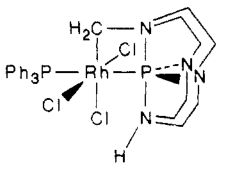
tensity peak in the ^{1}H NMR at 5.1 ppm[4] which disappears immediately upon addition of D_2O. Reaction 1 can be viewed as a simple displacement of two PPh_3 ligands with a phosphine and an amine ligand.

Compound 1 is insoluble in most common solvents and moderately soluble in halogenated solvents. However, 1 also reacts with halogenated solvents. After a few hours in CH_2Cl_2 solution, upfield resonances appear in the ^{31}P NMR spectrum while peaks due to 1 slowly diminish. Within 2 days, all traces of 1 are gone. The product shows an entirely different ABX pattern: δ 13 (dd, PC, $^1J_{RhP}$ = 84 Hz), -40 (dd, PN, $^1J_{RhP}$ = 132 Hz), $^2J_{PP}$ = 872 Hz. The appearance of the upfield resonance at -40 ppm suggests that a pentacoordinate phosphorus is present, and the extremely large $^2J_{PP}$ value is indicative of a trans arrangement of P atoms.[6] In addition, a broad singlet in the ^{1}H NMR spectrum at δ 3.19 is observed which is absent when the same reaction is run in CD_2Cl_2, indicating incorporation of a CH_2 group into the product.

The structure of the product **2**[7] was established by X-ray diffraction[8] and is illustrated in Figure 1. Selected bond distances and angles are collected in Table I. The geometry about Rh is distorted octahedral, while the geometry about P(2) is approximately trigonal-bipyramidal, as is usually observed in derivatives of cyclenP.[9] An intramolecular hydrogen bond is found between H(3) and Cl(2).



2

The formation of 2 may involve initial oxidative addition of CH_2Cl_2 to Rh to form a CH_2Cl–Rh–Cl species,[1] followed by rearrangement of the cyclenP group (from tetra- to pentacoordinate) and attack of nitrogen on carbon to displace Cl^-. Although nitrogen atoms bound to phosphorus are usually not very nucleophilic,[6a,10] such is not the case in cyclenP derivatives where the high nucleophilicity of the axial nitrogens is well-known.[9a-c] This may be due to the ring structure of the cyclenP group which holds the axial nitrogens in a more pyramidal geometry compared to the equatorial nitrogens.[9c,d,11] Another factor could be the hypervalent three-center, four-electron bond which places significantly more electron density at the axial positions in a trigonal bipyramid.[12]

The bonding in the Rh–C–N linkage can be viewed in a number of ways. One way is to consider the C–N(4) bond as an ylide, H_2C^-–N^+R_3, with the carbon donating a lone pair of electrons to rhodium. Indeed, *ionic* N, P, As, and S ylide–metal complexes have been isolated, and similar intermediates (i.e., CH_2X–M) have been proposed for their formation.[1a,2d,e,13] Alternatively, the carbon could be considered a neutral carbene, H_2C:, donating a lone pair to rhodium, with the nitrogen donating a lone pair into the vacant p orbital on carbon.[14]

We are currently investigating the scope of the addition reaction as well as the reactions of 2. Preliminary $^{31}P\{^1H\}$ NMR evidence suggests that a compound similar to 2 is formed immediately when 1 is dissolved in $CDCl_3$ (with a Rh–CDCl–N linkage): δ 9 (PC, dd, $^1J_{RhP}$ = 81 Hz), -37 (PN, dd, $^1J_{RhP}$ = 132 Hz), $^2J_{PP}$ = 856 Hz.

Acknowledgment. We wish to thank the Robert A. Welch Foundation (M.L. and S.S.C.C.) and the Research Corp. (M.L.) for generous financial support.

Registry No. 1, 104600-81-9; 2, 104619-50-3; 2·CH_2Cl_2, 104712-81-4; cyclenPH, 64317-97-1; $(Ph_3P)_3RhCl$, 14694-95-2.

Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles (4 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(7) The Rh(III) species **2** was isolated as follows: 1.1 g (1.8 mmol) of **1** was dissolved in 50 mL of CH_2Cl_2 and stirred for 2 days at ambient temperature. The CH_2Cl_2 was then removed and the residue washed with THF. The remaining solid was washed with CH_2Cl_2. Removal of the volatiles from the CH_2Cl_2 washings yielded 0.91 g of **2** as a yellow solid (79%). The ^{1}H NMR spectrum indicated the presence of free CH_2Cl_2 after overnight pumping (see ref 8). Analytically pure samples were obtained by recrystallization from CH_2Cl_2. Anal. Calcd for $C_{27}H_{34}Cl_3N_4P_2Rh \cdot CH_2Cl_2$: C, 43.63; H, 4.71; N, 7.27; Cl, 23.00. Found: C, 43.62; H, 4.71; N, 7.30; Cl, 22.32. ^{1}H NMR data (200 MHz, $CDCl_3$): δ 2.6–3.8 (comp m, CH_2CH_2) 3.19 (s br, $RhCH_2$) [18 H total], 7.26, 7.92 (m, CH, 15 H), 9.3 (br, NH, 1 H).

(8) Crystals of **2** were grown from CH_2Cl_2 solution. One molecule of CH_2Cl_2 crystallizes per molecule of **2**. *Crystal data*: $C_{27}H_{34}N_4Cl_3P_2$-$Rh \cdot CH_2Cl_2$, orthorhombic, space group *Pbca*, a = 18.649 (4) Å, b = 18.857 (3) Å, c = 17.984 (2) Å, V = 6325 (2) Å^3, D_{calcd} (Z = 8) = 1.644 g/cm^3, μ(Mo Kα) = 10.85 cm^{-1}. A crystal (0.64 × 0.30 × 0.06 mm) was used to collect the data on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. A total of 4165 independent reflections were measured in the range $3 < 2\theta < 45°$ using the $\theta/2\theta$ scan technique. Three standard reflections remeasured after every 100 reflections did not show any significant change in intensity during data collection. The data were corrected for Lorentz–polarization effects and for absorption. Only the 2607 observed reflections with $I > 3\sigma(I)$ were used subsequently. The structure was solved by standard Patterson and difference Fourier methods. All non-H atoms were refined anisotropically. All H atoms were located and refined isotropically except for the 16 H atoms on the methylene carbons of the cyclen ring. Owing to the large thermal motion of the cyclen C atoms, C(1)–C(8), the H atoms attached to them were calculated and included in the least-squares calculation with U's set at 0.15 Å^2 but not refined. Full-matrix least squares were carried out by using SHELX76 (Sheldrick, G. M., 1976, program for crystal structure determination, University of Cambridge, England), the function minimized being $\sum w(|F_o| - |F_c|)^2$. The final refinement converged [$(\Delta/\sigma)_{max}$ = 0.16] to R = 0.039 and R_w = 0.038, the weight used being $w^{-1} = \sigma_F^2 + 0.000415F^2$. $\Delta\rho_{max}$ = 0.42 e/Å^3 at 1.1 Å from Rh.

(9) (a) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Organometallics* **1986**, *5*, 677. (b) Dupart, J.-M.; LeBorgne, G.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 1202. (c) Dupart, J.-M.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 1051. (d) Richman, J. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3378. (e) Richman, J. E.; Day, R. O; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955. (f) Richman, J. E.; *Tetrahedron Lett.* **1977**, 559.

(10) Riess, J. G. In *Rings, Clusters and Polymers of the Representative Elements*; Cowley, A. H., Ed.; ACS Symposium Series 232, American Chemical Society: Washington, D.C., 1983; p 17.

(11) A few bicyclic aminophosphines have been shown to have basic nitrogen atoms. See, for example: Grec, D.; Hubert-Pfalzgraf, L. G.; Grand, A.; Riess, J. G. *Inorg. Chem.* **1985**, *24*, 4642, and references therein.

(12) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.

(13) (a) Feser, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 940. (b) Werner, H.; Paul, W.; Feser, R.; Zolk, R.; Thometzek, P. *Chem. Ber.* **1985**, *118*, 261.

(14) A related carbene compound, $[(C_2H_5)_3P]_2RhCl_3[CHN(CH_3)_2]$, has been structurally characterized: Cetinkaya, B.; Lappert, M. F.; McLaughlin, G. M.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1974**, 1591.

Competitive Carbon–Carbon Bond Formation and Cleavage and Cluster Formation in the Reaction between 3-Hexyne and Hexaisopropoxyditungsten

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Summary: At -20 °C, $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and 3-hexyne (1 equiv) react in pentane in the presence of pyridine (2

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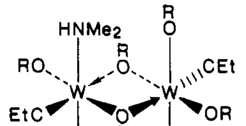
equiv) to give $[(HNMe_2)(EtC{\equiv})(i\text{-}PrO)_2W(\mu\text{-}O\text{-}i\text{-}Pr)]_2$ (I) which adopts an edge-shared bioctahedral geometry in the solid state. This confirms the metathesis reaction reported previously (Schrock, R. R., et al. *Bull. Soc. Chim. Fr.* **1985**, 349). At room temperature the same reactants yield a mixture of products including $W_3(\mu_3\text{-}CEt)(O\text{-}i\text{-}Pr)_9$ (II) and $W_2(\mu\text{-}C_4Et_4)(\eta^2\text{-}C_2Et_2)(O\text{-}i\text{-}Pr)_6$ (III). Compound II is formed by the comproportionation of $W_2(O\text{-}i\text{-}Pr)_6L_2$, where L = py or $HNMe_2$, with $^1/_2$I, while compound III is formed by the reaction between I and $EtC{\equiv}CEt$. Independent syntheses of II and III involve the reaction between $W_2(O\text{-}i\text{-}Pr)_6L_2$, where L = py or $HNMe_2$ and $EtC{\equiv}CEt$, in the mole ratio 3:1 and 1:3, respectively, at room temperature in hydrocarbon solvents.

When similar chemical reactions carried out in different laboratories yield different results, it is generally an indication that the chemistry is more complex than had been originally recognized. The report by Schrock and coworkers[1] of the alkyne scission reaction (eq 1) prompted us to determine why this result had not been obtained in our laboratory when a similar reaction had been carried out at room temperature. As we show here the chemistry is indeed more complex and interesting.[2]

$$W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2 + EtC{\equiv}CEt + 2py \xrightarrow[\text{pentane}]{-20\ °C} 2(i\text{-}PrO)_3W{\equiv}CEt + 2HNMe_2 + 2py \quad (1)$$

Repetition of reaction 1, using the experimental conditions described, confirmed that the alkyne scission is virtually quantitative. The crystalline compound $[(HNMe_2)(EtC{\equiv})(i\text{-}PrO)_2W(\mu\text{-}O\text{-}i\text{-}Pr)]_2$ (I) is obtained in high yield (ca. 60%) by crystallization from pentane. The molecular structure of the propylidyne complex I has a distorted edge-shared bioctahedral geometry, as shown below, and parallels that seen previously for $[(HNMe_2)(ON)(i\text{-}PrO)_2Mo(\mu\text{-}O\text{-}i\text{-}Pr)]_2$.[3,4]



I, R = *i*-Pr

The W-to-W distance in I is nonbonding, 3.528 (1) Å, and the W–O distances of the central $W_2(\mu\text{-}O\text{-}i\text{-}Pr)_2$ moiety are asymmetric, 2.360 (7) and 2.035 (6) Å, reflecting the high trans influence of the $W{\equiv}CEt$ moiety, W–C = 1.772 (11) Å. The $HNMe_2$ ligands in I are relatively strongly bound and not readily displaced by pyridine (py).

When reaction 1 is carried out at room temperature, a mixture of products is obtained including $W_3(\mu_3\text{-}CEt)(\mu_2\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ (II) and $W_2(\mu\text{-}C_4Et_4)(\eta^2\text{-}C_2Et_2)(O\text{-}i\text{-}Pr)_6$ (III). Direct and essentially quantitative formation of II and III is achieved by the stoichiometric reactions shown in eq 2 and 3, respectively.

$$3W_2(O\text{-}i\text{-}Pr)_6(py)_2 + EtC{\equiv}CEt \xrightarrow[\text{hexane}]{22°C} 2II + 6py \quad (2)$$

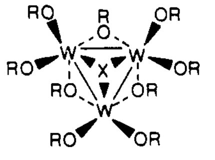
$$W_2(O\text{-}i\text{-}Pr)_6(py)_2 + 3EtC{\equiv}CEt \xrightarrow[\text{hexane}]{22°C} III + 2py \quad (3)$$

The failure of reaction 1, when carried out at room temperature, arises because cluster formation (eq 4) and carbon–carbon coupling (eq 5) are competitive with the $W{\equiv}W$ and $C{\equiv}C$ metathesis reaction.

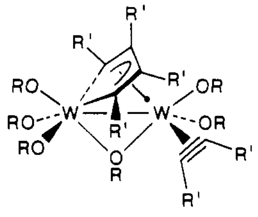
$$W_2(O\text{-}i\text{-}Pr)_6(py)_2 + {}^1/_2I \xrightarrow[\text{pentane}]{22\ °C} II + 2py + HNMe_2 \quad (4)$$

$$I + 2EtC{\equiv}CEt \xrightarrow[\text{pentane}]{22\ °C} III + 2HNMe_2 \quad (5)$$

The stoichiometric reactions (4) and (5) provide alternate (cf. eq 2 and 3 above) syntheses of II and III, respectively. These compounds are readily crystallized from alkanes (pentane or hexane), II, or alkane/*i*-PrOH solvents mixtures, III. NMR data[5] are consistent with the structures depicted below for which $W_3(\mu_3\text{-}CMe)(\mu_2\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$[6] and $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2)$[7] provide precedents. The proposed molecular structure for III was confirmed by a single-crystal X-ray study[8] for the compound $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Et_2H_2)(\eta^2\text{-}C_2H_2)$ (see below).[8]

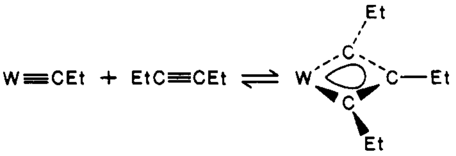


II, R = *i*-Pr; X = CEt

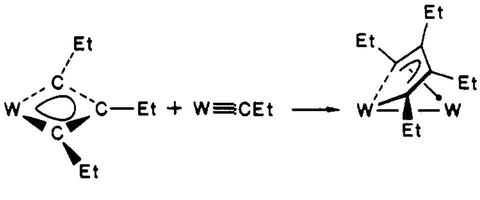


III, R = *i*-Pr; R' = Et

Reaction 5 is without precedent and could occur as a result of reaction sequences shown in either (6) or (7).



(6i)



(6ii)

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[1] Schrock, R. R.; Freudenberger, J. H.; Pedersen, S. F. *Bull. Soc. Chim. Fr.* **1985**, 349.

[2] For a recent review of reactions involving $W_2(OR)_6$ compounds and alkynes see: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, *14*, 69.

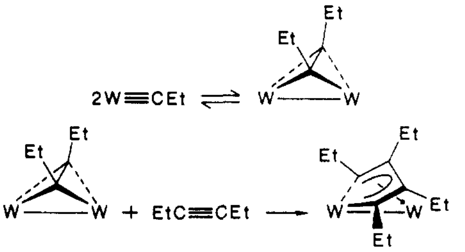
[3] Chisholm, M. H.; Huffman, J. C.; Kelly, R. C. *Inorg. Chem.* **1980**, *19*, 2762. A similar structure was proposed for $[(HNMe_2)(t\text{-}BuC{\equiv})(MeO)_3W]_2$: Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645.

[4] All reactions were carried out under a N_2 atmosphere by using dry and deoxygenated solvents. The alkyne was added rapidly to stirred hydrocarbon solutions of the tungsten-containing compounds by syringe. Reactions 2 and 3 and 4 and 5 are complete in ca. 1 h at 22 °C. Isolated crystalline yields of 50–60% were obtained from reactions employing ca. 500 mg of W-containing compounds in ca. 10 mL of hydrocarbon solvent. Crystal data for $[(HNMe_2)(EtC{\equiv})(i\text{-}PrO)_2W(\mu\text{-}O\text{-}i\text{-}Pr)]_2$: monoclinic, space group $P2_1/n$ with a = 11.098 (3) Å, b = 11.325 (3) Å, c = 14.187 (5) Å; D_{calcd} = 1.671 g cm^{-3} for Z = 2; temperature −153 °C. R = 0.0399 and R_w = 0.0364 for 2077 observed data to 2θ = 45°.

[5] ^1H NMR data for $W_3(\mu_3\text{-}CEt)(\mu_2\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ (22 °C, C_6D_6): $\delta(OCH(CH_3)_2)$ 1.48, 1.42, 1.28 (d, J_{HH} = 6 Hz) in a 1:1:1 integral ratio; $\delta(OCH(CH_3)_2$ 5.01, 3.50 (sept, J_{HH} = 6 Hz) in a 2:1 integral ratio, respectively; $\delta(CCH_2CH_3)$ 1.81 (t, J_{HH} = 7 Hz); $\delta(CCH_2CH_3)$ 4.09 (q with ^{183}W satellites, J_{HH} = 7 Hz, $^3J_{WH}$ = 6 Hz). ^1H NMR of $W_2(\mu\text{-}C_4Et_4)(\eta^2\text{-}C_2Et_2)(O\text{-}i\text{-}Pr)_6$ (22 °C, toluene-d_8): $\delta(OCH(CH_3)_2)$ 1.56, 1.47, 1.16, 0.95, 0.59 (d), 1.43–1.35 (overlapping doublets, J_{HH} = 6 Hz); δ-$(OCH(CH_3)_2)$ 5.35, 5.34, 5.15, 4.97, 4.88, 4.40 (sept, J_{HH} = 6 Hz); $\delta(\mu\text{-}C_4(CH_2CH_3)_4$ 1.43–1.35 (overlapping triplets); $\delta(\eta^2\text{-}C_2(CH_2CH_3)_2)$ 1.38 (t, J_{HH} = 6 Hz); $\delta(\mu\text{-}C_4(CH_2CH_3)_4)$ 4.13, 3.14, 2.65–2.34 (m); $\delta(\eta^2\text{-}C_2\text{-}(CH_2CH_3)_2)$ 3.58, 3.40 (ABX_3 patterns). $^{13}C\{^1H\}$ NMR of $W_2(\mu\text{-}C_4Et_4)(\eta^2\text{-}C_2Et_2)(O\text{-}i\text{-}Pr)_6$ (22 °C, toluene-d_8): $\delta(\mu\text{-}C_4Et_4)$ 218.3, 204.1, 156.0, 152.3; $\delta(\eta^2C_2Et_2)$ 185 (br).

[6] Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234.

Alkyne metathesis, which is known for $(t\text{-BuO})_3W{\equiv}CR$ compounds,[9] involves the reversibility of (6i) and would be terminated by (6ii).



(7i)

(7ii)

Evidence for equilibria involving tungsten alkylidynes and ditungstatetrahedra supported by alkoxide ligands, (7i), has previously been noted,[10] as has the coupling reaction (7ii).[7]

Reactions between I and C_2H_2, 2 equiv (also in separate experiments $^*C_2H_2$, 2 equiv, where $^*C$ represents 92 mol % ^{13}C), show formation of $W_2(\mu\text{-}C_4Et_2H_2)(\eta^2\text{-}C_2H_2)(O\text{-}i\text{-}Pr)_6$ in which the carbon atoms of the ethyne are scrambled over all four sites of the μ-C_4 ring, as might have been anticipated for a reversible reaction, (6i), followed by either (6ii) or (7).

Further studies are in progress.[11]

Registry No. I, 104240-17-7; II, 104215-35-2; III, 104240-18-8; $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$, 104215-36-3; $W_2(O\text{-}i\text{-}Pr)_6(py)_2$, 70178-75-5; $EtC{\equiv}CEt$, 928-49-4.

Supplementary Material Available: A summary of data collections, tables of program MU output, crystal and diffractometer data, fractional coordinates, anisotropic temperature factors, and bond distances and angles, a listing of standard data type, and figures of VERSORT drawings, ORTEP drawings, space-filling-model drawings, and a plot of standards (35 pages); a list of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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(7) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806.

(8) Chisholm, M. H.; Conroy, B. K.; Huffman, J. C., unpublished results.

(9) Schrock, R. R.; Sancho, J. *J. Mol. Catal.* **1982**, *15*, 75. Schrock, R. R. *ACS Symp. Ser.* **1983**, *No. 24*, 369.

(10) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794. Chisholm, M. H.; Conroy, B. K.; Huffman, J. C.; Marchant, N. S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 446.

(11) We thank the National Science Foundation and the Wrubel Computing Center for support.

Synthesis, Structure, and Electrical Properties of $[(MeCp)_5V_5S_6][(TCNQ)_2]$

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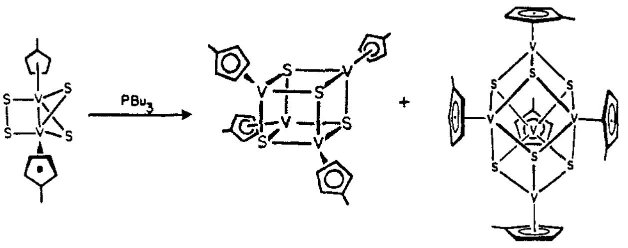
Received July 22, 1986

Summary: Desulfurization of $(MeCp)_2V_2S_4$ with PBu_3 gives $(MeCp)_4V_4S_4$ (**1**) and $(MeCp)_5V_5S_6$ (**2**). Compounds **1** and **2** were characterized by ^1H NMR spectroscopy and mass spectrometry. Compound **2** forms the charge-transfer salt $[\mathbf{2}][(TCNQ)_2]$ which was characterized by X-ray crystallography as its CH_2Cl_2 solvate. The cluster consists of a trigonal-bipyramidal V_5 core inside of a trigonal prism of six sulfur atoms. Four-probe conductivity measurements show that $[\mathbf{2}][(TCNQ)_2]$ is a *n*-type semiconductor ($E_g \approx 0.25$ eV).

We wish to describe the synthesis and characterization of $(MeCp)_5V_5S_6$ (MeCp = $\eta^5\text{-}CH_3C_5H_4$). This work provides some insights into how cyclopentadienyl metal chalcogenide clusters form from simple precursors. Furthermore our structural work establishes the presence of unusual intracluster sulfur–sulfur interactions. These results are supplemented by electrical measurements on $[(MeCp)_5V_5S_6][(TCNQ)_2]$.

The addition of tributylphosphine to a solution of $(MeCp)_2V_2S_4$[1] results in the rapid formation of the phosphine sulfide and two black compounds which were separated by sublimation at 150 °C (0.03 mmHg) (eq 1). The more volatile species is $(MeCp)_4V_4S_4$ (**1**). This 56e cubane was obtained in ca. 40% yield and was fully characterized.[2,3] The less volatile product of the desulfurization reaction is the weakly paramagnetic $(MeCp)_5V_5S_6$ (**2**).[4] The ^1H NMR spectrum of **2** is consistent with a trigonal-bipyramidal cluster as two sets of MeCp resonances are observed in a 2:3 ratio. The structure of a derivative of **2** lends credence to this assignment (*vide infra*) as does Bottomley's recent structural characterization of the closely related compounds $Cp_5Ti_5S_6$ and $Cp_5V_5O_6$.[5] In contrast to the present work, Bottomley's clusters were prepared from monometallic precursors and sources of atomic sulfur (H_2S) and oxygen (N_2O).



(1)

The formation of **1** and **2** occurs via an aggregation process induced by desulfurization of the V_2S_4 precursor. This aggregation is analogous to the well-known clusterification of metal carbonyls induced by decarbonylation.[6]

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*To whom correspondence should be addressed at the School of Chemical Sciences.

(1) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321.

(2) Many details can be found in C. M. Bolinger's Ph.D. Thesis (University of Illinois at Urbana-Champaign, 1984). The structures of $(MeCp)_4V_4S_4$ and its cation have been determined by Professor A. L. Rheingold at the University of Delaware and will be discussed in a full report of the V_4S_4 chemistry (Boyd, P. D. W.; Darkwa, J.; Rauchfuss, T. B.; Rheingold, A. L., in preparation). The reaction of *t*-BuSH and $(MeCp)_2V$ also gives $(MeCp)_4V_4S_4$: Eremenko, I. L.; Pasynskii, A. A.; Katugin, A. S.; Ellert, O. G.; Shkloyer, V. E.; Struchkov, Yu. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1669.

(3) Anal. Calcd for $C_{24}H_{28}S_4V_4$: C, 44.65; H, 4.35; V, 31.42. Found: C, 44.60; H, 4.44, V, 31.42. ^1H NMR ($CDCl_3$ solution): δ 59.2 ($\Delta\nu_{1/2}$ = 72 Hz), 58.4 (72 Hz), 7.6 (14 Hz). EIMS (*m/e*): 648, M^+; 569 $(M - MeCp)^+$; 490 $(M - 2MeCp)^+$; 411 $(M - 3MeCp)^+$; 332 $(M - 4MeCp)^+$.

(4) Anal. Calcd for $C_{30}H_{35}S_6V_5$: C, 42.76; H, 4.19. Found: C, 42.85; H, 4.36. ^1H NMR ($CDCl_3$): δ 5.18 (130 Hz), 4.72 (94 Hz), 2.09 (13 Hz), 1.86 (5 Hz). The yield of **2** was typically 10%. The $\mu_{eff} = 0.98\ \mu_B$ (uncorrected).

(5) $Cp_5V_5O_6$: Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 5651. $Cp_5Ti_5S_6$: Bottomley, F.; Egharevba, G. O.; White, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 4353.

(6) For an example see Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* 1976, *98*, 7433.

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