

These results indicate that phthalocyanine "molecular metal" chemistry is considerably broader than that involving only halogen counterions. In the case of highly conductive $\text{Ni}(\text{Pc})(\text{BF}_4)_{0.33}$, similarities to halogenated analogues in crystal and band structure are accompanied by significant differences in transport/metal-to-semiconductor transition characteristics. Further phthalocyanine counterion effects are under investigation.

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Organometallic Clusters Containing Oxygen Atoms: Preparation, Structure, and Properties of $(\eta\text{-C}_5\text{H}_5)_{11}\text{V}_{13}\text{O}_{18}(\text{N}(\text{CH}_3)_3)_2$ and $(\eta\text{-C}_5\text{H}_5)_{14}\text{V}_{16}\text{O}_{24}$, Dimeric Derivatives of $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6\text{O}_8$

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We described previously $\text{Cp}_5\text{V}_5\text{O}_6$ and $\text{Cp}_4\text{Cr}_4\text{O}_4$ ¹ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) which with $\text{Cp}_6\text{Ti}_6\text{O}_8$ described by Caulton et al.² form a series of $(\text{CpM})_m(\mu_3\text{-O})_n$ clusters. In a theoretical study we suggested that in each cluster there were 12 orbitals occupied by 2 ($\text{Cp}_6\text{Ti}_6\text{O}_8$), 8 ($\text{Cp}_5\text{V}_6\text{O}_6$), or 12 ($\text{Cp}_4\text{Cr}_4\text{O}_4$) electrons, and a variety of more or less distorted octahedral $(\text{CpM})_6\text{O}_8$, trigonal bipyramidal $(\text{CpM})_5\text{O}_6$, and tetrahedral $(\text{CpM})_4\text{O}_4$ clusters should be obtainable.³ We report here the preparation of $\text{Cp}_6\text{V}_6\text{O}_8$ and two remarkable derivatives of it, $[(\text{Cp}_5\text{V}_6(\mu_3\text{-O})_8)_2(\mu\text{-O})_2\text{Cp}(\text{N}(\text{CH}_3)_3)_2]$ (I) and $[(\text{Cp}_5\text{V}_6(\mu_3\text{-O})_8)_2(\text{CpV})_4(\mu_2\text{-O})_8]$ (II).

When Cp_2V was oxidized by $(\text{CH}_3)_3\text{NO}$ in toluene a black solid and a black-brown solution were obtained. The solid was not crystalline but mass spectrometry (all m/e peaks corresponding to $\text{Cp}_m\text{V}_6\text{O}_8^+$ with $m = 6 \rightarrow 0$), microanalysis (found, C, 42.5; H, 3.9%; calcd for $\text{C}_{30}\text{H}_{30}\text{V}_6\text{O}_8$, C, 43.7; H, 3.7%) and ¹H NMR (singlet at -171.4 ppm) established it as paramagnetic $\text{Cp}_6\text{V}_6\text{O}_8$.

The solution deposited large crystals on storage at 5 °C. These were shown to be I by X-ray crystallography (Figure 1).⁴ The cluster is derived from $\text{Cp}_6\text{V}_6\text{O}_8$ by removal of one Cp and linking of two $\text{Cp}_5\text{V}_6\text{O}_8$ fragments via the oxygen of $(\text{CpV}(\text{N}(\text{CH}_3)_3)_2(\mu\text{-O})_2)$. The $\text{Cp}_5\text{V}_6\text{O}_8$ units contain regular octahedra of vanadium with an average V-V distance of 2.906 (4, 29) Å.⁵ The oxygen atoms lie over the triangular faces with an average V-O distance of 1.940 (10, 55) Å. The V-V distances are similar to the Ti-Ti in $\text{Cp}_6\text{Ti}_6\text{O}_8$, 2.891 Å (1, 14).² The V-O distance to the linking oxygen is 1.679 (15) Å.

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(4) Crystallographic data: $\text{C}_{83}\text{H}_{105}\text{N}_2\text{O}_{18}\text{V}_{13}$ ($(\eta\text{-C}_5\text{H}_5)_{11}\text{V}_{13}\text{O}_{18}(\text{N}(\text{CH}_3)_3)_2 \cdot 4(\text{C}_6\text{H}_5\text{CH}_3)$), $M_r = 2081.12$, $C2/m$, $a = 17.969$ (4) Å, $b = 14.318$ (3) Å, $c = 18.853$ (4) Å, $\beta = 105.94$ (28)°; $Z = 2$; $D_c = 1.48$ g cm⁻³; $R = 0.095$, $R_w = 0.108$ for 1674 observed ($I > 3\sigma(I)$) reflections with $2\theta < 45^\circ$. Anisotropic V and O; the $\text{N}(\text{CH}_3)_3$ and C_5H_5 groups were refined as rigid bodies (137 variables). There is disorder in the $\text{CpV}(\mu\text{-O})_2(\text{N}(\text{CH}_3)_3)_2$ unit and in the toluenes.

(5) The first figure is the average standard deviation, the second the maximum deviation from the average.

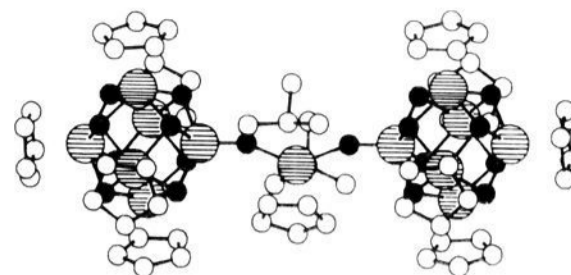


Figure 1. Structure of $(\eta\text{-C}_5\text{H}_5)_{11}\text{V}_{13}\text{O}_{18}(\text{N}(\text{CH}_3)_3)_2$.

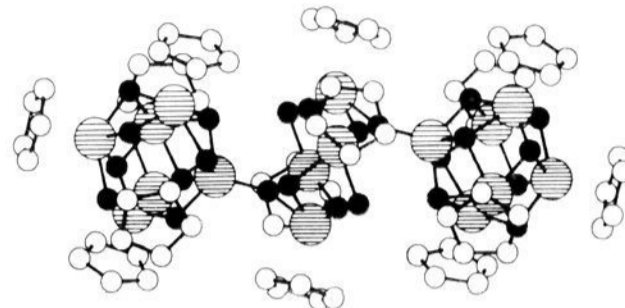


Figure 2. Structure of $(\eta\text{-C}_5\text{H}_5)_{14}\text{V}_{16}\text{O}_{24}$.

The ESR of I showed an asymmetrical eight-line spectrum typical of vanadium in a low-symmetry environment. The ¹H NMR showed a broad, weak, symmetrical resonance at -79.4, a multiplet at -7.15, and a singlet at -2.29 ppm. The latter resonances had an intensity ratio of 2.6:1. We assign the resonance at -79.4 ppm to an $\eta^5\text{-C}_5\text{H}_5$ group attached to paramagnetic vanadium, the resonance at -7.15 ppm to $\eta^5\text{-C}_5\text{H}_5$ attached to diamagnetic vanadium, and that at -2.29 ppm to the $\text{N}(\text{CH}_3)_3$. This interpretation means that the $\text{Cp}_5\text{V}_6\text{O}_8$ units are diamagnetic and the vanadium(III) in the bridge has two unpaired electrons.

The diamagnetism and regularity of the $\text{Cp}_5\text{V}_6\text{O}_8$ may be rationalized by arguments developed for $\text{Cp}_6\text{M}_6\text{O}_8$.³ The $\text{Cp}_5(\mu\text{-O})\text{V}_6\text{O}_8$ units are derivatives of $\text{Cp}_6\text{V}_6\text{O}_8$ in which an OR group replaces one Cp. This leaves the number of cluster electrons at eight but increases the cluster orbitals by two. If the unique vanadium lies on z the four orbitals it contributes to the cluster are the same two as in $\text{Cp}_6\text{V}_6\text{O}_8$, $d_{x^2-y^2}$ and d_{z^2} , plus d_{xz} and d_{yz} . Of these, $d_{x^2-y^2}$ is nonbonding and the other three are antibonding counterparts of V-O bonds. In addition d_{xz} is the antibonding counterpart of the π -bond between the bridging oxygen and vanadium. Therefore $d_{x^2-y^2}$ remains localized on the unique vanadium and is occupied by two electrons; d_{z^2} and d_{yz} contribute to the cluster and d_{xz} is of high energy. Only six electrons occupy the 12 cluster orbitals. The configuration is $a_{1g}^2e_g^4$; therefore $\text{Cp}_5\text{V}_6\text{O}_8$ is diamagnetic and undistorted.

When Cp_2V was oxidized by $(\text{CH}_3)_3\text{NO}$ in tetrahydrofuran a black, diamagnetic, crystalline solid of formula $\text{Cp}_{14}\text{V}_{16}\text{O}_{24}$ was obtained. It too is derived from $\text{Cp}_6\text{V}_6\text{O}_8$: two $\text{Cp}_5\text{V}_6\text{O}_8$ are linked by $(\text{CpV})_4(\mu_2\text{-O})_8$ (Figure 2).⁶ The latter is a rectangle of vanadium with pairs of oxygen along the edges; the connections to $\text{Cp}_5\text{V}_6\text{O}_8$ are diagonally opposed oxygens (V-O 1.701 (13) Å). The V-V distances in the $\text{Cp}_5\text{V}_6\text{O}_8$ units average 2.900 (5, 21) and the V-O distances 1.942 (14, 67) Å, very similar to I. In the $(\text{CpV})_4(\mu_2\text{-O})_8$ bridge the V-V distances are 2.989 (6) and 3.296 (6) Å and the V-O distance to the doubly bridging oxygens 2.020 (14, 29) Å but to the two triply bridging ones 2.179 (14, 26).

These clusters are extreme cases of those obtained by binding organometallic fragments to polyoxometalate ions;⁷⁻⁹ $\{[(\text{C}_7\text{H}_8)\text{-Rh}]_5(\text{cis-Nb}_2\text{W}_4\text{O}_{19})_2\}^{3-7}$ is a spectacular example. Both I and II are true molecular clusters, being highly soluble in toluene.

(6) Crystallographic data: $\text{C}_{77}\text{H}_{78}\text{O}_{24}\text{V}_{16}$ ($(\eta\text{-C}_5\text{H}_5)_{14}\text{V}_{16}\text{O}_{24} \cdot \text{C}_6\text{H}_5\text{CH}_3$), $M_r = 2202.5$, $P\bar{1}$, $a = 11.582$ (2) Å, $b = 13.099$ (2) Å, $c = 13.969$ (4) Å, $\alpha = 94.10$ (2)°, $\beta = 90.03$ (2)°, $\gamma = 104.72$ (2)°, $Z = 1$; $D_c = 1.78$ g cm⁻³; $R = 0.070$, $R_w = 0.076$ for 1657 observed ($I > 3\sigma(I)$) reflections with $2\theta < 45^\circ$. Anisotropic V and O; C_5H_5 groups as rigid bodies (287 variables).

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths for I and II (9 pages). Ordering information is given on any current masthead page.

Stereospecificity of 1,3-Dipolar Cycloadditions of *p*-Nitrobenzotrile Oxide to *cis*- and *trans*-Dideuterioethylene[†]

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The mechanism of 1,3-dipolar cycloadditions has been a topic of lively debate.²⁻⁴ For nitrile oxide cycloadditions, experimental data have been interpreted either as supportive of a concerted mechanism^{2,4} or in favor of a stepwise mechanism with diradical intermediates.³ Theory has compounded, rather than resolved, this problem: *ab initio* calculations on the reaction of formonitrile oxide with acetylene predict a concerted mechanism at the molecular orbital level⁵ but a stepwise mechanism after inclusion of extensive electron correlation.⁶ MNDO predicts a stepwise mechanism with a diradical intermediate.⁷ We have studied the stereospecificity of the cycloadditions of *p*-nitrobenzotrile oxide (**1**, Ar = *p*-NO₂Ph) to *cis*- and *trans*-1,2-dideuterioethylene and have obtained evidence that narrowly circumscribes the mechanism of this typical 1,3-dipolar cycloaddition.

The stereospecificity observed in many 1,3-dipolar cycloadditions⁸ is often considered to be compelling, if not conclusive, evidence for concert in these reactions.² However, if the rate constant for rotation (*k_r*) about bond **a** (Figure 1) in a diradical intermediate, **3a** or **3b**, were much smaller than the rate constant for cyclization (*k_c*), high stereospecificity would still be observed.³ The reported examples of stereospecific 1,3-dipolar cycloadditions involve di-, tri-, or tetrasubstituted alkenes.⁸ Barriers to rotation of simple primary, secondary, and tertiary alkyl radicals are only 0–1.2 kcal/mol,⁹ but more highly substituted radicals have barriers

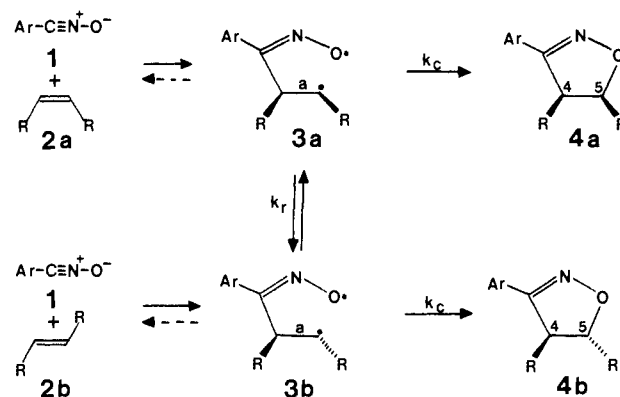


Figure 1. Hypothetical intermediates for stepwise 1,3-dipolar cycloadditions of nitrile oxides to *cis*- or *trans*-disubstituted alkenes.

to rotation estimated to be as high as 4 kcal/mol.¹⁰

Experimental evidence implies that barriers to rotation about single bonds in diradicals are similar to those of analogous monoradicals. For example, while the cupric chloride chlorinations of *cis*- and *trans*-2-butene are largely stereospecific, this reaction is nearly stereorandom with the dideuterioethylenes.¹¹ Similarly, while rotation is only 0.5–1.4 times the rate of cyclization for 1,2-dimethylbutane-1,4-diyl, rotation is 12 times faster than cyclization for 1,2-dideuterobutane-1,4-diyl.¹² For cycloadditions of tetrafluoroethylene to *trans*-2-butene, 72% of the *trans* adduct is obtained,¹³ while *cis*- and *trans*-dideuterioethylene give the same adduct ratio (probably 1:1) with tetrafluoroethylene.¹⁴ Thus, rotations about single bonds to deuterated primary radical centers in diradicals are very fast relative to cyclization.

If diradical intermediates were formed in the cycloadditions of *p*-nitrobenzotrile oxide (**1**, Ar = O₂NPh) to *cis*- and *trans*-1,2-dideuterioethylenes (**2**, R = D), then significant scrambling of stereochemistry should be observed in the product. The barrier to rotation of the *n*-propyl radical, a reasonable analogue to **3a** (R = D), is 0.1–0.4 kcal/mol.⁹ Even if the barrier to cyclization were only 0.1 kcal/mol, and the barrier to rotation were 0.4 kcal/mol, about 27% of the *cis* adduct should be formed from the *trans* reactant, and vice versa.

cis- and *trans*-dideuterioethylene were prepared for these studies by the methods of Nicholas and Carroll.¹¹ Infrared and mass spectral analyses indicated that the dideuterioethylenes were isomerically pure, but different preparations contained 2–9% of monodeuterated ethylene.¹⁵ The reaction of each dideuterioethylene with *p*-nitrobenzotrile oxide was carried out in methylene chloride solution at room temperature for 2–6 days under a slight pressure of ethylene-*d*₂. Evaporation of the solvent and thin layer chromatography gave the deuterated 3-(*p*-nitrophenyl)-2-isoxazolines (**4**, Ar = O₂NPh; R = D), mp 158–159 °C,¹⁶ plus some of the nitrile oxide dimer. The NMR spectrum of the undeuterated adduct is an AA'BB' multiplet, with the resonances due to the protons at C₄ and C₅ centered at 3.36 and 4.57 ppm, respectively. The couplings, *J*_{cis} = 11.5, *J*_{trans} = 8.7, *J*_{gem(4,4)} = –16.0, and *J*_{gem(5,5)} = –10.0 Hz, are similar to the

[†] Dedicated to Professor Rolf Huisgen on the occasion of his 65th birthday.

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