634 *Inorg. Chem.* **1986**, *25*, 634–643

The EHMO calculation of Meissner and Korol'kov predicts a $^3A_2(e^2)$ ground state for $Mo_5X_{13}^{3-}$ clusters.[4] Our results indicate that the $Mo_5X_{13}^{3-}$ ground state is paramagnetic, and at least for $Mo_5Br_{13}^{3-}$, the EPR spectrum is characteristic of a triplet state at low (10 K) temperatures.[9] At higher temperatures, the lowest electronic states are in thermal equilibrium in each cluster trianion. The low magnetic moments of these even electron clusters are not unprecedented for high nuclearity metal systems. Recent work has shown that $H_2Os_{10}C(CO)_{24}$ exhibits Curie paramagnetic behavior with $\mu_{eff} = 0.62\ \mu_B$ per cluster molecule.[10] Although more sophisticated electronic structural models undoubtedly will be required to understand in quantitative detail the magnetic properties of the $Mo_5X_{13}^{3-}$ clusters, it is worth pointing out in closing that the broad $g \sim 2$ EPR spectra and the low effective magnetic moments are reminiscent of conduction band electrons in bulk metals.

Acknowledgment. We thank L. G. Butler for assistance with the analysis of the magnetic susceptibility data, and R. E. McCarley for helpful discussions. This research was supported by National Science Foundation Grant CHE84-19828.

Registry No. $(n\text{-}Bu_4N)_3Mo_5Cl_{13}$, 99727-62-5; $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$, 55913-48-9; $(n\text{-}Bu_4N)Mo_5Cl_{13}$, 99727-64-7; $(n\text{-}Bu_4N)_2Mo_5Br_{13}$, 99748-38-6; $(n\text{-}Bu_4N)_3Mo_5Br_{13}$, 99727-66-9; $(n\text{-}Bu_4N)Mo_5Br_{13}$, 99766-94-6; $K_3[MoCl_6]$, 13600-82-3.

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(9) McCarley and co-workers have determined the crystal structure of $(PhEt_3N)_2Mo_5Cl_{13}$ (McCarley, R. E., private communication). They find that the cluster is distorted rhombically from C_{4v} symmetry, which would split the e level. Clearly, it would be of great interest to see if this distortion is retained in the structure of the reduced (3−) species, because our data indicate that the 3− ground state is a spin-triplet. The implication from our work is that the distortion in the 3− cluster is not large.

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Contribution from the School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, Department of Chemistry, University of Delaware, Newark, Delaware 19711, and Crystalytics Company, Lincoln, Nebraska 68501

$(CH_3C_5H_4)_2V_2S_4$ as an Organometallic Ligand: Preparation of Iron, Cobalt, Nickel, and Iridium Derivatives and Structures of a V_4Ni Cluster and Three V_2Fe Clusters

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Cynthia S. Day,[§] and Scott R. Wilson[†]

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The reactions of iron, cobalt, nickel, and iridium complexes with $(CH_3C_5H_4)_2V_2S_4$ (**1**) have been studied, resulting in the preparation of a series of new mixed-metal clusters. Reaction of **1** with $Fe(CO)_5/Me_3NO$ yields $(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (**2**) while $(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (**3**) is obtained from **1** and $Fe(CO)_2(NO)_2$. The μ-η^2-S_2 ligands in **2** and **3** are electrophilic and react with PBu_3 or $Pt(C_2H_4)(PPh_3)_2$ to give V_2FeS_3 or V_2FePtS_4 clusters, respectively. The compound $(CH_3C_5H_4)_2V_2S_4CoC_5H_5$ can be prepared from **1** and $C_5H_5Co(CO)_2$ or $CpCo(CO)I_2$ and Zn. The cluster $(CH_3C_5H_4)_2V_2S_4Ir(PPh_3)Cl$ can be prepared from **1** and $IrCl(N_2)(PPh_3)_2$; ^1H NMR studies on this compound show that the vanadium centers are equivalent. $[(C_5H_5)Ni(CO)]_2$ reacts with **1** to give $[(CH_3C_5H_4)_2V_2S_4]_2Ni$ (**4**), which can be desulfurized to give $[(CH_3C_5H_4)_2V_2S_3]_2Ni$. The V_4NiS_8 cluster also reacts with $Pt(C_2H_4)(PPh_3)_2$ to give V_4NiS_8Pt and $V_4NiS_8Pt_2$ derivatives. The compound $(CH_3C_5H_4)_2V_2S_3Fe(NO)_2$ reacts with $CoI(NO)_2$ and zinc to give $(CH_3C_5H_4)VS_3FeCo_2(NO)_6$, an analogue of Roussin's "black salt", $Fe_4S_3(NO)_7^-$. The structures of **2**, **2-S**, **3**, and **4** were determined by X-ray crystallographic techniques. The crystals of **2** were monoclinic, with $a = 9.853$ (2) Å, $b = 15.652$ (3) Å, $c = 12.821$ (3) Å, $\beta = 105.89$ (2)°, and $Z = 4$; the space group was $P2_1/c$. Conventional full-matrix least-squares refinement with non-hydrogen atoms anisotropic and hydrogen atoms isotropic gave $R = 0.028$ and $R_w = 0.036$ for 2889 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 moieties, with the V–V edge spanned by a μ-η^2-S_2 ligand. The V–Fe distances are unusually long, and the V–V distances are unusually short. The crystals of **2-S** were monoclinic with $a = 10.397$ (2) Å, $b = 25.504$ (7) Å, $c = 14.135$ (4) Å, $\beta = 106.63$ (2)°, and $Z = 8$; the space group was $P2_1/c$. Modified full-matrix least-squares refinement with non-hydrogen atoms anisotropic and fixed hydrogen atoms isotropic gave $R = 0.038$ and $R_w = 0.051$ for 8422 reflections having $2\theta < 55°$ and $I > 3\sigma(I)$. The structure is similar to that of **2** but with the V–V edge spanned by a μ-S ligand. The crystals of **3** were monoclinic with $a = 10.190$ (3) Å, $b = 12.680$ (5) Å, $c = 14.016$ (5) Å, $\beta = 103.01$ (3)°, and $Z = 4$; the space group was $P2_1/c$. Conventional full-matrix least-squares refinement with the non-hydrogen atoms anisotropic and the hydrogen atoms isotropic gave $R = 0.031$ and $R_w = 0.030$ for 5227 reflections having $2\theta < 55°$ and $I > 3\sigma(I)$. The structure of **3** is very similar to that for **2**, except that the iron is coordinated to two nearly linear nitrosyl ligands. The unusual V–Fe bond lengths of **2**, **2-S**, and **3** are rationalized by V–S(μ-S) and V–S(μ_3-S) π interactions, which are competitive with V–Fe bonding. Crystals of the V_4Ni cluster **4** were orthorhombic with $a = 16.014$ (4) Å, $b = 14.477$ (3) Å, $c = 12.990$ (3) Å, and $Z = 4$; the space group was *Pbcn*. Refinement with the least-squares matrix blocked into random units and with anisotropic non-hydrogen atoms gave $R = 0.081$ and $R_w = 0.081$ for 1693 reflections having $2\theta < 50°$ and $F_o > 3\sigma(F_o)$. The molecule consists of tetrahedral Ni situated on a crystallographic 2-fold axis bound via two μ_3-S atoms to each of two $[(CH_3C_5H_4)_2V_2(\mu\text{-}S_2)]$ fragments. The V–V distance is 2.484 (2) Å, and the V–Ni distances are 2.813 ± 0.03 Å.

Introduction

Sulfido complexes are known to function as ligands for other metals and this is the basis upon which a number of cluster compounds are prepared.[1] Along these lines, the coordination chemistry of bis(methylcyclopentadienyl)divanadium tetrasulfide $(CH_3C_5H_4)_2V_2S_4$ (**1**) has been the subject of our studies (Scheme I).[2–4] Two distinguishing characteristics of **1** are (i) it is formally highly electron-deficient and its complexes should exhibit novel structural and chemical properties, and (ii) the derivatives of **1**, i.e. V_2MS_4 complexes, are themselves ligands, thereby permitting

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[†] University of Illinois.
[‡] University of Delaware.
[§] Crystalytics Co.

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Table I. NMR and IR Data for New Compounds

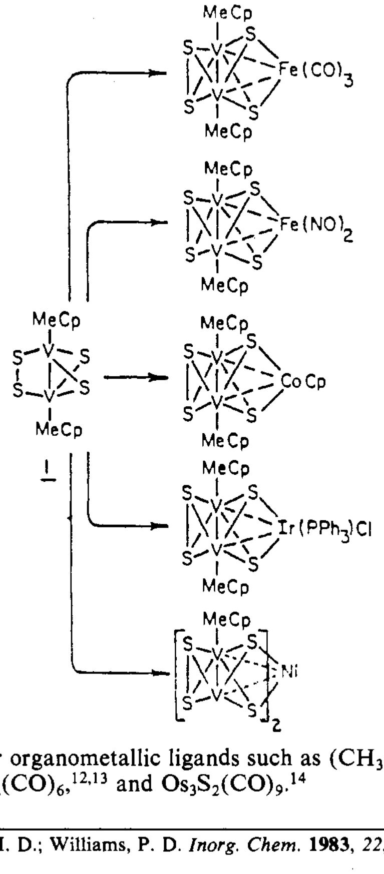
compd	^1H NMR[a] ($CDCl_3$), ppm	IR,[b] cm^{-1} (ν_{CO} and ν_{NO} only)	^{31}P NMR,[a] ppm
$(CH_3C_5H_4)_2V_2S_4FeCO)_3$ (**2**)	4.95 (2 H, m)	2028, 1978	
	4.94 (2 H, m)	1970	
	1.97 (3 H, s)		
$(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (**3**)	5.10 (2 H, m)	1758	
	4.95 (2 H, m)	1720	
	2.00 (3 H, s)		
$(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ (**2-S**)	5.98 (2 H, m)	2028, 1979	
	5.55 (2 H, m)	1970	
	2.10 (3 H, s)		
$(CH_3C_5H_4)_2V_2S_3Fe(NO)_2$	5.95 (2 H, m)	1763	
	5.45 (2 H, m)	1726	
	2.10 (3 H, s)		
$(CH_3C_5H_4)_2V_2S_4CoC_5H_5$	4.90 (5 H, s)		
	4.72 (8 H, m)		
	1.85 (6 H, s)		
$(CH_3C_5H_4)_2V_2S_4IrCl(PPh_3)$	7.70 (9 H, m)		−8.27
	7.15 (6 H, m)		
	6.00 (2 H, s)		
	5.55 (2 H, s)		
	5.25 (2 H, s)		
	4.95 (2 H, s)		
	1.98 (6 H, s)		
$(CH_3C_5H_4)_2V_2S_4Fe(CO)_3{\cdot}Pt(PPh_3)_2$	7.32 (15 H, m)	2014, 1954 (br)	2.08 ($^1J_{PPt}$ = 2688 s^{-1})[c]
	5.49 (2 H, m)		
	5.41 (2 H, m)		
	1.90 (3 H, s)		
$(CH_3C_5H_4)VS_3FeCo_2(NO)_6$	5.58 (4 H, s)	1858, 1825	
	1.95 (3 H, s)	1796, 1780	
		1745, 1709	
$(CH_3C_5H_4)_4V_4S_8Ni$ (**4**)	5.49 (2 H, m)		
	5.34 (2 H, m)		
	2.10 (3 H, m)		
$(CH_3C_5H_4)_4V_4S_8Ni{\cdot}2Pt(PPh_3)_2$	7.60 (m), 6.95 (m) (15 H)		
	6.10 (4 H, m)		
	2.30 (3 H, m)		

[a] Chemical shifts are quoted (upfield shifts being negative) relative to standards $Si(CH_3)_4$ (^1H) and 85% H_3PO_4 (^{31}P). [b] Carbonyl absorptions were measured on cyclohexane solutions by FTIR, except for those of $2{\cdot}Pt(PPh_3)_2$, which were measured in toluene. Nitrosyl absorptions were measured on CCl_4 solutions. [c] $^{31}P\{^1H\}$ NMR, measured in $CDCl_3$.

the stepwise assembly of novel $V_2MM'S_4$ clusters and eventually, perhaps, even metallic polymers. An interesting aspect of the compounds prepared in this work is the nature of the metal–metal and metal–sulfur interactions as indicated by the four structure analyses.

In work related to our own, the Pasynskii group has utilized the very stable $(C_5H_5)_2Cr_2(\mu\text{-S-}t\text{-Bu})_2(\mu\text{-S})$,[5] to prepare a variety of adducts,[6] trimetallic clusters,[7] and cubanes[8] (Scheme II). More recently these workers have described a series of "bow tie" clusters of the type $[(C_5H_5)_2Cr_2(S\text{-}t\text{-Bu})S_2]_2M$, where M = Cr, Mn, or Co.[9] Recent studies have also described the coordination chemistry of other organometallic ligands such as $(CH_3C_5H_4)_2Mo_2S_4$,[10,11] $Fe_2S_2(CO)_6$,[12,13] and $Os_3S_2(CO)_9$.[14]

Scheme I



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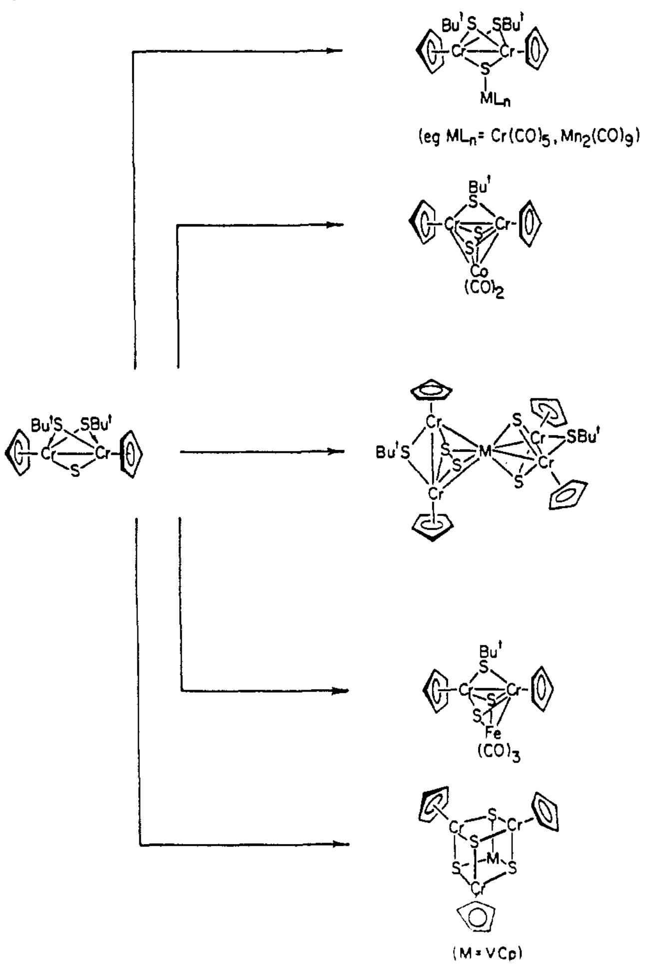
Scheme II



Results and Discussion

Synthesis of Metal Complexes of $(CH_3C_5H_4)_2V_2S_4$. This project started with the discovery that $Fe_3(CO)_{12}$ reacts with $(CH_3C_5H_4)_2V_2S_4$ (**1**) to give $(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (**2**) in low yield along with small amounts of $Fe_3S_2(CO)_9$ and $Fe_2S_2(CO)_6$. Subsequently, it was found that 35–45% yields could be obtained by decarbonylating $Fe(CO)_5$ with trimethylamine *N*-oxide in the presence of **1**. The compound $(CH_3C_5H_4)_2V_2S_5$[15] also reacts with $Fe(CO)_5$ in the presence of Me_3NO under the same conditions to give very low yields of both **2** and $(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ (**2-S**).

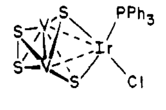
Compound **2** dissolves in most common organic solvents (sparingly in alkanes and alcohols) to give air-stable green solutions. ^1H NMR spectroscopy revealed a single resonance at 4.95 ppm for the ring protons of the methylcyclopentadienyl ligands, which was resolved at higher fields (360 MHz) into two multiplets (Table I). Three IR absorptions assignable to ν_{CO} were observed for cyclohexane solutions of **2** (Table I). Its elemental composition was established by elemental analysis and field-desorption (FD) mass spectroscopy.

The compound $(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (**3**) was found to be a minor product formed in the early stages of the reaction between **1** and an excess of $Hg[Fe(CO)_3NO]_2$ in refluxing toluene while the major product formed under these conditions is the cubane $(CH_3C_5H_4)_2V_2S_4Fe_2(NO)_2$.[4] Compound **3** can be prepared in improved yields from **1** and $Hg[Fe(CO)_3NO]_2$ at room temperature although the tricarbonyl **2** is also formed under these conditions. An improved method for the synthesis of **3** employs $Fe(CO)_2(NO)_2$ generated in situ as described by Gladfelter[16] from PPN$[Fe(CO)_3NO]$ (PPN is bis(triphenylphosphine)nitrogen(1+)) and $NOBF_4/Et_3N$ in THF.

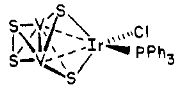
Compound **3** exists as black air-stable crystals, which are soluble in common organic solvents and give mildly air-sensitive purple solutions. The infrared spectrum of **3** shows two intense ν_{NO} bands at 1758 and 1720 cm^{-1}, well within the range of linear or nearly linear nitrosyls. The compound was also characterized by ^1H NMR spectroscopy and mass spectrometry.

A V_2Co cluster was prepared, initially in low yield, from **1** and $(C_5H_5)Co(COD)$ and $(C_5H_5)Co(CO)_2$. Higher yields were obtained by using $[(C_5H_5)Co(CO)]_2$ or Zn-reduced $(C_5H_5)_2CoI_2(CO)$. The compound $(CH_3C_5H_4)_2V_2S_4Co(C_5H_5)$ is green, air-stable, and diamagnetic.

Since the 14e fragments $Fe(CO)_3$, $Fe(NO)_2$, and $Co(C_5H_5)$ form stable adducts with **1**, we anticipated that the $IrCl(PPh_3)_2$ moiety could be similarly incorporated. Treatment of **1** with $IrCl(N_2)(PPh_3)_2$ gave a purple product concomitant with elimination of N_2 *and* 1 equiv of PPh_3. Air-stable purple crystals analyzing as $(CH_3C_5H_4)_2V_2S_4IrCl(PPh_3)$ were further characterized by FDMS, IR, and ^1H NMR spectroscopy. The 220-MHz ^1H NMR spectrum of this novel species shows *four* separate signals for $CH_3C_5H_4$ but only one signal for the methyl groups. It follows that the molecule contains a plane of symmetry lying on the bisector of the two $CH_3C_5H_4$ rings. This information is consistent with structure A but not structure B.



A



B

In an effort to extend the series of 48e trimetallic clusters to the species $(CH_3C_5H_4)_2V_2S_4Ni(CO)_2$, the reaction of **1** and $Ni(CO)_4$ was performed. The only isolable product, however, was an air-stable, dark purple compound, which was formulated as $[(CH_3C_5H_4)_2V_2S_4]_2Ni$ (**4**) on the basis of its elemental analysis and field desorption mass spectrum. At the very early stages of this reaction a green compound was detected by TLC but attempts to isolate this species were unsuccessful. The substituted nickel carbonyls $Ni(CO)_2(PPh_3)_2$ and $Ni(CO)_2(Ph_2PC_2H_4PPh_2)$ were reacted with $(CH_3C_5H_4)_2V_2S_4$, our rationale being that the phosphine would stabilize intermediates of the type $(CH_3C_5H_4)_2V_2S_4NiL_2$, but in both cases the pentanuclear cluster **4** was the only product obtained.

The yields of $(CH_3C_5H_4)_4V_4S_8Ni$ from the reaction of **1** and $Ni(CO)_4$ or its derivatives were low. Attempts were made to optimize the yield by utilizing $Ni(COD)_2$ (COD is 1,5-cyclooctadiene), but the yield of the V_4S_8Ni cluster was only 15%. Amazingly, the best synthesis of **6** involves the reaction of **1** and $[(C_5H_5)Ni(CO)]_2$, the yield was 80%.

Reactions of $(CH_3C_5H_4)_2V_2S_4FeL_n$ (L_n = $(CO)_3$, $(NO)_2$). The clusters $(CH_3C_5H_4)_2V_2S_4FeL_n$ (L_n = $(CO)_3$, $(NO)_2$) contain pendant μ-η^2-S_2 ligands which are susceptible to further reactions. Three reactions were studied: oxidative addition of Pt(0), desulfurization with phosphines, and hydride reduction.

Upon treatment with $Pt(C_2H_4)(PPh_3)_2$, the two V_2FeS_4 clusters are smoothly converted to **2**·$Pt(PPh_3)_2$ and **3**·$Pt(PPh_3)_2$. The ^1H NMR data for these tetrametallic species indicated symmetrical complexes in that the methyl groups were isochronous while the

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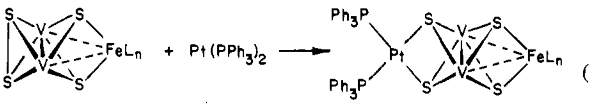
Table II. Mössbauer Data[a]

compd	isomer shift (δ_{Fe}), mm s^{-1}	quadrupole splitting (Δ), mm s^{-1}	line widths (Γ), mm s^{-1}
$(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (**2**)	0.05	1.17	0.13 0.12
$(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (**3**)	0.11	0.27	0.14 0.13
$(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ (**2**-S)	0.06	1.64	0.15 0.14
$(CH_3C_5H_4)_2V_2S_4Fe(CO)_3Pt(PPh_3)_2$	0.04	1.09	0.14 0.13
$Fe_3S_2(CO)_9$	0.02	0.58	0.14 0.14
$Fe_3S_2(CO)_9$ (85 K)[20]	0.04	0.56	0.27 0.27
$Fe_3S_2(CO)_9$ (80 K)[21]	0.03	0.57	

[a] All values were obtained at 150 K and are quoted relative to that of Fe foil (0.01 mm s^{-1}).

^{31}P NMR data indicated cis and equivalent phosphorus atoms (eq 1). In principle other metals should insert into the μ-η^2-S_2 group,

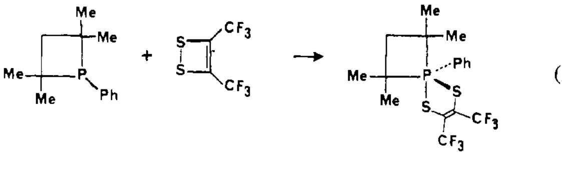


(1)

(FeL_n = $Fe(CO)_3$, $Fe(NO)_2$; Cp groups omitted for clarity)

but this aspect has not been studied (although $(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ does react with $Hg[Fe(CO)_3NO]_2$ to give the cubane $(CH_3C_5H_4)_2V_2S_4Fe_2(NO)_2$[4]).

Green solutions of **2** immediately assume a red color upon treatment with PBu_3. Thermally labile, dark red crystalline $(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ (**2**-S) was isolated in good yield and was thoroughly characterized. Whereas the ν_{CO} region of the IR spectra of **2** and **2**-S are virtually superimposable, the ^1H NMR signals for the ring protons of **2**-S are shifted ca. 1 ppm downfield relative to those for **2**. Similarly the ν_{NO} absorptions of **3** are affected little by conversion to **3**-S, but a substantial downfield shift in the ^1H NMR is observed. On the basis of an analogy to the structure of the V_2FePtS_4 structure, we conjecture that desulfurization of **2** and **3** proceeds via a pentacoordinate phosphorane intermediate that eliminates $SPBu_3$. The oxidative addition of disulfides to phosphorus(III) is a known process[17] (eq 2).



(2)

An attempt was made to synthesize the V_2S_4FePt cluster by reduction of **2** followed by treatment with *cis*-$PtCl_2(PPh_3)_2$. This procedure failed and the only silica-stable product was **2**-S. In a separate experiment, excess methyl iodide was added to solutions of **2** that had been treated with $LiBHEt_3$. On exposure to air, a thiol odor (presumably due to CH_3SH) was detected and the formation of **2**-S in low yield was again indicated by thin-layer chromatography. These results suggest that the anionic species presumed to be generated concomitant with cleavage of the sulfur–sulfur bond in **2** is unstable. This pattern is consistent with the ease with which **2** can be desulfurized by phosphines but contrasts with the reduction product of $(C_5H_5)_2V_2(\mu$-η^2-$S_2)(\mu$-η^2-$S_2C_2(CF_3)_2)$, which undergoes clean methylation to give $(C_5H_5)_2V_2(SCH_3)_2(\mu$-$\eta^2$-$S_2C_2(CF_3)_2)$.[18] This difference may be attributable to the fact that the 32e dithiolene dimer is too electron deficient to tolerate loss of S^{2-}.

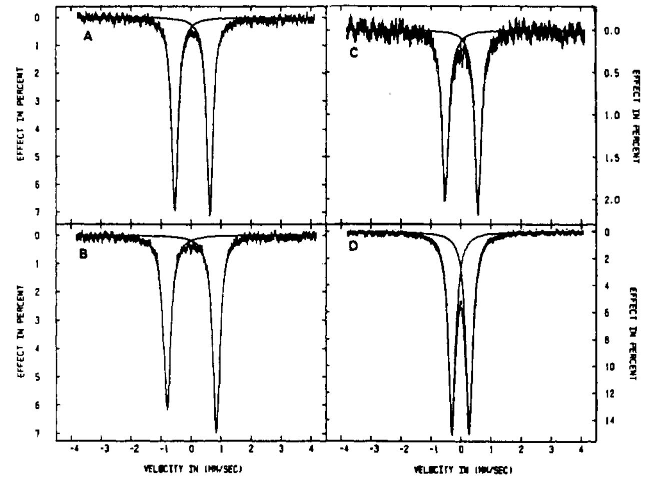
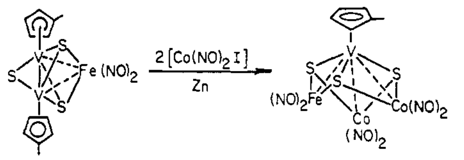


Figure 1. Mössbauer spectra of compounds **2** (A), **2**-S (B), **2**·$Pt(PPh_3)_2$ (C), and $Fe_2S_2(CO)_9$ (D).

In view of the great π-acceptor ability of the nitrosyl ligand, we investigated the chemistry of the reduction products of **3**. Reduction of this dinitrosyl with either $LiBHEt_3$ or MeLi followed by treatment with $[CoI(NO)_2]_x$ gave an inseparable mixture of the cubane $(CH_3C_5H_4)_2V_2S_4FeCo(NO)_2$[4] and a new compound characterized by several overlapping ν_{NO} bands. Computer simulation of the parent ion envelope in the FDMS spectrum of the new compound indicated the formula $(CH_3C_5H_4)VS_3FeCo_2(NO)_6$. A more efficient synthesis of this VCo_2Fe cluster involved the reaction of **3**-S with Zn-reduced $[CoI(NO)_2]_x$. The ^1H NMR spectrum for this cluster demonstrated that the $CH_3C_5H_4$ group lies on a time-averaged plane of symmetry. The valence shell electron configuration of this compound, assuming three μ_3-S ligands, is 66e, like that for Roussin's black salt, $Fe_4S_3(NO)_7^-$.[19] On the basis of this information, the structure shown in eq 3 is proposed.



(3)

Mössbauer Spectroscopy. The ν_{CO} IR data for **2** and **2**-S are essentially identical. We sought more direct insight into the nature of the iron centers in these molecules. Mössbauer spectra of **2**, **2**-S, **3**, **2**·$Pt(PPh_3)_2$, and $Fe_3S_2(CO)_9$ were recorded at 150 K and zero magnetic field (Figure 1, Table II). The isomer shifts for all of these compounds are quite similar, suggesting that changes in the electronic configuration of the cluster have little effect on

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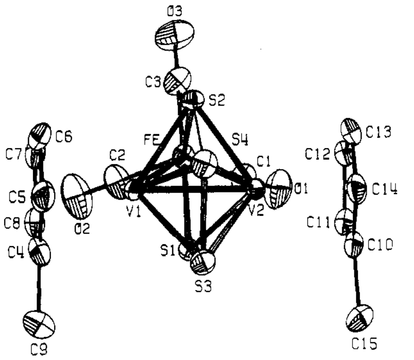
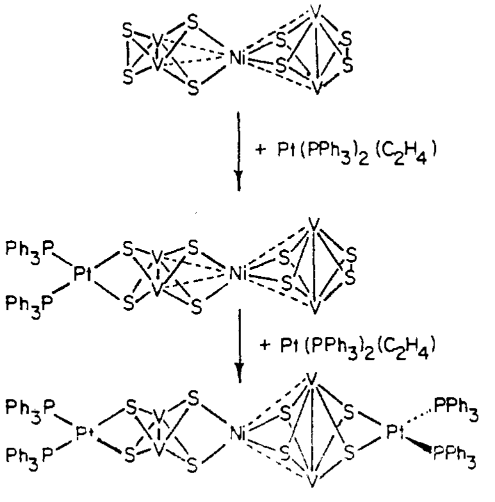


Figure 2. ORTEP plot of the $(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ molecule (**2**), with thermal ellipsoids drawn at the 35% probability level.

the oxidation state of the iron centers. On the other hand, the quadrupole splitting data indicate that there are substantial changes in the electronic environment about the iron centers. Since the structural results indicate V–Fe interactions, quadrupole splittings may reflect different V–Fe bond orders, supporting the notion that the V–Fe bonds in **2**-S are indeed stronger than those in **2**, **3**, and **2**·$Pt(PPh_3)_2$ in accord with the structural results. The limitations of the Mössbauer technique for this class of compounds are evident, however, in the case of $Fe_3S_2(CO)_9$ since its two types of Fe atoms have indistinguishable isomer shifts and quadrupole splittings.[20,25]

Reactions of the V_4NiS_8 Cluster. The V_4S_8Ni cluster **4**, by virtue of its *two* exocyclic disulfide moieties, sequentially added two $Pt(PPh_3)_2$ units (eq 4, $CH_3C_5H_4$ groups omitted for clarity).



(4)

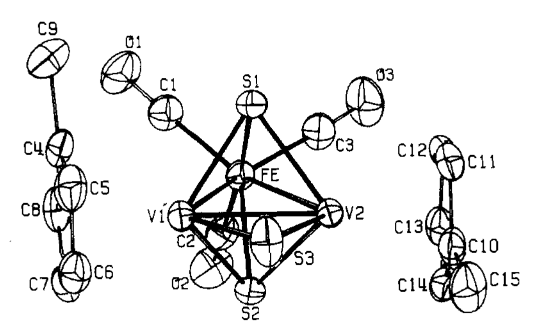


Figure 3. ORTEP plot of one of the two crystallographically independent $(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ molecules (**2**-S), with thermal ellipsoids drawn at the 35% probability level.

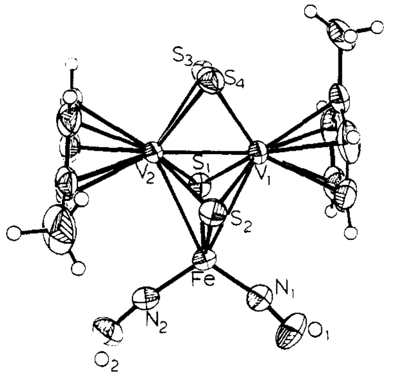


Figure 4. ORTEP plot of the $(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ molecule (**3**), with thermal ellipsoids drawn at the 35% probability level.

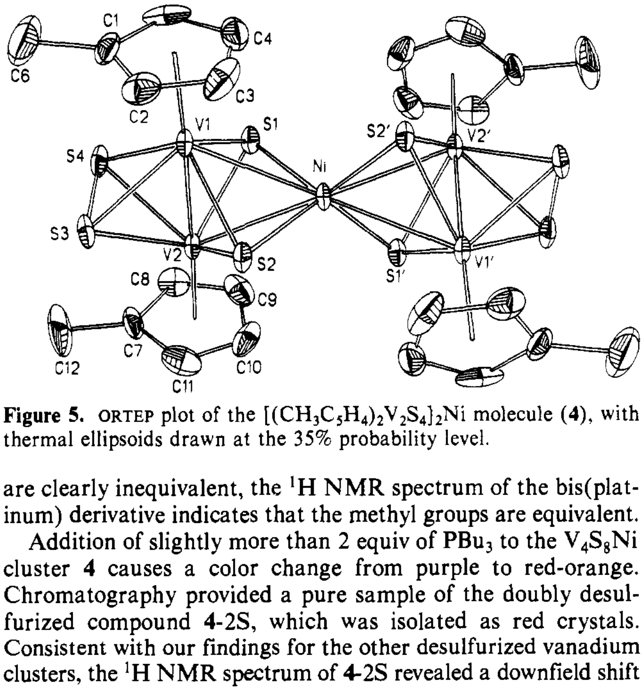


Figure 5. ORTEP plot of the $[(CH_3C_5H_4)_2V_2S_4]_2Ni$ molecule (**4**), with thermal ellipsoids drawn at the 35% probability level.

Treatment of a purple solution of **3** with 1 equiv of $Pt(C_2H_4)(PPh_3)_2$ induced an immediate color change to steel blue. Gel-permeation chromatography provided a sample of **4**·$Pt(PPh_3)_2$ isolated as a blue powder. The ^1H NMR spectrum of this compound proved to be informative in that it showed the presence of two different sets of $CH_3C_5H_4$ ligands. Together with the characteristic resonances for PPh_3, one broad singlet and a set of two multiplets were observed at 6.12, 5.50, and 5.24 ppm, respectively. We assign the lowest field resonance to the ring protons adjacent to the $Pt(PPh_3)_2$ moiety while the higher field set of resonances may be assigned to the ring protons of the underivatized V_2S_2 unit; these latter signals are not significantly shifted from those of the parent **4**. Addition of a second equivalent of $Pt(C_2H_4)(PPh_3)_2$ to the blue solution of **4**·$Pt(PPh_3)_2$ gave a Kelly green solution of **4**·$Pt_2(PPh_3)_4$. On the basis of its ^1H NMR spectrum, we assign the structure depicted above to this $V_4S_8NiPt_2$ cluster. The ring protons of the $CH_3C_5H_4$ ligands of the two $Pt(PPh_3)_2$ groups are shifted to even lower field relative to those of the parent **4**. Unlike the methyl groups in **4**·$Pt(PPh_3)_2$, which are clearly inequivalent, the ^1H NMR spectrum of the bis(platinum) derivative indicates that the methyl groups are equivalent.

Addition of slightly more than 2 equiv of PBu_3 to the V_4S_8Ni cluster **4** causes a color change from purple to red-orange. Chromatography provided a pure sample of the doubly desulfurized compound **4**-2S, which was isolated as red crystals. Consistent with our findings for the other desulfurized vanadium clusters, the ^1H NMR spectrum of **4**-2S revealed a downfield shift of the ring and methyl protons related to **4**. The field desorption mass spectrum of this V_4S_6Ni cluster showed the expected parent ion together with a small envelope corresponding to the *singly* desulfurized derivative of **4**, but no attempt was made to synthesize this species.

X-ray Crystallography of 2, 2-S, 3, and 4. Single crystal X-ray diffraction studies established the solid-state structures of **2**, **2**-S, **3**, and **4** (Figures 2–5). Important bond lengths and angles are collected in Table III, while complete listings are available as supplementary material.

The structures of **2** and **3** consist of an approximate isosceles triangle of two vanadium atoms and one iron atom with both faces of this triangle capped by bridging sulfides. These atoms define

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Table III. Important Structural Parameters for **2**, **3**, **2**-S, and **4**

			2-S		
	2	**3**	molecule 1	molecule 2	**4**
Distances (Å)					
V(1)–V(2)	2.5098 (7)	2.482 (1)	2.508 (1)	2.503 (1)	2.484 (2)
V(1)–M	2.8956 (7)	2.849 (1)	2.8132 (9)	2.7509 (9)	2.817 (2)
V(1)–S(1)(μ_3-S)	2.3265 (9)	2.354 (1)	2.308 (1)	2.321 (1)	2.320 (3)
V(1)–S(2)(μ_3-S)	2.3104 (9)	2.340 (1)	2.288 (1)	2.312 (1)	2.348 (3)
V(1)–S(3)(μ-S_1 or μ-S_2)	2.4067 (9)	2.398 (1)	2.242 (2)	2.233 (2)	2.406 (3)
V(1)–S(4)(μ-S_1 or μ-S_2)	2.4058 (9)	2.398 (1)			2.400 (3)
V(1)–Cp	1.952 (4)	1.958	1.955 (5)	1.947 (5)	
M–S(1)	2.2616 (9)	2.232 (1)	2.272 (1)	2.264 (1)	2.192 (3)
M–S(2)	2.2502 (8)	2.228 (1)	2.259 (1)	2.263 (1)	2.194 (3)
S(1)–S(3)	2.934 (1)	2.962 (1)			
S(3)–S(4)	2.020 (1)	2.012 (1)			2.020
M–C(1)(N(1))	1.799 (4)	1.666 (3)	1.802 (5)	1.806 (5)	
C(1)(N(1))–O	1.132 (5)	1.163 (4)	1.132 (7)	1.132 (7)	
Angles (deg)					
V(1)–S(1)–M	78.25 (3)	76.8 (1)	75.78 (4)	73.71 (4)	77.2 (1)
V(1)–S(2)–M	78.82 (3)	77.1 (1)	76.43 (4)	73.92 (4)	76.8 (1)
V(1)–S(3)–V(2)	62.83 (2)	62.2 (1)	68.23 (5)	68.24 (5)	62.2 (1)
V(1)–S(4)–V(2)	62.76 (3)	62.4 (1)			62.2 (1)
V(1)–M–V(2)	51.21 (2)	51.8 (1)	52.64 (2)	52.89 (2)	52.4 (0)
V(2)–V(1)–M	64.73 (2)	63.8 (1)	64.31 (3)	65.91 (3)	63.7 (1)
V(1)–S(1)–V(2)	65.24 (3)	63.8 (1)	66.07 (4)	66.12 (4)	64.4 (1)
V(1)–S(2)–V(2)	65.93 (3)	63.8 (1)	66.63 (4)	66.31 (4)	64.2 (1)
S(1)–M–S(2)	92.74 (3)	97.3 (1)	93.36 (4)	93.80 (4)	97.7 (1)
S(1)–V(1)–S(2)	89.54 (3)	91.0 (1)	91.67 (5)	91.02 (5)	90.1 (1)
V(1)–S(3)–S(4)	65.16 (3)	65.2 (1)			65.0 (1)
V(1)–S(4)–S(3)	65.21 (3)	65.2 (1)			65.3 (1)
V(2)–V(1)–Cp	177.2 (1)	177.7 (1)	175.6 (2)	175.7 (2)	
C(1)(N(1))–M–C(2)(N(2))	102.3 (2)	111.2 (1)	90.9 (2)	97.7 (3)	
M–C(1)(N(1))–O(1)	178.0 (3)	169.3 (2)	177.3 (5)	174.8 (5)	

Table IV. Vanadium–Vanadium Distances in Cyclopentadienyl Complexes

compd	d_{V-V}, Å	ref
$(C_5H_5)_2V_2(C_8H_8)$	2.439 (1)	22
$(C_5H_5)_2V_2(CO)_5$	2.462	23
$(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (**3**)	2.482 (1)	this work
$[(CH_3C_5H_4)_2V_2S_4]_2Ni$ (**4**)	2.484 (2)	this work
$(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ (**2-S**)	2.506 (1)	this work
$(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (**2**)	2.510 (1)	this work
$(CH_3C_5H_4)_2V_2S_3(PTD)Pt(PPh_3)_2$[a]	2.556 (2)	21
$(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$	2.574 (3)	2
$((CH_3)_2CHC_5H_4)_2V_2S_4$	2.610 (1)	2
$(CH_3C_5H_4)_2V_2S_5$	2.658 (1)	15
$(C_5H_5)_5V_5O_6$	2.748	24
$(CH_3C_5H_4)_2V_2Se_5$	2.779 (4)	18
$(CH_3C_5H_4)_4V_4S_4$	2.88	18
$(CH_3C_5H_4)_2V_2S_4Fe_2(NO)_2$	2.9572 (8)	4

[a] PTD = 4-phenyl-1,2,4-triazoline-3,5-dione.

a distorted trigonal bipyramid. The V–V edge is also spanned by a transverse (η^2) disulfide. The coordination spheres of the vanadium atoms are completed by methylcyclopentadienyl ligands while the iron atom is further coordinated by three carbonyl ligands in **2** and two nitrosyls in **3**.

The V–V distances in **2**, **2**-S, **3**, and **4** are all within the range 2.482 (1)–2.5098 (7) Å. V–V distances in other structurally characterized cyclopentadienylvanadium compounds are listed in Table IV. The V–V bond lengths in our compounds are shorter than those in $((CH_3)_2CHC_5H_4)_2V_2S_4$[2] and $(CH_3C_5H_4)_2V_2S_5$,[15] which were suggested to represent single V–V bonds. Evaluation of the metal–metal distances in these $(CH_3C_5H_4)V$ dimers is, however, complicated by the presence of different bridging ligand sets. The acute V–S(μ_3-S)–V angles of 65.8 ± 0.8° in **2**, **3**, **2**-S, and **4** in conjunction with V–S(μ-S_2)–V angles of 62.4 ± 0.2° in **2**, **3**, and **4** indicate comparable interactions between the vanadium atoms in these compounds.

The V–Fe distances are approximately 0.08 Å longer in **2** than in **2**-S. A V–Fe single bond length is expected to be 2.60–2.65 Å on the basis of structural results for the $(C_5H_4R)_2V_2S_x$ and $Fe_2(SR)_2(CO)_6$ systems. The iron atoms in both **2** and **2**-S are seven-coordinate by virtue of bonding to two vanadium atoms, two sulfur atoms, and three carbonyl ligands. This situation is very similar to that found for the unique iron in $Fe_3S_2(CO)_9$.[25]

The V–S bonds for **2**, **3**, and **2**-S fall into three categories (Table V). The longest, 2.40 (±0.01) Å, are associated with the μ-η^2-S_2 ligands in **2**, **3**, and **4**. In accord with previously suggested guidelines, this distance falls in the range for V–S single bonds (2.35–2.41 Å) as found, for example, for the μ-η^2-S_2 ligands in $(CH_3C_5H_4)_2V_2S_5$[15] and $(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$.[2] The shortest V–S bonds found in this work are associated with the μ_2-S ligand in **2**-S. This distance, 2.23 Å, is nearly as short as those found for the bridging sulfides in $((CH_3)_2CHC_5H_4)_2V_2S_4$, which average 2.21 Å. Accordingly, we conclude that this is a multiple bond. Intermediate V–S bond lengths are found for the "capping" μ_3-S ligands. These distances, 2.32 Å for **2** and 2.29 Å for **3**, may indicate some degree of π bonding between the vanadium and the μ_3-S atoms. The Fe–S bonds, which average 2.26 Å in **2** and **3**, are slightly elongated by 0.03 Å relative to those found for $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$.[25]

The V–S(μ_3-S) and V–Fe distances in the two crystallographically independent molecules of **2**-S merit closer examination.

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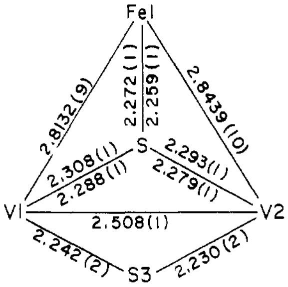
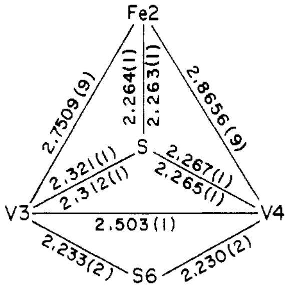
Table V. Vanadium–Sulfur Bond Lengths (Å)

divanadium compds	V–S(μ-S)	V–S(μ-η^1-S_2)	V–S(μ-η^2-S_2)	V–S(μ_3-S)	ref
$(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$			2.40	2.35	this work
$(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$	2.23			2.29	this work
$(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$			2.41	2.32	this work
$(CH_3C_5H_4)_4V_4S_8Ni$			2.403	2.33	this work
$(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$			2.38		2
$((CH_3)_2CHC_5H_4)_2V_2S_4$	2.21	2.27			2
$(CH_3C_5H_4)_2V_2S_5$	2.26	2.32	2.35, 2.40		15
$(CH_3C_5H_4)_2V_2S_4Fe_2(NO)_2$				2.28	4

monovanadium compds	V–S	ref
$(C_5H_5)_2VS_5$	2.45	26
$(NH_4)_3VS_4$	2.14	27
(acacen)VS	2.06	28

Schematic representations of the V_2S_3Fe cores are shown with the pair of μ_3-S atoms eclipsed:





A correlation exists between the V–Fe and the V–S(μ_3-S) distances: vanadium atoms with long V–Fe distances have short V–S(μ_3-S) distances and vanadium atoms with short V–Fe distances have long V–S(μ_3-S) distances. These distortions, which are probably induced by crystal packing forces, indicate complementary V–Fe and V–S(μ_3-S) bonding.

Compound **3** is an example of a $M(NO)_2$-containing *closo*-deltahedron. The Fe–N distances of 1.666 (3) Å compare well with 1.67 Å found in $Fe_2(\mu\text{-SEt})_2(NO)_4$[29] and 1.66 Å found in $Fe_4(\mu_3\text{-S})_3(NO)_7^-$ [19] and are normal for these formally NO^+ ligands. Although the Fe–N–O angles are not perfectly linear at 169.3 (2) and 172.6 (2)°, they still fall within the "near-linear" range and compare well with the Fe–N–O angles in $Fe_2(\mu\text{-SEt})_2(NO)_4$,[29] which average 167.5°. The nitrosyls are slightly bent toward each other with the O–Fe–O angle of 93.1°; for first-row transition-metal dinitrosyls, inward geniculation is not uncommon.[30]

The principal differences observed in the structures of the two V_2FeS_4 clusters **2** and **3** are the tightening of the V–(μ_3-S)–V and the V–S–Fe angles together with shorter V–V and V–Fe distances in the dinitrosyl.

The S–S bond lengths of 2.020 (1) Å in **2** and 2.012 (1) Å in **3** are within the range 2.00–2.10 Å found for c-S_8 and other transition-metal polysulfides.[31a] Slightly short S–S bonds appear to be a general property of the $M_2(\mu\text{-}\eta^2\text{-}S_2)$ functional group.[31b] For **2** the S(1)–S(3) and S(2)–S(4) distances are 2.934 (1) Å and 2.906 (1) Å, respectively, which are shorter than twice the van der Waals radius of sulfur, 3.6 Å. It seems unlikely, however, that they represent significant bonding interactions, and we attribute the close contacts to geometric constraints arising from the placement of a disulfide, two sulfides, and one iron tricarbonyl between the vanadium atoms.

The structure of the V_4S_8Ni cluster **4** consists of a nickel atom coordinated in a pseudotetrahedral fashion by four μ_3-S atoms of the two $(CH_3C_5H_4)_2V_2S_4$ ligands. The central nickel atom is located on a crystallographic 2-fold axis, and therefore the planes defined by V(1)NiV(2) and V(1′)NiV(2′) are required to be mutually perpendicular (Figure 6). The NiS_4 unit also conforms exactly to D_{2d} symmetry. The Ni–S distances of 2.194 (3) and 2.192 (2) Å compare well with the Ni–S distances seen in the structurally related complexes $[(C_5H_5)_2M(SMe)_2]_2Ni^{2+}$ (M = Mo, Nb).[32]

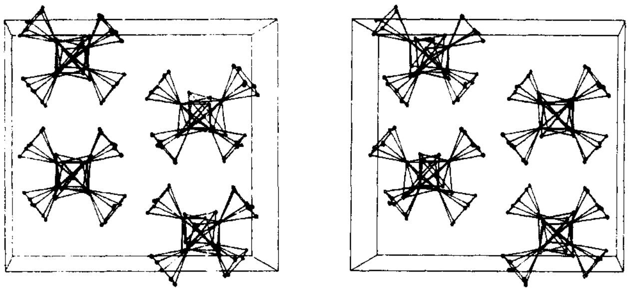


Figure 6. Crystal packing diagram for $[(CH_3C_5H_4)_2V_2S_4]_2Ni$ (**4**).

The pentanuclear spirane defined by the four vanadium atoms and the nickel atom is similar in appearance to the "bow tie" clusters $[(C_5H_5)_2Cr_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2M$ prepared by Pasynskii and co-workers.[9] As in our V_4Ni species, the two Cr_2M subunits in the Russian clusters are mutually perpendicular or nearly so. In an assessment of the electron configuration of **4**, each $(CH_3C_5H_4)_2V_2S_2(S_2)$ unit provides 2e; hence, the cluster has 14e in metal-based orbitals.[40]

Summary

The compound $(CH_3C_5H_4)_2V_2S_4$ has been shown to be an effective precursor for the preparation of cluster compounds containing both early and late transition metals. The $V_2S_4ML_n$ species themselves are kinetically well-behaved and may be further derivatized by virtue of the reactive exocyclic disulfide to form electron-deficient trimers and small cluster compounds. The bifunctional V_4NiS_8 species is of special interest and it may represent a building block for the construction of multimetallic chains. The feasibility of this approach is indicated by the syntheses of the V_4NiS_8Pt and $V_4NiS_8Pt_2$ compounds. Similar approaches can be envisioned starting from the related organometallic ligands $(C_5H_5)_2Cr_2(S)(S\text{-}t\text{-Bu})_2$[5-9] and $(CH_3C_5H_4)_2Mo_2S_4$.[10,11]

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_4O_{10}. All other solvents were reagent grade and were dried over 4A molecular sieves. $Fe(CO)_5$ (Alfa) was filtered through paper under a blanket of nitrogen. Trimethylamine *N*-oxide dihydrate (Aldrich) was repeatedly resublimed at 100 °C in a dynamic vacuum to afford the anhydrous reagent. $(CH_3C_5H_4)_2V_2S_4$,[2] $PPN[Fe(CO)_3NO]$,[16] $[CoI(NO)_2]_x$,[33] and $IrCl(PPh_3)_2(N_2)$[34] were pre-

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pared by the literature methods. All other reagents were obtained from standard commercial sources and used without further purification. $Pt(C_2H_4)(PPh_3)_2$ was prepared according to a recently published procedure[35] although it was sometimes found to be contaminated with significant quantities of *cis*-$PtCl_2(PPh_3)_2$ (20% by elemental analysis), which did not interfere with our syntheses.

Eastman 13181 silica gel thin-layer chromatography plates were used to monitor the reactions. Flash chromatography utilizing a 5 × 15 cm column proved to be the method of choice for purification of the compounds. For this purpose Woehm silica gel (32–63 μm) was employed.

The following instruments were used in this work: IR, Perkin-Elmer 599B or Nicolet 7199; ^1H NMR, Varian EM-390 (with internal frequency lock), Varian HR220 (with ^2H lock), and Nicolet NT-360 (with internal ^2H frequency lock). 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 were isolated as crystalline solids. Microanalytical data were obtained by the University of Illinois Microanalytical Laboratory.

$(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (2). A solution of Me_3NO, 0.092 g (1.23 mmol) in 5.0 mL of CH_2Cl_2, was slowly (1 h) dripped into a solution of $(CH_3C_5H_4)_2V_2S_4$, 0.100 g (0.256 mmol), and $Fe(CO)_5$, 0.175 mL (1.33 mmol), in 10.0 mL of CH_2Cl_2. The reaction mixture was evaporated to dryness and extracted with hexane. The hexane solution was evaporated to a small volume, filtered, and evaporated to dryness. The residue was twice recrystallized from CH_2Cl_2/MeOH, affording 0.060 g (44%) of lustrous black crystalline product. Field desorption mass spectrum: *m/e* 528 (M^+). Anal. Calcd for $C_{15}H_{14}FeO_3S_4V_2$: C, 34.10; H, 2.67; Fe, 10.57; V, 19.29. Found: C, 33.93; H, 2.58; Fe, 10.46; V, 19.08.

$(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (3) from $Hg[Fe(CO)_3NO]_2$. $(CH_3C_5H_4)_2V_2S_4$, 0.200 g (0.520 mmol), and $Hg[Fe(CO)_3NO]_2$, 0.280 g (0.520 mmol), were vigorously stirred together in 60 mL of THF for 9 h. The reaction mixture was filtered to remove insoluble materials, silica gel was added to the filtrate, and the mixture was evaporated to dryness. Flash chromatography of the residue with 1:10 benzene/hexane gave a small amount of unreacted $Hg[Fe(CO)_3NO]_2$ followed by an intense purple band, which was collected, filtered, and evaporated. Crystallization of the residue from CH_2Cl_2/MeOH gave 0.150 g (59%) of a purple-black crystalline product. Electron-impact mass spectrum (70 eV): *m/e* 504 (M^+). Anal. Calcd for $C_{12}H_{14}FeN_2O_2S_4V_2$: C, 28.58; H, 2.80; N, 5.55. Found: C, 29.20; H, 3.10; N, 5.28.

$(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ from $Fe(CO)_2(NO)_2$. PPN[$Fe(CO)_3NO$], 1.50 g (2.11 mmol), was partially dissolved in 50 mL of THF and treated with Et_3N, 0.420 mL (2.00 mmol), and freshly sublimed $NOBF_4$, 0.350 g (3.00 mmol). The PPN[$Fe(CO)_3NO$] completely dissolved with concomitant gas evolution and darkening of the solution. After 5 min, the $Fe(CO)_2(NO)_2$ solution was Schlenk-filtered through Celite into a solution of $(CH_3C_5H_4)_2V_2S_4$, 0.682 g (1.76 mmol), in 50 mL of THF. The solution was refluxed for 45 min and evaporated. The residue was extracted with CH_2Cl_2 and filtered through a bed of silica gel; the resulting filtrate was diluted with MeOH, and then concentrated to give 0.710 g (80%) of purple black crystalline **3**. TLC (3:7 CH_2Cl_2/hexane) and IR (CCl_4 solution) confirmed the identity and purity of this product.

$(CH_3C_5H_4)_2V_2S_4CoC_5H_5$. $(C_5H_5)CoI_2(CO)$[36] was generated by adding I_2, 0.09 g (0.35 mmol), to a concentrated THF solution of $(C_5H_5)Co(CO)_2$, 0.063 g (0.35 mmol). After being stirred at room temperature for 24 h, the purple solution was treated with compound **1**, 0.100 g (0.26 mmol), and Zn dust, 0.052 g (0.80 mmol). The mixture was heated at reflux for 4 h. Removal of the THF in vacuo followed by flash chromatography (30% CH_2Cl_2 in hexane) gave a green band, which was collected and crystallized from MeOH/CH_2Cl_2 to give 0.033 g (25%) of dark green crystals. Electron-impact mass spectrum: *m/e* 512 (M^+). Anal. Calcd for $C_{17}H_{19}CoS_4V_2$: C, 39.88; H, 3.74; S, 25.05. Found: C, 39.70; H, 3.72; S, 25.20.

Table VI. Positional Parameters for Non-Hydrogen Atoms of $(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (**2**)

	x/a	*y/b*	*z/c*
Fe	0.18117 (5)	0.13698 (3)	0.07823 (3)
V(1)	0.43783 (5)	0.21894 (3)	0.20299 (4)
V(2)	0.24040 (5)	0.31852 (3)	0.11405 (4)
S(1)	0.33233 (8)	0.21876 (5)	0.01694 (6)
S(2)	0.21705 (8)	0.21269 (4)	0.23260 (6)
S(3)	0.48375 (8)	0.36062 (5)	0.14808 (7)
S(4)	0.41254 (9)	0.35562 (5)	0.28144 (7)
O(1)	−0.0428 (3)	0.1606 (2)	−0.1239 (2)
O(2)	0.3178 (4)	−0.0189 (2)	0.0289 (3)
O(3)	−0.0039 (4)	0.0391 (2)	0.1774 (3)
C(1)	0.0437 (4)	0.1530 (2)	−0.0455 (3)
C(2)	0.2663 (4)	0.0420 (2)	0.0490 (3)
C(3)	0.0697 (4)	0.0773 (2)	0.1399 (3)
C(4)	0.6703 (3)	0.1783 (2)	0.2237 (3)
C(5)	0.6548 (4)	0.2070 (2)	0.3235 (3)
C(6)	0.5617 (4)	0.1516 (3)	0.3556 (3)
C(7)	0.5169 (4)	0.0893 (2)	0.2753 (3)
C(8)	0.5833 (4)	0.1058 (2)	0.1939 (3)
C(9)	0.7632 (5)	0.2163 (4)	0.1608 (5)
C(10)	0.1685 (3)	0.4354 (2)	0.0008 (3)
C(11)	0.0759 (3)	0.3668 (2)	−0.0389 (3)
C(12)	0.0057 (3)	0.3454 (2)	0.0395 (3)
C(13)	0.0560 (4)	0.4000 (2)	0.1291 (3)
C(14)	0.1567 (3)	0.4549 (2)	0.1057 (3)
C(15)	0.2596 (4)	0.4802 (3)	−0.0583 (3)

$(CH_3C_5H_4)_2V_2S_4IrCl(PPh_3)$. Compound **1**, 0.150 g (0.39 mmol), and $IrCl(PPh_3)_2(N_2)$, 0.362 g (0.46 mmol), were refluxed in THF for 15 min. Silica gel was added to the purple solution, which was then evaporated to dryness. The purple powder was placed atop of a 3-cm plug of silica gel in a 30-mL filter frit and washed extensively with hexane (ca. 250 mL) to remove the PPh_3. The desired product eluted with CH_2Cl_2, evaporation of which gave a purple oil. Two recrystallizations from CH_2Cl_2/hexane gave 210 mg (62%) of dark purple microcrystals. Field-desorption mass spectrum: *m/e* 878 (M^+). Anal. Calcd for $C_{30}H_{29}ClIrPS_4V_2$: C, 41.04; H, 3.32; S, 14.60; Cl, 4.04. Found: C, 41.69; H, 3.25; S, 14.25; C, 4.55.

$[(CH_3C_5H_4)_2V_2S_4]_2Ni$ (4). Compound **1**, 100 mg (0.26 mmol), and $[(C_5H_5)Ni(CO)]_2$, 45 mg (0.15 mmol), were brought to reflux in 30 mL of THF. After 1 h the solution was cooled to room temperature and stirred overnight. The THF was removed in vacuo and the residue extracted with CH_2Cl_2 and filtered through a bed of silica gel. Dilution of the filtrate with hexane and subsequent concentration gave 85 mg (79%) of purple microcrystals. Field-desorption mass spectrum: *m/e* 835 (M^+). Anal. Calcd for $C_{24}H_{28}NiS_8V_4$. C, 34.50; H, 3.38; S 30.70. Found: C, 34.73; H, 3.56; S, 30.19.

$(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ (2-S). PBu_3, 0.225 mL (0.903 mmol), was injected neat into a rapidly stirred solution of **2**, 0.251 g (0.502 mmol), in 10.0 mL of CH_2Cl_2. The red solution was evaporated to dryness, redissolved in hexane, and filtered through a plug (2.5 × 6 cm) of silica. The filtrate was evaporated to dryness, redissolved in CH_2Cl_2, diluted with methanol, and concentrated to incipient crystallization. After the filtrate was cooled to −78 °C and filtered, the yield of analytically pure product was 0.182 g (77%). Field-desorption mass spectrum: *m/e* 496 (M^+). Anal. Calcd for $C_{15}H_{14}FeO_3S_3V_2$: C, 36.31; H, 2.82; Fe, 11.26; V, 20.53. Found: C, 36.24; H, 2.85; Fe, 11.24; V, 20.43.

$(CH_3C_5H_4)_2V_2S_3Fe(NO)_2$ (3-S). Compound **3**, 0.125 g (0.250 mmol), in 25 mL of CH_2Cl_2 was treated with neat PBu_3, 0.080 mL (0.39 mmol). The red slurry was refluxed for 15 min and filtered through a bed of silica gel, and the filtrate diluted with MeOH. Slow evaporation of this solution afforded 0.095 g (80%) of red-black plates. Field-desorption mass spectrum: *m/e* 472 (M^+). Anal. Calcd for $C_{12}H_{14}FeN_2O_2S_3V_2$: C, 30.53; H, 2.99; N, 5.94; S, 20.34. Found: C, 30.90; H, 2.94; N, 5.57; S, 20.54.

$(CH_3C_5H_4)VS_3FeCo_2(NO)_6$. Compound **3-S**, 0.050 g (0.106), $[CoI(NO)_2]_x$, 0.065 g (0.26 mmol), and Zn dust, 0.017 g (0.26 mmol), were refluxed in 30 mL of THF for 30 min. The reaction mixture was filtered, silica gel was added to the filtrate, and the mixture was evaporated to dryness. Flash chromatography of this residue with 10% CH_2Cl_2 in hexane gave a trace of a green compound (ν_{NO} in CCl_4: 1844, 1804, and 1780 cm^{-1}), which was not further characterized, followed by the major red band, which was collected, filtered, and evaporated to dryness. Recrystallization from CH_2Cl_2/MeOH gave 0.027 g (44%) of red-black plates. Electron-impact mass spectrum (70 eV): *m/e* 580 (M^+). Anal. Calcd for $C_6H_7Co_2FeN_6O_6S_3V_2$: C, 13.72; H, 1.76; N, 13.72. Found: C, 13.73; H, 1.63; N, 13.17.

$[(CH_3C_5H_4)_2V_2S_3]_2Ni$ (4-2S). Compound **4**, 30 mg (0.036 mmol), was dissolved in 10 mL of CH_2Cl_2 and treated with neat PBu_3, 0.019 mL (0.075 mmol), to cause an immediate color change from purple to red-orange. The solution was stirred for 10 min, filtered through a bed of silica gel, diluted with EtOH, and concentrated to give 21 mg (75%) of red crystals. Field-desorption mass spectrum: *m/e* 771 (M^+).

$(CH_3C_5H_4)_2V_2S_4Fe(CO)_3Pt(PPh_3)_2$. Compound **2**, 0.057 g (0.107 mmol), and $Pt(PPh_3)_2(C_2H_4)$, 0.120 g (0.161 mmol), were dissolved in 5.0 mL of CH_2Cl_2 to give a wine red solution. The reaction mixture was

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Table VII. Positional Parameters for Non-Hydrogen Atoms of $(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ (**2**-S)

	x/a	*y/b*	*z/c*
Fe(1)	−0.01160 (6)	0.13219 (3)	0.36879 (4)
Fe(2)	0.49492 (6)	−0.04009 (3)	0.32520 (4)
V(1)	0.00213 (7)	0.18934 (3)	0.20106 (5)
V(2)	−0.21906 (7)	0.18783 (3)	0.24471 (5)
V(3)	0.34441 (7)	−0.08788 (3)	0.16399 (5)
V(4)	0.57740 (7)	−0.07038 (3)	0.15243 (5)
S(1)	−0.0336 (1)	0.22025 (5)	0.34659 (8)
S(2)	−0.1121 (1)	0.11393 (4)	0.21384 (8)
S(3)	−0.1762 (1)	0.23195 (6)	0.1189 (1)
S(4)	0.5278 (1)	−0.12144 (4)	0.27081 (8)
S(5)	0.4386 (1)	−0.00536 (4)	0.17451 (8)
S(6)	0.4283 (1)	−0.10975 (6)	0.0369 (1)
O(1)	0.2575 (4)	0.1520 (2)	0.4790 (3)
O(2)	0.0353 (4)	0.0190 (2)	0.3779 (3)
O(3)	−0.1467 (4)	0.1302 (2)	0.5313 (3)
O(16)	0.7495 (4)	0.0013 (2)	0.4306 (3)
O(17)	0.3356 (5)	0.0470 (2)	0.3680 (3)
O(18)	0.4308 (5)	−0.1018 (2)	0.4829 (3)
C(1)	0.1548 (5)	0.1442 (2)	0.4344 (4)
C(2)	0.0166 (5)	0.0630 (2)	0.3742 (4)
C(3)	−0.0979 (5)	0.1304 (2)	0.4663 (3)
C(4)	0.2188 (5)	0.2181 (2)	0.2303 (4)
C(5)	0.1502 (5)	0.2385 (2)	0.1419 (4)
C(6)	0.1061 (5)	0.1979 (2)	0.0763 (4)
C(7)	0.1488 (5)	0.1508 (2)	0.1243 (4)
C(8)	0.2179 (5)	0.1630 (2)	0.2183 (4)
C(9)	0.2901 (6)	0.2490 (3)	0.3183 (6)
C(10)	−0.4410 (4)	0.2094 (2)	0.1912 (3)
C(11)	−0.3900 (5)	0.2359 (2)	0.2782 (4)
C(12)	−0.3532 (5)	0.1991 (2)	0.3528 (4)
C(13)	−0.3779 (5)	0.1491 (2)	0.3117 (4)
C(14)	−0.4296 (4)	0.1555 (2)	0.2121 (4)
C(15)	−0.5016 (5)	0.2347 (3)	0.0960 (4)
C(16)	0.6543 (5)	−0.0158 (2)	0.3871 (4)
C(17)	0.3988 (6)	0.0137 (3)	0.3510 (4)
C(18)	0.4551 (6)	−0.0776 (2)	0.4216 (4)
C(19)	0.1347 (4)	−0.0555 (2)	0.1488 (3)
C(20)	0.1700 (4)	−0.0808 (2)	0.2394 (4)
C(21)	0.1916 (5)	−0.1342 (2)	0.2236 (4)
C(22)	0.1680 (5)	−0.1422 (2)	0.1229 (5)
C(23)	0.1335 (4)	−0.0938 (2)	0.0768 (4)
C(24)	0.0955 (5)	0.0013 (2)	0.1328 (4)
C(25)	0.8043 (4)	−0.0802 (2)	0.2076 (4)
C(26)	0.7662 (5)	−0.1040 (2)	0.1174 (4)
C(27)	0.7148 (5)	−0.0654 (3)	0.0480 (4)
C(28)	0.7194 (5)	−0.0178 (2)	0.0954 (4)
C(29)	0.7743 (4)	−0.0259 (2)	0.1939 (4)
C(30)	0.8716 (6)	−0.1070 (3)	0.2996 (5)

evaporated to dryness, redissolved in toluene, and filtered through a plug of silica (2.5 × 6.0 cm). The filtrate was evaporated to dryness and recrystallized from CH_2Cl_2/hexane to give 0.130 g (97%) of fibrous purple crystals. Fast-atom-bombardment mass spectrum: *m/e* 1163 ($C_{48}H_{44}FeP_2PtS_4V_2^+$). Anal. Calcd for $C_{48}H_{44}FeP_2PtS_4V_2$: C, 49.08; H, 3.55; Fe, 4.48; V, 8.16. Found: C, 48.93; H, 3.51; Fe, 4.45; V, 8.13.

$[(CH_3C_5H_4)_2V_2S_4]_2NiPt(PPh_3)_2$ (4·Pt(PPh$_3$)$_2$). Compound **4**, 20 mg (0.024 mmol), was dissolved in 15 mL of CH_2Cl_2 and treated with $Pt(PPh_3)_2(C_2H_4)$, 20 mg (0.026 mmol), to give a steel blue solution. After the mixture was stirred for 10 min, the solvent was removed in vacuo and the residue chromatographed on a 2 × 8 in. Bio-Beads SX-2 column packed with CH_2Cl_2. The blue band was collected, diluted with hexane, and concentrated to give 30 mg (82%) of blue powder.

$[(CH_3C_5H_4)_2V_2S_4]_2NiPt_2(PPh_3)_4$ (4·2Pt(PPh$_3$)$_2$). Compound **4**, 30 mg (0.035 mmol), was dissolved in 15 mL of benzene and treated with $Pt(C_2H_4)(PPh_3)_2$, 75 mg (0.10 mmol), to give a Kelly green solution, which was heated to 40 C for 10 min, cooled, filtered, and evaporated to dryness. The residue was chromatographed on a 5 × 20 cm Bio-Beads column packed with benzene. The green fraction was collected and stripped to dryness. Slow recrystallization of the residue from hexane/CH_2Cl_2 gave 75 mg (94%) of green microcrystals. Anal. Calcd for $C_{96}H_{98}NiP_4Pt_2S_8V_4$: C, 50.68; H, 3.90; Ni, 2.58. Found: C, 51.09; H, 4.14; Ni, 2.29.

Mössbauer Spectroscopy. Mössbauer transmission spectra were collected with a vertical arrangement of source (^{57}Co/Rh), sample, and detector. Calibration of the system was made with known spectral values for metallic iron foil (12 μm). The regulated sample temperature was measured with a Cu/Cu–Ni thermocouple. Spectral parameters of δ, Δ, Λ, and peak area were obtained with the computer program MOSBFIT using least-squares fitting to a sum of Lorentzian components.[37]

Table VIII. Positional Parameters (×10^4) for $(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (**3**)

atom	*x/a*	*y/b*	*z/c*
Fe	2572 (1)	4294 (1)	3372 (1)
V(1)	322 (1)	3645 (1)	1887 (1)
V(2)	2573 (1)	3414 (1)	1514 (1)
S(1)	1819 (1)	5066 (1)	1921 (1)
S(2)	2009 (1)	2646 (1)	2899 (1)
S(3)	597 (1)	3710 (1)	233 (1)
S(4)	741 (1)	2260 (1)	829 (1)
O(1)	1397 (3)	5106 (2)	4855 (2)
O(2)	5381 (2)	4448 (2)	4177 (2)
N(1)	1762 (2)	4752 (2)	4194 (2)
N(2)	4235 (2)	4375 (2)	3785 (2)
C(a1)	−1969 (3)	3410 (3)	1349 (2)
C(a2)	−1539 (3)	2874 (3)	2242 (3)
C(a3)	−1042 (3)	3601 (3)	2972 (2)
C(a4)	−1153 (3)	4599 (3)	2551 (3)
C(a5)	−1721 (3)	4475 (3)	1563 (3)
C(a6)	−2618 (3)	2970 (4)	361 (3)
C(b1)	4672 (3)	2615 (3)	1867 (2)
C(b2)	4862 (3)	3702 (3)	1835 (2)
C(b3)	4299 (3)	4085 (3)	901 (2)
C(b4)	3760 (3)	3212 (3)	340 (2)
C(b5)	3977 (3)	2322 (3)	916 (3)
C(b6)	5177 (4)	1895 (4)	2727 (4)

Table IX. Positional Parameters (×10^4) for $(CH_3C_5H_4)_4V_4S_8Ni$ (**4**)

atom	*x/a*	*y/b*	*z/c*
V(1)	1959 (1)	6810 (1)	3074 (1)
V(2)	1929 (1)	5709 (1)	1884 (1)
Ni	0	6268 (1)	2500
S(1)	1119 (2)	5399 (2)	3158 (2)
S(2)	1102 (2)	7133 (2)	1816 (2)
S(3)	3320 (2)	6786 (2)	2055 (2)
S(4)	3328 (2)	5720 (2)	2869 (2)
C(1)	2942 (8)	7598 (9)	4046 (7)
C(2)	2390 (11)	8246 (11)	3580 (9)
C(3)	1363 (12)	8104 (10)	3705 (10)
C(4)	1248 (11)	7378 (12)	4252 (8)
C(5)	2210 (15)	7058 (9)	4473 (7)
C(6)	4077 (13)	7525 (18)	4125 (11)
C(7)	2888 (9)	4922 (10)	891 (8)
C(8)	2343 (10)	4283 (9)	1375 (8)
C(9)	1305 (12)	4404 (9)	1296 (9)
C(10)	1134 (11)	5122 (11)	736 (8)
C(11)	2080 (14)	5439 (10)	490 (8)
C(12)	4009 (12)	4989 (15)	792 (11)

X-ray Crystallography. The details of the crystal data, data collection methods, and refinement procedures are presented in Table X. All data collections were obtained at room temperature, 22 ± 2 °C.

$(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (2). Dark green single crystals were grown by cooling a saturated hexane solution to −25 °C. A prismatic crystal was mounted on a glass fiber with the long dimension parallel to the spindle axis.

The structure was solved by direct methods;[38] positions for two of the metal atoms were deduced from an *E* map. A weighted difference Fourier map gave positions for the four sulfur atoms along with the third metal atom and subsequent least-squares–difference Fourier calculations revealed positions for all remaining atoms including the hydrogens. The final cycle of least-squares refinement, which employed anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms, converged to R = 0.028 and R_w = 0.036 with a maximum change/error of 0.03.[39] Fractional atomic co-

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(37) Chrisman, B. L.; Tumolillo, T. A. Technical Report No. 178; Physics Department, University of Illinois: Urbana, IL.

(38) Sheldrick, G. M. "SHELX 76, A Program for Crystal Structure Determination", University of Cambridge, England, 1976.

(39) $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = [\sum_w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The function minimizes was $\sum w||F_o| - |F_c||^2$. Scattering factor tables for neutral atoms were taken from: Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101. Anomalous dispersion corrections for non-hydrogen atoms were taken from pp 149–150.

Table X. Crystal Data Collection and Refinement Parameters

	$C_{15}H_{14}FeV_2S_4O_3$ (**2**)	$C_{12}H_{14}FeV_2S_4N_2O_2$ (**3**)	$C_{24}H_{28}NiV_4S_8$ (**4**)
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	*Pbcn*
a, Å	9.853 (2)	10.90 (3)	16.014 (4)
b, Å	15.652 (3)	12.680 (5)	14.477 (3)
c, Å	12.821 (3)	14.016 (5)	12.990 (3)
α, deg	90	90	90
β, deg	105.89 (2)	103.01 (3)	90
γ, deg	90	90	90
V, Å^3	1901.7 (7)	1765 (1)	3011.6 (20)
Z	4	4	4
cryst dimens, mm	0.24 × 0.25 × 0.50	0.48 × 0.65 × 0.22	0.06 × 0.26 × 0.34
radiation	Mo Kα	Mo Kα	Mo Kα
diffractometer	Syntex $P2_1$	Nicolet P$\bar{1}$	Nicolet R3
abs coeff, cm^{-1}	21.24	22.8	24.3
scan technique	$2\theta/\theta$	ω	$2\theta/\theta$
2θ scan range, deg	3–55	3–60.4	4–50
no. of unique data	4917	5227	2458
no. of data processed	4380	3926	1693
R_F	0.028	0.031	0.081
R_{wF}	0.036	0.030	0.081

ordinates are presented in Table VI.

$(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ (2-S). Opaque single crystals were grown by cooling a saturated hexane solution to −25 °C. A prismatic crystal was mounted on a glass fiber with its longest dimension along the spindle.

The structure was solved by direct methods;[38] positions for the six metal atoms were deduced from an *E* map. A weighted difference Fourier map gave positions for the six sulfur atoms, and subsequent least-squares–difference Fourier calculations revealed positions for the remaining nonhydrogen atoms. In the latter stages of refinement, most of the hydrogen atoms appeared in difference Fourier maps; however, the hydrogen positions did not refine in a satisfactory manner so they were placed in fixed positions. Since the total number of variables exceeded the current software limits, the structure factors were refined with the least-squares matrix blocked into molecular units. The parameters for molecule one were refined while those for molecule two were held constant and then the reverse was done, a "blocked-cascade" procedure. Since the scattering of two molecules is independent, the blocked least-squares refinement converged without problems. The only consequence of this technique is slightly underestimated positional errors. In the final cycle of least-squares refinement, all non-hydrogen positional parameters were varied with anistropic thermal parameters in two molecular blocks. The hydrogen atoms were fixed in calculated positions and assigned a fixed isotropic thermal parameter of 0.078 Å^2. R and R_w converged to 0.038 and 0.051, respectively, with a maximum change/error of 0.002. Fractional atomic coordinates are presented in Table VII.

$(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (3). Black single crystals were grown by slow diffusion of methanol into a CH_2Cl_2 solution of **3**. The crystallographic experiments were conducted at the Crystalytics Co. A rectangular parallelepiped crystal was mounted on a 0.15-mm glass fiber with its longest dimension nearly parallel to the ϕ axis of the diffractometer.

The structure was solved by direct methods. The 23 non-hydrogen atoms were located by using the SHELXTL direct-methods program, while the hydrogen atoms were located after three refinement cycles by least-squares–difference Fourier calculations. The final cycle of the refinement, which employed anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms, converged to $R = 0.031$ and $R_w = 0.030$ with a "goodness-of-fit" of 1.61. Fractional atomic coordinates are presented in Table VIII.

$[(CH_3C_5H_4)_2V_2S_4]_2Ni$ (4). A black, thin plate obtained by recrystallization from CH_2Cl_2/EtOH, was affixed to a fine glass fiber. Preliminary photographic characterization indicated Laue symmetry *mmm*; systematic absences uniquely provided the orthorhombic space group *Pbcn*.

ψ-Scans were taken in 10° increments about the diffraction vector. The nonsinusoidal character of these ψ-scan data indicated the presence of significant edge effects in the diffraction data. Corrections for absorption were made by using the ψ-scan data and a procedure for fitting data to a thin plate. Data were discarded for which the incident or diffracted beam was close (<3°) to the plate face (100). Minimum/maximum transmission = 0.622/0.875. Although these results were superior (by final *R* factor) to those obtained by Gaussian integration methods, the rather high final residuals likely reflect a less than satisfactory correction for absorption.

The structure was solved by direct methods (SOLV-SHELXTL), which provided the metal and S atom positions. The C atoms were obtained from a subsequent difference Fourier synthesis. Ring hydrogen atoms were placed in idealized locations (d(C–H) = 0.96 Å), but no attempt was made to incorporate contributions from methyl groups hydrogen atoms due to the uncertainty in their rotational orientation. In the final cycles of a blocked-cascade refinement, (see above) all non-hydrogen atoms were refined with anisotropic temperature factors. The final difference map contained a peak (1.87 e Å^{-3}) displaced by (0, $y/2$, 0) from Ni along the crystallographic 2-fold symmetry axis, which also passes through the Ni atom; other map features (next ten, 0.81–0.64 e Å^{-3}) were contained within the heavy-atom structure and are further indication of unresolved problems associated with the absorption correction. Fractional atomic coordinates are presented in Table IX.

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Note Added in Proof. Toluene slurries of unactivated nickel powder react directly with $(CH_3C_5H_4)_2V_2S_4$ to give the V_4Ni cluster **4** in good yield.

Registry No. **1**, 87174-39-8; **2**, 83587-85-3; **2**-S, 83587-86-4; **3**, 87174-43-4; **3**-S, 99606-61-8; **4**, 99606-60-7; **4**-2S, 99606-62-9; **6**·Pt$(PPh_3)_2$, 99617-59-1; **6**·2Pt$(PPh_3)_2$, 99617-60-4; $Fe(CO)_5$, 13463-40-6; $Hg[Fe(CO)_3NO]_2$, 63270-61-1; $Fe(CO)_2(NO)_2$, 13682-74-1; PPN$[Fe(CO)_3NO]$, 61003-17-6; $(CH_3C_5H_4)_2VS_4CoC_5H_5$, 99595-28-5; $(C_5H_5)CoI_2(CO)$, 12012-77-0; $(C_5H_5)Co(CO)_2$, 12078-25-0; $(CH_3C_5H_4)_2V_2S_4IrCl(PPh_3)$, 99606-59-4; $IrCl(PPh_3)_2(N_2)$, 15695-36-0; $[(C_5H_5)Ni(CO)]$, 63912-73-2; $(CH_3C_5H_4)VS_3FeCo_2(NO)_6$, 99595-29-6; $CoI(NO)_2$, 44387-12-4; $(CH_3C_5H_4)_2V_2S_4Fe(CO)_3Pt(PPh_3)_2$, 99606-63-0; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; V, 7440-62-2; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0; Ir, 7439-88-5.

Supplementary Material Available: Tables for compounds **2**, **2**-S, and **4** of thermal parameters, hydrogen atom parameters, complete bond angles and bond distances, and observed and calculated structure factors (55 pages). Supplementary crystallographic data for $(CH_3C_5H_4)_2V_2S_3Fe(CO)_3$ were submitted with ref 4. Ordering information is given on any current masthead page.

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(40) Compound **4** and the so-called "bow tie" clusters of Pasynskii are relatives of $(C_5H_5)_4Ni_5S_4$: Vahrenkamp, H.; Dahl, L. F. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 144.