

## Communications

### Ring-Induced Rhombicity in Chlorin and Isobacteriochlorin Complexes of Square-Planar Iron(II)

Sir:

Our interest in the chemical,<sup>1-3</sup> structural,<sup>3,4</sup> and magnetic<sup>1,4</sup> properties of iron chlorins and isobacteriochlorins derives from their occurrence in a wide variety of heme proteins and enzymes.<sup>4-6</sup> Magnetic properties are of fundamental importance to biochemists who isolate and work with heme proteins, because data such as EPR and Mössbauer spectra, paramagnetic <sup>1</sup>H NMR spectra, and effective magnetic moments have been used to elucidate the molecular and electronic structure of the heme active site, usually by comparison with well-defined iron porphyrin models.<sup>7,8</sup>

Early EPR studies on model compounds found no significant macrocycle effect on the spin state or *g* values for high-spin Fe(III) derivatives or for Co(II) or Cu(II) derivatives, supporting the view that metalloporphyrins are competent magnetic models for metallochlorin- and metalloisobacteriochlorin-containing proteins.<sup>1,9-13</sup>

- (1) Stolzenberg, A. M.; Strauss, S. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4763-4778.
- (2) Strauss, S. H.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 863-868.
- (3) Strauss, S. H.; Silver, M. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4108-4109.
- (4) Strauss, S. H.; Silver, M. E.; Long, K. M.; Thompson, R. G.; Hudgens, R. A.; Spartalian, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4207-4215.
- (5) (a) Andersson, L. A.; Loeher, T. M.; Lim, A. R.; Mauk, A. G. *J. Biol. Chem.* **1984**, *259*, 15340-15349. (b) Koland, J. G.; Miller, M. J.; Gennis, R. B. *Biochemistry* **1984**, *23*, 445-453. (c) Timkovich, R.; Cork, M. S.; Gennis, R. B.; Johnson, P. Y. *J. Am. Chem. Soc.* **1985**, *107*, 6069-6075. (d) Kim, C.-H.; Hollocher, T. C. *J. Biol. Chem.* **1984**, *259*, 2092-2099. (e) Timkovich, R.; Cork, M. S.; Taylor, P. V. *J. Biol. Chem.* **1984**, *259*, 1577-1585. (f) *Ibid.* **1984**, *259*, 15089-15093. (g) Sibbett, S. S.; Hurst, J. K. *Biochemistry* **1984**, *23*, 3007-3013. (h) Ikedo-Saito, M.; Prince, R. C. *J. Biol. Chem.* **1985**, *260*, 8301-8305.
- (6) Christner, J. A.; Munck, E.; Kent, T. A.; Janick, P. A.; Salerno, J. C.; Siegel, L. M. *J. Am. Chem. Soc.* **1984**, *106*, 6786-6794.
- (7) *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. I-VII.
- (8) *Iron Porphyrins*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; Parts I and II.
- (9) Stolzenberg, A. M.; Spreer, L. O.; Holm, R. H. *J. Chem. Soc., Chem. Commun.* **1979**, 1077-1078.
- (10) (a) Richardson, P. F.; Chang, C. K.; Hanson, L. K.; Spaulding, L. D.; Fajer, J. *J. Phys. Chem.* **1979**, *83*, 3420-3424. (b) Chang, C. K.; Fajer, J. *J. Am. Chem. Soc.* **1980**, *102*, 848-851. (c) Chang, C. K.; Hansen, L. K.; Richardson, P. F.; Young, R.; Fajer, J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2652-2656. (d) Chang, C. K. In *The Biological Chemistry of Iron*; Dunford, H. B., Dolphin, D., Raymond, K. N., Sieker, L., Eds.; Reidel: Dordrecht, Holland, 1982; pp 313-334. (e) Fujita, E.; Fajer, J. *J. Am. Chem. Soc.* **1983**, *105*, 6743-6745.
- (11) Murphy, M. J.; Siegel, L. M.; Kamin, H.; Rosenthal, D. *J. Biol. Chem.* **1973**, *248*, 2801-2814.
- (12) Peisach, J.; Blumberg, W. E.; Adler, A. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 310-327.

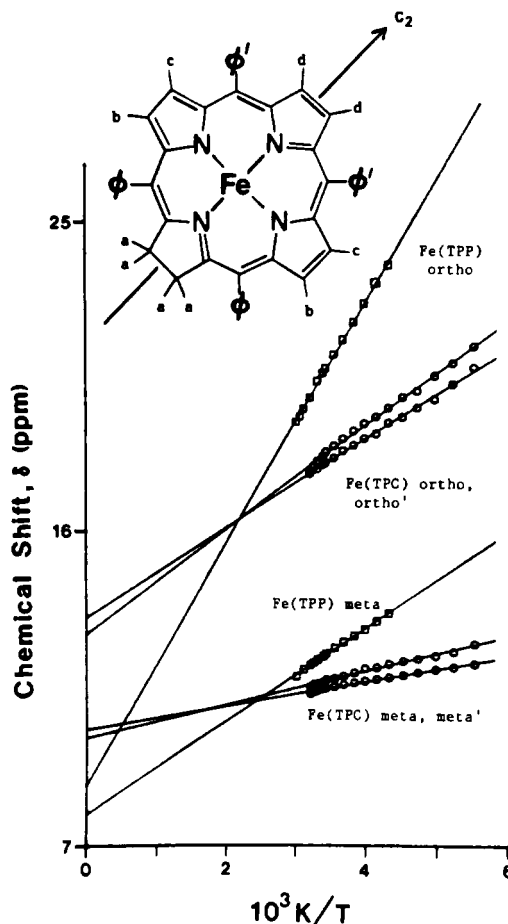
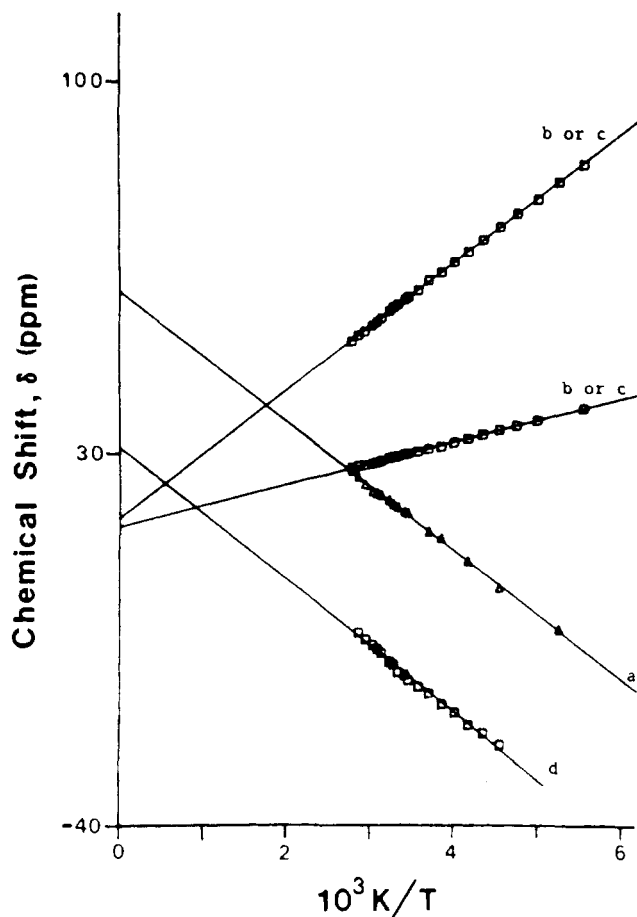


Figure 1.  $\delta$  vs.  $1/T$  plots for phenyl protons in 200-MHz <sup>1</sup>H NMR spectra of Fe(TPP) and Fe(TPC) in toluene-*d*<sub>8</sub>. The solid lines are linear least-squares fits to the data and are extrapolated to  $1/T = 0$ .

Some authors have used *g* values to calculate ligand field parameters for low-spin Fe(III) complexes.<sup>1,10d,14</sup> With respect to ring-induced rhombicity, the results of these calculations are ambiguous in that any differences in axial and rhombic components are a convolution of axial ligand effects (including axial ligand orientation) as well as macrocycle effects. However, we have recently shown that ring-induced rhombicity in a hydrophorphyrin complex can be demonstrated unambiguously.<sup>4</sup> Fe(OEP)<sup>15</sup> possesses axial magnetic anisotropy while Fe(OEC)<sup>15</sup>

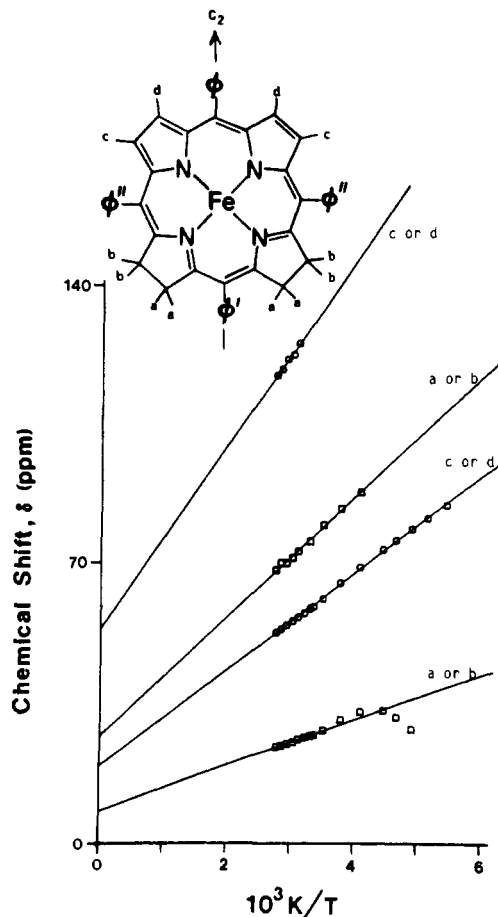
- (13) Fuhrhop, J. H.; Wasser, P. K. W.; Subramian, J.; Schroeder, U. *Justus Liebig's Ann. Chem.* **1974**, 1450-1466.
- (14) (a) Muhoherac, B. B.; Wharton, D. C. *J. Biol. Chem.* **1983**, *258*, 3019-3027. (b) Muhoherac, B. B. *Arch. Biochem. Biophys.* **1984**, *233*, 682-697.



**Figure 2.**  $\delta$  vs.  $1/T$  plots for pyrrole and pyrroline protons in 200-MHz  $^1\text{H}$  NMR spectra of Fe(TPC) in toluene- $d_8$ . The solid lines are linear least-squares fits to the data and are extrapolated to  $1/T = 0$ .

is magnetically rhombic. The two compounds have significantly different magnetic moments and Mössbauer quadrupole coupling constants. Since there are no axial ligands in these four-coordinate square-planar complexes, these differences are the result of a macrocycle effect. We now report variable-temperature  $^1\text{H}$  NMR spectra that show that a second iron chlorin, Fe(TPC),<sup>15</sup> is significantly different magnetically from its porphyrin homologue, the well-studied compound Fe(TPP).<sup>15-18</sup> In addition, we report variable-temperature  $^1\text{H}$  NMR spectra for Fe(TPiBC)<sup>15</sup> that demonstrate for the first time that the isobacteriochlorin ring system can produce resolvable rhombicity in the electronic structure of a metal.

Samples of Fe(TPP), Fe(TPC), and Fe(TPiBC) dissolved in toluene- $d_8$  were prepared by methods analogous to those reported for Fe(OEP) and Fe(OEC).<sup>2,4</sup> Plots of  $\delta$  vs  $1/T$  for 200-MHz  $^1\text{H}$  NMR spectra of Fe(TPC) are linear for all resonances over the temperature range  $-90$  to  $+75$  °C (Figures 1 and 2). Similar plots for Fe(TPiBC) pyrrole and pyrroline resonances are shown in Figure 3. Three of the four plots are linear over the accessible temperature range, which is limited in some cases because all of the resonances broaden appreciably at low temperatures. The Fe(TPiBC) phenyl proton region is very complicated, with many overlapping resonances shifting both *upfield* and *downfield* as the



**Figure 3.**  $\delta$  vs.  $1/T$  plots for pyrrole and pyrroline protons in 200-MHz  $^1\text{H}$  NMR spectra of Fe(TPiBC) in toluene- $d_8$ . The solid lines are linear least-squares fits to the data and are extrapolated to  $1/T = 0$ . For the bottom plot, the solid line is fit to the first nine data points only. Chemical shifts for the last five data points have a large uncertainty because this resonance is very broad below 280 K.

**Table I.** Linear Least-Squares Parameters for  $\delta$  vs.  $1/T$  Plots<sup>a</sup>

compd	resonance	$10^{-3} \times$ slope, ppm·K	$\delta^b$	$\delta^c$
Fe(TPP)	pyrrole	-4.4	19.5	8.8
	ortho	3.3	9.4	8.3, 8.1
	meta	1.2	8.5	7.8, 7.7
Fe(TPC)	a pyrroline	-12.2	60.5	4.1
	b, c pyrrole	4.1	16.2	8.6, 8.2
	b, c pyrrole	12.1	17.8	8.6, 8.2
	d pyrrole	-12.5	31.1	8.6, 8.2
	ortho, ortho'	1.3	13.3	8.1, 7.9
	ortho, ortho'	1.6	12.5	8.1, 7.9
	meta, meta'	0.54	9.8	7.7
meta, meta'	0.40	10.0	7.7	
Fe(TPiBC)	c, d pyrrole	22.9	53.3	7.4, 6.9
	a, b pyrroline	14.9	26.4	3.3
	c, d pyrrole	12.0	18.8	7.4, 6.9
	a, b pyrroline	5.6 <sup>d</sup>	7.7 <sup>d</sup>	3.3

<sup>a</sup> Chemical shifts for  $^1\text{H}$  NMR spectra for samples dissolved in toluene- $d_8$ . <sup>b</sup> Chemical shift at  $1/T \approx 0$ , extrapolated. <sup>c</sup> Chemical shift for diamagnetic reference compounds Ni(TPP),  $\text{H}_2(\text{TPC})$ , and  $\text{H}_2(\text{TPiBC})$ . <sup>d</sup> These parameters were calculated from the first nine data points only.

temperature is lowered.<sup>19</sup> Linear least-squares parameters for these plots are collected in Table I.

Large isotropic shifts with significant dipolar contributions and narrow line widths are characteristic of Fe(OEP), Fe(OEC), and

- (15) Abbreviations: TPP, 5,10,15,20-tetraphenylporphyrinate dianion; TPC, 7,8-dihydro-5,10,15,20-tetraphenylporphyrinate dianion; TPiBC, 2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphyrinate dianion; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinate dianion; OEC, 7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinate dianion.  
 (16) Goff, H.; La Mar, G. N.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 3641-3646.  
 (17) Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676-2681.  
 (18) Boyd, P. D. W.; Buckingham, D. A.; McMeeking, R. F.; Mitra, S. *Inorg. Chem.* **1979**, *18*, 3585-3591.

- (19) Accurate Curie plots of these resonances cannot be made with 200-MHz data because of many overlapping resonances. We plan to collect data at 500 MHz, which will be used to construct more meaningful plots, and will report these in the full paper.

all other four-coordinate intermediate-spin ( $S = 1$ ) Fe(II) porphyrins studied to date.<sup>4,16,20</sup> The spin delocalization mechanism for  $S = 1$  Fe(II) porphyrins has been shown to be  $P \rightarrow Fe \pi$  charge transfer.<sup>16,21,22</sup> It has been argued<sup>16</sup> that contact contributions to the isotropic shifts of the *phenyl* protons of Fe(TPP) are very small, so that these isotropic shifts are dominated by dipolar contributions.<sup>23,24</sup>

$$(\Delta H/H)^{\text{dip}} = (-1/3N)[\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})]\langle(3 \cos^2 \theta - 1)/r^3\rangle - (1/2N)[\chi_{xx} - \chi_{yy}]\langle(\sin^2 \theta \cos 2\phi)/r^3\rangle$$

Note that for Fe(TPP)  $\chi_{xx} = \chi_{yy}$  so that the second (rhombic) term does not contribute to  $(\Delta H/H)^{\text{dip}}$ . For simplicity, we treat the loss of 4-fold symmetry from the reduction of one or two pyrrole rings as a perturbation. Thus,  $z$  is perpendicular to the plane of Fe(TPC) and Fe(TPiBC) and  $y$  is coincident with the molecular  $C_2$  axis in each compound (see Figures 1 and 3). Since  $\cos 2\phi \approx 0$  for the phenyl protons of Fe(TPC), a comparison of Curie plot slopes for the phenyl protons of Fe(TPP) and Fe(TPC) allows the ratio of the terms  $[\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})]\langle(3 \cos^2 \theta - 1)/r^3\rangle$  for these two compounds to be estimated: the term for Fe(TPC) is *less than half* that for Fe(TPP). The solid-state structure of Fe(TPC),<sup>25</sup> while disordered, is nearly identical with that of Fe(TPP).<sup>17</sup> If the conformations in solution are also similar for the two compounds, then  $\Delta\chi_{\parallel}$  for Fe(TPC) may be considerably less than  $\Delta\chi_{\parallel}$  for Fe(TPP).

An analysis of isotropic shifts for protons situated parallel or perpendicular to the molecular  $C_2$  axis for Fe(TPC) (pyrrole and pyrroline protons, Figure 2) and Fe(TPiBC) (phenyl protons,<sup>19</sup> not shown) shows the same upfield and downfield pattern observed for Fe(OEC)<sup>4</sup> and *strongly suggests in-plane magnetic anisotropy for these two compounds* (i.e.  $\chi_{xx} \neq \chi_{yy}$ ). Even though the pyrrole and pyrroline protons for Fe(TPC) should have large dipolar and contact contributions to their isotropic shifts, the phenyl protons for Fe(TPiBC) should only experience sizable dipolar shifts. Thus, our data provide unambiguous proof that the isobacteriochlorin ring system *can* induce rhombicity in the magnetic properties of a metal.

Curie plots for Fe(TPC) and Fe(TPiBC) show large apparent temperature-independent paramagnetism (TIP) for these compounds, as was seen for Fe(OEC) (large deviations in  $1/T = 0$  intercepts, as much as  $\sim 60$  ppm, from diamagnetic values). While none of the protons in Fe(OEP) is chemically similar to those in Fe(TPP), the compounds Fe(OEC) and Fe(TPC) have  $\beta$ -pyrroline protons that are similar. The Curie plot slopes and intercepts for these protons in the two compounds *are nearly identical*:  $-12.2 \times 10^3$  ppm·K and 65.5 ppm for Fe(OEC)<sup>4</sup> and  $-12.2 \times 10^3$  ppm·K and 60.5 ppm for Fe(TPC). Since these two chlorins must have some structural and electronic differences, this coincidence suggests that there is something fundamental about the magnetic properties that can be induced in metals by chlorins.

In summary, the hydroporphyrin complexes Fe(TPC) and Fe(TPiBC) are magnetically different from Fe(TPP) despite their common  $S = 1$  ground state: they are rhombic instead of axial and they exhibit sizable apparent TIP. In addition,  $\Delta\chi_{\parallel}$  may be much smaller for Fe(TPC) than for Fe(TPP). Experiments designed to probe further the molecular and electronic structures of these compounds are in progress.

- (20) (a) Mispelter, J.; Momenteau, M.; Lhoste, J. M. *J. Chem. Phys.* **1980**, *72*, 1003-1012. (b) *Mol. Phys.* **1977**, *33*, 1715-1728. (c) Wayland, B. B.; Mehne, L. F.; Swartz, J. J. *Am. Chem. Soc.* **1978**, *100*, 2379-2383. (d) Migita, K.; La Mar, G. N. *J. Phys. Chem.* **1980**, *84*, 2953-2957. (e) Latos-Grazynski, L.; Cheng, R.-J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 5992-6000.
- (21) Goff, H. M. In ref 7; Part I, pp 237-281.
- (22) La Mar, G. N.; Walker, F. A. In ref 8; Vol IV, pp 61-157.
- (23) Jesson, J. P. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic: New York, 1973; pp 1-52.
- (24)  $N$  is Avogadro's number,  $\chi_{xx}$ ,  $\chi_{yy}$ , and  $\chi_{zz}$  are the magnetic susceptibilities along the three principal magnetic axes,  $r$ ,  $\theta$ , and  $\phi$  are the spherical polar coordinates of a proton with respect to the metal atom origin, and  $\Delta\chi_{\parallel} = \chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$ .
- (25) Strauss, S. H.; Pawlik, M. J.; Anderson, O. P., unpublished data, 1985.

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**Registry No.** Fe(TPC), 52155-40-5; Fe(TPiBC), 102133-42-6.

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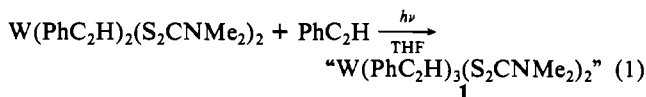
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### Substituted Cyclopentadienyl(dithiolene)tungsten(IV) Products from Alkyne Addition to Tungsten(II) Dithiocarbamate Reagents

Sir:

Reactions that form or cleave C-C<sup>1</sup> or C-S<sup>2</sup> bonds are important in organometallic chemistry. Protonation of  $M(\text{RC}\equiv\text{CR})_2(\text{S}_2\text{CNMe}_2)_2$  ( $M = \text{Mo}$  or  $\text{W}$ ) has been shown to induce alkyne coupling and form  $\eta^4\text{-C}_4\text{R}_4\text{H}$  ligands.<sup>3</sup> We now report that photochemical addition of  $\text{PhC}\equiv\text{CH}$  to  $\text{W}(\text{PhC}_2\text{H})_2(\text{S}_2\text{CNMe}_2)_2$  involves dissection of a dithiocarbamate ligand into three components which are ultimately coupled to alkyne units in the isolated product.

A compound of stoichiometry  $\text{W}(\text{PhC}_2\text{H})_3(\text{S}_2\text{CNMe}_2)_2$  (**1**) is formed in low yield upon photolysis of  $\text{W}(\text{PhC}_2\text{H})_2(\text{S}_2\text{CNMe}_2)_2$ <sup>3</sup> in the presence of excess phenylacetylene (eq 1).<sup>4</sup> Two sets of



signals in both <sup>1</sup>H and <sup>13</sup>C NMR spectra indicated a 1.4:1.0 mixture of isomers. The magnitudes of the <sup>1</sup>J<sub>CH</sub> coupling constants of the CH moieties derived from the original three  $\text{PhC}\equiv\text{CH}$  units were less than 200 Hz (171-183 Hz), from which we inferred that no simple alkyne ligands were retained in the product.<sup>5</sup>

Efforts to unravel the connectivity of the coupled alkyne product from NMR data were unsuccessful, and an X-ray structural determination was undertaken.<sup>6</sup> The structure of "W-(PhC<sub>2</sub>H)<sub>3</sub>(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>" revealed a  $\pi$ -bound 1-(dimethyl-

- Carbon-carbon bond formation is central to organometallic chemistry; see: (a) Swan, J. M.; Black, D. S. C. *Organometallics in Organic Synthesis*; Chapman Hall: London, 1974. (b) Heck, R. F. *Organotransition Metal Chemistry*; Academic: New York, 1974.
- Heterogeneous hydrodesulfurization is the dominant industrial reaction involving C-S bond cleavage; see: Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265.
- Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5004.
- A tetrahydrofuran solution of  $\text{W}(\text{PhC}_2\text{H})_2(\text{S}_2\text{CNMe}_2)_2$  (0.5 mmol in 200 mL) and a 10-fold excess of  $\text{PhC}_2\text{H}$  was photolyzed with a Hanovia 750W medium-pressure Hg arc lamp for 1 h. Solvent evaporation followed by alumina chromatography with an increasing ratio of  $\text{CH}_2\text{Cl}_2$  to  $\text{PhCH}_3$  as the eluant first yielded a band of reagent bis(alkyne), which was followed by a dark gold product band. Solvent removal and recrystallization from  $\text{Et}_2\text{O}$  gave pure **1** in yields of 8-12%.
- In our experience <sup>1</sup>J<sub>CH</sub> values for  $\text{RC}\equiv\text{CH}$  ligands lie between 200 and 240 Hz: (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532. (b) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248. (c) Herrick, R. S.; Templeton, J. L. *Organometallics* **1982**, *1*, 842.
- The crystal selected was triclinic (space group  $P\bar{1}$ ) with unit cell dimensions of  $a = 18.803$  (4) Å,  $b = 10.291$  (3) Å,  $c = 16.186$  (3) Å,  $\alpha = 80.42$  (2)°,  $\beta = 84.79$  (3)°, and  $\gamma = 89.81$  (3)° with  $Z = 2$ . Of the 6141 reflections monitored, 4210 independent reflections with  $I > 3\sigma(I)$  were used in the structure solution and refinement, which converged to 2.6 and 2.1% for  $R_w$  and  $R$ , respectively. Hydrogen positions were calculated, and all other atoms were refined anisotropically.