

The Chemistry of Bis(cyclopentadienyl)divanadium Tetrasulfide:  
Elucidation of Ligand Dependent Reactivity and the Influence of  $\pi$ -Bonding

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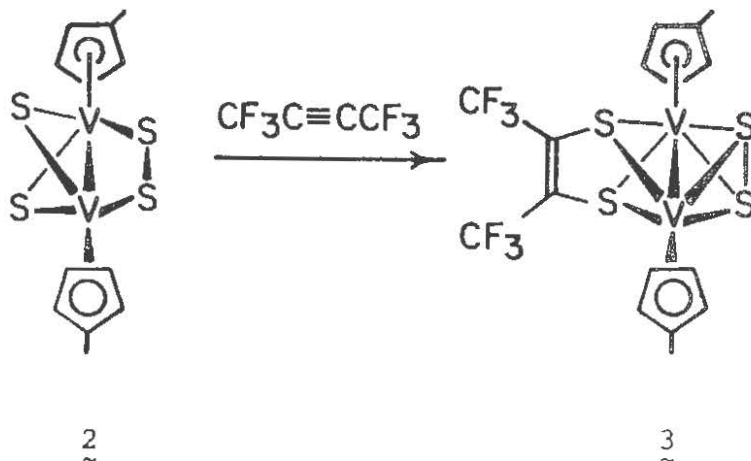
Final Seminar

October 13, 1983

There is now reason to suggest that binding and activation of unsaturated organic [1] and inorganic substrates [2,3] by metal sulfides occurs at the sulfur ligands and not at the metal. These exciting developments considerably broaden the scope and chemical significance of the nonmetal component in transition metal-nonmetal hybrids.

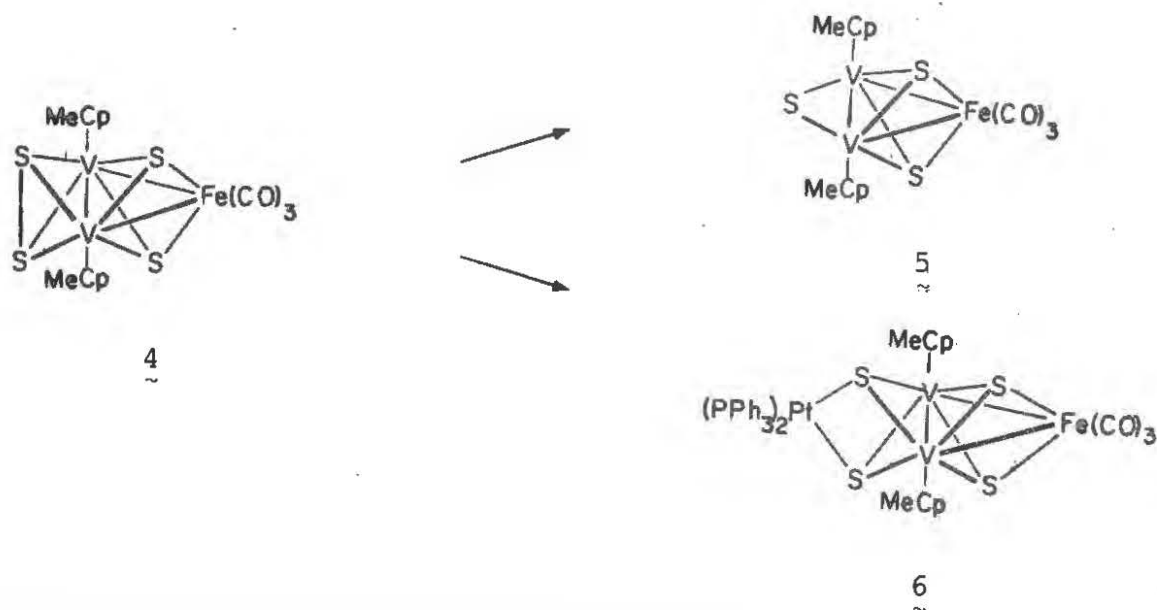
The concept of ligand to metal donation of electron density [4] via  $\pi$ -type orbitals is especially important for understanding the chemistry of the cyclopentadienyl vanadium sulfides since it is the sulfur ligands which interact with external reagents. Furthermore, systematic investigations of  $\pi$  bonding in multinuclear complexes are relatively rare [5] and are important for understanding the chemistry of both discrete and nonmolecular metal sulfides.

The synthetic entry into cyclopentadienylvanadium sulfide chemistry is provided by  $(RC_5H_4)_2V_2S_5$  (1), which was first reported in 1966 [6]. The disposition of the sulfur ligands in this compound was unknown until the preparation and structural characterization of  $(CH_3C_5H_4)_2V_2S_5$ , which revealed the presence of a transverse disulfide ( $\mu-\eta^2-S_2$ ), a parallel disulfide ( $\mu-\eta^1-S_2$ ), and a bridging sulfide ( $\mu-S$ ) [7]. Desulfurization of the  $30e^-$  complex 1 by tri-*n*-butyl phosphine ( $PBu_3$ ) produces the  $26e^-$  complex  $(RC_5H_4)_2V_2S_4$  (2).



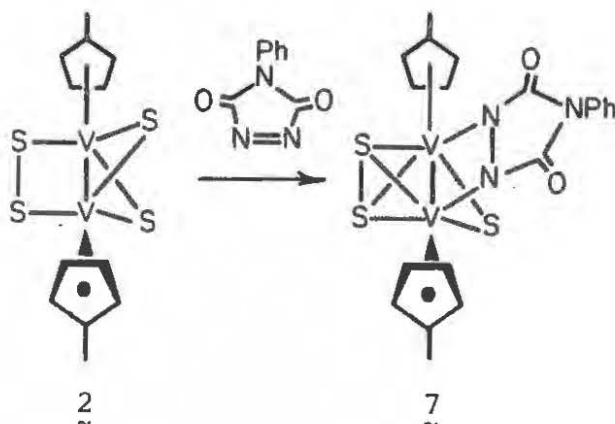
An analysis of the V-S distances in the electron deficient 2 provides evidence for efficient  $\pi$  donation from the bridging sulfides. Reaction of 2 with the electrophilic acetylene hexafluoro-2-butyne results in the formation of a dithiolene complex,  $(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$  (3) via attack at the nucleophilic  $\mu-S$  ligands. During this process, the  $\mu-\eta^1-S_2$  rotates to a  $\mu-\eta^2$  geometry, apparently as a result of decreased  $\pi$  donation from the bridging sulfides.

Treatment of **2** with  $\text{Fe}(\text{CO})_5$  in the presence of  $(\text{CH}_3)_3\text{NO}$  results in the formation of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4\text{Fe}(\text{CO})_3$  (**4**), the first example of a vanadium-iron cluster. Like the product of the acetylene reaction,



**4** contains a  $\mu\text{-}\eta^2\text{-S}_2$  ligand. This  $\mu\text{-}\eta^1\text{-S}_2$  ligand is electrophilic, reacting with  $\text{PBU}_3$  to produce  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4\text{Fe}(\text{CO})_3$  (**5**) and with  $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$  to produce  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4\text{Fe}(\text{CO})_3\text{Pt}(\text{PPh}_3)_2$  (**6**) [8]. The solid state structures of **4** ( $48e^-$ ) and **5** ( $44e^-$ ) suggest that both V-Fe and V-S  $\pi$ -interactions are important for understanding the electronic structure of these clusters.

Compound **2** reacts with 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) [9] to yield  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_3$  (PTD) (**7**). Structural characterization



of the  $\text{Pt}(\text{PPh}_3)_2$  derivative indicates that **7** possesses  $\mu\text{-S}$ ,  $\mu\text{-}\eta^2\text{-S}_2$ , and  $\mu\text{-}\eta^1\text{-PTD}$  ligands. Desulfurization of **7** produces  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_2$  (PTD) (**8**) which is structurally analogous to **2**. Further reaction

of 8 with PTD forms  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_2(\text{PTD})_2$  (9). The  $\mu\text{-}\eta^2\text{-S}_2$  ligand of 9 apparently results from oxidative coupling of two  $\mu\text{-S}$  ligands and is the first direct observation of this type of reaction.

Compound 2 can be further desulfurized by  $\text{PBU}_3$  to form higher nuclearity vanadium clusters,  $(\text{RC}_5\text{H}_4)_4\text{V}_4\text{S}_4$  (10) (a cubane [10]) and  $(\text{RC}_5\text{H}_4)_5\text{V}_5\text{S}_6$  (11) (structurally analogous to the known  $(\text{C}_5\text{H}_5)_5\text{V}_5\text{O}_6$  [11]), with interesting structural and magnetic properties. The  $56e^-$  complex 10 is the most electron deficient organotransition metal cubane to date. Theoretical studies on  $(\text{C}_5\text{H}_5)_4\text{M}_4\text{A}_4$  compounds predict that a  $56e^-$  cluster should be diamagnetic with  $\text{D}_{2d}$  symmetry [12]. However, compound 10 is paramagnetic with nearly ideal  $\text{T}_d$  symmetry.

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