

compared to the very mild cyanotrihydroborate anion ( $\text{BH}_3\text{CN}^-$ ).<sup>7</sup>

The reactivity of the amine-( $\alpha$ -cyanoorgano)boranes also differs from that of amine-cyanoborane. For instance, the reaction of trimethylamine-cyanoborane,  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$ , with 2 equiv of Meerwein's reagent in refluxing  $\text{CH}_2\text{Cl}_2$  gives the intermediate product  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}^+\text{C}_2\text{H}_5\text{BF}_4^-$ , which, upon hydrolysis, is known to yield the protonated boron analogue of betaine,  $(\text{C}_2\text{H}_5)_3\text{N}\cdot\text{BH}_2\text{COOH}$ .<sup>3</sup> Numerous attempts to extend this synthesis to the amine-( $\alpha$ -cyanoorgano)borane system were unsuccessful. In all cases, the product isolated did not contain the  $\text{BH}_2^-$  group, as monitored by  $^{11}\text{B}$  NMR and infrared spectroscopies. Very mild conditions (room temperature) did not result in a reaction. The observed decomposition of the amine-( $\alpha$ -cyanoorgano)boranes under conditions successful for the synthesis of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{COOH}$  from the amine-cyanoborane must result from the presence of the CRR' moiety in the former. Thus, insertion of CRR' changes the reactivity of the CN and/or the B-H moieties. Research is under way to further study the preparation, stability, and reactivity of amine-( $\alpha$ -cyanoorgano)boranes in selected chemical systems, to compare their reactivity to that of their carbon analogues, and to evaluate the biological activity of this new class of compounds.

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### Synthesis and X-ray Structure of $\text{Na}_{10}[\text{Pt}_2(\mu\text{-PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2]\cdot 22\text{H}_2\text{O}$ , a Complex with Doubly Deprotonated Guanine Anions Coordinated to Diplatinum(III)

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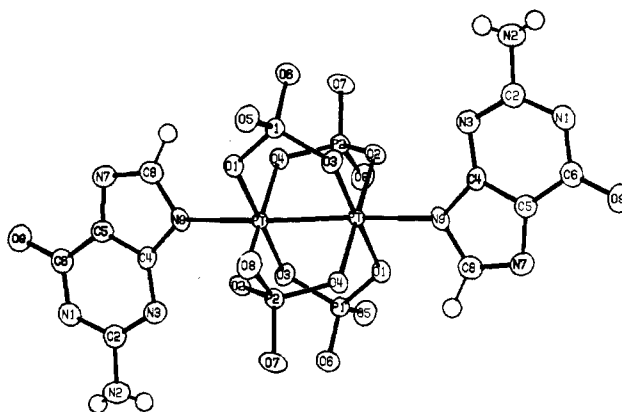
Although there have been many structural studies of complexes that have 9-substituted guanine derivatives coordinated to a transition metal, there have been very few structures solved where guanine itself is complexed to these metal ions.<sup>2</sup> No structural data have been reported for guanine bonded to platinum, and in the two published structures of transition-metal complexes, namely  $\text{ZnCl}_3(\text{guH}_2)$  and  $\text{CuCl}_3(\text{guH}_2)\cdot 2\text{H}_2\text{O}$  (guanine =  $\text{guH}$ ), the guanine is protonated as the guaninium cation  $\text{guH}_2^+$ .<sup>3</sup>

We have found that guanine will replace the axial water ligands in  $\text{Na}_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2]$  to give the product complex  $\text{Na}_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{guH})_2]$  with the guanine ligands coordinated to the axial positions.<sup>4</sup> This complex is soluble in aqueous sodium hydroxide, and crystals of the compound can be grown by slow evaporation of water with this solution. The crystals have the composition  $\text{Na}_{10}[\text{Pt}_2(\mu\text{-PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2]$ , where  $\text{C}_5\text{H}_3\text{N}_5\text{O}$  is the dianion derived from guanine. This structure is significant because it is the first structural example of a complexed guanine dianion, because it is the first diplatinum(III) structure with a

**Table I.** Crystallographic Data for  $\text{Na}_{10}[\text{Pt}_2(\mu\text{-PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2]\cdot 22\text{H}_2\text{O}$

formula	$\text{Pt}_2\text{P}_4\text{Na}_{10}\text{C}_{50}\text{H}_{50}\text{N}_{10}\text{O}_{40}$
fw	1694.5
space group	P1
a, Å	9.4077 (5)
b, Å	10.9588 (5)
c, Å	12.2968 (16)
$\alpha$ , deg	72.746 (11)
$\beta$ , deg	86.223 (8)
$\gamma$ , deg	88.095 (8)
Z	1
V, Å <sup>3</sup>	1208.0 (3)
$d_{\text{calcd}}$ , g/cm <sup>3</sup>	2.329
$\lambda$ , Å (graphite monochromated)	0.71073
$\mu$ (Mo K $\alpha$ ) cm <sup>-1</sup>	61.79
T, °C	17
data collecn instrument	Enraf-Nonius CAD 4
radiation	Mo K $\alpha$
scan method	$\omega$ -2 $\theta$
data collecn range, deg	1-28, $\theta$
no. of unique data	5824
no. of data with $F_o^2 \geq 3\sigma(F_o^2)$	5403
no. of parameters refined	420
extinction coeff	$3.7(1) \times 10^{-7}$
$R^a$	0.019
$R_w^b$	0.025

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$



**Figure 1.** ORTEP view of the anion  $\text{Pt}_2(\mu\text{-PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2^{10-}$  with 75% probability ellipsoids.

fully deprotonated phosphate bridge, because the lattice contains a rather unusual decanegative anion, and because the thermal parameters obtained for the crystal are very small, which leads to a very precise structure determination of the anion in the molecule.

### Experimental Section

Potassium tetrachloroplatinate(II) was purchased from Matthey Bishop Inc. The complex  $\text{Na}_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2]$  was prepared by the literature procedure.<sup>5</sup> Guanine was purchased from Sigma Co. The complex  $\text{Na}_{10}[\text{Pt}_2(\mu\text{-PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2]$  ( $\text{C}_5\text{H}_3\text{N}_5\text{O}$  = doubly deprotonated guanine dianion) was prepared by the addition of guanine hydrochloride to a solution of  $\text{Na}_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2]$  in aqueous sodium hydroxide.<sup>4</sup> Slow evaporation of the solvent gave the crystals as yellow rhombohedra.

**Structure Solution.** A yellow rhombic crystal of dimensions  $0.20 \times 0.32 \times 0.40$  mm was sealed in a capillary tube. Intensity data were obtained on an Enraf-Nonius CAD4 diffractometer equipped with Mo K $\alpha$  radiation and a graphite monochromator by  $\omega$ -2 $\theta$  scans designed to yield  $\sigma(I) = 0.04I$  for all observable data, subject to a maximum scan time of 60 s. The scan rates were  $1.0$ - $4.0^\circ/\text{min}$ . One hemisphere of data was collected ( $-12 \leq h \leq 12$ ,  $0 \leq k \leq 14$ ,  $-16 \leq l \leq 16$ ) and corrected for Lp, background, and absorption effects. The absorption correction was made by using  $\psi$  scans, and the minimum relative transmission

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**Table II.** Coordinates for  $\text{Na}_{10}[\text{Pt}_2(\text{PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2]\cdot 22\text{H}_2\text{O}$ 

atom	x	y	z	atom	x	y	z
Pt	0.03511 (1)	0.38630 (1)	0.05299 (1)	N3	0.1258 (3)	0.1661 (2)	0.3387 (2)
P1	0.15307 (8)	0.47801 (7)	-0.20367 (6)	N7	0.1374 (3)	-0.0169 (2)	0.1391 (2)
P2	0.25213 (8)	0.59149 (7)	0.06622 (6)	N9	0.0942 (3)	0.1920 (2)	0.1352 (2)
Na1	0.1074 (1)	0.3927 (1)	0.3297 (1)	C2	0.1565 (4)	0.0715 (3)	0.4316 (3)
Na2	0.4237 (1)	0.4056 (1)	0.9189 (1)	C4	0.1208 (3)	0.1229 (3)	0.2458 (2)
Na3	0.0621 (2)	0.7555 (1)	0.1910 (1)	C5	0.1457 (3)	-0.0032 (3)	0.2472 (2)
Na4	0.3946 (2)	0.8206 (1)	0.1956 (1)	C6	0.1788 (3)	-0.0947 (3)	0.3501 (3)
Na5	0.4613 (2)	0.6852 (2)	0.6479 (1)	C8	0.1063 (3)	0.1014 (3)	0.0788 (3)
O1	0.1650 (2)	0.3805 (2)	-0.0816 (2)	O1W	0.2474 (3)	0.8037 (2)	0.6594 (2)
O2	0.1935 (2)	0.4521 (2)	0.1232 (2)	O2W	0.3389 (3)	0.4519 (2)	0.3593 (2)
O3	0.0939 (2)	0.6093 (2)	-0.1890 (2)	O3W	0.0326 (3)	0.3532 (2)	0.5262 (2)
O4	0.1229 (2)	0.6811 (2)	0.0150 (2)	O4W	0.4422 (3)	0.2831 (2)	0.1909 (2)
O5	0.3038 (2)	0.4971 (2)	-0.2572 (2)	O5W	0.3451 (3)	0.5997 (2)	0.5092 (2)
O6	0.0525 (2)	0.4333 (2)	-0.2740 (2)	O6W	0.2472 (3)	0.8991 (3)	0.8404 (3)
O7	0.3035 (2)	0.6391 (2)	0.1606 (2)	O7W	0.4183 (3)	0.1798 (3)	0.9452 (3)
O8	0.3684 (2)	0.5878 (2)	-0.0223 (2)	O8W	0.1661 (3)	0.1518 (3)	0.7896 (3)
O9	0.2040 (3)	-0.2125 (2)	0.3551 (2)	O9W	0.4227 (3)	0.2903 (3)	0.6832 (2)
N1	0.1831 (3)	-0.0530 (2)	0.4424 (2)	O10W	0.5259 (4)	0.8582 (4)	0.4880 (3)
N2	0.1736 (4)	0.1053 (3)	0.5308 (2)	O11W	0.5282 (3)	0.9707 (3)	0.8221 (3)

coefficient was 87.29%. No crystal decay was observed. Data having  $I > 3\sigma(I)$  were used in the refinement. The structure was solved by the heavy-atom method, followed by an analysis of the close-contact separations. All hydrogen atoms were located on Fourier difference maps, and all but those on water molecules O9, O10, and O11 were refined. Refinement was by full-matrix least squares with weights  $w = \sigma^{-2}(F_o)$ . The maximum final residual density was  $0.94 \text{ e } \text{Å}^{-3}$  in the vicinity of platinum. Scattering factors and anomalous coefficients, along with computer programs used for the structure solution, are part of the Enraf-Nonius SDP.<sup>6</sup> Final residuals are given in Table I. The small thermal parameters allow the ORTEP figure (Figure 1) to be drawn with 75% probability ellipsoids. Atom coordinates are given in Table II and in the supplementary material, and Table III gives the selected bond distances and bond angles.

### Results and Discussion

When  $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$  reacts with guanine, the axially substituted complex  $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{guH})_2^{2-}$  is formed.<sup>4</sup> The complex is insoluble in water, but it will dissolve in strong aqueous base to give a yellow solution. When sodium hydroxide is used as the base, the complex can be crystallized from solution. Structure solution by X-ray crystallography shows the complex to consist of the anion  $\text{Pt}_2(\mu\text{-PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2^{10-}$ , where  $\text{C}_5\text{-H}_3\text{N}_5\text{O}$  is the dianion derived from guanine. As with the zinc and copper structures of the protonated guaninium cation,<sup>3</sup> we find that the guanine moiety is complexed through N9.

The Pt-Pt distance of 2.5342 (4) Å is closely similar to that of 2.494 (1) Å found in the diplatinum(III) pyridine complex  $(\text{pyH})_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{py})_2]$ .<sup>7</sup> In each case the Pt-N distances are long, the values being 2.141 (2) Å in the anion  $\text{Pt}_2(\mu\text{-PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2^{10-}$  and 2.11 (2) and 2.18 (1) Å in the pyridine complex. This long distance to the axial substituents is due to the high trans influence of the Pt(III)-Pt(III) bond.<sup>4,7,8</sup> The Pt-Pt-N9 angle of 177.32 (6)° is close to linear.

Although several structures of diplatinum(III) complexes have been solved where the bridging  $\mu\text{-O,O'}$ -ligand is a hydrogen phosphate moiety, no diplatinum(III) complex has yet been characterized where the bridging ligands are fully deprotonated phosphate groups. In agreement with this premise, the P-O distances fall into two distinct ranges. For the coordinated oxygens the P-O distances are long (1.572 (2)-1.581 (2) Å), and for the terminal oxygens the P-O distances are much shorter (1.500 (2)-1.518 (2) Å). By comparison with the literature for simple

**Table III.** Selected Distances and Angles for the Anion in  $\text{Na}_{10}[\text{Pt}_2(\mu\text{-PO}_4)_4(\text{C}_5\text{H}_3\text{N}_5\text{O})_2]\cdot 22\text{H}_2\text{O}$ 

Distances (Å)			
Pt-Pt	2.5342 (4)	P1-O1	1.572 (2)
Pt-O1	2.007 (2)	P1-O3	1.581 (2)
Pt-O2	2.023 (2)	P1-O5	1.518 (2)
Pt-O3	2.012 (2)	P1-O6	1.508 (2)
Pt-O4	2.014 (2)	P2-O2	1.581 (2)
Pt-N9	2.141 (2)	P2-O4	1.579 (2)
N1-C2	1.348 (4)	P2-O7	1.517 (2)
N1-C6	1.347 (4)	P2-O8	1.500 (2)
C2-N2	1.396 (4)	C6-O9	1.289 (3)
C2-N3	1.336 (3)	C5-N7	1.389 (3)
N3-C4	1.364 (3)	N7-C8	1.322 (3)
C4-C5	1.389 (3)	C8-H	1.076 (34)
C4-N9	1.381 (3)	N2-H21	0.73 (5)
C5-C6	1.408 (4)	N2-H22	0.84 (4)
N2-O5	5.843 (3)	N2-O7	6.355 (3)
N2-O6	4.946 (3)	N2-O8	6.918 (3)

Angles (deg)			
O1-Pt-O2	91.28 (7)	O1-P1-O3	108.2 (1)
O1-Pt-O3	179.40 (7)	O1-P1-O5	106.2 (1)
O1-Pt-O4	89.16 (7)	O1-P1-O6	112.1 (1)
O2-Pt-O3	88.46 (7)	O3-P1-O5	108.8 (1)
O2-Pt-O4	179.22 (6)	O3-P1-O6	108.2 (1)
O3-Pt-O4	91.09 (7)	O5-P1-O6	113.2 (1)
Pt-Pt-N9	177.32 (6)	O2-P2-O4	108.0 (1)
C2-N1-C6	119.1 (2)	O2-P2-O7	107.5 (1)
N1-C2-N3	129.1 (3)	O2-P2-O8	109.3 (1)
N1-C2-N2	114.0 (3)	O4-P2-O7	106.6 (1)
N2-C2-N3	116.8 (3)	O4-P2-O8	112.7 (1)
C2-N3-C4	111.4 (2)	O7-P2-O8	112.5 (1)
N3-C4-C5	124.4 (2)	C5-N7-C8	101.4 (2)
N3-C4-N9	126.3 (2)	C4-N9-C8	102.9 (2)
C5-C4-N9	107.3 (2)	C5-C6-O9	121.3 (3)
C4-C5-N7	111.1 (2)	N1-C6-O9	121.9 (2)
C4-C5-C6	119.2 (3)	N1-C6-C5	116.8 (2)
C6-C5-N7	129.7 (2)		

phosphate salts, the former distances correspond with the P-O single bond and the latter with a P=O double bond.<sup>9</sup> Furthermore, the nonbonded O...O distances between the terminal oxygen atoms around the periphery of the complex are long: O6-O7 = 3.563 (3) Å; O5-O8 = 3.416 (3) Å. By comparison, hydrogen-bonded structures of type O...H...O typically show O...O

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separations in the range of 2.4–2.6 Å.<sup>4,8–10</sup> In support of our claim that the phosphate ligands are fully deprotonated, we also find that each terminal oxygen has contacts to two sodium ions at distances ranging between 2.288 (2) and 2.765 (2) Å. Finally we should add that we cannot observe any electron density in the region of the terminal oxygens to indicate the presence of any hydrogen atoms, even though all the other hydrogen atoms in the structure were observed on difference maps.

The terminal guanine ligands are doubly deprotonated  $C_5H_3N_5O_2^{2-}$  anions. As evidence for this claim, we find that the N9 hydrogen present in guanine monohydrate<sup>11</sup> is clearly missing, with N9 in this complex being coordinated to platinum in a planar fashion. The N1 hydrogen, also present in guanine monohydrate, is also missing. This is shown by the fact that no peak is apparent from difference maps, and also that N1 accepts a hydrogen bond from the water molecule O1W. The hydrogen atom involved in this contact is 1.90 (4) Å from N1, and is in the plane of the guanine ligand. The N–C distances involving N1, N1–C6 and N1–C2, have shortened from the values 1.398 and 1.371 Å in guanine monohydrate, to 1.347 (4) and 1.348 (4) Å in this complex anion. The corresponding change in the C2–N1–C6 angle is from 124.6 to 119.1 (2)°. No hydrogens are observed on N3 and N7 in our complex anion, and there are also no differences in the bond distances and angles about these atoms between this structure and that of guanine monohydrate. Furthermore, N3 has a close contact to  $Na^+$  ( $N3\cdots Na1 = 2.453$  (2) Å), N7 has contacts to two  $Na^+$  ions ( $N7\cdots Na3 = 2.499$  (3) Å;  $N7\cdots Na4 = 2.951$  (3) Å, and the carbonyl oxygen O9 has two close contacts to  $Na^+$  ( $O9\cdots Na3 = 2.604$  (2) Å;  $O9\cdots Na4 = 2.520$  (3) Å). This formulation corresponds to a decanegative anionic complex with two platinum(III) centers.

Since the  $\mu$ -phosphato bridges are fully deprotonated, the only plausible interligand H-bonding is between the hydrogens on N2 and one of the terminal phosphato oxygens.<sup>12</sup> It is clear from the long internuclear separations between N2 and O5, O6, O7, and O8 that there are no interligand H-bonds within this structure.

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**Registry No.**  $Na_{10}[Pt_2(\mu-PO_4)_4(C_5H_3N_5O_2)_2]\cdot xH_2O$ , 103883-58-5; Pt, 7440-06-4.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, hydrogen atom coordinates and isotropic thermal parameters, and least-squares planes (4 pages); table of observed vs. calculated structure factors for  $Na_{10}[Pt_2(\mu-PO_4)_4(C_5H_3N_5O_2)_2]\cdot 22H_2O$  (25 pages). Ordering information is given on any current masthead page.

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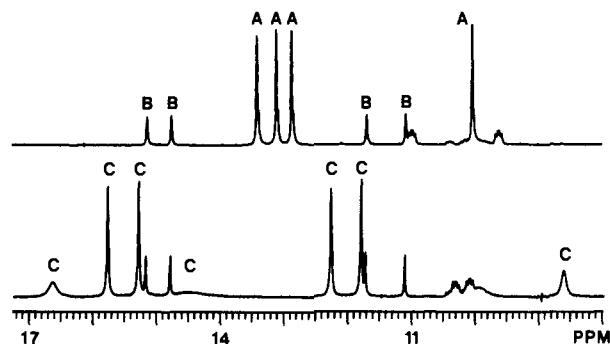
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### Characterization of Iron(III) Porphyrins Bearing Aliphatic Amine Ligands

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The facile autoreduction of Fe(III) porphyrins by electron-rich ligands has been known for many years. Ligands such as aliphatic amines,<sup>1–4</sup> cyanide,<sup>3,5</sup> thiols,<sup>6</sup> imidazolates,<sup>7</sup> pyridine/hydroxide<sup>1b,8</sup>



**Figure 1.**  $Fe^{III}PPIXDME$  in  $Me_2SO-d_6$ : upper, 1 equiv of  $CN^-$ ; lower, 1 equiv of  $CN^-$  and 4 equiv of  $n-BuNH_2$ ; (A) mono-cyano complex; (B) dicyano complex; (C)  $CN^-$ ,  $n-BuNH_2$  complex.

and alcoholates<sup>8b,9</sup> all reduce the Fe(III) complex to its Fe(II) oxidation state. In fact, autoreduction has been used to prepare Fe(II) species for investigation by Mössbauer,<sup>1</sup> X-ray,<sup>2</sup> flash photolysis,<sup>4</sup> and electron-transfer<sup>5</sup> techniques. In many other instances, however, autoreduction precludes study of a desired Fe(III) species. In particular, aliphatic amines generally induce rapid and complete autoreduction and it is generally supposed that Fe(III) porphyrin–aliphatic amine complexes cannot be formed. We are aware of only two counterexamples: the tetraphenylporphyrin derivatives  $Fe^{III}TPP(pip)_2Cl^{3c}$  and  $(T(2,4,6-EtO)_3PP)Fe^{III}(pip)_2Cl$ .<sup>10</sup> These were observed by  $^1H$  NMR in  $CD_2Cl_2$  ( $-78^\circ C$ ) and  $CDCl_3$  (room temperature), respectively; autoreduction is usually very slow in these solvents.<sup>3</sup> In this paper we report that aliphatic amines bind to ferric porphyrins in the presence of cyanide to give  $Fe^{III}(\text{porphyrin})(RR'NH)(CN^-)$  complexes. At low ligand concentration under air, these species remain for days even in  $Me_2SO$ , a solvent in which autoreduction is generally very rapid.<sup>3</sup>

When aliphatic amines are added to an NMR tube containing a ferric porphyrin and 1 equiv of cyanide in  $Me_2SO-d_6$ , a new species grows in. In the case of iron(III) protoporphyrin IX dimethyl ester ( $Fe^{III}PPIXDME$ ) and  $n-BuNH_2$ , this species had a new set of resonances corresponding to the hemin ring protons as well as four new peaks corresponding to the resonances of the bound  $n-BuNH_2$ , as seen in Figure 1. Integration showed that only one butylamine was bound. Different species, with much broader line widths, were formed in the absence of cyanide, indicating that cyanide rather than  $Me_2SO$  was the sixth ligand.

The chemical shifts of the axial butyl group were at 14.4, 16.6, 8.6, and 3.8 ppm down the chain with line widths of 173, 44, 27, and 15 Hz, respectively. The assignment of the  $\beta$ ,  $\gamma$ , and  $\delta$

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