If this step is followed by an oxidative-addition of 1-methylpentaborane at a basal position, the selective formation of the 1:2′-$[B_4H_9][1'-CH_3B_5H_7]$ isomer would then result following reductive-elimination. A similar reaction sequence could lead to formation of 1:1′-$[B_4H_9]_2$; however, the oxidative-addition of the second tetraborane(10) molecule must also occur at a 1-boron position to account for the formation of the symmetrical isomer.

In contrast to the results with 1-methylpentaborane, 2-methylpentaborane was found to react readily in the presence of $PtBr_2$ to give a coupled-cage product, 1:2′-$[2-CH_3B_5H_7][3'-CH_3B_5H_7]$. The fact that no 1:2′-$[2-CH_3B_5H_7][4'-CH_3B_5H_7]$ isomer is observed in the reaction indicates that the oxidative-addition of 2-methylpentaborane(9) must occur at a B–H position adjacent (cis) to the basal methyl substituent. A similar cis preference has been observed in the formation of dimethyl-substituted pentaboranes and has been proposed to result from steric repulsions between the methyl group and adjacent bridge hydrogens.[52]

It is significant that the reaction of hexaborane(10) with $PtBr_2$ does not result in the formation of a coupled-cage product but instead gives the metalloborane complex, $[4,5;4',5'\text{-}\mu\text{-}trans\text{-}PtCl_2(B_6H_{10})_2]_2$,[35] in which each hexaborane(10) is bound in an η^2-fashion across a basal boron–boron bond. Thus, hexaborane(10), because of its unique basal single bond, is able to coordinate in an olefin-like bonding fashion that is not possible for other boron hydrides and carboranes. As a result, processes such as oxidative-addition of a cage B–H bond to platinum are less likely and no coupling occurs.

Platinum(II) bromide was also found to be effective for catalyzing the reactions of the small carboranes, 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$, to give the corresponding boron–boron linked coupled carboranes, 2:2′-$[1,5-C_2B_3H_4]_2$ and 2:2′-$[1,6-C_2B_4H_5]_2$. There was no evidence for the formation of any carbon–carbon or boron–carbon linked isomers in the reactions, which agrees both with the proposed electrophilic nature of the catalyst and with the relative bond strengths of B–H (~91 kcal) and C–H (~98 kcal) bonds.[53] The observation of only boron–boron linked products is also consistent with our earlier studies of the transition-metal-catalyzed reactions of small carboranes with acetylenes, which was found to yield only boron-substituted alkenylcarborane products.[54]

In conclusion, we feel that the results described herein represent a major step toward the development of rational, high-yield procedures for the formation of multicage polyhedral boranes and carboranes. Furthermore, this work again illustrates the potential for the use of transition-metal catalysts, which until now have been primarily employed in organic chemistry, to promote analogous reactions of inorganic compounds. Work is now continuing in this laboratory aimed toward both the discovery of new types of dehydrodimerization catalysts, which may exhibit higher reactivity and different selectivity, and the development of new classes of metal-catalyzed borane and carborane reactions.

Acknowledgment. We thank the Army Research Office and the National Science Foundation for the support of this work.

---

(52) Onak, T.; Friedman, L. B.; Hartsuck, J. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1966**, *88*, 3439–3440.

(53) Jolly, W. L. "The Principles of Inorganic Chemistry"; McGraw-Hill: New York, 1976; p 41.

(54) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 506–514.

4-Phenyl-1,2,4-triazoline-3,5-dione: A Prosthesis for the μ-η^1-S_2 Ligand in Organovanadium Sulfide Chemistry

C. Mark Bolinger, Thomas B. Rauchfuss,*[1] and Scott R. Wilson

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received February 6, 1984*

Abstract: 4-Phenyl-1,2,4-triazoline-3,5-dione (PTD) reacts with $(CH_3C_5H_4)_2V_2(\mu\text{-}S)_2(\mu\text{-}\eta^1\text{-}S_2)$ (**1**) to yield primarily $(CH_3C_5H_4)_2V_2(\mu\text{-}S)(\mu\text{-}\eta^2\text{-}S_2)(\mu\text{-}\eta^1\text{-}PTD)$ (**2**) along with other minor products. The structure of **2** was inferred from the structure of its $Pt(PPh_3)_2$ adduct $(CH_3C_5H_4)_2V_2S_3(PTD)Pt(PPh_3)_2$ (**5**), which was determined by single-crystal X-ray diffraction techniques. The crystals of **5** belong to space group $P2_1/c$ with $a = 22.181$ (7) Å, $b = 13.176$ (4) Å, $c = 19.303$ (5) Å, $\beta = 111.10$ (2)°, $Z = 4$. Conventional full-matrix least-squares refinement with non-carbon atoms anisotropic, carbon atoms independently isotropic, and hydrogen atoms identically isotropic gave $R = 0.059$ and $R_w = 0.065$ for 6934 reflections having $2\theta < 55°$ and $I > 3\sigma(I)$. The structure consists of an isosceles triangle of metal atoms capped by two μ_3-S ligands, with the V–V edge spanned by a μ-S and a μ-η^1-PTD ligand. An evaluation of the V–S and V–Pt distances indicates that formation of the $Pt(PPh_3)_2$ adduct effects only minor perturbations on the electronic structure of **2**. Compound **2** is efficiently desulfurized by tri-*n*-butylphosphine to yield $(CH_3C_5H_4)_2V_2(\mu\text{-}S)_2(\mu\text{-}\eta^1\text{-}PTD)$ (**3**). Compound **3** reacts further with PTD to yield $(CH_3C_5H_4)_2V_2S_2(PTD)_2$ (**4**). Both **3** and **4** are minor products of the reaction of **1** with PTD. The high symmetry of **3** and **4** is supported by spectroscopic measurements. Compound **4** forms a stable $Pt(PPh_3)_2$ adduct, $(CH_3C_5H_4)_2V_2S_2(PTD)_2Pt(PPh_3)_2$ (**6**), whose properties indicate a structure consisting of a $[(CH_3C_5H_4)V]_2$ moiety bridged by two μ-η^1-PTD ligands and a μ-η^2-$S_2Pt(PPh_3)_2$ ligand. The structure of **4** thus arises from oxidative coupling of the two μ-S ligands in **3**. Comparison of **2** and **3** with $(CH_3C_5H_4)_2V_2(\mu\text{-}S)(\mu\text{-}\eta^1\text{-}S_2)(\mu\text{-}\eta^2\text{-}S_2)$ and $(CH_3C_5H_4)_2V_2(\mu\text{-}S)_2(\mu\text{-}\eta^1\text{-}S_2)$ illustrates that the μ-η^1-PTD ligand functions as prosthesis for the μ-η^1-S_2 ligand in these cyclopentadienylvanadium dimers.

Recent work has shown that organometallic sulfide complexes can exhibit considerable sulfur-centered reactivity. Compounds of the type $(RC_5H_4)_2TiS_5$ (R = H, CH_3),[2] $(RC_5H_4)_2V_2S_4$ (R = H, CH_3, $(CH_3)_2CH$),[3] $(C_5H_5)_2Cr_2S(S\text{-}t\text{-}Bu)_2$,[4] $(CH_3R_4C_5)_2Mo_2S_4$ (R = CH_3, H)[5], and $Fe_2(S_2)(CO)_6$[6] have been employed for organic synthesis, for the assembly of unusual mixed-metal

---

(1) Fellow of the Alfred P. Sloan Foundation (1983–1985); Camille and Henry Dreyfus Teacher-Scholar (1983–1988).

(2) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947. Giolando, D. M.; Rauchfuss, T. B. *Organometallics* **1984**, *2*, 487.

(3) (a) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321. (b) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L., submitted for publication.

(4) Pasynskii, A. A.; Eremenko, I. L.; Rakitin, Y. V.; Novotortsev, V. M.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1979**, *165*, 57.

0002-7863/84/1506-7800$01.50/0

Table I. Analytical Data for New Compounds[a]

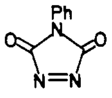
compound	C	H	N	V	P
$(CH_3C_5H_4)_2V_2S_3(PTD)$	45.40 (45.20)	3.56 (3.60)	7.89 (7.91)	19.10 (19.17)	
$(CH_3C_5H_4)_2V_2S_2(PTD)$	47.80 (48.10)	3.58 (3.84)	8.37 (8.42)		
$(CH_3C_5H_4)_2V_2S_2(PTD)_2{\cdot}CH_2Cl_2$	46.61 (45.86)	3.50 (3.45)	11.37 (11.06)	13.69 (13.42)	
$(CH_3C_5H_4)_2V_2S_3(PTD)Pt(PPh_3)_2$	53.43 (53.76)	3.78 (3.95)	3.44 (3.36)	8.15 (8.14)	4.89 (4.95)
$(CH_3C_5H_4)_2V_2S_2(PTD)_2Pt(PPh_3)_2{\cdot}CH_2Cl_2$	52.89 (52.78)	3.82 (4.02)	5.96 (5.68)	6.91 (6.89)	

[a] Calculated values in parentheses.

clusters, and as hydrogenation catalysts. All of these cases involve reactions of coordinated inorganic sulfur ligands.

The present report is concerned with the use of an organic heterocycle as a chemical probe in organometallic sulfide chemistry. The work has yielded unexpected dividends in terms of the reactions and rearrangements that occur when organovanadium sulfur compounds interact with diazenes. In particular, the displacement of a bridging sulfide by an unsaturated organic molecule and coupling of two sulfide ligands to a disulfide have been observed in discrete, molecular species. These fundamental processes are potentially important to the chemistry of both molecular metal sulfides and nonmolecular metal sulfide catalysts.

The reagent employed in this project is 4-phenyl-1,2,4-triazoline-3,5-dione (PTD).[7] PTD is a highly electrophilic diazene that



PTD

is well-known in organic circles, particularly in its role as a dienophile.[8] The transition metal chemistry of PTD and related diazenes has been systematically developed over the past 20 years. Briefly summarized, they are known to coordinate metals in either a terminal olefin-like fashion or a bridging acetylene-like fashion. A classic example of diazene coordination is provided by $Ni(Ph_2N_2)(P(tol)_3)_2$ (tol = *p*-tolyl)[9] where the bonding appears to resemble that for $Ni(C_2H_4)(PPh_3)_2$.[10]

We were struck by similarities in the coordination chemistry of diazenes and disulfur. For instance, $IrCl(CO)(PPh_3)_2(Z_2N_2)$[11] is related to $[Ir(dppe)_2S_2]^+$[12] as is $MoO(Z_2N_2)(dtc)_2$[13] to $MoO(S_2)(dtc)_2$[14] (Z = CO_2CH_3, dtc = S_2CNR_2, dppe = 1,2-$(Ph_2P)_2C_2H_4$). $Fe_2((CH_3)_2N_2)(CO)_6$[15] is obviously related to $Fe_2S_2(CO)_6$[16] as well as $Fe_2(t\text{-}Bu_2P_2)(CO)_6$[17] and $Co_2As_2(CO)_6$.[18] Bimetallic complexes in which the diazene bridges the metals in an μ-η^1 mode are generally derived from the pyrazolide anion, e.g., $((C_5H_5)_2Ti)_2(N_2C_3H_3)_2$.[19] The chair conformation of this compound resembles that of 1,4-$[((CH_3)_2CHC_5H_4)_2Ti]_2S_4$.[20] Planar complexes are also known as in $(Ni(NO)(N_2C_5H_7))_2$ (maximum deviation of the Ni_2N_4 ring is 0.005 (3) Å).[21] It is interesting and relevant that $(Fe(NO)_2(N_2C_5H_7))_2$[22] is similar to $(Fe(NO)_2)_2(S)_2^{2-}$[23] and $(Fe(NO)_2)_2(SEt)_2$,[24] which have single sulfur atom bridges.

In previous reports from this laboratory we have described the preparation, properties, and structures of $(RC_5H_4)_2V_2S_5$[25] and $(RC_5H_4)_2V_2S_4$.[3] Both compounds possess structurally and electronically unique cores that have not yet been duplicated in other systems. Our studies on the PTD–$(CH_3C_5H_4)_2V_2S_x$ system have afforded such analogues, and the new compounds provide a context within which this new generation of early transition metal sulfides can be better understood.

Experimental Section

Materials and Methods. All preparative reactions were performed under an atmosphere of prepurified nitrogen, and unless otherwise noted, workups were done aerobically in an efficient hood. Tetrahydrofuran (THF), hexanes (bp 68–72 °C), and toluene were obtained as reagent grade and were redistilled from sodium benzophenone ketyl (THF, hexane) or sodium metal (toluene). Dichloromethane was technical grade and was redistilled from $CaCl_2$ and P_2O_5. All other solvents were reagent grade and were dried over 4A molecular sieves. 4-Phenyl-1,2,4-triazoline-3,5-dione (PTD) (Fluka) and tri-*n*-butylphosphine (PBu_3) (Aldrich) were used without further purification. $(CH_3C_5H_4)_2V_2S_4$ (**1**) was prepared according to published procedures.[3] $Pt(PPh_3)_2C_2H_4$ was prepared according to a recently published procedure.[26] Invariably, it was found to be contaminated with significant quantities of *cis*-$PtCl_2(PPh_3)_2$ (20% by elemental analysis), which does not affect the syntheses.

Thin-layer chromatography (analytical scale) was performed on Eastman 13181 silica gel plates; flash chromatography (preparative scale) was performed with columns packed with Woehm 32-63 silica gel.

The following instruments were used in this work: IR, Perkin-Elmer 599B; ^1H NMR, Varian EM-390 (with internal frequency lock) or Varian HR-220 (with internal ^2H frequency lock); ^{13}C NMR, Nicolet NT-360 (with internal ^2H frequency lock); ^{31}P NMR, Varian XL-100 (with external ^2H frequency lock). The 70-eV electron-impact (EI) and field desorption (FD) mass spectra were measured as a service on Varian CH-5 and 731 spectrometers at the University of Illinois Mass Spectrometry Laboratory. All new compounds showed molecular ions in EI (**2**, **3**) or FD (**4**–**6**) mass spectrum.

All new compounds were isolated as crystalline solids that gave satisfactory analyses (Table I). These data were obtained by the University of Illinois Microanalytical Laboratory.

Reaction of $(CH_3C_5H_4)_2V_2S_4$ with PTD. Compound **1** (0.508 g, 1.31 mmol) and PTD (0.509 g, 2.91 mmol) were dissolved in 10 mL of THF. After 1 h the reaction mixture was filtered through Celite, evaporated, and extracted with CH_2Cl_2. Chromatography on a 2.5 × 20 cm silica gel column eluting with CH_2Cl_2 afforded black, red, purple, and blue fractions; in some cases the red and purple bands were only poorly resolved and rechromatography was required. The black, red, and purple bands were shown to be $(CH_3C_5H_4)_2V_2S_5$ (0.01 g), $(CH_3C_5H_4)_2V_2S_2(PTD)$ (0.057 g, 8.8%), and $(CH_3C_5H_4)_2V_2S_3(PTD)$ (**2**) (0.373 g, 53.7%), respectively. The blue band afforded 0.0154 g of an unidentified stable solid. Elution with acetone gave a small quantity of $(CH_3C_5H_4)_2V_2S_2(PTD)_2$.

$(CH_3C_5H_4)_2V_2S_2(PTD)$ (3) from 2 and PBu_3. A CH_2Cl_2 solution of PBu_3 (0.130 mL, 0.522 mmol) was dripped into a slurry of **2** (0.241 g, 0.454 mmol) in 5.0 mL of CH_2Cl_2 over a period of 5 min. The resultant red solution was filtered, and analytically pure **3** was obtained by diluting the filtrate with hexane, concentrating to a small volume, cooling to −25

---

(5) (a) Rakowski-DuBois, M.; DuBois D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064. (b) Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 107.

(6) (a) Day, V. W.; Lesch, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 1290. (b) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(7) Stickler, J. C.; Pirkle, W. H. *J. Org. Chem.* **1966**, *31*, 3444.

(8) Moody, C. J. *Adv. Heterocycl. Chem.* **1982**, *30*, 1.

(9) Ittel, S. D.; Ibers, J. A. *J. Organomet. Chem.* **1973**, *57*, 389.

(10) Cheng, P. T.; Cook, C. D.; Koo, C. H.; Nyburg, S. C.; Shiomi, M. T. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1904.

(11) Green, M.; Osborn, R. B. L.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 3083.

(12) Bond, W. D., Jr.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1313.

(13) Schneider, P. W.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 8460.

(14) Dirand, J.; Ricard, L.; Weiss, R. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 661.

(15) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2709.

(16) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1.

(17) Vahrenkamp, H.; Wolters, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 154.

(18) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5633.

(19) Fieselmann, B. F.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2074.

(20) Giolando, D. M.; Rauchfuss, T. B., unpublished results.

(21) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1979**, *57*, 3090.

(22) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1979**, 3119.

(23) Rauchfuss, T. B.; Weatherill, T. D. *Inorg. Chem.* **1982**, *21*, 827.

(24) Thomas, J. T.; Robertston, J. H.; Cox, E. G. *Acta Crystallogr.* **1958**, *11*, 599.

(25) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551.

(26) Nogel, U. *Chem. Ber.* **1982**, *115*, 1998.

Table II. NMR and IR Data for New Compounds

compound	^1H NMR,[a] ppm	IR,[b] cm^{-1}	^{13}C, ^{31}P NMR,[a] ppm
$(CH_3C_5H_4)_2V_2S_3(PTD)$	(CD_2Cl_2) 7.35 (5 H, m), 6.95 (2 H, m), 6.68 (2 H, m), 6.50 (2 H, m), 6.50 (2 H, m), 6.27 (2 H, m), 2.28 (6 H, s)	1731 (s), 1695 (s), 1492 (m), 1395 (vs), 1235 (s), 1141 (s), 1038 (w), 1014 (m), 834 (w), 820 (s), 772 (m), 710 (w), 641 (m)	
$(CH_3C_5H_4)_2V_2S_2(PTD)$	($CDCl_3$) 7.27 (5 H, m), 6.96 (4 H, m), 6.62 (4 H, m), 2.40 (6 H, s)	1730 (s), 1697 (s), 1490 (m), 1390 (vs), 1235 (s), 1105 (m), 1038 (m), 1020 (m), 1012 (m), 821 (s), 769 (m), 709 (w), 639 (m)	
$(CH_3C_5H_4)_2V_2S_2(PTD)_2 \cdot CH_2Cl_2$	(CD_2Cl_2) 7.49 (10 H, m), 7.10 (4 H, m), 6.74 (4 H, m), 2.35 (6 H, s)	1680 (br, vs), 1501 (m), 1380 (s), 1223 (s), 1175 (m), 1066 (m), 1009 (s), 997 (m), 822 (m), 766 (m), 723 (m), 691 (m), 630 (m)	$^{13}C\{^1H\}$ NMR (CD_2Cl_2) 133.5, 129.2, 127.8, 126.3, 125.3, 111.7, 111.4, 16.6
$(CH_3C_5H_4)_2V_2S_3(PTD)Pt(PPh_3)_2$	($CDCl_3$) 7.28 (35 H, m), 6.85 (2 H, m), 6.70 (2 H, m), 6.28 (2 H, m), 5.97 (2 H, m), 2.25 (6 H, s),	1710 (s), 1680 (s), 1500 (m), 1385 (vs), 1230 (s), 1129 (m), 1095 (m), 1014 (m), 997 (w), 908 (w), 803 (m), 738 (m), 694 (s), 641 (m)	$^{31}P\{^1H\}$ NMR (CH_2Cl_2) 20.6 (d), 17.8 (d), $^1J_{PPt} = 3030$ s^{-1}, $^1J_{P'Pt} = 2706$ s^{-1}, $^2J_{PP'} = 21.4$ s^{-1}
$(CH_3C_5H_4)_2V_2S_2(PTD)_2Pt(PPh_3)_2 \cdot CH_2Cl_2$	($CDCl_3$) 7.37 (40 H, m), 6.98 (4 H, m), 6.60 (4 H, m), 2.05 (6 H, s)	1715 (s), 1666 (vs), 1511 (m), 1380 (vs), 1266 (m), 1224 (s), 1099 (m), 1074 (m), 1012 (s), 998 (s), 825 (m), 696 (m), 627 (m)	$^{31}P\{^1H\}$ NMR ($CDCl_3$) 14.0 (s), $^1J_{PPt} = 3021$ s^{-1}

[a] Chemical shifts are quoted (upfield shifts being negative) relative to the following standards: $Si(CH_3)_4$ (^1H and ^{13}C), 85% H_3PO_4 (^{31}P). [b] The IR spectrum of free PTD as a mineral oil mull: 1780 (vs), 1765 (vs), 1170 (s), 712 (s), 670 (s). The IR spectrum of phenylurazole as a mineral oil mull: 3200–3000 (s, br), 1685 (vs, br), 1230 (s) 790–760 (s).

°C, and filtering to yield 0.213 g (94%) of **3**.

$(CH_3C_5H_4)_2V_2S_2(PTD)_2$ (4) from 3 and PTD. Compound **3** (0.109 g, 0.218 mmol) and PTD (0.101 g, 0.578 mmol) were dissolved in 5.0 mL of THF and heated to reflux. After 2.5 h, the reaction mixture was cooled, filtered, evaporated to dryness, and extracted with toluene. The filtered extracts were concentrated to a small volume, cooled to −25 °C, and filtered to yield a tan powder. This crude product was recrystallized from CH_2Cl_2/MeOH and CH_2Cl_2/hexane to yield 0.060 g of dark brown crystalline $(CH_3C_5H_4)_2V_2S_2(PTD)_2 \cdot CH_2Cl_2$. The combined filtrates were filtered through a plug of silica as described for the reaction of **1** with PTD to yield **2** (0.011 g), a trace of the unidentified blue species, and **4** (0.009 g). The total yield of **4** was 42%.

$(CH_3C_5H_4)_2V_2S_3(PTD)Pt(PPh_3)_2$ (5). Compound **2** (0.074 g, 0.140 mmol) and $Pt(PPh_3)_2C_2H_4$ (0.199 g, 0.266 mmol) were dissolved in 5.0 mL of CH_2Cl_2. The resultant blue solution was evaporated to dryness, and the residue was extracted with toluene (5 × 5 mL). The filtered toluene extracts were concentrated to a small volume, cooled to −25 °C for 2 h, and filtered. The crude product was recrystallized from CH_2Cl_2/MeOH to yield 0.129 g (74%) of analytically pure material.

$(CH_3C_5H_4)_2V_2S_2(PTD)_2Pt(PPh_3)_2$ (6). A filtered toluene solution of $Pt(PPh_3)_2C_2H_4$ (0.205 g, 0.274 mmol) was added to a solution of **4** (0.062 g, 0.092 mmol) in 5.0 mL of CH_2Cl_2. The green solution was concentrated and filtered, washing with toluene. The CH_2Cl_2 extract of the crude product was diluted with toluene, cooled to −25 °C, and filtered to yield 0.062 mg (45%) of green, microcrystalline $(CH_3C_5H_4)_2V_2S_2(PTD)_2Pt(PPh_3)_2 \cdot C_6H_5CH_3$.

X-ray Crystallography of 5. Dark blue, opaque single crystals were grown by slow diffusion of methanol into a CH_2Cl_2 solution of **5** at 25 °C. A prismatic crystal, ca. 0.28 × 0.40 × 0.45 mm, was mounted on a glass fiber about 9° off normal to the (1, 0, −2) planes. The crystals were monoclinic of space group $P2_1/c—C_{2h}^5$ (No. 14) with $a = 22.181$ (7) Å, $b = 13.176$ (4) Å, $c = 19.303$ (5) Å, $\beta = 111.10°$, $Z = 4$, p(calcd) = 1.579 g cm^{-3}, $F(000) = 2496.0$ e, and $\mu = 32.33$ cm^{-1}.

Intensity measurements were made on a Syntex $P2_1$ automated diffractometer using graphite-monochromated Mo $K\bar{\alpha}$ ($\lambda = 0.71069$ Å) radiation. A total of 12818 independent reflections having $2\theta \leq 55°$ were measured in two concentric shells. Three standard reflections measured every 100 reflections as a monitor for possible disalignment and/or deterioration of the crystal gave no indication of either. A total of 6934 nonzero reflections were obtained at the 3σ significance level. The data were corrected for Lorentz and polarization effects and numerically for absorption.[27]

Coordinates for the platinum atom were deduced from a Patterson map. A weighted difference Fourier incorporating the Pt atom revealed positions for 46 of the other 68 non-hydrogen atoms. Subsequent least-squares difference Fourier calculations gave positions for all of the remaining non-hydrogen atoms. The final difference Fourier had two peaks which were significantly above background (2.7 and 1.7 e/Å). Both of these peaks were less than 1 Å from the Pt atom and may be attributed to inadequacies with the absorption correction. In the final cycle of least squares, coordinates for all of the non-hydrogen atoms were refined and the hydrogen atoms were fixed in idealized positions. Of the refined atomic positions, all of the non-carbon atoms were varied with anisotropic thermal coefficients and all of the carbon atoms were refined with independent isotropic thermal coefficients. A single isotropic thermal parameter was refined for the hydrogen atoms as a group. The final cycle of least squares converged to $R = 0.059$ and $R_w = 0.065$ with a maximum change/error of 0.11.[28]

Results

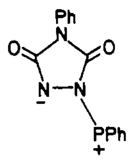
$(CH_3C_5H_4)_2V_2S_3(PTD)$. 4-Phenyl-1,2,4-triazoline-3,5-dione (PTD) reacts with $(CH_3C_5H_4)_2V_2S_4$, **1**, to give a complex mixture of products. In THF at room temperature, the major product of this reaction is purple, crystalline $(CH_3C_5H_4)_2V_2S_3(PTD)$, **2**, which is isolated in 53% yield after chromatography workup. Minor products (<10% yield) include $(CH_3C_5H_4)_2V_2S_5$, $(CH_3C_5H_4)_2V_2S_2(PTD)$ (**3**), $(CH_3C_5H_4)_2V_2S_2(PTD)_2$ (**4**), and a blue-green paramagnetic compound which we have been unable to isolate in a pure state. The formulation of these new compounds is based on elemental analysis (Table I), mass spectrometry, and IR and NMR spectroscopy (Table II). The transformation of **1** to **2**–**4** involves loss of sulfur, the fate of which we are unable to determine exactly. An off-white insoluble solid is removed from the reaction mixture by filtration, but this material contains no sulfur (Anal. $C_8H_5N_2$. IR absorptions similar to PTD). Optimum conversion of **1** to **2** requires an excess of PTD.

Other synthetic routes to **2** were less successful. Reaction of $(CH_3C_5H_4)_2V_2S_5$ with PTD is much less facile than **1**, producing **2** in low yield and requiring a large excess of PTD. The adduct formed by PTD and PPh_3 (A) reacts with **1** over a period of 6 days to produce a low yield of **2** (22%) and $(CH_3C_5H_4)_2V_2S_5$ (48%). The latter probably arises from slow thermal decompo-

---

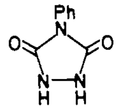
(27) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180.

(28) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = k/((\sigma(F_o))^2 + (p|F_o|)^2$, $k = 5.43$, and $p = 0.02$. Scattering factor tables for neutral atoms were taken from: "International Tables for X-Ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101. Anomalous dispersion corrections for non-hydrogen atoms were taken from pp 149–50.



A

sition of **1**. 4-Phenyl-1,2,4-triazolidine-3,5-dione (B) (also known as phenylurazole) reacts very sluggishly with **1** in refluxing THF. After 16 h, thin-layer chromatography of the reaction mixture indicated formation of **2** (trace) and no **3** or **4**.



B

Solutions of **2**, **3**, and **4** are stable to both air and silica gel. The infrared spectra of these compounds (Table II) reveal characteristic and intense absorptions for the methylcyclopentadienyl and PTD ligands. The IR spectra of these PTD complexes were characterized by intense absorptions in the range 1730–1680 cm^{-1}. Similar absorption are also observed in IrCl(CO)$(PPh_3)_2$PTD, $Pt(PPh_3)_2$PTD,[11] and phenylurazole. These bands, assigned to ν_{CO}, occur at lower frequency than those in free PTD (1780, 1765 cm^{-1}) and indicate that substantial reduction of this heterocycle occurs upon coordination.

The ^{1}H NMR spectra of **3** and **4** indicated the equivalency of the two methylcyclopentadienyl ligands, the presence of a plane of symmetry parallel with the V–V axis, and the ratio of methylcyclopentadienyl ligands to phenyltriazolinedione ligands. Unfortunately, neither of these techniques indicated the disposition of the sulfur ligands or the bridging mode of the PTD ligand (transverse vs. parallel).

Bis(triphenylphosphine)platinum ethylene reacts instantly with **2** to give blue solutions from which crystalline $(CH_3C_5H_4)_2V_2S_3$(PTD)$Pt(PPh_3)_2$, **5**, can be isolated in good yield (Scheme I). Like that for **2**, the ^{1}H NMR spectrum of **5** revealed only one methyl resonance and four multiplets for the methylcyclopentadienyl ring protons indicating the absence of a plane of symmetry parallel with the V–V vector. Furthermore, ^{31}P NMR spectroscopy (102 MHz) revealed the presence of inequivalent phosphorus ligands with coupling constants, $^1J_{PPt}$ = 3030 Hz, $^1J_{P'Pt}$ = 2706 Hz, and $^2J_{PP'}$ = 21 Hz, in the range expected for a *cis*-$Pt^{II}(PPh_3)_2$ complex. Since the molecule possesses a plane of symmetry perpendicular to the V–V vector as indicated by the equivalent methylcyclopentadienyl ligands, the ^{31}P NMR data indicates that the coordination plane of the platinum is also perpendicular to the V–V vector. Based on this data, we assigned a $V_2(\mu\text{-}S)(\mu\text{-}\eta^1\text{-PTD})(\mu_3\text{-}S)_2Pt$ geometry to the core of **5**.

The Structure of $(CH_3C_5H_4)_2V_2S(PTD)(\mu\text{-}S_2Pt(PPh_3)_2)$. The geometry of **5** was confirmed by X-ray crystallography. Views of the entire molecule and the $V_2S_3(PTD)PtP_2$ core are presented in Figures 1 and 2. Important bond distances and angles are collected in Table III. Atomic positional and thermal parameters are presented in Tables IV and V.

The structure of **5** consists of an isosceles triangle defined by two vanadium atoms and one platinum atom. The triangle is capped on both sides by bridging sulfides while the V–V edge is spanned by a bridging sulfide and the PTD ligand. The coordination spheres of the vanadium atoms are completed by methylcyclopentadienyl ligands, and the platinum is further coordinated to two triphenylphosphine ligands. If the phenyl rings and the methyl substituents of the cyclopentadienyl rings are disregarded, there is a plane of symmetry bisecting the V–V and N1–N2 vectors and containing S1, S2, S3, N3, Pt, P1, and P2.

The vanadium–vanadium distance at 2.566 (2) Å is at the short end of the range assigned to V–V single bonds; it is within 0.01 Å of the V–V distance in $(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$ that appears to have partial double bond between the vanadium centers.[3] The V–S–V angles are quite acute (V–S1–V = 63.78 (9)°; V–S2–V = 63.54 (8)°; V–S3–V = 68.1 (3)°) and are indicative of a strong metal–metal interaction. The V–Pt distances at 3.563 (2) and 3.651 (2) Å are nonbonding.

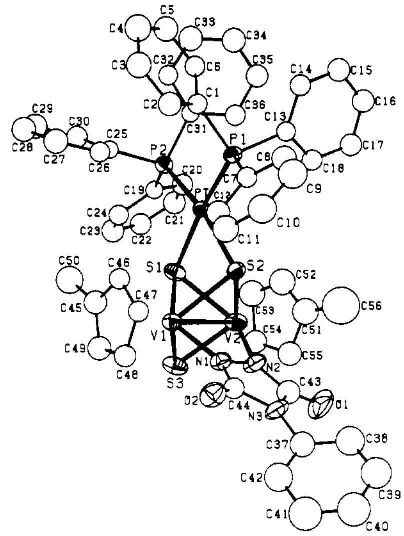


Figure 1. ORTEP plot of the non-hydrogen atoms of the $(CH_3C_5H_4)_2V_2S_2$(PTD)$Pt(PPh_3)_2$ molecule with the thermal ellipsoids for the non-carbon atoms drawn at the 35% probability level.

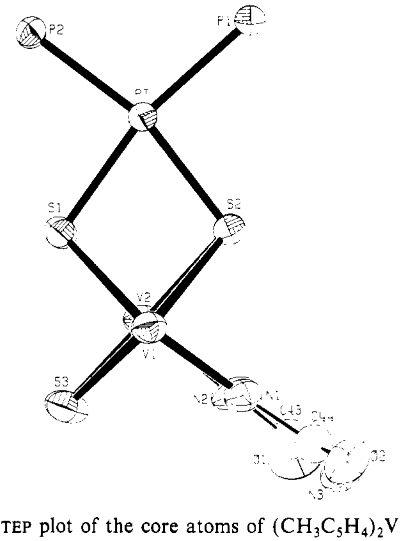
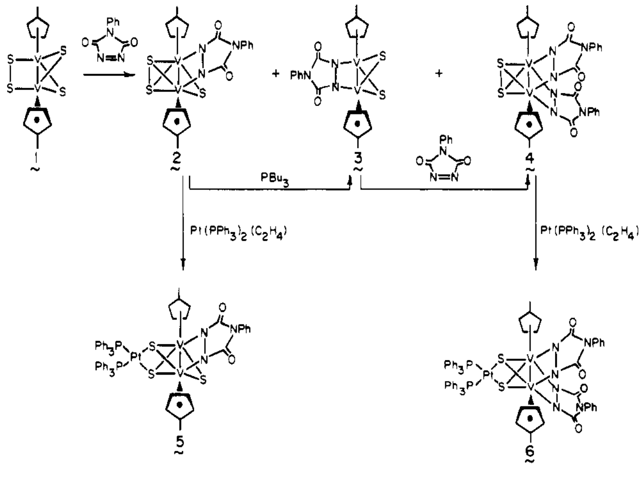


Figure 2. ORTEP plot of the core atoms of $(CH_3C_5H_4)_2V_2S_3$(PTD)Pt$(PPh_3)_2$ molecule.

Scheme I



We have previously shown that V–S distances provide a consistent indication of sulfur to vanadium π donation: V–S bond distances less than 2.35 Å reflect some π-bonding while longer

Table III. Important Structural Parameters for **5**[a]

	Distances (Å)		
V1–V2	2.556 (2)	Pt–S1	2.316 (3)
V1–S1	2.420 (3)	Pt–S2	2.327 (2)
V1–S2	2.443 (3)	Pt–P1	2.338 (2)
V1–S3	2.263 (3)	Pt–P2	2.298 (2)
V1–N1	1.990 (8)	S1–S2	2.784 (4)
N1–N2	1.39 (1)	N1–C44	1.39 (1)
O2–C44	1.20 (1)	N3–C44	1.43 (1)
V1–CP1	1.98 (1)		
	Angles (deg)		
V1–S1–V2	63.78 (9)	S1–Pt–S2	73.65 (9)
V1–S2–V2	63.54 (8)	P1–Pt–P2	101.31 (9)
V1–S3–V2	68.3 (1)	S1–Pt–P2	91.35 (9)
V1–N1–N2	107.9 (6)	S2–Pt–P1	93.97 (9)
N2–N1–C44	108.2 (8)	Pt–S1–V1	97.5 (1)
N1–C44–N3	106.7 (8)	Pt–S2–V1	96.61 (10)
C44–N3–C43	107.7 (9)	V2–V1–CP1	175.0 (4)
N1–C44–O2	127.8 (10)		

[a] Only distances and angles that are unique with respect to the molecular symmetry plane are included.

V–S bonds indicate relatively innocent σ bonds.[3] In **5** the V–S (μ-S) distance of 2.27 Å indicates significant V–S π bonding and is quite similar to that observed for the μ-S ligand in $(CH_3C_5H_4)_2V_2S_5$, 2.26 Å.[25] In contrast, the long V–S(μ_3-S) distances reflect the $V_2(\mu\text{-}\eta^2\text{-}S_2)$ parentage of the V_2S_2Pt fragment and clearly indicate V–S σ bonding that is uncomplicated by π effects. The V–S(μ_3-S) bonds average 2.42 Å in **5** and are slightly longer than the V–S(μ-η^2-S_2) distances of $(CH_3C_5H_4)_2V_2S_5$ (2.35 and 2.40 Å).[25] The V–S(μ_3-S) distances are longer than those in $(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (2.32 Å).[29]

The V–N distances of 1.990 (8) and 1.997 (10) Å are significantly longer than those in $(C_5H_5)_2VNSi(CH_3)_3$ (1.665 Å)[30] and $(C_5H_5)_2VNN(Si(CH_3)_3)_2$ (1.666 (6) Å),[31] that formally contain vanadium–nitrogen double bonds. The V–N distance in **5** is slightly shorter than those in compounds that formally contain single bonds such as $[(\mu\text{-}\eta^{10}\text{-}C_{10}H_8)_2V_2(CH_3CN)_2][PF_6]_2\cdot CH_3CN$ (2.02 (2) Å).[32] The V–N bond lengths in VS(acen) (acen = *N,N'*-ethylenebis(acetylacetonylideniminato))[33] and VO(acen)[34] average 2.028 (3) and 2.054 (8) Å, respectively.

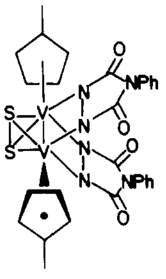
Parameters within the phenyltriazolinedione ligand are similar to other nitrogen heterocycles that coordinate two metals in a similar fashion. The N–N distance of 1.39 (1) Å is in the range of 1.36–1.40 Å commonly observed for these ligands (1.366 (1) Å for $(\mu\text{-}CH_3NNCH_3)Fe_2(CO)_6$[15] and 1.381 (2) Å for $[Fe(NO)_2(\mu\text{-}N_2C_5H_7)]_2$[22]) although distances can range from 1.312 (6) Å ($[(C_5H_5)_2Ti(\mu\text{-}N_2C_3H_3)]_2$[19]) to 1.463 ($[Ni(NO)(\mu\text{-}N_2C_5H_7)]_2$[21]). For comparison, the single bond radius of nitrogen is ~0.70 Å[35] and the N–N distance in free azobenzene is 1.247 (3) Å.[36] The C–N bond lengths are not unusual, the bonds to N1 and N2 being slightly shorter than those to N3. The ligand is planar (maximum deviation = 0.028 (10) Å) and is canted slightly relative to the V–V vector; V1 and V2 are 0.103 and 0.104 Å above and below the plane, respectively. The dihedral angle between the phenyl ring and the triazoline ring is 40°.

The platinum atom is in a square-planar environment containing cis-sulfur and cis-phosphorus atoms; the PtP_2S_2 fragment is coplanar within 0.097 Å. This plane nearly bisects the V–V vector; the dihedral angle between this plane and the plane containing S1, S2, and S3 is 6.7°. All other parameters pertaining to the coordination sphere of the platinum are quite normal.

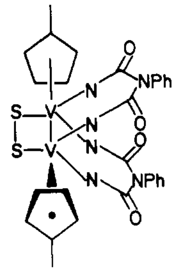
The methylcyclopentadienyl ligands in **5** are symmetrically bonded to the vanadium atoms and are tilted away from the nitrogen ligand such that the dihedral angle between them is 13°. It has been noted that V–Cp(centroid) distances vary with the oxidation state of the metal: 1.87–1.92 Å for V(I), 1.91–1.92 Å for V(II), 1.94–1.96 Å for V(III), and 1.96–2.05 Å for V(IV).[37] The V–Cp(centroid) distances of 1.98 (1) and 1.97 (1) Å are indicative of a formal oxidation state of V(IV) for these compounds.

$(CH_3C_5H_4)_2V_2S_2(PTD)$ and $(CH_3C_5H_4)_2V_2S_2(PTD)_2$. Compound **2** reacts readily with $P(n\text{-}Bu)_3$ to give $(CH_3C_5H_4)_2V_2S_2(PTD)$, **3**, in high yield. Compound **3** forms red solutions but crystallizes as a green solid; its formulation is based on analytical data and the observation of a molecular ion in its electron-impact mass spectrum. ^1H NMR spectroscopy established that **3** possesses symmetry planes along the V–V axis and the bisector thereof. The ν_{CO} bands for the PTD ligand are closely similar to those for **2**, indicating that here again the PTD moiety adopts the μ-η^1 geometry. On the basis of these data, we suggest that **3** possesses a core structure similar to that of $((CH_3)_2CHC_5H_4)_2V_2S_4$.[3]

Compound **3** reacts quickly with a second equivalent of PTD to give $(CH_3C_5H_4)_2V_2S_2(PTD)_2$ isolated as a brown crystalline solid. NMR analysis indicated a 1:1 $CH_3C_5H_4$:PTD ratio and a highly symmetrical $V_2S_2(PTD)_2$ core. Two candidate structures are indicated below (C and D), structures with both μ-η^1-PTD and μ-η^2-PTD being incompatible with the NMR data. The isomer featuring two μ-η^2-PTD units would be unacceptably sterically crowded. Structure C is supported by its reactivity towards $Pt(PPh_3)_2C_2H_4$ (vide infra). We therefore conclude that the conversion of **3** to **4** involves coupling of the two μ-S ligands to give a μ-η^2-S_2.



C



D

Discussion

$(CH_3C_5H_4)_2V_2S_4$ (**1**) reacts with 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) to form a series of compounds in which the sulfur ligands of **1** have been replaced by PTD (Scheme I). Although specific mechanistic information is not available, it is clear that PTD functions as both a sulfur abstracting agent and as a ligand. The former probably involves attack by an electrophilic PTD nitrogen at a bridging sulfide atom similar to reaction of **1** with hexafluoro-2-butyne,[3] $Fe(NO)_2$,[39] or $Fe(CO)_x$.[29] The exceptional electrophilicity of PTD has been extensively documented in organic synthetic studies.[8]

Compound **2** is efficiently desulfurized by PBu_3. This process is proposed to involve removal of a sulfur atom from the μ-η^2-S_2 ligand, converting it to a μ-S ligand.[3,29]

The conversion of $(CH_3C_5H_4)_2V_2S_2(PTD)$ to the bis(PTD) adduct **4** is unusual in several aspects. The formation of **4** from **3** implies that at some stage in the reaction, the unsaturated substrate directly attacks the metal centers. This reaction is

---

(29) (a) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 7313. (b) Bolinger, C. M.; Rauchfuss, T. B., submitted for publication.

(30) Wilberg, N.; Häring, H.-W.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 599.

(31) Veith, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 387.

(32) Smart, J. C.; Pinsky, B. L.; Fredrich, M. F.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 4371.

(33) Sato, M.; Miller, K. M.; Enemark, J. H.; Strouse, C. E.; Callahan, K. P. *Inorg. Chem.* **1981**, *20*, 3571.

(34) Bruins, D.; Weaver, D. L. *Inorg. Chem.* **1970**, *9*, 130.

(35) Cotton, F. A.; Wilkinson, G. In "Advanced Inorganic chemistry: A Comprehensive Text", 3rd ed.; Interscience: New York, 1972; p 117.

(36) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146.

(37) Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 5651.

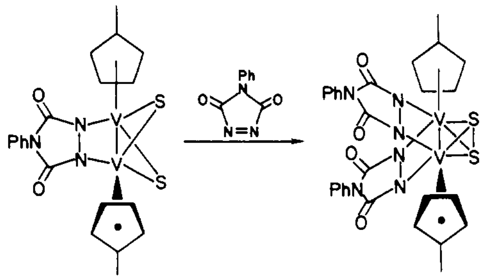
(38) Braunstein, P.; Jud, J.-M.; Tiripicchio, A.; Tiripicchio-Camellini, M.; Sappa, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 307.

(39) Rauchfuss, T. B.; Weatherill, T. D.; Wilson, S. R.; Zebrowski, J. P. *J. Am. Chem. Soc.* **1983**, *185*, 6508.

Table IV. Positional Parameters for **5**

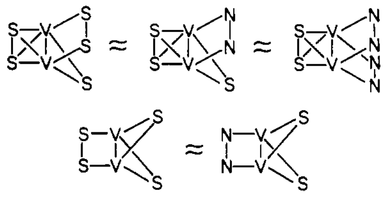
	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Pt	0.28963 (2)	0.12791 (3)	0.13045 (2)	C47	0.2496 (5)	0.3379 (8)	0.2956 (5)
V1	0.28861 (8)	0.3758 (1)	0.20380 (8)	C48	0.2780 (6)	0.4366 (9)	0.3101 (6)
V2	0.2804 (1)	0.3913 (1)	0.06869 (9)	C49	0.3448 (6)	0.425 (1)	0.3248 (6)
S1	0.3534 (1)	0.2724 (2)	0.1536 (1)	C50	0.4253 (7)	0.277 (1)	0.3374 (8)
S2	0.2191 (1)	0.2654 (2)	0.1059 (1)	C51	0.2329 (8)	0.377 (1)	−0.0576 (8)
S3	0.3472 (2)	0.4871 (2)	0.1646 (2)	C52	0.2757 (8)	0.308 (1)	−0.0366 (8)
P1	0.2079 (1)	0.0076 (2)	0.1127 (1)	C53	0.3373 (8)	0.337 (1)	−0.0087 (8)
P2	0.3786 (1)	0.0255 (2)	0.1537 (1)	C54	0.3294 (7)	0.451 (1)	−0.0077 (6)
O1	0.1453 (6)	0.5736 (8)	−0.0196 (5)	C55	0.2637 (7)	0.477 (1)	−0.0403 (7)
O2	0.1456 (4)	0.5170 (7)	0.2135 (4)	C56	0.169 (1)	0.361 (2)	−0.092 (1)
N1	0.2121 (4)	0.4619 (6)	0.1512 (4)	H2	0.1924	−0.0497	0.2497
N2	0.2095 (5)	0.4761 (7)	0.0788 (5)	H3	0.2255	−0.1896	0.3316
N3	0.1283 (5)	0.5656 (7)	0.0911 (5)	H4	0.2734	−0.3279	0.3005
C1	0.2275 (5)	−0.1054 (7)	0.1717 (5)	H5	0.2947	−0.3281	0.1910
C2	0.2140 (5)	−0.1056 (9)	0.2378 (6)	H6	0.2644	−0.1911	0.1104
C3	0.2331 (6)	−0.190 (1)	0.2862 (7)	H8	0.0701	−0.0276	0.0551
C4	0.2617 (7)	−0.271 (1)	0.2683 (7)	H9	−0.0157	0.0254	0.0900
C5	0.2740 (6)	−0.271 (1)	0.2031 (6)	H10	0.0021	0.1413	0.1856
C6	0.2565 (5)	−0.1891 (8)	0.1555 (5)	H11	0.1023	0.2102	0.2458
C7	0.1386 (5)	0.0573 (8)	0.1312 (5)	H12	0.1886	0.1574	0.2129
C8	0.0775 (6)	0.0194 (10)	0.0947 (7)	H14	0.1515	−0.1854	0.0368
C9	0.0264 (8)	0.052 (1)	0.1148 (8)	H15	0.1187	−0.2391	−0.0860
C10	0.0372 (8)	0.121 (1)	0.1717 (7)	H16	0.1210	−0.1240	−0.1783
C11	0.0960 (6)	0.161 (1)	0.2076 (7)	H17	0.1502	0.0420	−0.1493
C12	0.1469 (6)	0.1296 (10)	0.1879 (6)	H18	0.1879	0.0945	−0.0260
C13	0.1744 (5)	−0.0395 (8)	0.0183 (5)	H20	0.4215	0.0387	0.0294
C14	0.1525 (5)	−0.1394 (8)	−0.0007 (5)	H21	0.5083	0.1151	0.0086
C15	0.1328 (6)	−0.1712 (9)	−0.0732 (6)	H22	0.5868	0.1983	0.0999
C16	0.1336 (6)	−0.1018 (9)	−0.1283 (6)	H23	0.5764	0.2185	0.2145
C17	0.1519 (5)	−0.0049 (9)	−0.1112 (6)	H24	0.4902	0.1522	0.2374
C18	0.1734 (5)	0.0266 (8)	−0.0379 (5)	H26	0.3309	0.0129	0.2704
C19	0.4463 (5)	0.0847 (7)	0.1365 (5)	H27	0.3731	−0.0350	0.3964
C20	0.4527 (6)	0.0756 (9)	0.0682 (6)	H28	0.4805	−0.0825	0.4510
C21	0.5050 (6)	0.121 (1)	0.0562 (7)	H29	0.5444	−0.0976	0.3797
C22	0.5507 (6)	0.1706 (9)	0.1088 (6)	H30	0.5039	−0.0499	0.2554
C23	0.5444 (6)	0.182 (1)	0.1764 (7)	H32	0.4280	−0.1859	0.1752
C24	0.4937 (5)	0.1416 (9)	0.1904 (6)	H33	0.4102	−0.3267	0.0965
C25	0.4132 (5)	−0.0142 (7)	0.2504 (5)	H34	0.3420	−0.3146	−0.0240
C26	0.3744 (5)	−0.0092 (8)	0.2922 (5)	H35	0.2860	−0.1707	−0.0708
C27	0.3999 (6)	−0.0368 (10)	0.3675 (6)	H36	0.3037	−0.0216	0.0060
C28	0.4633 (6)	−0.067 (1)	0.3995 (7)	H38	0.0287	0.5846	−0.0279
C29	0.5012 (6)	−0.074 (1)	0.3579 (6)	H39	−0.0632	0.6837	−0.0485
C30	0.4767 (5)	−0.0467 (9)	0.2839 (6)	H40	−0.0606	0.8062	0.0344
C31	0.3682 (5)	−0.0913 (7)	0.0980 (5)	H41	0.0161	0.8096	0.1524
C32	0.3995 (5)	−0.1810 (8)	0.1250 (5)	H42	0.1090	0.6958	0.1767
C33	0.3887 (7)	−0.264 (1)	0.0783 (7)	H46	0.2948	0.1982	0.2968
C34	0.3479 (6)	−0.257 (1)	0.0074 (7)	H47	0.2052	0.3221	0.2831
C35	0.3154 (6)	−0.1722 (10)	−0.0209 (6)	H48	0.2559	0.4984	0.3100
C36	0.3256 (5)	−0.0832 (9)	0.0250 (5)	H49	0.3753	0.4972	0.3354
C37	0.0742 (6)	0.634 (1)	0.0770 (7)	H501	0.4203	0.2060	0.3309
C38	0.0259 (8)	0.629 (1)	0.0095 (8)	H502	0.4528	0.2918	0.3869
C39	−0.0268 (9)	0.690 (1)	−0.0038 (9)	H503	0.4438	0.3039	0.3038
C40	−0.0264 (9)	0.758 (2)	0.0472 (9)	H52	0.2640	0.2386	−0.0412
C41	0.0194 (9)	0.764 (2)	0.1159 (10)	H53	0.3754	0.2974	0.0064
C42	0.0742 (8)	0.695 (1)	0.1302 (8)	H54	0.3637	0.4986	0.0122
C43	0.1597 (6)	0.539 (1)	0.0412 (7)	H55	0.2444	0.5422	−0.0493
C44	0.1603 (5)	0.5131 (8)	0.1593 (6)	H561	0.1466	0.4244	−0.1019
C45	0.3583 (6)	0.3246 (10)	0.3217 (6)	H562	0.1538	0.3218	−0.0603
C46	0.2995 (5)	0.2696 (9)	0.3032 (5)	H563	0.1611	0.3261	−0.1372

proposed to involve the conversion of two μ-S moieties to a μ-η^2-S_2 (eq 1). Similar internal redox processes would explain the prevalent formation of μ-S_2 ligands in the chemistry of binary molybdenum sulfides.[40] Such oxidative couplings may accompany substrate binding in catalytic processes involving metal sulfides.



(1)

It is apparent that the V_2S_5 and V_2S_3(PTD) cores are analogous as are the V_2S_4 and V_2S_2(PTD) cores: This similarity supports



---

[40] Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321.

Table V. Thermal Parameters for **5**

	U(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
Pt	0.0348 (2)	0.0325 (2)	0.0419 (2)	0.0010 (2)	0.0149 (1)	0.0006 (2)
V1	0.0487 (9)	0.0377 (8)	0.0467 (8)	−0.0014 (7)	0.0221 (7)	0.0006 (8)
V2	0.078 (1)	0.0405 (10)	0.0532 (9)	0.0009 (7)	0.0381 (9)	−0.0050 (9)
S1	0.045 (2)	0.042 (1)	0.066 (2)	−0.012 (1)	0.028 (1)	−0.008 (1)
S2	0.041 (1)	0.037 (1)	0.047 (1)	0.004 (1)	0.014 (1)	0.003 (1)
S3	0.079 (2)	0.044 (1)	0.078 (2)	−0.013 (1)	0.045 (2)	−0.017 (1)
P1	0.037 (1)	0.034 (1)	0.050 (1)	0.004 (1)	0.014 (1)	0.000 (1)
P2	0.037 (1)	0.039 (1)	0.045 (1)	−0.0038 (10)	0.017 (1)	0.002 (1)
O1	0.138 (10)	0.105 (8)	0.070 (6)	0.044 (5)	0.025 (6)	0.029 (7)
O2	0.074 (6)	0.075 (6)	0.079 (5)	0.005 (4)	0.037 (5)	0.019 (5)
N1	0.058 (5)	0.039 (4)	0.050 (5)	0.005 (3)	0.025 (4)	0.004 (4)
N2	0.084 (7)	0.043 (5)	0.058 (5)	0.016 (4)	0.031 (5)	0.022 (5)
N3	0.063 (6)	0.043 (5)	0.083 (7)	0.019 (4)	0.018 (5)	0.016 (5)

			U_{iso}, Å^2				
C1	0.047 (2)	C28	0.073 (3)	C54	0.072 (3)	H29	0.097
C2	0.064 (3)	C29	0.076 (3)	C55	0.078 (4)	H30	0.097
C3	0.073 (3)	C30	0.060 (3)	C56	0.19 (1)	H32	0.097
C4	0.082 (4)	C31	0.043 (2)	H2	0.097 (6)	H33	0.097
C5	0.071 (3)	C32	0.052 (2)	H3	0.097	H34	0.097
C6	0.050 (2)	C33	0.080 (4)	H4	0.097	H35	0.097
C7	0.049 (2)	C34	0.077 (3)	H5	0.097	H36	0.097
C8	0.071 (3)	C35	0.067 (3)	H6	0.097	H38	0.097
C9	0.093 (4)	C36	0.057 (3)	H8	0.097	H39	0.097
C10	0.089 (4)	C37	0.073 (3)	H9	0.097	H40	0.097
C11	0.077 (3)	C38	0.097 (4)	H10	0.097	H41	0.097
C12	0.064 (3)	C39	0.110 (5)	H11	0.097	H42	0.097
C13	0.046 (2)	C40	0.124 (6)	H12	0.097	H46	0.097
C14	0.054 (3)	C41	0.125 (6)	H14	0.097	H47	0.097
C15	0.064 (3)	C42	0.094 (4)	H15	0.097	H48	0.097
C16	0.063 (3)	C43	0.068 (3)	H16	0.097	H49	0.097
C17	0.061 (3)	C44	0.054 (3)	H17	0.097	H501	0.097
C18	0.054 (3)	C45	0.067 (3)	H18	0.097	H502	0.097
C19	0.043 (2)	C46	0.053 (2)	H20	0.097	H503	0.097
C20	0.063 (3)	C47	0.051 (2)	H21	0.097	H52	0.097
C21	0.075 (3)	C48	0.059 (3)	H22	0.097	H53	0.097
C22	0.068 (3)	C49	0.070 (3)	H23	0.097	H54	0.097
C23	0.074 (3)	C50	0.097 (4)	H24	0.097	H55	0.097
C24	0.057 (2)	C51	0.094 (4)	H26	0.097	H561	0.097
C25	0.042 (2)	C52	0.094 (4)	H27	0.097	H562	0.097
C26	0.052 (2)	C53	0.095 (4)	H28	0.097	H563	0.097
C27	0.074 (3)						

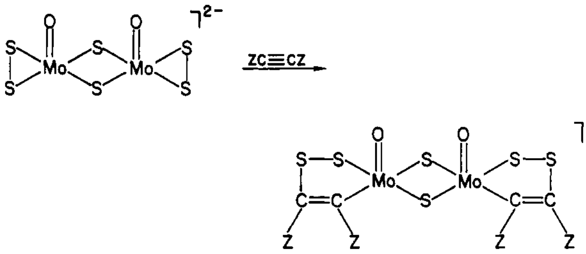
our view that PTD is a prosthesis for the μ-η^1-S_2 moiety. Compound **4** is unique in this series and may be considered to be a model for the unknown $(CH_3C_5H_4)_2V_2S_6$. The deviations of the chemistry of the PTD derivatives from that for $(CH_3C_5H_4)_2V_2S_x$ (x = 4, 5) can be largely attributed to the greater electronegativity of PTD relative to S_2. For example, $(CH_3C_5H_4)_2V_2S_4$ is especially air sensitive in solution, while **2**–**6** are quite robust under comparable conditions. The considerable electron-withdrawing power of PTD and its resistance to formation of μ-η^2-PTD derivatives also provides an explanation for the reluctance of **3** to form an adduct with hexafluoro-2-butyne, in contrast to **1**.[3]

In this project we have employed the reagent $Pt(PPh_3)_2C_2H_4$ to derivitize the μ-η^2-S_2-containing complexes **2** and **4**. In both cases stable, crystalline derivatives were obtained whose ^{31}P NMR spectra provided useful structural information from which we deduced the structure of their precursors. It is important to recognize that the presence of a μ-η^2 geometry appears to be a necessary but *not* a sufficient condition for the successful formation of a stable $Pt(PPh_3)_2$ derivative. The structurally characterized species $(CH_3C_5H_4)_2V_2S_5$ and $(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$ do react readily with $Pt(PPh_3)_2C_2H_4$ but fail to give stable derivatives.

The electronic structure of **5** can be evaluated by consideration of the V–S distances. For example, the V–S(μ-S) bond lengths are 2.26 and 2.27 Å for $(CH_3C_5H_4)_2V_2S_5$ and **5**, respectively. This indicates a similar degree of π interaction for the μ-S ligand in these two compounds and supports the proposal that the V_2S_5 and V_2S_3PTD centers are similar electronically and that the PTD ligand is similar to the μ-η^1-S_2 ligand. The V–S(μ_3-S) bond lengths (average 2.42 Å) are comparable to the V–S(μ-η^2-$S_2C_2(CF)_3)_2$) distances of $(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$ (2.43 Å) which suggests structural and electronic equivalence of the μ-η^2-$S_2Pt(PPh_3)_2$ fragment with the transverse bridging dithiolene.

Summary

This report illustrates several new aspects of the reactivity of metal sulfides. The displacement of sulfide ligands by an organic molecule has been established in the synthesis of **2** from **1** and PTD. This direct metal–substrate interaction is related to a recent report on the insertion of acetylene in a transition metal–sulfur bond (eq 2).[41] These results demonstrate that the reactivity of



(2)

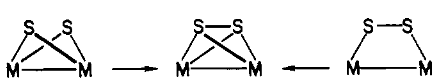
transition metal sulfides need not be localized entirely on the sulfur ligands, as might be inferred from previous reports from this and other laboratories. Instead, substrate activation at *both* the nonmetal and metallic components may be a more viable picture of catalysis by binary and ternary metal sulfides.[42]

We have provided evidence for the oxidative coupling of two μ-S ligands in the conversion of **3** to **4** (eq 3). This result is

---

[41] Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

[42] Weisser, O.; Landa, S. "Sulfide Catalysts, Their Properties and Applications"; Pergamon Press: New York, 1973.



particularly germane to the large number of complexes that contain terminal and bridging sulfides. This conversion represents the second pathway elucidated for the intramolecular assembly of μ-η^2-S_2 ligands, the first being rotation of a μ-η^1-S_2 ligand in response to electron deficiency at the metal centers.[3,29] These arrangements are induced by substrate binding. Similar cooperativity may be anticipated for other metal sulfides.

Acknowledgment. This research was supported by the National Science Foundation (NSF CHE 81-06781). C.M.B. acknowledges fellowships provided by the University of Illinois. The 360-MHz NMR spectra were obtained at the NSF Midwest Regional NMR facility (NSF 79-16100). Platinum was provided by Engelhardt Industries.

Appendix

See Tables IV and V for positional and thermal parameters for **5**.

Registry No. 1, 87174-39-8; **2**, 92641-95-7; **3**, 92641-96-8; **4**, 92641-97-9; **5**, 92641-98-0; **6**, 92641-99-1; PTD, 4233-33-4; $(CH_3C_5H_4)_2V_2S_5$, 82978-84-5; $Pt(Ph_3)_2C_2H_4$, 12120-15-9; phenylurazole, 15988-11-1.

Supplementary Material Available: Complete lists of distances and angles and calculated and observed structure factor amplitudes (33 pages). Ordering information is given on any current masthead page.

Enhanced Base Hydrolysis of Coordinated Phosphate Esters: The Reactivity of an Unusual Cobalt(III) Amine Dimer

David R. Jones,[1a] Leonard F. Lindoy,*[1a] and Alan M. Sargeson*[1b]

Contribution from the Department of Chemistry and Biochemistry, James Cook University of North Queensland, QLD. 4811 Australia, and Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia. *Received April 16, 1984*

Abstract: The hydrolysis of the dimeric cation bis(μ-4-nitrophenyl phosphato)bis[bis(1,2-ethandiamine)cobalt(III)](2+) has been studied at pH 10 and over the hydroxide concentration range 0.05–1.0 M. Product distribution, kinetics (involving 4-nitrophenol release), and ^{31}P NMR and ^{18}O tracer studies were carried out to establish the course of the reaction. In a rapid first step, the eight-membered ring of the dimer is opened by rupture of one of the Co–O bonds (S_N1cB) to give a cis hydroxo complex. The ring-opened species reacts further via two competing pathways: (a) intramolecular attack of the coordinated hydroxide upon the bridging phosphate ester moiety and (b) further cleavage of the dimer by base-catalyzed (S_N1cB) rupture of some Co–O bonds. Route a results in ester hydrolysis with the concomitant formation of a chelated bridging phosphate species whereas route b yields *cis*- and *trans*-hydroxy(*p*-nitrophenyl phosphate)bis(1,2-ethanediamine)cobalt(III). The phosphate chelate ring in the initial product of path a is subsequently opened by Co–O bond rupture and the resultant dimeric bridging phosphato species slowly decomposes to *cis*- and *trans*-hydroxo(phosphato)bis(1,2-ethanediamine)cobalt(III). Comparison of the rate data for hydrolysis of the dimer and the *cis*-hydroxo(4-nitrophenyl phosphato)bis(1,2-ethanediamine)cobalt(III) ion indicates that the attack by the intramolecular nucleophile is largely responsible for the enhanced rate of ester hydrolysis ($\sim 10^5$) with a smaller contribution from charge neutralization at the P center by the metal ion (~ 10–10^2). Parallel kinetic studies on the analogous dimer bis(μ-4-nitrophenyl phosphato)bis[bis(1,3-propanediamine)cobalt(III)](2+), previously incorrectly formulated as a monomeric species containing chelated phosphate ester, indicate that ester hydrolysis in this complex proceeds by a similar mechanism to that for the 1,2-ethanediamine complex. In total, the results are rationalized in relation to a possible mechanism for the Zn^{2+} containing enzyme E. coli alkaline phosphatase.

Most of the enzymes responsible for the metabolism of phosphate compounds require divalent metal ions such as Mn, Zn, or Mg for activation.[2] The most studied of these enzymes (the alkaline phosphatase[3] and nucleotide kinases[4]) have been shown to have the metal ion present in the active site during the catalytic cycle. However, the precise roles of these ions in the mechanism of catalysis are still far from clear and they need to be displayed in reactive model systems where the route can be defined.

In previous studies, we have investigated the role of metal ions in phosphate ester hydrolysis using structurally well-characterized model compounds and have demonstrated that the hydroxide[5] and amido (NH_2^-)[6] ions coordinated to cobalt(III) are efficient intramolecular nucleophiles for cleaving 4-nitrophenol from coordinated 4-nitrophenyl phosphate. Rate enhancements of 10^5 and 10^8, respectively, relative to the uncoordinated ester were obtained for these (mononuclear) complexes. There is evidence that the coordination of a phosphate ester simultaneously to two metal ions will also lead to a considerable increase in the rate of ester hydrolysis. For example, the rate of hydrolysis of ATP is enhanced 60–300-fold[7] in the presence of Cu(II) and this has been attributed to the formation of the dimeric chelate, $[(ATP)Cu(OH)]_2^{6-}$. Binuclear complexes have been implicated as the reactive entities that are responsible for the increased rates of hydrolysis of ATP in the presence of the lanthanide ions[8] and [Co(1,3-propanedi-

---

(1) (a) James Cook University. (b) Australian National University.

(2) Dixon, M.; Webb, E. C. "Enzymes", 2nd ed.; Longman, Green and Co.: New York, 1971; pp 422–424. Morrison, J. F.; Heyde, E. *Annu. Rev. Biochem.* **1972**, *41*, 29.

(3) Reid, T. W.; Wilson, I. B. "The Enzymes", 3rd ed.; Boyer, P. D., Ed.; Academic Press: New York, 1971; Vol. 4, pp 373–409.

(4) (a) Watts, D. C. "The Enzymes", 3rd ed.; Boyer, P. D., Ed.; Academic Press: New York, 1973; Vol. 8A, pp 384–431. (b) Morrison, J. F. ref 4a, 1973; Vol. 8, pp 475–485. (c) Mildvan, A. S. ref 4a, 1973; Vol. 2, pp 499–501.

(5) Jones, D. R.; Lindoy, L. F.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7327.

(6) Harrowfield, J. MacB; Jones, D. R.; Lindoy, L. F.; Sargeson, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7733.

(7) Spiro, T. G.; Kjellstrom, W. A.; Zydel, M. C.; Butow, R. A. *Biochemistry* **1968**, *7*, 859. Sigel, H.; Hofstetter, F. *Eur. J. Biochem.* **1983**, *132*, 569.

0002-7863/84/1506-7807$01.50/0