

$\text{PPh}_2\text{Cl}$  in 5 mL of toluene. The orange suspension rapidly turned yellow. After 0.5 h, 5 mL of hexane was added and the bright yellow product filtered off, washed with hexane, and vacuum-dried. The yield was 520 mg (98%).

**Hydrolysis of  $\text{cis-Cl}_2\text{Pd}(\text{PPh}_2\text{Cl})_2$ .** (a) A sample of the complex was suspended in aqueous acetone (1:1) and stirred for 2-3 days at room temperature. The greyish yellow solid was isolated and recrystallized from  $\text{CH}_2\text{Cl}_2$ /ethanol to give light yellow crystals. IR and  $^1\text{H}$  and  $^{31}\text{P}$  NMR data were identical with literature values.<sup>8</sup> Osmometric molecular weight determination gave 1062 (1090.1 theory). Anal. Calcd: C, 52.87; H, 3.89; Cl, 6.50. Found: C, 52.65; H, 3.82; Cl, 7.05. The product was therefore identified as  $[(\text{Ph}_2\text{P}-\text{O}-\text{H}-\text{O}-\text{PPh}_2)\text{PdCl}]_2$ .

(b) A sample of the complex was suspended in acetone. An equal volume of concentrated HCl was added slowly with stirring. After 1 h, the clear, yellow solution was concentrated and diluted with water. Filtration yielded the light yellow product of  $[(\text{Ph}_2\text{P}-\text{O}-\text{H}-\text{O}-\text{PPh}_2)\text{PdCl}]_2$ .

(c) An amount of 250 mg (0.4 mmol) of the complex was suspended in 10 mL of aqueous acetone (1:3). A total of 3 mL of triethylamine was added and the suspension stirred for 2 h. After reduction in volume, the reaction mixture was diluted with water to give a yellow-orange solid (180 mg). IR absorptions are as follows: 1100 (s), 1030 (s), 1020 (s), 995 (s), 735 (m), 705 (m), 683 (s)  $\text{cm}^{-1}$ . The aqueous filtrate was evaporated to dryness and washed with ether to give 220 mg (100% of theory) of  $\text{NEt}_3\text{HCl}$ . Anal. Calcd for  $[\text{Pd}(\text{PPh}_2\text{O})_2]$ : C, 56.68; H, 3.93. Found: C, 56.99; H, 4.03.

**Reaction of  $[\text{Pd}(\text{PPh}_2\text{O})_2]_n$  with HCl.** To a suspension of the solid in acetone was added an equal volume of concentrated HCl. An immediate formation of a clear yellow-orange solution resulted. After volume reduction, the light yellow, water-insoluble solid was recrystallized from  $\text{CH}_2\text{Cl}_2$ /ethanol to give  $[(\text{Ph}_2\text{P}-\text{O}-\text{H}-\text{O}-\text{PPh}_2)-\text{PdCl}]_2$ .

**Acknowledgment.** We are grateful to the National Science Foundation for an instrumental grant toward the purchase of the FT NMR spectrometer.

**Registry No.** *cis*-(CO)<sub>4</sub>Mo(PPh<sub>2</sub>Cl)<sub>2</sub>, 42724-61-8; *trans*-(CO)<sub>4</sub>Mo(PPh<sub>2</sub>Cl)<sub>2</sub>, 37834-17-6;  $[\text{NEt}_3\text{H}][(\text{CO})_4\text{Mo}(\text{Ph}_2\text{P}-\text{O}-\text{H}-\text{O}-\text{PPh}_2)]$ , 66245-44-1;  $[(\text{Ph}_2\text{P}-\text{O}-\text{H}-\text{O}-\text{PPh}_2)\text{PdCl}]_2$ , 77071-72-8;  $[\text{Pd}(\text{PPh}_2\text{O})_2]_n$ , 36560-97-1; *cis*-Cl<sub>2</sub>Pd(PPh<sub>2</sub>Cl)<sub>2</sub>, 61567-62-2; Mo(CO)<sub>6</sub>, 13939-06-5; *cis*-(CO)<sub>4</sub>Mo(piperidine)<sub>2</sub>, 65337-26-0; (PhCN)<sub>2</sub>PdCl<sub>2</sub>, 14220-64-5.

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### Crystal and Molecular Structure of Tetramethylbis[ $\mu$ -(phenylethynyl)]-digallium

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Our initial observation that the vinyl group stabilized the electron-deficient bridged dimeric molecule  $\text{Ga}_2(\text{CH}=\text{CH}_2)_6$  lead us to postulate that the stabilization of this dimer resulted from metal- $\pi$ -electron interactions.<sup>1</sup> This stimulated our group, and others, to explore the structures of a variety of compounds including  $\text{Al}_2[\textit{trans}-(\mu-\text{CH}=\text{CHC}(\text{CH}_3)_3)]_2(i\text{-Bu})_4$ ,<sup>2</sup>  $\text{Al}_2(\textit{c-Pr})_6$ ,  $\text{Al}_2(\mu-\text{C}\equiv\text{CPh})_2\text{Ph}_4$ ,<sup>4</sup>  $\text{Al}_2(\mu-\text{C}\equiv$

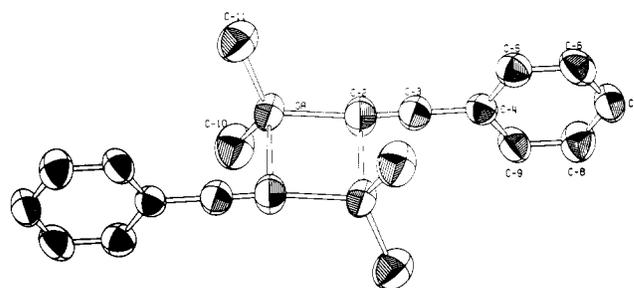


Figure 1. Molecular structure of  $\text{Ga}_2(\mu-\text{C}\equiv\text{CPh})_2\text{Me}_4$  with the atoms labeled.

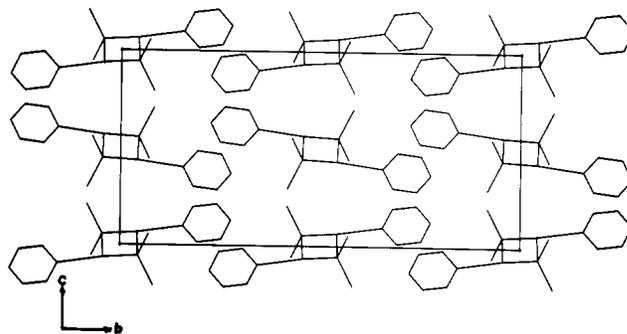


Figure 2. Projection along the *a* axis of  $\text{Ga}_2(\mu-\text{C}\equiv\text{CPh})_2\text{Me}_4$  showing the molecular packing.

$\text{CMe}_2\text{Me}_4$ ,<sup>5</sup> and  $\text{In}_2(\mu-\text{C}\equiv\text{CMe})_2\text{Me}_4$  as well as several studies on aromatic species.<sup>7-9</sup> These studies have shown that there are two distinct types of bridge bonds which may be formed. The first of these is that initially predicted from our studies<sup>1</sup> and involves the formation of a symmetrically bridged species. The second, and the subject of this report, involves an asymmetric bridge as first reported for  $\text{Al}_2(\mu-\text{C}\equiv\text{CPh})_2\text{Ph}_4$ <sup>4</sup> and subsequently observed in  $\text{Al}_2(\mu-\text{C}\equiv\text{CMe})_2\text{Me}_4$ <sup>5</sup> in the gas phase and for  $\text{In}_2(\mu-\text{C}\equiv\text{CPh})_2\text{Me}_4$ .<sup>6</sup> We now report the structure of the phenylethynyl-bridged gallium analogue.

### Experimental Section

**Synthesis and Crystal Selection of  $\text{Ga}_2(\mu-\text{C}\equiv\text{CPh})_2\text{Me}_4$ .** Tetramethylbis[ $\mu$ -(phenylethynyl)]-digallium was prepared as described by Jeffrey and Mole.<sup>10</sup> The compound was recrystallized from a toluene-hexane mixed solvent which yielded well-defined prisms suitable for X-ray crystallography. The vessel containing the crystals was placed in an argon-filled drybox where the air-sensitive crystals were removed. Suitable crystals were then selected by viewing with a microscope (external to the drybox) and placed in 0.2-mm diameter thin-walled glass capillaries. These were initially plugged with silicon grease and then flame sealed on removal from the drybox.

**Data Collection.** A suitable crystal, selected by examination with a polarizing microscope, was mounted on a goniometer head with an epoxy adhesive and placed on a Syntex P2, diffractometer. The data were collected with use of Mo  $K\alpha$  radiation diffracted from a highly oriented graphite crystal in the parallel mode with a  $\theta$ - $2\theta$  scan in the bisecting mode. The specific conditions, unit cell, and unit cell dimensions are given in Table I.

**Solution and Refinement.** The gallium atoms were initially located with the use of Patterson synthesis in three dimensions. Subsequent

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(9) Barber, M.; Oliver, J. P. unpublished observations  
(10) Jeffrey, E. A.; Mole, T. J. *J. Organomet. Chem.* **1968**, *11*, 393.

**Table I.** Experimental Data from X-ray Diffraction Study on  $\text{Ga}_2(\mu\text{-C}\equiv\text{CPh})_2\text{Me}_4$ 

mol formula:  $\text{C}_{20}\text{H}_{22}\text{Ga}_2$   
 mol wt: 401.83  
 cryst system: orthorhombic  
 space group: *Pbca*  
 cell dimens<sup>a</sup>  
 $a = 7.741(2) \text{ \AA}$   
 $b = 22.887(5) \text{ \AA}$   
 $c = 10.967(3) \text{ \AA}$   
 $V = 1943.2(8) \text{ \AA}^3$   
 $Z = 4$   
 $D_{\text{calcd}} = 1.374 \text{ g/cm}^3$   
 radiation: Mo  $\text{K}\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ )  
 monochromator: graphite  
 rflctns measd:  $+h, +k, +l$   
 $2\theta$  range:  $0-45^\circ$   
 scan type:  $\theta-2\theta$ ; moving crystal-moving counter  
 scan speed:  $2.0^\circ/\text{min}$  (in  $2\theta$ )  
 scan width:  $[2\theta(\text{Mo K}\alpha_1) - 1.0]^\circ \rightarrow [2\theta(\text{Mo K}\alpha_2) + 1]^\circ$   
 bkgd measurement: stationary crystal-stationary counter at beginning and end of  $2\theta$ , each for one-fourth the time taken for the  $2\theta$  scan  
 std rflctns: 3 measured every 97 reflections; no significant deviation from the mean was observed  
 unique data: 1529  
 unique data with  $F_o^2 > 2.5\sigma(F_o^2)$ : 811  
 abs coeff:  $\mu = 28.65 \text{ cm}^{-1}$   
 $F_{000} = 816$  electrons  
 $R_F = 0.041$   
 $R_{wF} = 0.052$

<sup>a</sup> Lattice parameters were obtained with the use of an auto indexing program and a least-squares fit to the setting angles at the unresolved Mo  $\text{K}\alpha$  components of 15 reflections with  $2\theta$  values between  $16.4$  and  $29.0^\circ$ .

**Table II.** Atomic Coordinates for  $\text{Ga}_2(\mu\text{-C}\equiv\text{CPh})_2\text{Me}_4$ 

atoms	x	y	z
Ga	0.13845 (9)	0.04467 (3)	0.05466 (7)
C(2)	0.1168 (9)	-0.0424 (3)	0.0655 (7)
C(3)	0.1185 (9)	-0.0936 (3)	0.0805 (6)
C(4)	0.1196 (8)	-0.1558 (3)	0.0986 (6)
C(5)	0.0380 (9)	-0.1809 (3)	0.1977 (6)
C(6)	0.0418 (9)	-0.2407 (3)	0.2130 (7)
C(7)	0.1246 (9)	-0.2761 (3)	0.1305 (7)
C(8)	0.2053 (9)	-0.2522 (3)	0.0315 (8)
C(9)	0.2040 (9)	-0.1923 (3)	0.0157 (7)
C(10)	0.3204 (9)	0.0709 (4)	-0.0557 (8)
C(11)	0.0650 (10)	0.0825 (3)	0.2056 (7)
H(12)	-0.0283	-0.1537	0.2633
H(13)	-0.0216	-0.2599	0.2912
H(14)	0.1263	-0.3229	0.1441
H(15)	0.2695	-0.2800	-0.0342
H(16)	0.2697	-0.1734	-0.0619
H(17)	0.2940	0.0550	-0.1466
H(18)	0.4432	0.0542	-0.0250
H(19)	0.3239	0.1181	-0.0567
H(20)	0.1446	0.0673	0.2799
H(21)	-0.0683	0.0718	0.2234
H(22)	0.0785	0.1292	0.1962

examination of difference maps gave the locations of all of the carbon atom positions. The hydrogen atoms were placed in idealized positions with the use of HFINDER.<sup>11</sup> The function  $\sum w(|F_o| - |F_c|)^2$  was minimized by least-square refinement by using the weighting scheme  $w = F_o^2/(\sigma(F_o^2))^2$ . Scattering factors<sup>12</sup> for neutral gallium and carbon

**Table III.** Isotropic Thermal Factors of Hydrogen Atoms and Anisotropic<sup>a</sup> Thermal Factors of Nonhydrogen Atoms in  $\text{Ga}_2(\mu\text{-C}\equiv\text{CPh})_2\text{Me}_4$ 

atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Ga	5.26 (4)	3.54 (4)	5.37 (4)	-0.2 (3)	0.56 (4)	-0.51 (3)
C(2)	6.2 (4)	4.4 (4)	5.7 (4)	-0.4 (4)	0.3 (4)	0.1 (3)
C(3)	5.0 (4)	3.8 (4)	5.0 (4)	0.0 (3)	-0.5 (3)	-0.0 (3)
C(4)	4.0 (3)	4.0 (3)	4.0 (3)	-0.1 (3)	-0.4 (3)	0.1 (3)
C(5)	5.1 (4)	5.0 (4)	4.2 (3)	0.1 (3)	0.2 (3)	0.0 (3)
C(6)	5.7 (4)	5.2 (4)	4.7 (4)	-1.0 (3)	-0.1 (3)	1.2 (3)
C(7)	5.9 (4)	4.0 (3)	5.7 (4)	-0.4 (3)	-0.8 (4)	0.9 (3)
C(8)	5.5 (4)	4.4 (4)	6.1 (5)	0.8 (3)	0.2 (4)	-0.0 (3)
C(9)	5.5 (4)	4.4 (4)	4.6 (4)	0.1 (3)	0.6 (3)	1.1 (3)
C(10)	5.8 (4)	6.0 (4)	7.4 (5)	0.0 (3)	0.8 (4)	-0.6 (4)
C(11)	6.1 (4)	6.9 (4)	6.0 (4)	0.2 (4)	0.1 (4)	-1.4 (4)

atom	$B, \text{ \AA}^2$	atom	$B, \text{ \AA}^2$	atom	$B, \text{ \AA}^2$
H(12)	5.2	H(16)	5.1	H(20)	6.8
H(13)	5.5	H(17)	7.0	H(21)	6.8
H(14)	5.5	H(18)	7.0	H(22)	6.8
H(15)	5.8	H(19)	7.0		

<sup>a</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

**Table IV.** Selected Interatomic Distances ( $\text{\AA}$ ) and Angles (Deg) in  $\text{Ga}_2(\mu\text{-C}\equiv\text{CPh})_2\text{Me}_4$ 

Ga-Ga	3.196 (2)	C(3)-C(4)	1.438 (9)
Ga-C(10)	1.952 (8)	C(4)-C(5)	1.382 (9)
Ga-C(11)	1.953 (7)	C(4)-C(9)	1.397 (9)
Ga-C(2)	2.004 (4)	C(5)-C(6)	1.378 (9)
Ga-C(2')	2.375 (7)	C(6)-C(7)	1.37 (1)
Ga-C(3')	2.722 (7)	C(7)-C(8)	1.37 (1)
C(2)-C(3)	1.183 (9)	C(8)-C(9)	1.38 (1)
C(10)-Ga-C(11)	126.8 (3)	C(2)-Ga-C(2')	86.7 (3)
C(10)-Ga-C(2)	113.8 (3)	Ga-C(2)-C(3)	172.8 (7)
C(10)-Ga-C(2')	105.2 (3)	Ga-C(2)-Ga'	93.3 (3)
C(11)-Ga-C(2)	111.5 (3)	Ga'-C(2)-C(3)	93.9 (5)
C(11)-Ga-C(2')	103.7 (3)	C(2)-C(3)-C(4)	180 (2)

were used. Hydrogen atom positions were refined by use of the Stewart et al. scattering factors.<sup>13</sup> In the final cycle, the real and imaginary component of the anomalous dispersion<sup>12</sup> were included for gallium. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for nonhydrogen atoms, leaving the hydrogens in their idealized positions, converged with  $R_F = 4.1\%$  and  $R_{wF} = 5.2\%$ ,<sup>14</sup> and the goodness of fit was 1.77 for 100 variables. No absorption correction was applied.

The final difference Fourier showed a maximum residual electron density of  $0.4 \text{ e/\AA}^3$ ,  $1.3 \text{ \AA}$  away from gallium. The atomic coordinates are presented in Table II and thermal parameters in Table III. Observed and calculated structure factors are available.<sup>15</sup>

## Results and Discussions

The structure with labeling is shown in Figure 1, and a projection of the crystal packing is given in Figure 2. From these two figures, it is readily apparent the I forms discrete molecular units which are packed efficiently in the unit cell where the closest approach is  $2.45 \text{ \AA}$  between hydrogen atoms on adjacent molecules. The interatomic distances are pertinent angles are listed in Table IV. From these data, and the selected data given in Table V, it is clear that the structure of the ethynyl-bridged aluminum and gallium species are very similar in both the solid state and gas phase. The indium derivative differs with the formation of an infinite structure in the solid state. However, a comparison of the data in Table

(11) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for generation of normalized structure factors; (2) FORDAP, A. Zalkin's Fourier program; (3) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (4) ORTEP, C. K. Johnson's program for drawing crystal models; (5) HFINDER, A. Zalkin's idealized hydrogen program.

(12) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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(14) Values for the  $R$  factors are defined as  $R_F = \sum |F_o| - |F_c| / \sum |F_o|$  and  $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ .

(15) See the paragraph at the end of the paper regarding supplementary material.

Table V. Selected Interatomic Distances (Å) and Angles (Deg) for Ethynyl-Bridged Metal Derivatives

compd	bridging dist		C≡C (bridging)	M-C (terminal)	∠C≡C-C	∠M-C-M (bridge)	∠M-C≡C	∠M'-C≡C	∠C-M-C (terminal)
	short M	long M							
Al <sub>2</sub> (μ-C≡CMe) <sub>2</sub> Me <sub>4</sub> <sup>a</sup> (gas phase)	2.050 (15)	2.15 (3)	1.229 (4)	1.956 (5)	167.8 (1.6)	92.0 (1)	158.3 (1.9)	109.7 (1.3)	120.8
Al <sub>2</sub> (μ-C≡CPh) <sub>2</sub> Ph <sub>4</sub> <sup>b</sup>	1.992	2.184	1.207	1.904		91.73	171.6		
Ga <sub>2</sub> (μ-C≡CPh) <sub>2</sub> Me <sub>4</sub> <sup>c</sup>	2.004 (7)	2.375 (7)	1.183 (6)	1.952 (8)	180 (2)	86.7 (3)	172.8 (7)	93.8 (5)	126.86
In <sub>2</sub> (μ-C≡CMe) <sub>2</sub> Me <sub>4</sub> <sup>d</sup>	2.193 (14)	2.933 (23)	1.212 (20)	2.185 (av)	178.6 (1.3)		177 (1)		129.8 (4)
Be <sub>2</sub> (μ-C≡CPh) <sub>2</sub> Me <sub>2</sub> <sup>e</sup>	1.85	1.89	1.17	1.75	178	77	147	1.36	
[Cu <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> -2) <sub>2</sub> ] <sup>-</sup> (C≡CC <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> ] <sub>2</sub> <sup>f</sup> HC≡CH <sup>g</sup>	2.028	2.054	1.17		177.9	75	148.1	137.2	
			1.204 (2)						

<sup>a</sup> Reference 5. <sup>b</sup> Reference 4. <sup>c</sup> This work. <sup>d</sup> Reference 6. Note that the In-C<sub>β</sub> distance is 2.989 (24) Å, i.e., nearly equivalent to the In-C<sub>α</sub> distances. <sup>e</sup> Reference 17. <sup>f</sup> Reference 16. <sup>g</sup> Reference 18.

V and a careful review of the behavior of the indium species in solution<sup>6,10</sup> suggests that the major differences are observed only in the solid state since the indium derivative forms a relatively stable dimer in solution with behavior similar to that observed for the aluminum and gallium derivative and presumably, therefore, with a similar structure.

Other studies have shown that both copper<sup>16</sup> and beryllium<sup>17</sup> form derivatives which contain ethynyl-bridge bonds. The bonding in these species has been discussed in detail, and it has been concluded that the ethynyl moiety contributes one electron to the bridge bond in the copper compound. This conclusion was based on the short (compared to 1.204 (2) Å in acetylene) C≡C distance of 1.17 Å observed and on the large separation between the bridged copper atoms of 2.47 Å.<sup>16</sup> A similar proposal was made for the beryllium system which again has a 1.17 Å C≡C distance and no available "low energy" metal orbitals for interaction with the π-electron system on the ethynyl groups.<sup>16</sup>

In both aluminum derivatives, for which structures are known, and for the gallium derivative studied in this work, it is quite clear that the molecular unit is held together by bridging ethynyl groups which enter into two distinctly different bonding interactions: one, as evidenced by the Ga-C bond distance of 2.004 (7) Å and the C≡C-Ga angle of 172.8 (7)°, is essentially a gallium-carbon σ bond while the second is best described as a strong interaction between the second gallium atom and the π electrons of the carbon-carbon triple bond and is characterized by the location of the gallium atom which permits significant metal-π-electron interaction. This is shown in the indium derivatives where the metal atom is shifted toward the π electrons and is located almost at the midpoint of the carbon-carbon triple bond with the two metal-carbon distances nearly equivalent at 2.93 and 2.99 Å, respectively.

Variations in carbon-carbon triple bond lengths were suggested by ten Hoedt et al.<sup>16</sup> as a measure of the metal-π-electron interaction. These bond distances for several ethynyl-bridged derivatives, along with other parameters, have been collected in Table V. Examination of these data show that the carbon-carbon triple bond distances for the aluminum and indium derivatives are greater than that observed in acetylene, as expected from ten Hoedt's proposal, but that the carbon-carbon triple bond distance found in the gallium derivative is significantly less than that in acetylene and is within the values reported for species which presumably have no metal-π-electron interaction. Therefore, it appears that the carbon-carbon triple bond length does not serve as an effective

measure of the metal-π-electron interaction, and other criteria must be sought.

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**Registry No.** Ga<sub>2</sub>(μ-C≡CPh)<sub>2</sub>Me<sub>4</sub>, 18744-50-8.

**Supplementary Material Available:** Listings of observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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### Preparation and Molecular Stereochemistry of Fluoro(meso-tetraphenylporphinato)iron(III)

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The molecular stereochemistry of a number of five-coordinate high-spin (porphinato)iron(III) complexes, Fe(P)(X), has been determined, including those for X = Cl,<sup>3</sup> Br,<sup>4</sup> and I.<sup>5</sup> We have completed the series of halide derivatives by preparing and determining the molecular stereochemistry of a fluoro complex, fluoro(meso-tetraphenylporphinato)iron(III), hereinafter written as Fe(TPP)(F).

### Experimental Section

Fe(TPP)(F) was prepared by the reaction of a CHCl<sub>3</sub> solution of [Fe(TPP)]<sub>2</sub>O<sup>6,7</sup> (500 mg/100 mL) with an aqueous 5% HF solution in a polyethylene separatory funnel. After the CHCl<sub>3</sub> layer was washed with water, the CHCl<sub>3</sub> solution was concentrated. Crystals (about 300 mg) were obtained by allowing pentane to diffuse into the solution. This material was recrystallized by dissolving it in CHCl<sub>3</sub> and diffusing pentane into the solution. The IR spectrum exhibits a Fe-F band<sup>8</sup> at 600 cm<sup>-1</sup>. Anal. Calcd for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>FFe: C, 76.86; H, 4.10; N,

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