

This value is reminiscent of a number of other exocyclic phosphorus-nitrogen bond lengths that have been reported.<sup>12,14-16</sup> For example, octakis(dimethylamino)cyclo-tetraphosphazene,  $[\text{NP}(\text{N}(\text{CH}_3)_2)_2]_4$ , has an average exocyclic P-N bond length of 1.69 Å.<sup>12</sup> From this structural consideration alone, a difference cannot be detected between (alkylamino)-, (arylamino)-, or imidazolylcyclophosphazenes that would explain the enhanced ease of hydrolysis of the latter species.

**Bonding within the Imidazole Rings.** The imidazole groups in **1** are aromatic in character. The average bond distance within each imidazole group is 1.353 Å. This bond length value provides a clue to the hydrolytic instability of **1**. The amino nitrogen (bound to phosphorus) lone-pair electrons can be delocalized into the phosphazene ring in (alkylamino)- or (arylamino)phosphazenes. However, in **1**, the lone pairs are delocalized into the aromatic  $\pi$  system of the imidazole substituents. Hence, these lone-pair electrons cannot enhance the electron density on the skeletal phosphorus or nitrogen atoms in a way that would inhibit (nucleophilic) hydrolysis reactions. This also suggests that the second nitrogen atom within the imidazole group may constitute an alternative site for protonation. This, in turn, could assist in the hydrolysis process by stabilizing the imidazole substituent as a leaving group.

**Bond Angles at Phosphorus.** The geometry around the phosphorus atoms in **1** provides a second explanation for the ease of hydrolysis of this compound. Although the exocyclic N-P-N bond angle ( $102.34^\circ$  average) is comparable to those in related phosphazenes,<sup>10,12,16</sup> the planarity of both the phosphazene and imidazole rings exposes the phosphorus atoms to nucleophilic attack. Moreover, the presence of a five-membered ring as a substituent further reduces the shielding power of the side group.

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**Registry No.** **1**, 74868-58-9.

**Supplementary Material Available:** Table II, a listing of the observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

- (14) Mani, N. V.; Wagner, A. J. *J. Chem. Soc., Chem. Commun.* **1968**, 658.  
 (15) Wagner, A. J.; Vos, A. *Acta Crystallogr., Sect. B* **1968**, *B24*, 1423; **1971**, *B27*, 51.  
 (16) Bullen, G. J.; Mallinson, P. R. *J. Chem. Soc., Chem. Commun.* **1969**, 691.

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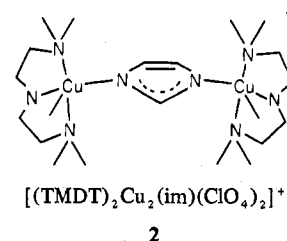
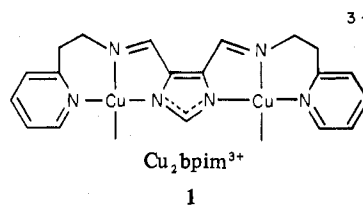
### An Asymmetric Imidazolate-Bridged Dicopper(II) Complex

Robert N. Katz, Gary Kolks, and Stephen J. Lippard\*

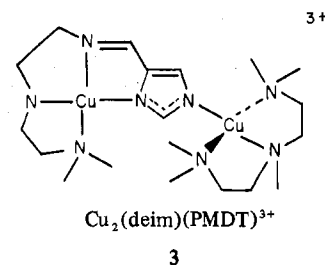
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The discovery<sup>1</sup> of an imidazolate-bridged copper(II)-zinc(II) center in bovine erythrocyte superoxide dismutase and the postulated existence of a histidine-bridged copper(II)-iron(III) unit in cytochrome *c* oxidase<sup>2</sup> have stimulated recent interest

in the imidazolate ion (im) as a bridging ligand. In particular, a variety of imidazolate-bridged dicopper(II) complexes has been synthesized and characterized.<sup>3-8</sup> In all cases, for example, **1**<sup>3</sup> and **2**,<sup>5</sup> the  $\text{Cu}_2(\text{im})^{3+}$  ion was part of a symmetric complex where, except for weakly coordinating anions or solvent molecules,<sup>3b</sup> the two copper coordination spheres were identical.



The magnetic exchange coupling constants in the imidazolate-bridged dicopper(II) complexes fall into two categories.<sup>4-8</sup> When the bridging imidazolate ion is part of the chelating ligand and therefore constrained to lie in the copper coordination plane, as for compounds containing the  $\text{Cu}_2(\text{bpm})^{3+}$  unit (**1**), the value of  $J$  is  $\sim -85 \text{ cm}^{-1}$ . Complexes such as **2**, where the bridging ligand is an independent unit that can rotate out of the principal copper coordination plane, have  $J$  values that lie in the range  $-15$  to  $-40 \text{ cm}^{-1}$ , vary smoothly with the  $\text{pK}_a$  of the bridging ligand,<sup>4b</sup> and are usually  $\sim -30 \text{ cm}^{-1}$ . It was therefore of interest to learn how the spin-exchange interaction in asymmetric **3**, which may be



viewed as a hybrid of **1** and **2**, would relate to that of its symmetric analogues. The present note reports the synthesis and magnetic exchange properties of **3** and also describes the

- (1) (a) Richardson, J. S.; Thomas, K. A.; Rubin, B. H.; Richardson, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1349-1353. (b) Beem, K. M.; Richardson, D. C.; Rajagopalan, K. V. *Biochemistry* **1977**, *16*, 1930-1936.

- (2) Palmer, G.; Babcock, G. T.; Vickery, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2206-2210.  
 (3) (a) Kolks, G.; Frihart, C. R.; Rabinowitz, H. N.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 5720-5721. (b) Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 2079-2082.  
 (4) (a) Kolks, G.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 5804-5806. (b) Kolks, G.; Lippard, S. J., to be submitted for publication.  
 (5) (a) O'Young, C.-L.; Dewan, J. C.; Lilienthal, H. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 7291-7300. (b) Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E.-i.; Lehn, J.-M. *Ibid.* **1979**, *101*, 265-266.  
 (6) (a) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2622-2630. (b) Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Ibid.* **1979**, *18*, 141-148.  
 (7) Mori, W.; Nakahara, A.; Nakao, Y. *Inorg. Chim. Acta* **1979**, *37*, L507-L508.  
 (8) Hendricks, H. M. J.; Reedijk, J. *Inorg. Chim. Acta* **1979**, *37*, L509-L510.

related mononuclear and polymeric complexes [Cu-(deimH)](ClO<sub>4</sub>)<sub>2</sub> and [Cu(deim)(ClO<sub>4</sub>)<sub>n</sub>]<sub>n</sub>, respectively, where deimH is 4(5)-[[(2-((2-(dimethylamino)ethyl)amino)ethyl)imino)methyl]imidazole.

### Experimental Section

**Materials and Methods.** 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDT) and 1,1-dimethyldiethylenetriamine were distilled prior to use; the latter was stored at 4 °C. 4(5)-Formylimidazole was prepared by manganese dioxide oxidation of 4(5)-(hydroxymethyl)imidazole<sup>9</sup> in dioxane<sup>10</sup> or dimethylacetamide<sup>3a</sup> and purified by chromatography on silica. The complex (PMDT)Cu(ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>CN was prepared from methanol solutions.<sup>4b</sup> Elemental analyses were obtained from Galbraith Laboratories, Knoxville, Tenn. Melting points were taken on a Nalge hot-stage microscope and are uncorrected.

Variable-temperature (4.2 K < T < 280 K) magnetic susceptibility measurements were made on a locally constructed Faraday balance equipped with a Varian 12-in. magnet, Cahn 1000 electrobalance, Janis dewar, and Lakeshore Cryotronics variable-temperature controller.<sup>4b</sup> Electron spin resonance spectra were obtained at 295 and 77 K on powders and frozen glasses as described previously.<sup>5a</sup> Infrared spectral data were recorded on a Perkin-Elmer 621 spectrophotometer using 2% KBr pellets and polystyrene as the calibrant. Optical spectra were taken on a Cary 118C spectrometer.

**Preparation of Compounds.** [4-[(2-((2-(Dimethylamino)ethyl)amino)ethyl)imino)methyl]imidazole]copper(II) Perchlorate, Cu-(deimH)(ClO<sub>4</sub>)<sub>2</sub>. To a 10-mL methanol solution of 3.96 g (10.7 mmol) of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O heated to reflux was added 1.59 mL (10.7 mmol) of 1,1-dimethyldiethylenetriamine. A solution of 1.04 g (10.7 mmol) of 4(5)-formylimidazole dissolved in 50 mL of methanol was then added dropwise, followed by another 10 mL of methanol used to rinse the dropping funnel. The reaction was continued at reflux for 18 h after which time the volume was reduced to 10 mL in a beaker with heating. A blue powder collected upon cooling was dried in vacuo overnight. A 3.49-g (69%) yield of Cu(deimH)(ClO<sub>4</sub>)<sub>2</sub>, mp 255 °C dec, was isolated.

Anal. Calcd for C<sub>10</sub>H<sub>19</sub>N<sub>5</sub>Cl<sub>2</sub>O<sub>8</sub>Cu: C, 25.46; H, 4.06; N, 14.85; Cl, 15.03. Found: C, 25.69; H, 4.23; N, 14.85; Cl, 14.45.

IR: 1658 (s), 1587 (w), 1558 (w), 1517 (m), 1470 (s), 1442 (s), 1388 (w), 1338 (m), 1329 (sh), 1319 (w), 1280 (s), 1240 (m), 1225 (w), 1095 (vs, br), 1035 (sh), 970 (m), 955 (w), 931 (m), 901 (w), 873 (m), 830 (m), 780 (m), 622 (vs), 602 (s), 562 (w), 500 (m), 475 (w), 455 (m), 420 (w) cm<sup>-1</sup>.

Optical spectra: Nujol mull, 553 (br) nm; dimethylformamide solution, 592 and 355 nm; Me<sub>2</sub>SO solution, 595 nm.

**μ-[4-[(2-((2-(Dimethylamino)ethyl)amino)ethyl)imino)methyl]imidazolato]-(1,1,4,7,7-pentamethyldiethylenetriamine)dicopper(II) Perchlorate, Cu<sub>2</sub>(deim)(PMDT)(ClO<sub>4</sub>)<sub>3</sub> (3).** A solution containing 509 mg (1.08 mmol) of Cu(deimH)(ClO<sub>4</sub>)<sub>2</sub> and 540 mg (1.07 mmol) of Cu(PMDT)(ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>CN in 15 mL of methanol was refluxed for 1 h at which time 1.11 mL of an ~1 M methanol solution of sodium methoxide was added in 100-μL amounts through the condenser. After refluxing for 18 h the reaction mixture was allowed to cool and 750 mg (86%) of purple powder was isolated by filtration (mp 239 °C dec).

Anal. Calcd for C<sub>19</sub>H<sub>41</sub>N<sub>8</sub>Cl<sub>3</sub>O<sub>12</sub>Cu<sub>2</sub>: C, 28.28; H, 5.12; N, 13.88; Cl, 13.18. Found: C, 28.20; H, 5.09; N, 13.71; Cl, 13.36.

IR: 1641 (vs), 1561 (s), 1471 (vs), 1446 (sh), 1428 (m), 1417 (sh), 1404 (w), 1388 (w), 1366 (m), 1336 (sh), 1324 (s), 1294 (s), 1256 (m), 1235 (w), 1225 (w), 1211 (sh), 1171 (sh), 1096 (vs, br), 1031 (sh), 1013 (sh), 981 (m), 967 (m), 944 (m), 936 (m), 926 (w), 891 (w), 861 (m), 836 (m), 816 (m), 798 (sh), 786 (s), 766 (w), 704 (w), 661 (s), 626 (vs), 576 (w), 506 (m), 486 (m), 425 (w) cm<sup>-1</sup>.

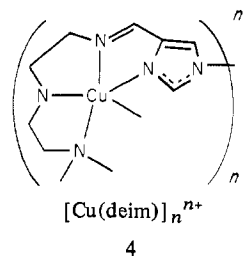
**Polymeric μ-[4-[(2-((2-(dimethylamino)ethyl)amino)ethyl)imino)methyl]imidazolato]copper(II) Perchlorate, [Cu(deim)(ClO<sub>4</sub>)<sub>n</sub>]<sub>n</sub> (4).** Rapid addition of sodium methoxide to the reaction mixture of Cu-(deimH)(ClO<sub>4</sub>)<sub>2</sub> and Cu(PMDT)(ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>CN or to Cu-(deimH)(ClO<sub>4</sub>)<sub>2</sub> alone caused the precipitation of a green microcrystalline material (mp 260 °C dec).

Anal. Calcd for C<sub>10</sub>H<sub>18</sub>N<sub>5</sub>ClO<sub>4</sub>Cu: C, 32.35; H, 4.89; N, 18.86; Cl, 9.55. Found: C, 32.49; H, 4.85; N, 18.67; Cl, 9.78.

IR: 1736 (w), 1634 (vs), 1561 (s), 1474 (s), 1447 (sh), 1434 (sh), 1414 (w), 1389 (w), 1381 (w), 1356 (m), 1334 (s), 1325 (s), 1294 (s), 1275 (s), 1261 (m), 1254 (m), 1235 (m), 1225 (m), 1186 (sh), 1175 (sh), 1106 (s, br), 1056 (w), 1035 (m), 1013 (w), 1001 (m), 975 (m), 951 (m), 938 (m), 921 (m), 876 (m), 831 (m), 815 (s), 796 (s), 771 (s), 691 (m), 656 (vs), 637 (sh), 626 (vs), 561 (m), 514 (m), 457 (s) cm<sup>-1</sup>.

### Results and Discussion

The complexes formed in the reaction of Cu(deim)<sup>2+</sup> with (PMDT)Cu<sup>2+</sup> or with itself in the presence of base correspond, respectively, to the imidazolate-bridged species **3** and **4** as



shown from the analytical, magnetic, and spectroscopic data. A 0.5 mM solution of **3** in Me<sub>2</sub>SO exhibits a broad maximum at 615 nm. Addition of a fourfold excess of aqueous sulfuric acid shifts the absorbance maximum to 595 nm, the exact position observed for a Me<sub>2</sub>SO solution of Cu(deimH)(ClO<sub>4</sub>)<sub>2</sub>. This result is consistent with previous studies<sup>3,5</sup> which show that the imidazolate bridge of the Cu<sub>2</sub>(im)<sup>3+</sup> moiety cleaves in the presence of acid to form mononuclear copper(II) complexes. The spectrum of the Cu(PMDT)<sup>2+</sup> half of **3**, which has a λ<sub>max</sub> at 683 nm, was not observed when **3** was treated with excess acid, presumably because the ligand is released under these conditions. Solutions of **3** in dry dimethylformamide (DMF) do not obey Beer's law and slowly deposit **4**. The green complex **4** formed during all attempts to obtain crystals of **3** unless excess Cu(PMDT)<sup>2+</sup> was present. Even in these cases, and in several different solvent systems, crystals suitable for X-ray study could not be obtained. Supporting evidence for the imidazolate-bridged formulation of **3** was obtained from electron spin resonance spectra at 77 K in a 1:1 DMF/CH<sub>2</sub>Cl<sub>2</sub> glass which showed a weak ΔM = ±2 transition at half-field (g = 4.28) with seven copper hyperfine lines.<sup>5a</sup>

The antiferromagnetic coupling observed for solid samples of **3** is also consistent with the proposed imidazolate-bridged structure. Magnetic susceptibility data plotted as a function of temperature exhibit the broad maximum (~85 K) characteristic<sup>4-6</sup> of the Cu<sub>2</sub>(im)<sup>3+</sup> unit; a table of observed and calculated atomic susceptibilities and temperatures is available.<sup>11</sup> Analysis of the data in the usual manner<sup>4,5</sup> revealed g = 2.068 (5) and J = -45.2 (2) cm<sup>-1</sup>. It is interesting that this value is slightly less than the average of the exchange coupling constants previously determined<sup>4,5</sup> for Cu<sub>2</sub>(bpm)<sup>3+</sup> (**1**) and [(TMDT)<sub>2</sub>Cu<sub>2</sub>(im)(ClO<sub>4</sub>)<sub>2</sub>]<sup>+</sup> (**2**), -81.3 (1) and -25.8 (2) cm<sup>-1</sup>, respectively. Whatever the structural and electronic features that determine the magnitude of the exchange coupling constant in Cu<sub>2</sub>(im)<sup>3+</sup> complexes,<sup>4,6</sup> the J value for the asymmetric complex **3** is close to the value predicted by interpolation of the results for the symmetric complexes formed by its two separate components.

(9) Totter, J. R.; Darley, W. J. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, pp 460-462.

(10) Papadopoulos, E. P.; Jarrar, A.; Issidorides, C. H. *J. Org. Chem.* **1966**, *31*, 615-616.

(11) Supplementary material.

by its two separate components.

The plot of susceptibility vs. temperature for compound 4 showed behavior typical of an antiferromagnetically coupled linear-chain polymer<sup>12</sup> and, upon analysis, gave  $g = 2.139$  (8) and  $J = -36.3$  (2)  $\text{cm}^{-1}$ . Data are available in Table S1.<sup>11</sup>

Differences in the solid-state infrared spectra of 3 and 4 compared with that of the mononuclear complex (Experimental Section) in the 1500–1700- $\text{cm}^{-1}$  (C=N, C=C) region may be diagnostic of the mode of imidazole binding.

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**Registry No.** 3, 74911-59-4; 4, 74911-55-0; Cu(deimH)(ClO<sub>4</sub>)<sub>2</sub>, 74947-52-7; Cu(PMDT)(ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>CN, 74911-61-8; 1,1-dimethyldiethylenetriamine, 24229-53-6; 4(5)-(formyl)imidazole, 3034-50-2.

**Supplementary Material Available:** Table S1 reporting the observed and calculated temperature dependent magnetic susceptibilities for Cu<sub>2</sub>(deim)(PMDT)(ClO<sub>4</sub>)<sub>3</sub> and [Cu(deim)(ClO<sub>4</sub>)<sub>n</sub>]<sub>n</sub> (2 pages). Ordering information is given on any current masthead page.

(12) Estes, W. E.; Gavel, D. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* 1978, 17, 1415-1421.

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### Carbonyl Sulfide Activation: COS Disproportionation to Dithiocarbonate and Carbon Monoxide Promoted by Vanadocene

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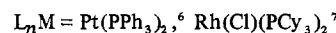
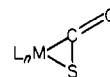
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Two strategies for studying molecular activation promoted by transition-metal complexes are the utilization of "model compounds" and "equivalent molecules". These approaches were recently applied to the problems associated with the activation of CO<sub>2</sub> by transition-metal complexes.<sup>2a</sup> While carbodiimides,<sup>2b</sup> phenyl isocyanate,<sup>3</sup> and diphenylketene<sup>4</sup> imitate CO<sub>2</sub> in many respects, carbon disulfide, which appears as the most obvious CO<sub>2</sub> analogue and which has a very rich organometallic chemistry,<sup>5</sup> is apparently a poor model. We expect that COS would more closely resemble CO<sub>2</sub> in its activation by transition metals. Very few reports have been concerned, however, with the reaction of COS with transition-metal complexes. In these cases,  $\pi$  coordination to the

**Table I.** Summary of Crystal Data and Intensity Data Collection for [Cp<sub>2</sub>V]<sub>2</sub>(COS<sub>2</sub>)·C<sub>6</sub>H<sub>6</sub>

|   |   |
|---|---|
| <i>a</i> , Å                                  | 16.317 (5)  |
| <i>b</i> , Å                                  | 10.566 (2)  |
| <i>c</i> , Å                                  | 15.416 (5)  |
| $\alpha$ , deg                                | 90.0  |
| $\beta$ , deg                                 | 114.72 (4)  |
| $\gamma$ , deg                                | 90.0  |
| <i>Z</i>                                      | 4   |
| <i>M<sub>r</sub></i>                          | 532.5   |
| <i>d</i> <sub>calc</sub> , g cm <sup>-3</sup> | 1.465   |
| space group                                   | <i>P</i> <sub>2</sub> / <i>c</i>                      |
| radiation                                     | Nb-filtered Mo K $\alpha$<br>( $\lambda = 0.71069$ Å) |
| $\mu$ , mm <sup>-1</sup>                      | 0.93  |
| $\mu$ <sub>r</sub>                            | 0.1   |
| scan type                                     | $\theta$ -2 $\theta$                                  |
| scan range                                    | $\pm 0.5^\circ$ from peak center                      |
| scan speed, deg $\theta$ /min                 | 2.5-10  |
| bkgd  | stationary cryst at $\pm 0.5^\circ$                   |
| 2 $\theta$ limits, deg                        | 5-48  |
| criterion for obsn                            | $I > 2\sigma(I)$                                      |
| unique obsd data                              | 2318  |
| unique total data                             | 3791  |
| cryst dims, mm <sup>3</sup>                   | 0.34 × 0.10 × 0.48                                    |

metal center through the C=S double bond has been proposed.<sup>6,7</sup>



With group 8 metals in low oxidation states, COS tends to resemble CS<sub>2</sub> more than CO<sub>2</sub>. We report here the reaction between COS and vanadocene, whose reactivity with other CO<sub>2</sub> equivalents has been described recently.<sup>8,9</sup> Vanadocene promotes a disproportionation of COS to COS<sub>2</sub><sup>2-</sup> and CO, resulting in the complexes (Cp<sub>2</sub>V)<sub>2</sub>(COS<sub>2</sub>) and Cp<sub>2</sub>V(CO).

### Experimental Section

All the experimental operations were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Vanadocene was prepared as described in the literature.<sup>10</sup> Carbonyl sulfide is commercially available from Aldrich. IR spectra were recorded with a Perkin-Elmer 282 spectrophotometer. Magnetic susceptibility measurements were made with a Faraday balance.

**Reaction of Vanadocene with Carbonyl Sulfide.** A 250-mL flask containing the violet solution of vanadocene (1.0 g, 5.52 mmol) in benzene (30 mL) was evacuated and then filled with COS at room temperature. The color of the solution turned suddenly to blue. When the solution was allowed to stand, gas evolution occurred along with change of the color to deep maroon. A crystalline maroon solid separated (ca 60%). Anal. Calcd for C<sub>21</sub>H<sub>20</sub>V<sub>2</sub>OS<sub>2</sub>: C, 55.50; H, 4.40; S, 14.10. Found: C, 55.12; H, 4.88; S, 14.10. The complex has a magnetic moment of 2.72  $\mu_B$  at 297 K. The IR spectrum (Nujol) does not show any significant band above 1600  $\text{cm}^{-1}$ . The solid is very sensitive to air and contains variable amounts of solvent, which is lost very easily. The X-ray analysis was performed on [(Cp<sub>2</sub>V)<sub>2</sub>(COS<sub>2</sub>)]·C<sub>6</sub>H<sub>6</sub>.

The same reaction was carried out with an excess of vanadocene over COS as follows: a toluene solution (30 mL) of vanadocene (2.13 g, 11.76 mmol) was reacted with 100 mL of COS (ca 4 mmol). The IR spectrum shows the presence in solution of a strong carbonylic band at 1880  $\text{cm}^{-1}$  corresponding to that of Cp<sub>2</sub>V(CO).<sup>11</sup>

- (1) (a) Università di Pisa. (b) Università di Parma.  
 (2) (a) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1979, 101, 1767. (b) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1979, 101, 4740 and references cited therein.  
 (3) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* 1979, 792 and references cited therein.  
 (4) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1978, 100, 1921; *Inorg. Chem.* 1978, 17, 2995.  
 (5) Butler, I. S.; Fenster, A. *J. Organomet. Chem.* 1974, 66, 161. Yaneff, P. V. *Coord. Chem. Rev.* 1977, 23, 183.

- (6) Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* 1967, 865.  
 (7) Van Gaal, H. L. M.; Verlaan, J. P. *J. Organomet. Chem.* 1977, 133, 93.  
 (8) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.*, in press.  
 (9) Pasquali, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.*, in press.  
 (10) Fischer, E. O.; Vigoureux, S. *Chem. Ber.* 1958, 51, 2205.