe-Cl3	90.9 (1)	N2-Fe-N3	81.9 (2)
N3-Fe-Cl1	89.5 (1)	N3-Fe-Cl2	89.2 (1)
N3-Fe-Cl3	169.2 (1)	B-N4-N1	118.5 (4)
B-N5-N2	119.8 (4)	B-N6-N3	119.6 (5)
N4-B-N5	107.1 (5)	N4-B-N6	107.0 (5)
N5-B-N6	109.0 (5)	B-N4-C3	132.9 (5)
B-N5-C6	130.9 (5)	B-N6-C9	131.5 (5)

mation of the byproduct  $FeL_2$ . As a half-sandwich iron complex with tris(pyrazolyl)borate ligand, the only example reported so far is  $(HB(pz)_3)Fe(C_3F_7)(CO)_2$ , but its structure was not elucidated.<sup>8</sup> Therefore, the structure of **2** was determined by X-ray crystallography. The crystal structure of the anion in **2** is given in Figure 1 and the selected bond distances and angles are listed in Table IV. The iron has a slightly distorted octahedral coordination geometry. The distances between the iron and the nitrogens on the ligand are close to each other (2.15–2.18  $\text{\AA}$ ). These are considerably longer than those found in  $Fe(HB(pz)_3)_2$  (1.96–1.98  $\text{\AA}$ )<sup>6</sup> but are in the range of values found in  $(HB(pz)_3)FeO(OAc)_2Fe(HB(pz)_3)$  (2.13–2.34  $\text{\AA}$ ).<sup>2</sup> Other distances, including the Fe-Cl distances, are not exceptional.

The reaction of  $FeCl_3$  and  $KHB(pz)_3$  (or  $KHB(3,5-Me_2pz)_3$ ) in the presence of  $Et_4NCl$ , which was expected as a more straightforward synthetic route, resulted in the sole formation of  $FeL_2$  and  $FeL_2^+$ . Therefore, the effectiveness of the binuclear complex **1** as a reactant for preparing the half-sandwich complexes **2** and **3** is striking. This may be indicative of the facile cleavage of the Fe-O bond rather than Fe-Cl in **1**. On the other hand, the reaction of **1** and  $KHB(pz)_3$  in the presence of  $NaOAc$  is known to give an acetate bridging  $\mu$ -oxo binuclear complex  $(HB(pz)_3)FeO(OAc)_2Fe(HB(pz)_3)$ .<sup>2</sup> The formation of **2** from **1** led us to the speculation that the binuclear complex is formed by a self-assembly of **2** rather than via unknown  $[(HB(pz)_3)-$

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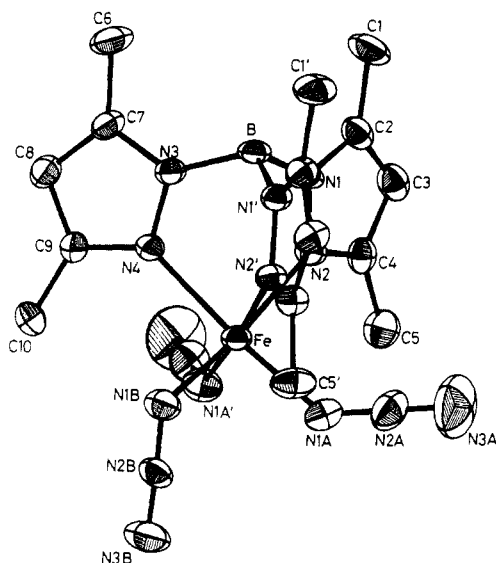


Figure 2. ORTEP drawing of the crystal structure of the anion in 4.

Table V. Selected Bond Distances (Å) and Angles (deg) for  $[(\text{HB}(3,5\text{-Me}_2\text{pz})_3)_2\text{Fe}(\text{N}_3)_3]^-$

Distances			
Fe-N1A	2.014 (7)	Fe-N1B	2.032 (8)
Fe-N2	2.224 (7)	Fe-N4	2.163 (5)
N1A-N2A	1.159 (10)	N2A-N3A	1.158 (16)
N1B-N2B	1.189 (8)	N2B-N3B	1.124 (9)
N1-N2	1.376 (8)	N1-C2	1.354 (11)
N1-B	1.521 (13)	N3-N4	1.382 (4)
N3-C7	1.354 (7)	N3-B	1.543 (6)
C1-C2	1.492 (10)	C2-C3	1.391 (16)
C3-C4	1.406 (9)	C4-C5	1.499 (14)
C4-N2	1.332 (15)	C6-C7	1.500 (6)
C7-C8	1.386 (6)	C8-C9	1.401 (7)
C9-C10	1.481 (6)	C9-N4	1.346 (7)

Angles			
N1-N2A-N3A	179.3 (1.6)	N1B-N2B-N3B	177.0 (1.2)
N1A-Fe-N1B	93.0 (3)	Fe-N1A-N2A	135.1 (5)
Fe-N1B-N2B	122.4 (8)	N2-Fe-N1A	92.6 (2)
N2-Fe-N1B	172.0 (3)	N4-Fe-N1A	174.6 (2)
N4-Fe-N1B	90.5 (2)	N2-Fe-N4	83.5 (2)
B-N1-C2	130.5 (6)	B-N1-N2	119.8 (6)
B-N3-C7	130.6 (3)	B-N3-N4	119.4 (4)
N1-B-N3	108.9 (4)		

$\text{FeOFe}(\text{HB}(\text{pz})_3)]^{2+}$ . In fact, Wieghardt et al. reported that an aerobic treatment of  $\text{LFeCl}_3$  with  $\text{NaOAc}$  gives  $\text{LFeO}(\text{OAc})_2\text{FeL}$ .<sup>3a,3c</sup> However, attempts to synthesize  $(\text{HB}(\text{pz})_3)\text{FeO}(\text{OAc})_2\text{Fe}(\text{HB}(\text{pz})_3)$  by treating **2** with  $\text{NaOAc}$  under various reaction conditions were all unsuccessful.

Although **2** and **3** were found to not be useful as a starting material for the synthesis of a binuclear iron complex, they may be suited as reagents for preparing a class of mononuclear iron complexes by substitution of the chloride. This possibility is demonstrated in the reaction of **3** and  $\text{NaN}_3$  to give  $(\text{Et}_4\text{N})\text{-}[(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Fe}(\text{N}_3)_3]$  (**4**). **4** is also obtained by the direct reaction of **1** and  $\text{KHB}(3,5\text{-Me}_2\text{pz})_3$  in the presence of  $\text{NaN}_3$ . A similar mononuclear azido complex  $\text{LFe}(\text{N}_3)_3$  ( $\text{L} = 1,4,7\text{-triazacyclononane}$  and  $1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$ ) was reported.<sup>3b</sup> The structure of  $[(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Fe}(\text{N}_3)_3]$  anion of **4** is shown in Figure 2, and the bond lengths and angles are summarized in Table V. The complex contains a crystallographically imposed miller plane. One azide ion ( $\text{N1B-N2B-N3B}$ ) lies on the Miller plane, whereas the other two ( $\text{N1A-N2A-N3A}$  and  $\text{N1A'-N2A'-N3A'}$ ) are related by the symmetric operation. The azide ion ( $\text{N1B-N2B-N3B}$ ) positions itself along the axis formed by the boron and iron, whereas the other azide ions are almost perpendicular. The bond distances  $\text{Fe-N1A}$  and  $\text{Fe-N1B}$  are close to each other (ca. 2.0 Å) and are shorter than those between the iron and nitrogens from the tris(pyrazolyl)borate

ligand (ca. 2.2 Å). The distances between the iron and azide nitrogens are slightly longer than one reported for an azido iron(III) porphyrin complex  $(\text{TPP})\text{Fe}(\text{N}_3)(\text{py})$ <sup>9</sup> ( $\text{TPP} = \text{tetraphenylporphyrinato}$ ,  $\text{py} = \text{pyridine}$ ) (1.925 (7) Å). The  $\text{Fe-N1A-N2A}$  angle (135.1 (5)°) is higher than that of  $\text{Fe-N1B-N2B}$  (122.4 (8)°). The latter value is typical for azido transition-metal complexes whereas the former is not; for instance, the angle found in  $(\text{TPP})\text{Fe}(\text{N}_3)(\text{py})$  is 125.6 (7)°.<sup>9</sup> The spreading of the angle of  $\text{Fe-N1A-N2A}$  may be due to the steric hindrance of the ligand, since the azide ion ( $\text{N1A-N2A-N3A}$  or  $\text{N1A'-N2A'-N3A'}$ ) positions itself closer to the methyl groups from the tris(pyrazolyl)borate ligand than the other azide ion ( $\text{N1B-N2B-N3B}$ ).

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**Supplementary Material Available:** Tables SI-SV, listing crystallographic details, thermal and hydrogen atom parameters, and bond distances and angles for **2** and **4** (12 pages); Table SVI, listing observed and calculated structure amplitudes for **2** and **4** (11 pages). Ordering information is given on any current masthead page.

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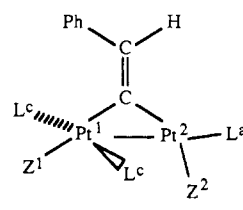
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### <sup>31</sup>P and <sup>195</sup>Pt NMR Data of Several "T-Frame" Diplatinum Complexes That Exhibit Unusual Structure, Bonding, and Reactivity

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We reported recently the results of an initial, though comprehensive, study of the synthesis, structure, bonding, and reactivity of several new dinuclear complexes, including the diplatinum compounds **1a-g**.<sup>1</sup> The molecular structures of complexes **1a**,



$\text{L}^a = \text{L}^c = \text{PEt}_3$

cpd#	Z <sup>1</sup>	Z <sup>2</sup>
<b>1a</b>	PhC≡C	PbEt <sub>3</sub> <sup>+</sup>
<b>1b</b>	PhC≡C	Cl
<b>1c</b>	PhC≡C	Br
<b>1d</b>	PhC≡C	I
<b>1e</b>	Cl	Cl
<b>1f</b>	Br	Br
<b>1g</b>	I	I

**1b**, **1d**, and **1f** have been determined by X-ray diffraction.<sup>1a,2</sup> The more interesting results of this study are as follows. (1) The molecules possess a "T-frame" structure of  $C_2$  symmetry in which the principal coordination planes of the two platinum atoms have an orthogonal relative orientation. (2) The Pt-Pt distance decreases from 2.750 (2) Å for **1a** to 2.685 (1) Å for **1f** as the electronegativity of the ancillary set of ligands increases. (3) Theoretical calculations of the electronic structure of the cationic complex **1a** indicate a large negative charge localization (nearly -1.0) on each platinum atom and a net repulsive interaction

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