Table **I.** Percent Abundance of Products Observed in the Reactions of MD^+ Ions with Various Hydrocarbons

		metal hydride ion		
hydrocarbon	products	FeD^+	CoD^+	NiD^+
H_2	$MH^+ + HD$	NR	100	100
CH_4	$MH^+ + CH_3D$	NR	NR	20
	$MCH_3^+ + HD$			80
C_2H_6	$MC_2H_5^+ + HD$	NR	100	100
C_3H_8	$MC_3H_5^+ + HD, H_2$		100	100
	$MC_3H_7^+ + HD$	100		
n-C_4H_{10}	$MC_3H_5^+ + HD, CH_4$			77
	$MC_4H_7^+ + HD, H_2$	60	100	23
	$MC_4H_9^+ + HD$	40		
i-C_4H_{10}	$MC_3M_5^+ + HD, CH_4$			67
	$MC_4H_7^+ + HD, H_2$	55	100	33
	$MC_4H_9^+ + HD$	45		
neo-C_5H_{12}	$MC_4H_7^+ + HD, CH_4$	12	100	100
	$MC_5H_{11}^+ + HD$	88		
C_2H_4	$MH^+ + C_2H_3D$	100	77	17
	$MC_2H_3^+ + HD$		10	28
	$MC_2H_2D^+ + H_2$		13	55
C_3H_6	$MH^+ + C_3H_5D$	18		
	$MCH_3^+ + C_2H_3D$	11	6	9
	$MCH_2D^+ + C_2H_4$	6	4	4
	$MC_2H_4^+ + CH_2D$			9
	$MC_2H_3D^+ + CH_3$			8
	$MC_3H_5^+ + HD$	28	36	37
	$MC_3H_4D^+ + H_2$	37	54	33
c-C_6H_6	$MC_6H_5^+ + HD$			17
	$MC_6H_6^+ + D$	31	100	37
	$MC_6H_5D^+ + H$	52		43
	$MC_6H_6D^+$	17		3

major product differences between the two butane isomers, in contrast to the bare metals whose reactivity differs with the change in the carbon skeleton.[3] FeD^+ forms both an alkyl and allyl product, while CoD^+ forms exclusively a metal–allyl product. Once again NiD^+ is an exceptional case, losing CH_4 and HD as its major pathway. CoD^+ and NiD^+ both react with neopentane by sequential HD and CH_4 loss to form metal–allyl products exclusively. FeD^+, however, loses predominantly HD to form initially the neopentyl-iron ion. In this case multiple dehydrogenations are not observed due to the absence of β-hydrogens.

While none of the bare metal ions under consideration react with ethene, all three hydrides are reactive producing D/H exchange and (except for FeD^+) dehydrogenation products. Where dehydrogenation does occur, so does considerable scrambling of the deuterium label. Similarly, all three hydrides dehydrogenate propene as the major product with considerable retention of deuterium. Both of these results require a reversible β-hydrogen transfer in the reaction complex. Minor products corresponding to loss or retention of $CH_3\cdot$ are consistent with CID results on metal–allyl complexes formed by an alternate route.[12]

Benzene displaces D· from CoD^+ as the only product. This is consistent with collisional activation of an intact benzene–hydride complex of Co^+ which produced $Co(C_6H_6)^+$ exclusively.[12] In the case of FeD^+, loss of H· is the main product indicating that the deuterium and the ring protons exchange. NiD^+ reacts similarly to FeD^+ but also produces a dehydrogenation product suggesting a metal phenyl structure for the exchange intermediate.

These preliminary results demonstrate the ability of small ligands bound to the metal center to alter dramatically the inherent reactivity of gas-phase metal ions. In sharp contrast to the bare metal ions Fe^+, Co^+, and Ni^+, which add nearly exclusively across C–C bonds of linear alkanes, the corresponding metal hydrides favor initial oxidative addition across C–H bonds. Furthermore, it is striking that Co^+ and Ni^+ are rendered more reactive by a hydride ligand bound to the metal center. The apparent order of reactivity $NiD^+ > CoD^+ > FeD^+$ is certainly the opposite of what would be expected on the basis of the bare metal reactivity. The effects of other ligands such as CH_2, CH_3, O, and S on the reactivity of gas-phase metal ions are being actively pursued in our laboratory.

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Synthesis and Structures of $(i\text{-}PrC_5H_4)_2V_2S_4$ and $(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$: The Influence of π-Bonding on the Geometry of the μ-S_2 Ligand

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The compound $(MeCp)_2V_2S_4$[2] (MeCp = η^5-methylcyclopentadienyl) has been shown to be useful in the preparation of vanadium sulfide cluster compounds and has proven to be a versatile precursor for a host of other derivatives.[3] Although we have been unable to obtain single crystals of $Cp_2V_2S_4$ or $(MeCp)_2V_2S_4$ suitable for X-ray diffraction, the relatively high symmetry of the V_2S_4 core was suggested by the ^1H NMR spectrum of the MeCp derivative. On the basis of these data and IR measurements, we indicated[3] that precedented structural possibilities for the V_2S_4 core included $V_2(\mu\text{-}\eta^2\text{-}S_2)_2$ (cf. $(VS_4)_n$[4]) and $V_2(\mu\text{-}S)_2(\mu\text{-}\eta^2\text{-}S_2)$ (cf. Wachter's isomer of $(Me_5C_5)_2Mo_2S_4$[5]). In this report we describe the unanticipated (and unprecedented) structures of $(i\text{-}PrCp)_2V_2S_4$ and the acetylene adduct of $Cp_2V_2S_4$. In a broader context, our results provide fresh insights into the important effects of π-bonding in electron-deficient transition-metal compounds.

$(i\text{-}PrCp)_2V_2S_4$ was prepared in three steps from $(i\text{-}PrCp)_2VCl_2$[6] by established procedures[7] and was shown to be closely related to $(MeCp)_2V_2S_4$ based on the superimposability of their optical spectra.[8] The structure[9] of $(i\text{-}PrCp)_2V_2S_4$ (**1**) is depicted in Figure 1. The two $(i\text{-}PrCp)V$ moities are bridged by one $\mu\text{-}\eta^1\text{-}S_2$ and two μ-S ligands. The V···V distance of 2.610 (1) Å is appropriate for a single bond. The average V–S(μ-S) and V–S(S_2) distances

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

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[8] Anal.: C, H, V. IR (mineral oil mull) 1418 (m), 1316 (s), 1061 (m), 1046 (s), 925 (s), 818 (vs) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.87 (m, 2 H), 6.70 (m, 2 H), 3.05 (septet, 1 H, $J_{HH} = 7\ s^{-1}$), 1.38 (d, 6 H, $J_{HH} = 7\ s^{-1}$); electron-impact mass spectrum (70 eV), m/e 444 (100%, M^+), 410 (14.6%, $C_{16}H_{20}S_3V_2^+$), 376 (85.4%, $C_{16}H_{18}S_2V_2^+$); UV–vis (THF) λ_{max} 366 nm (6900 L mol^{-1} cm^{-1}).

[9] $(i\text{-}PrCp)_2V_2S_4$ (**1**) crystallizes in the monoclinic space group $P2_1/c$ with a = 10.390 (3) Å, b = 10.103 (2) Å, c = 18.485 (5) Å, β = 102.08 (2)°, V = 1897.5 (7) $Å^3$, Z = 4, and μ = 13.71 cm^{-1} (Mo K_α). A total of 3255 reflections ($4° \leq 2\theta \leq 47°$) were collected on a Nicolet R3 diffractometer of which 2799 were unique. Of these reflections 2072 with $F_o \geq 3\sigma(F_o)$ were used in the subsequent direct-methods solution and refinement. The final discrepancy indices with anisotropic refinement of all non-hydrogen atoms were R_f = 5.90%, R_wF = 5.91%, and GOF = 1.420.

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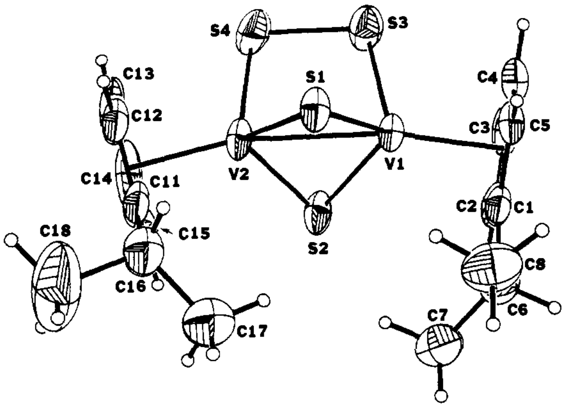


Figure 1. Molecular structure and labeling scheme for $(i\text{-PrCp})_2V_2S_4$ (**1**). The angle between the planes of the Cp rings is 25.7 (3)°. Important metrical parameters: V(1)–V(2), 2.610 (1); V(1)–S(1), 2.217 (2); V(1)–S(2), 2.210 (2); V(1)–S(3), 2.268 (2); V(2)–S(1), 2.219 (2); V(2)–S(2), 2.213 (2); V(2)–S(4), 2.280 (2); S(3)–S(4), 2.027 (3) Å.

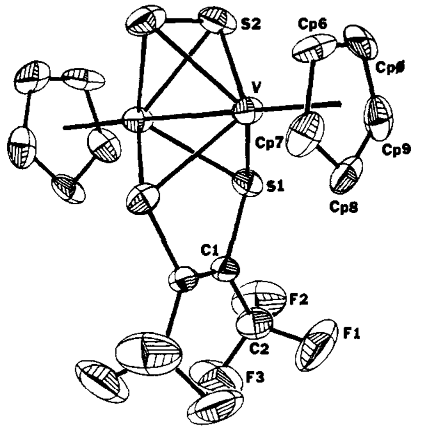
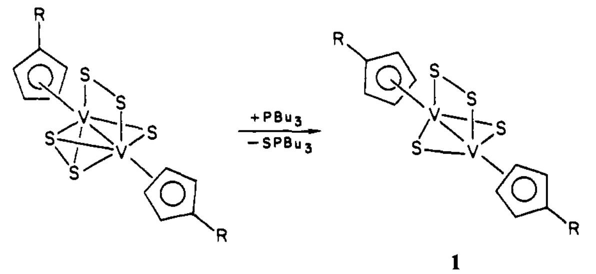


Figure 2. Molecular structure and labeling scheme for $Cp_2V_2S_4{\cdot}C_2(CF_3)_2$ (**2**). For clarity only one of the two rotational orientations of Cp ring is shown. The four sulfur atoms are coplanar (max deviation ±0.0004 Å). Important metrical parameters: V–V′, 2.574 (3); V–S(1), 2.429 (2); V–S(1′), 2.430 (2); V–S(2), 2.380 (2); V–S(2′), 2.380 (2); S(2)–S(2′), 2.040 (4); S(1)–C(1), 1.778 (6); C(1)–C(1′), 1.321 (11); C(1)–C(2), 1.511 (10) Å.

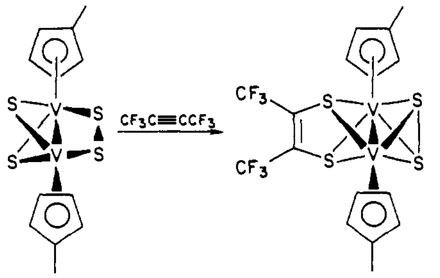
of 2.21 and 2.27 Å, respectively, are quite short (vide infra). It is mechanistically appealing to propose that **1** is formed from $(i\text{-PrCp})_2V_2S_5$ via S-atom abstraction from the μ-η^2-S_2 unit in the latter (eq 1). Obviously this regiochemistry is difficult to prove in the present case although it is well established in the conversions of $(MeCp)_2V_2Fe(CO)_3S_4$ to $(MeCp)_2V_2Fe(CO)_3S_3$[2] and of $[Mo_3S_7(S_2PR_2)_3]^+$ to $[Mo_3S_4(S_2PR_2)_4]$.[10]



(1)

1

$Cp_2V_2S_4$ reacts readily with hexafluoro-2-butyne (2 equiv, 5 mL of toluene/mmol $Cp_2V_2S_4$, 60 °C) to give dark green solutions. After evaporation, vacuum sublimation of the crude product affords lustrous black crystals of $Cp_2V_2S_4{\cdot}C_2(CF_3)_2$ (**2**) in 45% yield.[11] This species is weakly paramagnetic, and its structure[12] (Figure 2) consists of the Cp_2V_2 frame to which is attached μ-η^2-$S_2C_2(CF_3)_2$ and μ-η^2-S_2 ligands. We propose that the addition of the acetylene to **1** occurs to the two μ-S ligands concomitant with the rearrangement of the μ-S_2 ligand (eq 2). Two key

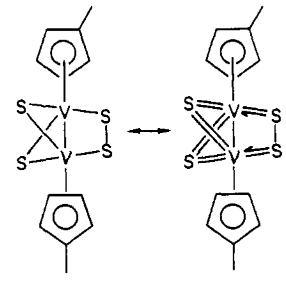


(2)

1 **2**

differences between **1** and **2** are (i) the presence of μ-η^1-S_2 in **1** and a μ-η^2-S_2 in **2** and (ii) the considerable elongation of the V–S(μ-S) distances upon conversion of **1** (av 2.21 Å) to **2** (av 2.43 Å).

Our structural results can be understood upon consideration of the bonding interactions of the Cp_2V_2 unit with its sulfur ligands. By conventional valence-shell electron count[13] (i.e., considering only S to M σ bonding), **1** is a 26e⁻ dimer, 8e⁻ short of the closed-shell configuration found for the majority of M–M bonded organobimetallics. If we invoke *full* S to V π-donation, **1** assumes a 34e⁻ configuration; such an interaction would involve the four π electrons of sp^2 hybridized μ-S moieties and the four π and π^* electrons of the acetylene-like μ-η^1-S_2 ligand:



26e⁻ 34e⁻

Extensive multiple bonding is reasonable in view of the electron deficiency of the d^1 CpV fragments; furthermore the t_{2g}-like orbitals of the pseudooctahedral vanadium centers are suitably poised for π-bonding with the bridging sulfur ligands.[14] The bonding in **1** is similar to that in $Cp_2Rh_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)(\mu\text{-}CO)_2$, also a 34e⁻ dimer, with which it is in fact nearly isolobal.[15] The

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[11] Anal.: C, H, S, V. IR (mineral oil mull) 1575 (s), 1254 (vs), 1171 (vs), 1128 (vs), 1018 (m), 890 (s), 835 (m), 810 (vs), 719 (s), 690 (m) cm^{-1}; ^{1}H NMR (90 MHz, CD_2Cl_2) δ +11.0 ($W_{1/2}$ = 600 s^{-1}); electron-impact mass spectrum (70 eV), *m/e* 522 (100%, M^+), 315 (61.9%, $C_{10}H_{10}FS_2V_2^+$), 296 (56.6%, $C_{10}H_{10}S_2V_2^+$); effective magnetic moment (25 °C) with diamagnetic correction 0.53 μ_B/V.

[12] $Cp_2V_2S_4{\cdot}C_2(CF_3)_2$ (**2**) crystallizes in the monoclinic space group *C*2/*c* with a = 13.206 (3) Å, b = 15.294 (4) Å, c = 10.086 (1) Å, β = 114.40 (1)°, V = 1855.0 (6) Å^3, Z = 4 (crystallographic 2-fold axis bisecting the C(1)–C(1′) and S(2)–S(2′) bonds), and μ = 14.61 cm^{-1} (Mo K_α). A total of 1793 reflections ($4° \le 2\theta \le 50°$) were collected of which 1630 were unique. Of these reflections 1316 with $F_o \ge 3\sigma(F_o)$ were used in the subsequent direct-methods solutions and refinement. The cyclopentadienyl ring is disordered; two equal-occupancy orientations were refined as independent rigid bodies. The final discrepancy indices with anisotropic refinement of all non-hydrogen atoms were R_F = 7.47%, R_{wF} = 7.29%, and GOF = 1.655. Due to the presence of Cp ring disorder, we attempted refinement in the noncentrosymmetric, alternative space group *Cc*. This led to severe correlation effects and unreasonably large variations in chemically identical bond parameters and was not considered further.

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[15] $Cp_2Rh_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)(\mu\text{-}CO)_2$ is the proposed intermediate in the CO scrambling reaction of $Cp_2Rh_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)(CO)_2$.[16]

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J. Am. Chem. Soc. 1983, 105, 6323-6324

net effect of π-donating ligands on d^0 or d^1 metals is electronically comparable to that of π acid ligands on later transition metals.

Conversion of **1** to **2** involves a net $2e^{-1}$ reduction of the $Cp_2V_2S_4$ subunit. The resultant d^4 Cp_2V_2 fragment is, however, deprived of π-interactions with the sulfur atoms of the dithiolene ligand, thereby inducing the μ-S_2 ligand to reorient so as to function more effectively as a σ-electron donor.

The conversion of an η^1-S_2 to an η^2-S_2 ligand has not been previously observed although several examples of each type exist. This work highlights the ability of the S_2 moiety to function as a facultative ligand and suggests that $\eta^1 \rightleftharpoons \eta^2$ interconversions may be an important facet of the reaction chemistry of other metal sulfide systems.

Acknowledgment. This research was supported by NSF (CHE81-06781). We thank D. M. Giolando for assistance with the preparation of $(i\text{-PrCp})_2V_2S_4$.

Supplementary Material Available: Tables of atomic coordinates, bond angles, bond distances, structure factors, and thermal parameters for **1** and **2** (34 pages). Ordering information is given on any current masthead page.

ESR Study of Cation-Crown Ether Induced Dimerization of a Water-Soluble Porphyrin

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Water-soluble porphyrins have found use as photocatalysts mediating the photoproduction of H_2 and O_2 in water.[1] For this reason their photophysics and photochemistry is of current interest. It is known that the porphyrins may be present as dimers or higher aggregates in aqueous solution.[2] Evidently this may have a strong effect on the photocatalytic activity. This prompted us to study the conditions that promote aggregation and the structure of the aggregates. During the course of this investigation we found that dimerization in some cases can be strongly promoted by the presence of a cation–crown ether complex. This communication deals with this crown ether induced dimerization.

Figure 1 shows the ESR spectra of photoexcited triplets of tetra(4-sulfonatophenyl)porphyrin (H_2(TPPS), Strem Chemicals) in frozen H_2O/glycerol. The spectra were recorded using field and light modulation with phase-sensitive detection at the modulation frequencies. This detection method takes advantage of the signal enhancement provided by spin polarization.[3] Moreover, it eliminates a strong doublet radical signal. The spin-polarization pattern (cf. Figure 1A) is the same as that found in the spectrum of H_2(TPP).[4] Also, the zero-field-splitting (zfs) parameters of the H_2(TPPS) monomer giving rise to the spectrum shown in Figure 1A (D = 423, E = 81 G) are similar to those of H_2(TPP) in toluene-chloroform (D = 410, E = 84 G). Apparently, the introduction of the sulfonate groups does not have a pronounced effect on the triplet-state characteristics of H_2(TPP).

Previous studies[2] disagree on whether or not H_2(TPPS) forms aggregates. We confirmed earlier findings that the optical absorption bands of H_2(TPPS) exhibit red shifts with increasing concentration and upon addition of cations (K^+, Na^+).[5] The optical absorption data are consistent with the presence of a monomer–dimer equilibrium.

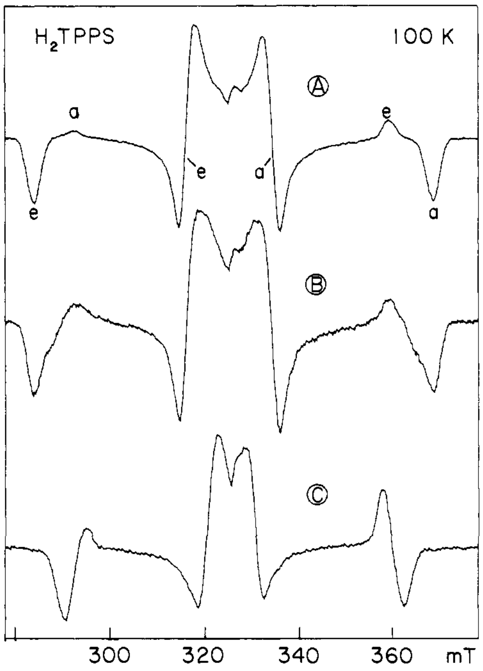

Figure 1. ESR spectra of the photoexcited tripets of H_2(TPPS) in frozen H_2O/glycerol (1:1) at 100 K. Spectra were recorded with a Varian E-9 spectrometer, microwave power 0.5 mW, field modulation 40 G at 100 kHz, 1000-W Xe/Hg light source modulated at 83 Hz. (A) 5×10^{-4} M H_2(TPPS), (B) 5×10^{-4} M H_2(TPPS) with 10^{-1} M KCl, (C) 5×10^{-4} M H_2(TPPS) with 10^{-2} M KCl and 10^{-3} M 18-crown-6. The spectra exhibit enhanced absorption (a) and emission (e) peaks as marked in spectrum A.

Addition of cations results in a loss of the monomer ESR signal (Figure 1A) and the appearance of a triplet signal attributed to the dimer. As shown in Figure 1B, with a H_2(TPPS) concentration of 5×10^{-4} M, a K^+ concentration in excess of 10^{-1} M is required for complete dimerization.

Since cations play a role in aggregation, it appeared likely that crown ethers would affect the equilibrium. In fact, we expected that cation–crown ether complexation would inhibit ion-pair formation, driving the equilibrium to the monomer side. Addition of 18-crown-6 (Aldrich) to an aqueous solution of H_2(TPPS) and KCl indeed has a strong effect. However, spectroscopic data show that the equilibrium shifts to the dimer rather than the monomer side. Figure 1C illustrates the pronounced effect on the ESR spectrum. In the absence of K^+ the optical absorption and ESR spectra are virtually unaffected by 18-crown-6 addition. On the other hand, in the presence of 18-crown-6, complete dimerization is attained with a K^+ concentration more than 2 orders of magnitude lower than that required in its absence. It is evident that it is the cation–crown complex that participates in the dimerization reaction. Studies of the effect of 18-crown-6 and K^+ concentration on the equilibrium indicate that the dimer encompasses less than four K^+ 18-crown-6 moieties.

The ESR spectrum establishes that the dimer has a well-defined structure. The change in zfs values (for the dimer D = 362, E = 87 G) is similar to the changes found in the triplet ESR spectra of chlorophylls upon dimerization.[6] Assuming that these changes stem from rapid triplet energy transfer between the dimer constituents (exciton model), they give an insight in the dimer structure.[7] It is noteworthy that the exciton model can account satisfactorily for the pronounced, dimerization-induced change in zfs values. It requires a geometry in which the porphyrin planes make an angle of about 35°. Furthermore, one in-plane principal axis of the zfs tensor in one porphyrin molecule must be roughly parallel to the corresponding axis in the other molecule. For this

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