

# Organometallic Oxides: Oxidation of $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$ with $\text{O}_2$ To Form $[(\mu\text{-}\eta^3\text{-C}_5\text{Me}_5\text{O}_3)\text{V}(\text{O})]_2$ , $[(\eta\text{-C}_5\text{Me}_5)\text{V}]_4(\mu\text{-O})_6$ , and $(\eta\text{-C}_5\text{Me}_5)_6\text{V}_8\text{O}_{17}$

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The reaction between  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  (1) and  $\text{O}_2$  (1:2 mole ratio) in hexane at  $-30^\circ\text{C}$  for 12 h gave  $[(\mu\text{-}\eta^3\text{-C}_5\text{Me}_5\text{O}_3)\text{V}(\text{O})]_2$  (3) in 20% yield. In this reaction three oxygen atoms were inserted into adjacent V-C bonds in an all-cis fashion. The reaction between 1 and traces of  $\text{O}_2$  in hexane at  $20^\circ\text{C}$  for 24 h gave  $[(\eta\text{-C}_5\text{Me}_5)\text{V}]_4(\mu\text{-O})_6$  (4). Cluster 4 was more conveniently prepared by oxidation of 1 with  $\text{N}_2\text{O}$  (85% yield) and was also formed on reduction of  $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\mu\text{-O})]_3$  with  $\text{PMe}_2\text{Ph}$ . Oxidation of 1 or 4 with a large excess of  $\text{O}_2$  in toluene at  $20^\circ\text{C}$  for 48 h gave  $(\eta\text{-C}_5\text{Me}_5)_6\text{V}_8\text{O}_{17}$  (5) in 80% yield. Reaction of  $(\eta\text{-C}_5\text{Me}_4\text{H})_2\text{V}$  with  $\text{O}_2$  gave the  $\eta\text{-C}_5\text{Me}_4\text{H}$  analogues of 4 and 5, but the analogue of 3 was not formed. Treatment of 5, or its  $\text{C}_5\text{Me}_4\text{H}$  analogue, with  $\text{SOCl}_2$  gave  $(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2(\text{O})$  (2) in 70% yield. The structures of 3 and 4 were previously determined by X-ray crystallography. Compound 3 is an alkoxide in which each V(V) atom has five-coordinate, square-pyramidal,  $(\text{RO})_4\text{V}(\text{O})$  coordination. Cluster 4 has an adamantane-like  $\text{V}_4(\mu\text{-O})_6$  core ( $T_d$  symmetry) and a magnetic moment of  $2.90 \mu_B$  at 295 K. The electronic structure of 4 has been investigated by extended Hückel molecular orbital methods; the core has the  $a_1^2e^2t_2^0t_1^0t_2^0$  configuration. Cluster 5 is proposed, on the basis of chemical and spectroscopic evidence, to contain two  $[\text{V}(\text{O})(\mu\text{-O})]_4$  units linked by a bridging oxygen.

## Introduction

The oxidation of  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  and  $(\eta\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$  by  $\text{O}_2$  was one of the earliest reactions of cyclopentadienyl derivatives of vanadium to be investigated. In 1958 Fischer and Vigoureux reported that  $(\eta\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$  was oxidized by  $\text{O}_2$  (air) in the presence of HCl to give  $(\eta\text{-C}_5\text{H}_5)\text{VCl}_2(\text{O})$  in 75% yield.<sup>1,2</sup> Attempts by Fischer and Ulm to characterize the products of the oxidation of  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  by excess  $\text{O}_2$  were not successful; only an intractable polymer of approximate formula  $[(\text{C}_5\text{H}_5)\text{VO}]_n$  was obtained.<sup>3</sup> In 1965 De Liefde Meijer and Van der Kerk reported that oxidation of  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  with  $\text{O}_2$  gave an ill-characterized material formulated as  $\text{C}_{10}\text{H}_{12}\text{V}_2\text{O}_5$ ; this could be chlorinated with  $\text{SOCl}_2$  to give  $(\eta\text{-C}_5\text{H}_5)\text{VCl}_2(\text{O})$  in 52% yield.<sup>4</sup>

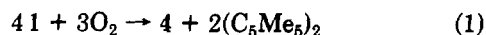
Over the last 10 years we have used oxides of nitrogen to oxidize  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  to organometallic oxides such as  $[(\eta\text{-C}_5\text{H}_5)\text{V}]_5(\mu_3\text{-O})_6$ ,<sup>5</sup>  $(\eta\text{-C}_5\text{H}_5)_{10}\text{V}_{12}\text{O}_{17}$ ,<sup>6</sup> and  $(\eta\text{-C}_5\text{H}_5)_{14}\text{V}_{16}\text{O}_{24}$ .<sup>7</sup> We periodically attempted to use  $\text{O}_2$  as the oxidizing agent, using controlled amounts rather than the large excesses used by the earlier workers. However, we obtained only very small quantities of the clusters. The major products were the intractable materials described by Fischer and Ulm.<sup>3</sup>

Recently, we have turned our attention to the oxidation of  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  (1). Oxidation of 1 with excess  $\text{O}_2$  in toluene at room temperature gave an unidentified brown material, which on treatment with  $\text{SOCl}_2$  gave  $(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2(\text{O})$  (2) in 82% yield.<sup>8</sup> Herberhold and co-workers oxidized  $(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{CO})_4$  with  $\text{O}_2$  in toluene at

room temperature, giving a brown material formulated as  $(\text{C}_5\text{Me}_5)_3\text{V}_4\text{O}_9$ .<sup>9</sup> When the oxidation of  $(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{CO})_4$  was accompanied by chlorination with  $\text{Cl}_2$ ,  $(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2(\text{O})$  was obtained in 84% yield.<sup>9</sup> It appeared from our experiments, and from the work of Herberhold et al., that the oxidation of 1 with  $\text{O}_2$  would prove to be more tractable than that of  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$ . We have therefore investigated the reaction between 1 and  $\text{O}_2$  under various conditions and have identified three remarkable products:  $[(\mu\text{-}\eta^3\text{-C}_5\text{Me}_5\text{O}_3)\text{V}(\text{O})]_2$  (3),  $[(\eta\text{-C}_5\text{Me}_5)\text{V}]_4(\mu\text{-O})_6$  (4), and  $(\eta\text{-C}_5\text{Me}_5)_6\text{V}_8\text{O}_{17}$  (5). The results of these investigations are reported here in detail, as are the physical and chemical properties of 3-5, as well as a discussion of the electronic structure of 4. Preliminary communications on 3 and 4 have appeared previously.<sup>10,11</sup>

## Results and Discussion

**Controlled Oxidation of  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  (1) by  $\text{O}_2$ .** We had observed that 1, which is red-pink, often took on a green patina when stored for long periods under argon or vacuum. We suspected this was due to slow ingress of  $\text{O}_2$  and therefore exposed a solution of 1 in hexane to traces of  $\text{O}_2$  at  $20^\circ\text{C}$ . A dark green solution was formed over 12 h. The same result was achieved with a mole ratio of 1 to  $\text{O}_2$  of 1:2 at  $-70^\circ\text{C}$  in a reaction time of 3 min. The solution contained unreacted 1 and a green compound, identified as  $[(\eta\text{-C}_5\text{Me}_5)\text{V}]_4(\mu\text{-O})_6$  (4, Figure 1) by mass spectrometry and by comparison with an authentic sample. The reaction occurring may be represented by eq 1. Since



4 was very sensitive to  $\text{O}_2$ , it could not be obtained in reasonable yield by reaction 1; two other methods of preparation are discussed below. Essentially identical results were obtained when  $(\eta\text{-C}_5\text{Me}_4\text{H})_2\text{V}$  or  $(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{CO})_4$

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 (7) Bottomley, F.; Paez, D. E.; White, P. S. J. *Am. Chem. Soc.* 1985, 107, 7226.  
 (8) Bottomley, F.; Sutin, L. *J. Chem. Soc., Chem. Commun.* 1987, 1112.

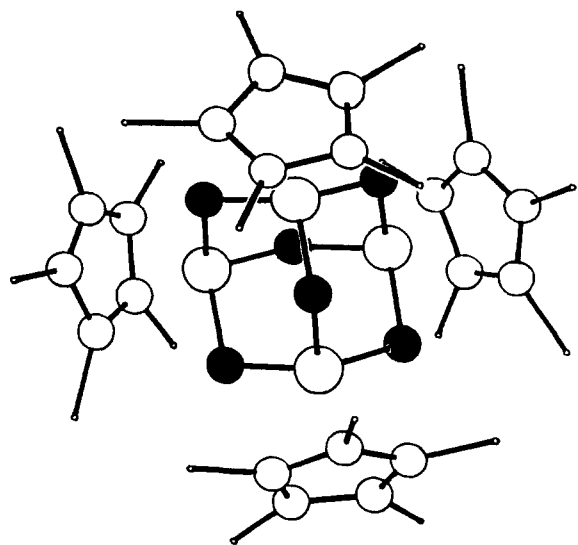


Figure 1. Structure of  $[(\eta\text{-C}_5\text{Me}_5\text{V})_4(\mu\text{-O})_6]$  (4).

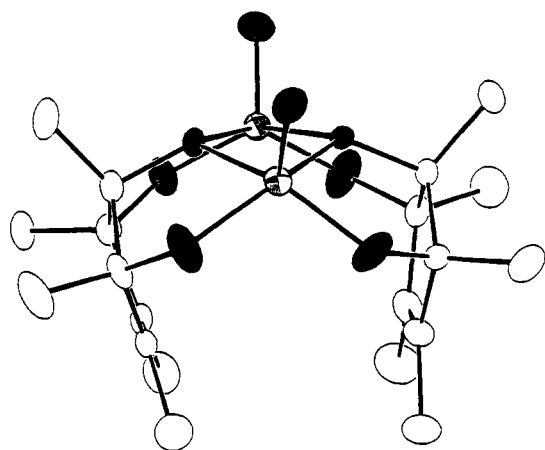


Figure 2. Structure of  $[(\mu\text{-}\eta^3\text{-C}_5\text{Me}_5\text{O}_3)\text{V}(\text{O})]_2$  (3).

$\text{C}_5\text{Me}_4\text{Et})_2\text{V}$  was treated with  $\text{O}_2$  under conditions similar to those for formation of 4.

When 1 was incubated with  $\text{O}_2$  (1:2 mole ratio) in hexane at  $-30^\circ\text{C}$  for 12 h, the color of the solution changed from pink to red-brown; a red oil was formed when the solvent was removed. Separation and purification of the products was complicated because they were highly soluble in hexane and other organic solvents and one of them readily formed an oil. Two products were identified after chromatography of the product solution on controlled-pore glass beads. These were  $(\text{C}_5\text{Me}_5)_2$ , which readily formed an oil but could be crystallized and identified by comparison with the literature<sup>12,13</sup> (see the Experimental section), and  $[(\mu\text{-}\eta^3\text{-C}_5\text{Me}_5\text{O}_3)\text{V}(\text{O})]_2$  (3, Figure 2). The reaction occurring can be represented by eq 2, although the

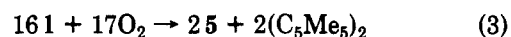


yield of 3 was only 20%. It is believed that the majority of the remaining 80% of product is  $(\eta\text{-C}_5\text{Me}_5)_6\text{V}_8\text{O}_{17}$  (5) (see below), which remained on the column during elution.

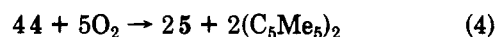
The reaction between  $(\eta\text{-C}_5\text{Me}_4\text{H})_2\text{V}$  and  $\text{O}_2$  was investigated under the same conditions as reaction 2 between 1 and  $\text{O}_2$ . The same color changes were observed, and NMR spectroscopy indicated that a product analogous to 3 was formed. However, it was very much less stable than

3, and it decomposed on workup, even when rigorous precautions to remove all traces of water were taken. It is possible that the decomposition was thermal, since 3 also decomposed slowly at room temperature. No reaction of the type shown in eq 2 was observed for  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$ . Since reaction 2 represents the insertion of three oxygen atoms on adjacent carbons in an all-cis fashion, it was hoped that it would have synthetic utility in the synthesis of carbohydrates. However, the reaction appears to be confined to  $\eta\text{-C}_5\text{Me}_5$  or to  $\text{C}_5\text{R}_5$  compounds containing no ring hydrogen atoms attached to the ring carbons.

When a solution of 1 in toluene was oxidized with a large excess of  $\text{O}_2$  at  $20^\circ\text{C}$ , the solution initially turned brown and then olive green over a period of 48 h. Workup of the solution gave  $(\text{C}_5\text{Me}_5)_2$  and olive green microcrystalline  $(\eta\text{-C}_5\text{Me}_5)_6\text{V}_8\text{O}_{17}$  (5) in essentially quantitative yield according to eq 3. Oxidation of 4 with excess  $\text{O}_2$  also gave



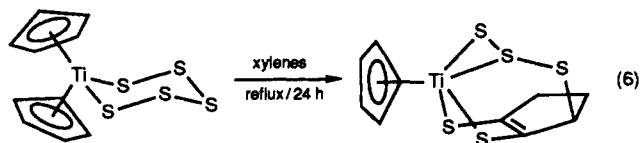
5 very rapidly according to eq 4. Oxidation of  $(\eta\text{-C}_5\text{Me}_4\text{Et})_2\text{V}$  or  $(\eta\text{-C}_5\text{Me}_4\text{Et})_2\text{V}$  with excess  $\text{O}_2$  readily gave the  $\text{C}_5\text{Me}_4\text{H}$  and  $\text{C}_5\text{Me}_4\text{Et}$  analogues of 5. Finally, oxidation of  $(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{CO})_4$  with excess  $\text{O}_2$  gave cluster 5, according to eq 5, the product being identical with that



obtained from 1 and  $\text{O}_2$ . From the latter result we conclude that  $(\eta\text{-C}_5\text{Me}_5)_6\text{V}_8\text{O}_{17}$  (5) is identical with the " $(\text{C}_5\text{Me}_5)_3\text{V}_4\text{O}_9$ " described by Herberhold and co-workers.<sup>9</sup> The results clearly show that 4 is an intermediate in the formation of 5 from 1. It is equally clear that 3 cannot be an intermediate in the formation of 4 or 5 from 1, since gross disruption of the  $\eta\text{-C}_5\text{Me}_5$  ring has occurred in 3. However, it is not clear whether 4 is an intermediate in the transformation of 1 into 3. We did not observe any species other than 4 when 1 was oxidized by traces of  $\text{O}_2$  or when larger quantities of  $\text{O}_2$  but short reaction times were used. None of the insertion product 3 was observed when 4 was oxidized to 5. Since 1, 4, and  $\text{O}_2$  are all paramagnetic, and since each has more than one unpaired electron, it was not possible to study any of the reactions between 1 and  $\text{O}_2$  by either NMR or ESR spectroscopy. However, we believe that 4 is not an intermediate in the formation of 3 from 1 because 4 formally contains four vanadium(IV) atoms and insertion of three oxygen atoms into the V-C bonds of a vanadium(IV) compound would require impossibly high formal oxidation states of vanadium ( $>5$ ). The oxidation of 1 by  $\text{O}_2$  is therefore best represented by the reactions shown in Scheme I.

The insertion of three oxygen atoms into adjacent V-C bonds, as in the conversion of 1 into 3, is an unprecedented reaction. Insertion of three sulfur atoms has been observed in the thermal rearrangement of  $(\eta\text{-C}_5\text{H}_5)_2\text{TiS}_5$  to  $(\eta\text{-C}_5\text{H}_5)\text{Ti}(\eta^3\text{-C}_5\text{H}_5\text{S}_3)$  (eq 6).<sup>14</sup> Bercau and Parkin were able

to insert one oxygen atom between an  $\eta\text{-C}_5\text{Me}_5$  ring and tungsten in the reaction of  $(\eta\text{-C}_5\text{Me}_5)_2\text{W}(\text{O})$  with  $\text{O}_2$  to give



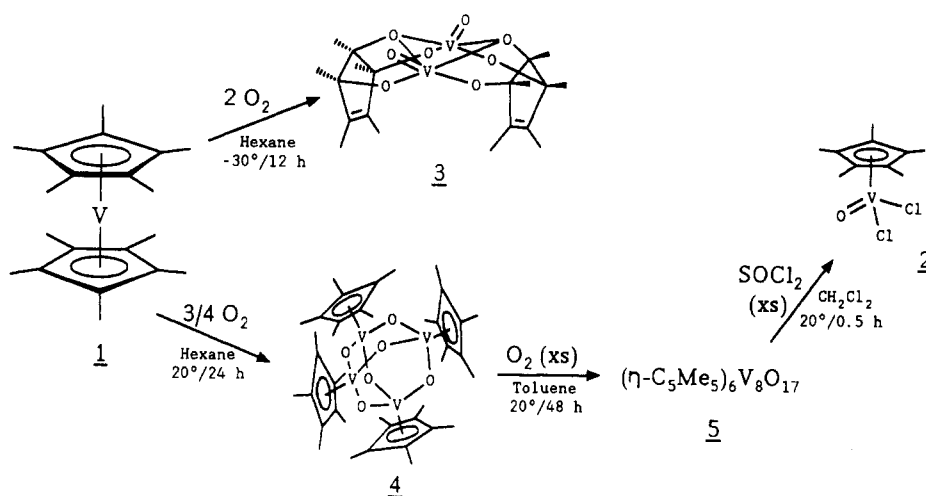
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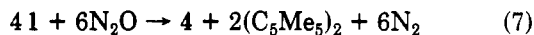
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Scheme I



$(\eta\text{-C}_5\text{Me}_5)\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$ .<sup>15-17</sup> Insertion of further oxygen atoms is impossible in the tungsten case because the product  $(\eta\text{-C}_5\text{Me}_5)\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$  contains the maximum oxidation state of tungsten, W(VI). It was shown by labeling that the inserted oxygen atom came from the  $\text{O}_2$  molecule, not from the W–O moiety.<sup>16</sup> In the present case the V(IV) intermediate  $(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\text{OC}_5\text{Me}_5)$  would be the analogue of  $(\eta\text{-C}_5\text{Me}_5)\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$ . As discussed above, it was not possible to observe any intermediates, and the mechanism of the remarkable reaction (2), as well as the reason why it does not proceed when the  $\eta\text{-C}_5\text{R}_5$  ring has even one R equal to H, remains unknown.

**Preparation of  $[(\eta\text{-C}_5\text{Me}_5)\text{V}]_4(\mu\text{-O})_6$  (4) from  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  and  $\text{N}_2\text{O}$ .** As noted above, the reaction between 1 and  $\text{O}_2$  was not a suitable method of preparation of 4. This was because 4 reacted very readily with  $\text{O}_2$  to form 5 (eq 4). When the conditions of reaction 1 were arranged to prevent formation of 5 (low temperature, excess 1, low partial pressure of  $\text{O}_2$  (achieved by dilution of  $\text{O}_2$  with argon)) either 3 was formed as well as 4 or 4 was formed in such low yield that workup was very difficult. However, when 1 was reacted with  $\text{N}_2\text{O}$ , 4 was readily obtained according to eq 7. The yield of 4 after workup and puri-



fication was 85%. Workup was difficult because of the presence of oily  $(\text{C}_5\text{Me}_5)_2$  and the extreme air sensitivity of 4. There was no reaction between  $(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{CO})_4$  and  $\text{N}_2\text{O}$ .

We did not observe any product except 4 when 1 was oxidized with  $\text{N}_2\text{O}$ ; specifically, neither 3 nor 5 could be detected by mass or NMR spectroscopy. We believe that reaction 7 is the sole process occurring under the conditions described. This result shows a clear difference in the oxidizing properties of  $\text{N}_2\text{O}$  and  $\text{O}_2$ . The fact that  $\text{O}_2$  oxidized 4 to 5, but  $\text{N}_2\text{O}$  did not, can be ascribed to the stronger oxidizing properties of  $\text{O}_2$  compared to  $\text{N}_2\text{O}$ . The fact that  $\text{N}_2\text{O}$  was unable to insert oxygen atoms into the V–C bonds of  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$ , whereas  $\text{O}_2$  inserted readily, must be due to different reaction mechanisms. In this respect the observations of Parkin and Bercaw,<sup>16</sup> that one oxygen atom of  $\text{O}_2$  was inserted into the W–C bonds of  $(\eta\text{-C}_5\text{Me}_5)_2\text{W}(\text{O})$  while the second oxygen atom of  $\text{O}_2$  be-

came attached to tungsten (to form  $(\eta\text{-C}_5\text{Me}_5)\text{W}(\text{OC}_5\text{Me}_5)(\text{O})_2$ ) may be relevant, since such a concerted reaction is impossible with  $\text{N}_2\text{O}$ . It is also noteworthy that Hillhouse and Vaughan observed that the insertion of a single oxygen atom into the M–C bond of  $(\eta\text{-C}_5\text{Me}_5)_2\text{M}(\eta^2\text{-PhC}_2\text{Ph})$  (M = Ti, Zr) to form  $(\eta\text{-C}_5\text{Me}_5)_2\text{M}(\text{OCPH}=\text{CPh})$  was preceded by insertion of the whole  $\text{N}_2\text{O}$  molecule, giving the isolable and structurally characterized intermediate  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{N}(\text{O})\text{NC}(\text{Ph})=\text{CPh})$ .<sup>18,19</sup> Insertion of the whole  $\text{N}_2\text{O}$  molecule into the V–C bonds of 1 seems to be mechanistically impossible because of the  $\eta^5$ -nature of the  $\text{C}_5\text{Me}_5\text{-V}$  interaction.

The reaction between 1 and  $\text{N}_2\text{O}$  to give 4 can be contrasted with that between  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  and  $\text{N}_2\text{O}$  and with that between  $(\eta\text{-C}_5\text{Me}_5)_2\text{Cr}$  and  $\text{N}_2\text{O}$ . The latter reaction gave  $[(\eta\text{-C}_5\text{Me}_5)\text{Cr}(\mu_3\text{-O})]_4$  as the sole product.<sup>20</sup> This may be due to the stability of Cr(III) versus Cr(IV), which would be formally present in  $[(\eta\text{-C}_5\text{Me}_5)\text{Cr}]_4(\mu\text{-O})_6$ , the chromium analogue of 4. The reaction between  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  and  $\text{N}_2\text{O}$  gave several products.<sup>5-7</sup> However,  $[(\eta\text{-C}_5\text{H}_5)\text{V}]_4(\mu\text{-O})_6$  has not been identified as one of them. There is no obvious reason why  $[(\eta\text{-C}_5\text{H}_5)\text{M}]_4(\mu\text{-O})_6$  compounds should not exist for titanium, vanadium or for their heavier congeners ( $[(\eta\text{-C}_5\text{Me}_5)\text{Ti}]_4(\mu\text{-O})_6$  is known<sup>21</sup>).

**Preparation of  $[(\eta\text{-C}_5\text{Me}_5)\text{V}]_4(\mu\text{-O})_6$  (4) from  $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\mu\text{-O})]_3$  and  $\text{PMe}_2\text{Ph}$ .** The cluster 4 was also prepared by reducing the cyclic trimer  $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\mu\text{-O})]_3$  with  $\text{PMe}_2\text{Ph}$ . The reaction proceeded according to eq 8. Reaction 8 did not appear to be accompanied by



side or subsequent reactions. However, workup of the product 4 was complicated by the presence of residual  $\text{PMe}_2\text{Ph}$  and  $\text{OPMe}_2\text{Ph}$ , as well as by the very similar solubilities of the products and starting materials in the same solvents. There was no reaction between  $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\mu\text{-O})]_3$  and  $\text{PPh}_3$ . The usefulness of phosphines as an abstractor of oxygen has been noted previously.<sup>22</sup>

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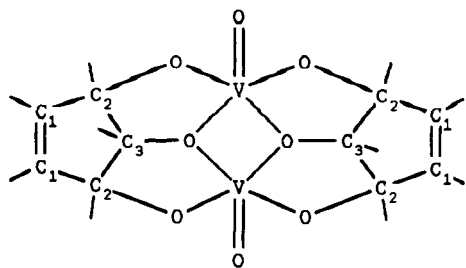


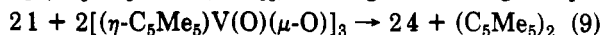
Figure 3. Numbering scheme for the atoms of 3.

Table I. Important Distances (Å) in 3<sup>a</sup>

|                     |                        |                   |          |
|---------------------|------------------------|-------------------|----------|
| V-O(1) <sup>b</sup> | 1.581 (6) <sup>c</sup> | C(1)-C(2)         | 1.47 (1) |
| V-O(2)              | 1.770 (7)              | C(2)-C(3)         | 1.57 (1) |
| V-O(3)              | 1.956 (6)              | C-O               | 1.45 (1) |
| C(1)-C(1)           | 1.335 (10)             | C-CH <sub>3</sub> | 1.51 (1) |

<sup>a</sup> A full list of distances and angles is given in the supplementary material for ref 10. <sup>b</sup> The distances have been averaged for the two halves of the molecule. <sup>c</sup> For the numbering scheme, see Figure 3.

Interestingly, 1 could also be used to abstract oxygen from  $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\mu\text{-O})]_3$ , forming 4 according to eq 9.



Reaction 8 must involve dissociation of trimeric  $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\mu\text{-O})]_3$  into monomeric and/or dimeric units. This disproportionation was caused by  $\text{PMe}_2\text{Ph}$ , since  $(\eta\text{-C}_5\text{Me}_5)\text{VO}_2$  only existed as the trimer  $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\mu\text{-O})]_3$ .<sup>8</sup>

**Chlorination of  $(\eta\text{-C}_5\text{Me}_5)_3\text{V}_3\text{O}_{17}$  (5).** Chlorination of 5 with  $\text{SOCl}_2$  in  $\text{CH}_2\text{Cl}_2$  rapidly gave 2 in 70% yield (i.e. essentially quantitative based on  $(\eta\text{-C}_5\text{Me}_5)$ ). An insoluble residue, presumed to be a vanadium oxide or oxychloride, was also formed. Since 5 was the ultimate product of the oxidation of 1 with  $\text{O}_2$ , and since 5 was formed via 4, the sequence of steps 1  $\rightarrow$  4  $\rightarrow$  5  $\rightarrow$  2 (see Scheme I) represents the mode of formation of 2 from 1 by the method described previously.<sup>8</sup> The  $\eta\text{-C}_5\text{H}_5$  analogues of 4 or 5 have not been isolated, and therefore, the intermediates in the original preparations of  $(\eta\text{-C}_5\text{H}_5)\text{VCl}_2(\text{O})$  from  $(\eta\text{-C}_5\text{H}_5)_2\text{V}^{2,4}$  remain unknown. Formation of 2 by oxidation (with  $\text{O}_2$ ) and chlorination (with  $\text{Cl}_2$ ) of  $(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{CO})_4$ , as described by Herberhold and co-workers,<sup>9</sup> also proceeds via chlorination of 5, since 5 appears to be identical with " $(\text{C}_5\text{Me}_5)_3\text{V}_4\text{O}_9$ ". Chlorination of 4 with  $\text{HCl}$  did not give  $[(\eta\text{-C}_5\text{Me}_5)\text{VCl}(\mu\text{-O})]_4$ ,<sup>23</sup> the vanadium analogue of  $[(\eta\text{-C}_5\text{Me}_5)\text{TiCl}(\mu\text{-O})]_4$ , which was formed from  $[(\eta\text{-C}_5\text{Me}_5)\text{Ti}]_4(\mu\text{-O})_6$  and  $\text{HCl}$ .<sup>24</sup> This reaction is still under investigation.

**Physical Properties of  $[(\mu\text{-}\eta^3\text{-C}_5\text{Me}_5\text{O}_3)\text{V}(\text{O})]_2$  (3).** The structure of 3, as determined by X-ray crystallography, was briefly reported previously<sup>10</sup> and is shown in Figures 2 and 3. The insertion of the oxygen atoms in the V-C bonds has converted the organometallic compound 1 into the alkoxide 3. It appears that only one alkoxide of the type  $[\text{V}^{\text{V}}(\text{OR})_2(\text{O})]_2(\mu\text{-OR})_2$ , with which 3 can be compared, has been structurally characterized.<sup>25,26</sup> This is  $[\text{V}(\text{OMe})_2(\text{O})]_2(\mu\text{-OMe})_2$ .<sup>25</sup> The structure was determined from visually estimated photographic data and only refined to  $R = 0.17$ . The average V=O distance was 1.54 Å, the V-OMe terminal distance 1.79 Å, and the bridging V-OMe distance 2.02 Å. These distances may be compared to the analogous distances of 1.581 (4), 1.770 (7), and

Table II. Important Distances (Å) and Angles (deg) in 4<sup>a</sup>

|                   |                          |       |             |
|-------------------|--------------------------|-------|-------------|
| V-V               | 3.003 (3,3) <sup>b</sup> | O-V-O | 108.0 (3,5) |
| V-O               | 1.808 (6,16)             | V-O-V | 112.2 (3,8) |
| V-Cp <sup>c</sup> | 2.023 (10,13)            |       |             |

<sup>a</sup> A full list of distances and angles is given in the supplementary material for ref 11. <sup>b</sup> The distances and angles have been averaged. The first figure in brackets is the average standard deviation; the second figure is the maximum deviation from the average. <sup>c</sup> Cp is the centroid of the  $\text{C}_5$  ring of the  $\eta\text{-C}_5\text{Me}_5$  ligand.

1.957 (6) Å in 3 (Table I and Figure 3). In  $[\text{V}(\text{OMe})_2(\text{O})]_2(\mu\text{-OMe})_2$  there was clear evidence for a rather long (2.27 Å) intermolecular interaction between a terminal OMe and a neighboring vanadium atom. As a result, the coordination about the vanadium atoms is best regarded as distorted octahedral, whereas in 3 the coordination is square pyramidal. Such square-pyramidal vanadium(V) compounds with an  $(\text{RO})_4\text{V}(\text{O})$  coordination sphere do not appear to be known, though many vanadium(IV) examples have been characterized.<sup>26</sup> As would be expected, all the V-O distances in 3 are shorter than those in the vanadium(IV) compounds. Recently, a second alkoxide of this type has been isolated,  $\text{V}(\text{OCH}_2\text{CH}_2\text{Cl})_3(\text{O})$ .<sup>27</sup> It is monomeric, although association between adjacent molecules of the type found in the structure of  $[\text{V}(\text{OMe})_2(\text{O})]_2(\mu\text{-OMe})_2$  occurs, making the coordination about the vanadium trigonal bipyramidal. The structure of  $\text{V}(\text{OCH}_2\text{CH}_2\text{Cl})_3(\text{O})$  is therefore not directly comparable with that of 3.

The distances within the  $\eta^3\text{-C}_5\text{Me}_5\text{O}_3$  ligand support the localized valence bond description of this ligand shown in Figure 3. The C(1)-C(1) distances (the C=C double bond) average 1.33 (1) Å, the C(2)-C(1) distances 1.47 (1) Å, and the C(2)-C(3) distances 1.56 (1) Å. The C-CH<sub>3</sub> distances are the same, 1.51 (1) Å, regardless of the nature of the ring carbon (C(1), C(2), or C(3)). The C-O distances are likewise all the same, at 1.43 (1) Å.

The distances within the  $\eta^3\text{-C}_5\text{Me}_5\text{O}_3$  ligand support the localized valence bond description of this ligand shown in Figure 3. The C(1)-C(1) distances (the C=C double bond) average 1.33 (1) Å, the C(2)-C(1) distances 1.47 (1) Å, and the C(2)-C(3) distances 1.56 (1) Å. The C-CH<sub>3</sub> distances are the same, 1.51 (1) Å, regardless of the nature of the ring carbon (C(1), C(2), or C(3)). The C-O distances are likewise all the same, at 1.43 (1) Å.

The NMR spectra of 3 are of some interest. The single <sup>51</sup>V signal at -672.5 ppm (relatively to  $\text{VOCl}_3$ ) showed the equivalence of the two vanadium atoms. The <sup>1</sup>H spectrum was surprising in that at 200 MHz only two resonances were observed, a singlet at 2.12 ppm (12 H) and a singlet at 2.05 ppm (18 H). The former singlet is readily assigned to the CH<sub>3</sub> groups attached to the olefinic carbons (C(1) in Figure 3). The latter singlet must be assigned to the CH<sub>3</sub> groups attached to the alkoxy carbons (C(2) and C(3) in Figure 3). The coincidence of the resonances must be fortuitous. In  $(\eta\text{-C}_5\text{Me}_5)\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$  the alkoxy methyl resonance was observed at 1.40 ppm and the olefinic methyls were observed at 1.62 and 1.78 ppm.<sup>15</sup> The <sup>13</sup>C spectrum of 3 showed signals at 10.5, 27.2, and 29.8 ppm due to CH<sub>3</sub> carbons attached to C(1), C(2), and C(3), respectively, and at 125.3, 128.1, and 128.9 ppm due to ring carbons C(1), C(2), and C(3). These may be compared to values of 10.2, 11.4, and 23.9 ppm for the CH<sub>3</sub> carbons of the -OC<sub>5</sub>Me<sub>5</sub> ligand in  $(\eta\text{-C}_5\text{Me}_5)\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$  and 93.4, 134.7, and 137 ppm for the ring carbons in the same ligand in the tungsten complex.<sup>15</sup> The values for  $(\text{C}_5\text{Me}_5)_2$  were 10.9, 12.5, and 19.3 ppm for the CH<sub>3</sub> carbons and 59.8, 133.2, and 141.7 ppm for the ring carbons. It is seen that in 3 the ring carbons resonate over a much narrower range than either the tungsten complex or  $(\text{C}_5\text{Me}_5)_2$ . This is due to the three adjacent cis oxygen atoms, which are substituted on the  $\text{C}_5\text{Me}_5$  ring in 3. In  $\alpha$ -ribose, which has three adjacent hydroxyl groups arranged in a cis fashion, the ring carbons C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> carrying the cis-OH groups resonate at 123.6, 122.0, and 124.7 ppm, respectively.<sup>28</sup>

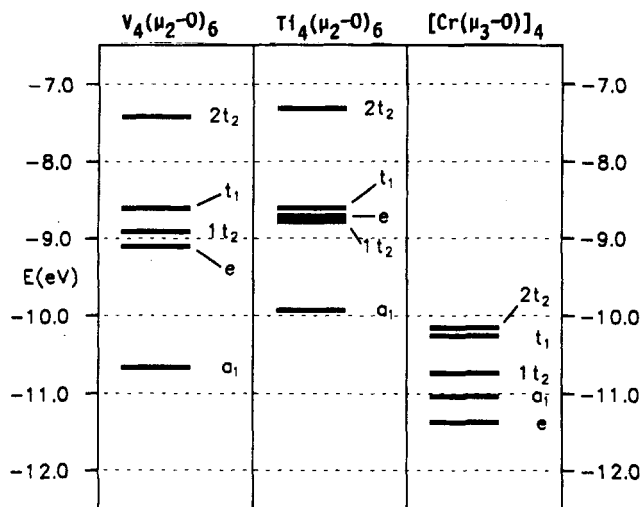
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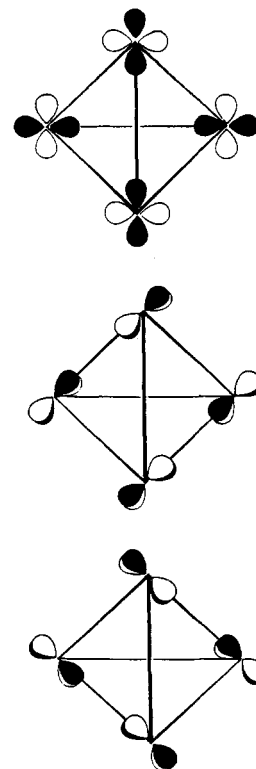
**Figure 4.** Energies and symmetries of the 12 cluster orbitals of the  $[M_4(\mu-O)_6]$  core of **4**, of  $[(\eta-C_5H_5)Ti]_4(\mu-O)_6$ , and of  $[(\eta-C_5H_5)Cr(\mu_3-O)]_4$ .

**Table III.** Composition of the 12 Cluster Orbitals of  $[(\eta-C_5H_5)V]_4(\mu-O)_6$

| orbital | vanadium |    | oxygen, |    |
|---------|----------|----|---------|----|
|         | d, %     | %  | orbital | %  |
| $2t_2$  | 76       | 14 | e       | 87 |
| $t_1$   | 78       | 19 | $a_1$   | 66 |
| $1t_2$  | 70       | 30 |         | 21 |

**Physical Properties of  $[(\eta-C_5Me_5)V]_4(\mu-O)_6$  (**4**).** The structure of **4**, as determined by X-ray crystallography, was reported previously<sup>11</sup> and is shown in Figure 1. A list of important distances and angles is given in Table II. The average V–V distance is 3.003 (3,3), and that for V–O, 1.806 (6,16) Å; the V–O–V angles average 112.3 (3,8), and the O–V–O angles, 108.0 (3,5)°. The molecule has  $T_d$  symmetry within experimental error. In this respect **4** resembles  $[(\eta-C_5Me_5)Ti]_4(\mu-O)_6$ , which has average Ti–Ti distances of 3.228 (1) Å, with Ti–O = 1.837 (3) Å, Ti–O–Ti = 123.0 (1)°, and O–Ti–O = 101.9 (1)°.<sup>21,29</sup> The larger O–V–O angle (108.0 versus the O–Ti–O angle of 101.9°) is due to the four cluster electrons present in **4**. The larger O–V–O angle forces the V–O–V angle to be smaller than the Ti–O–Ti angle in  $[(\eta-C_5Me_5)Ti]_4(\mu-O)_6$  (see below). Whereas  $[(\eta-C_5Me_5)Ti]_4(\mu-O)_6$  is diamagnetic (as expected, since it contains Ti(IV)), **4** has a magnetic moment (Faraday method) of 2.90  $\mu_B$  at 295 K (2.15  $\mu_B$  independent of temperature between 213 and 295 K by the Evans NMR method<sup>30</sup>).

In order to understand the magnetic moment of **4**, we performed extended Hückel molecular orbital calculations on the model compounds  $[(\eta-C_5H_5)M]_4(\mu-O)_6$  (M = Ti, V). Cluster **4** is composed of four piano-stool  $(\eta-C_5R_5)V(O)_3$  fragments. In each of these fragments six vanadium orbitals are required for bonding to the ligands. This leaves three nonbonding orbitals on each vanadium, these being the remnants of the  $t_{2g}$  set of an octahedron. The orbitals interact to form the 12 cluster orbitals of the  $[V_4(\mu-O)_6]$  core of **4**. The energies and symmetries of these orbitals are shown in Figure 4; their approximate composition is given in Table III. The order of the energy levels is  $a_1 \ll e \leq 1t_2 \leq t_1 < 2t_2$ . Because the  $(\eta-C_5H_5)M(O)_3$  frag-



**Figure 5.** Composition of the occupied  $a_1$  orbital of the  $[V_4(\mu-O)_6]$  core of **4**.

ments are similar, the results superficially resemble those for  $[(\eta-C_5H_5)Cr(\mu_3-O)]_4$ ,<sup>31,32</sup> which are also shown in Figure 4.

From Table III it is seen that the assumption that the cluster orbitals are pure metal d in character is valid only for the e set. There is considerable oxygen character in the other sets. This result is different from  $[(\eta-C_5H_5)Cr(\mu_3-O)]_4$ , where the oxygen contribution to the 12  $[Cr(\mu_3-O)]_4$  cluster orbitals was much smaller. The reason for the difference is that the oxygen atoms in  $[(\eta-C_5H_5)Cr(\mu_3-O)]_4$  are three-coordinate and will only donate electrons reluctantly from their remaining filled orbital. In **4** the oxygen atoms are two-coordinate and  $\pi$  donation of electrons from the oxygens to the metals is more facile. A second difference between the results for  $[(\eta-C_5H_5)Cr(\mu_3-O)]_4$  and  $[(\eta-C_5H_5)V]_4(\mu-O)_6$  is that in the former case the energies of the 12 cluster orbitals lay within a 1.5-eV range; in the present case they span 3.5 eV. Most of the increase in the total range is due to the low energy of the  $a_1$  orbital (see Figure 4), which is 1.6 eV below the e orbital. The marked stabilization of the  $a_1$  orbital occurs because it is strongly bonding between the vanadium atoms (Figure 5). The e,  $1t_2$ , and  $t_1$  orbitals are essentially nonbonding and are grouped within a narrow band of energy (0.5 eV). A calculation on  $[(\eta-C_5H_5)Ti]_4(\mu-O)_6$  with the Ti–Ti and Ti–O distances taken from the structure of  $[(\eta-C_5Me_5)Ti]_4(\mu-O)_6$ <sup>21</sup> in fact gave the order of energies as  $a_1 \ll 1t_2 \leq e \leq t_1 < 2t_2$  (i.e.  $1t_2$  and e were inverted with respect to **4**; see Figure 4).

Four electrons must be placed in the 12 cluster orbitals shown in Figure 4. This leads to a ground state configuration for **4** of  $a_1^2 e^2$  and a predicted spin-only paramagnetism of 2.83  $\mu_B$ , appropriate to two unpaired electrons. The observed value in the solid state is 2.90  $\mu_B$ ; the value in solution is lower, 2.15  $\mu_B$ , possibly because of the

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presence of diamagnetic  $(C_5Me_5)_2$  as an impurity. The observed magnetic moment and the undistorted  $T_d$  geometry of **4** suggest that the energy level ordering shown in Figure 4 is correct. The order  $a_1 < 1t_2 < e < t_1 < 2t_2$  would give a ground state of  $a_1^2t_2^2$ . This would lead to a Jahn-Teller distortion of the core, which is not observed.

The  $a_1$  orbital of **4** is strongly bonding with respect to the V-V interaction in the  $[V_4(\mu-O)_6]$  core (Figure 5). The effect of the occupation of this orbital by two electrons becomes clear when the core distances in **4** are compared to the distances in the  $[Ti_4(\mu-O)_6]$  core of  $[(\eta-C_5Me_5)-Ti]_4(\mu-O)_6$ . The average V-O distance in **4** is 1.806 Å, only 0.031 Å shorter than the Ti-O distance (1.837 Å). When the Ti-O-Ti angle (123.0°) is combined with the V-O distance, a calculated V-V distance of 3.174 (3) Å results. The observed V-V distance is 3.003 (3) Å. The shortening in the V-V distance of 0.17 Å is mainly due to the bonding effect of the two electrons in the  $a_1$  orbital. There are however only two bonding electrons for the six vanadium-vanadium interactions. The V-V distance is therefore longer than the 2.659 (1) Å in  $[(\eta-C_5H_4Me)V]_2(\mu-S)_2(\mu-S)$ ,<sup>33</sup> in which a single V-V bond is considered to be present. In  $[(\eta-C_5H_5)V]_5(\mu_3-O)_6$ , which has eight electrons for nine interactions, the V-V distances average 2.740 (2) (equatorial-equatorial) and 2.752 (2) Å (equatorial-axial).<sup>5</sup> In  $[(\eta-C_5H_4Me)V(\mu_3-S)]_4$ , which has eight electrons for six interactions, the average V-V distances are 2.884 (3) and 2.868 (3) Å.<sup>34</sup> An interesting example of an adamantane-like structure in which the metals are clearly not bonded is  $\{[(C_6H_{15}N_3)Mn]_4(\mu-O)_6\}^{4+}$ , which has a magnetic moment of 3.96  $\mu_B$ /manganese atom, corresponding to 12 unpaired electrons per cluster, and a Mn-Mn distance of 3.21 (1) Å.<sup>35</sup>

Although **4** was paramagnetic in the solid state (Faraday method) and in solution (Evans' NMR method), the  $^1H$  NMR spectrum at 295 K and 200 MHz in  $C_6D_6$  showed a single sharp signal at 2.00 ppm. Paramagnetic molecules usually show considerable shifting of the  $^1H$  signal. This is most pronounced with  $C_5H_5$  derivatives, less so with  $C_5(CH_3)_5$ , which are often found in the diamagnetic region (0–10 ppm). However, **4** is the first example that we have encountered in which the  $CH_3$  protons are apparently not shifted at all by the paramagnetic  $[V_4(\mu-O)_6]$  core. The result is even more surprising, since we were able to obtain a solvent shift in the determination of the magnetic moment by the Evans method, although the moment was lower than that determined in the solid state.

**Structure and Properties of  $(\eta-C_5Me_5)_6V_8O_{17}$  (**5**).** Exhaustive oxidation of **1** gave olive green, air-stable **5**. Analogous compounds were obtained on oxidation of  $(\eta-C_5Me_4H)_2V$  and  $(\eta-C_5Me_4Et)_2V$ ; **5** was also obtained by oxidation of **4** or of  $(\eta-C_5Me_5)V(CO)_4$  with excess  $O_2$ . All the reactions were very reproducible. Purification of **5** was achieved by repeated recrystallization from toluene/hexane. Microcrystalline samples were always obtained. As noted above, the formula proposed for **5**,  $(\eta-C_5Me_5)_6V_8O_{17}$ , is very close to that proposed by Herberhold and co-workers for the product of oxidation of  $(\eta-C_5Me_5)V(CO)_4$  with  $O_2$ : " $(\eta-C_5Me_5)_3V_4O_9$ ".<sup>9</sup> The last formula has been placed in quotes, since it contains vanadium in an oxidation state greater than five.

Microanalysis (C/H) and atomic absorption analysis (V) on both the  $C_5Me_5$  and  $C_5Me_4H$  derivatives of **5** indicated

a  $C_5R_5V$  ratio of 3:4. Molecular weight determination by osmometry in benzene gave a value of 1220. No parent ion peak was observed in the mass spectrum under a wide variety of conditions and ionization methods. Fragments of the type  $(C_5Me_5)_xV_yO_z^+$  were observed to  $m/e$  1082 (EI mode).

The  $^1H$  NMR spectrum of **5** showed only a sharp singlet at 2.11 ppm, assigned to the  $CH_3$  protons of a  $C_5Me_5$  ligand. The  $^{13}C$  spectrum showed two sharp singlets at 129.5 ( $C_5(CH_3)_5$ ) and 11.7 ppm ( $C_5(CH_2)_5$ ). The  $^1H$  spectrum was unchanged between +20 and -40 °C. Hence, there is only one type of  $\eta-C_5Me_5$  ligand in **5**. The  $^1H$  and  $^{13}C$  spectra of the  $C_5Me_4H$  derivative of **5** also showed signals expected for a single type of  $\eta-C_5Me_4H$  ligand. However, the  $^{51}V$  spectrum of **5** showed two resonances, a broad one at -481 (line width 1650 Hz) and a much narrower one at -578 ppm (line width 850 Hz). The  $C_5Me_4H$  derivative showed two similar resonances at -517 and -592 ppm. The observation of only one type of  $C_5R_5$  ligand but two types of vanadium is only compatible with a structure in which some vanadium atoms carry no  $C_5R_5$  ligand. The analytical evidence clearly indicated that the ratio of vanadium carrying  $C_5Me_5$  to vanadium without  $C_5Me_5$  was 3:1. The  $^{51}V$  NMR spectrum indicated an approximate ratio of 1:1; the integration may suffer from relaxation effects.

The  $^{17}O$  NMR spectrum ( $C_5Me_4H$  derivative) showed a broad signal at 635 ppm and two resonances at 1153 and 1186 ppm. The ratio of the resonances was approximately 2:1.1:1.1. Klemperer and co-workers found that  $V=O$  resonated in the 1150 ppm region,  $V-(\mu-O)-V$  in the 900–760 ppm region, and  $V_3(\mu_3-O)$  in the 390 ppm region.<sup>36</sup> The two resonances at 1153 and 1186 ppm can be assigned to an oxygen of the  $V=O$  type. The broad signal at 635 ppm may be due to either  $\mu_2-O$  or  $\mu_3-O$ . Heteronuclear decoupling experiments ( $C_5Me_4H$  derivative) established that the vanadium resonance at 592 ppm was coupled to the terminal  $V=O$  resonance at 1153 ppm and to the broad bridging oxygen resonance at 635 ppm. There was no observable coupling between the  $^{51}V$  resonance at 517 ppm and any of the three  $^{17}O$  resonances. It has been observed previously that broad resonances such as that at -517 ppm cannot always be decoupled.<sup>36</sup> The infrared spectrum of **5** showed two absorption bands assignable to  $\nu(V=O)$ , at 960 and 975  $cm^{-1}$ .

The spectroscopic data on the vanadium-oxygen units is in good agreement with structures I–III (Figure 6) for **5**. Structure III can have several isomers. Because III is extremely rigid, the isomers would not readily interconvert and there is no steric preference for one or the other isomer. The NMR results clearly showed that only one isomer was present at room temperature or below. Therefore we do not believe that III represents the structure of **5**. Structures I and II would also show several isomers. However, these structures are nonrigid, and interconversion between isomers is possible. There is also a very marked preference for the isomers shown in Figure 6, because of the steric repulsion of the bulky  $C_5Me_5$  rings.

Structures I and II might be expected to show two  $^1H$ ,  $^{13}C$ , and  $^{51}V$  resonances, since there are two types of  $(\eta-C_5Me_5)V$  units. The types differ only in their location symmetry; the coordination about the vanadium is the same. The resonance at -481 ppm in the  $^{51}V$  spectrum is broader than that at -578 ppm, and we therefore believe that it arises from the vanadium carrying the  $\eta-C_5Me_5$  ligands.

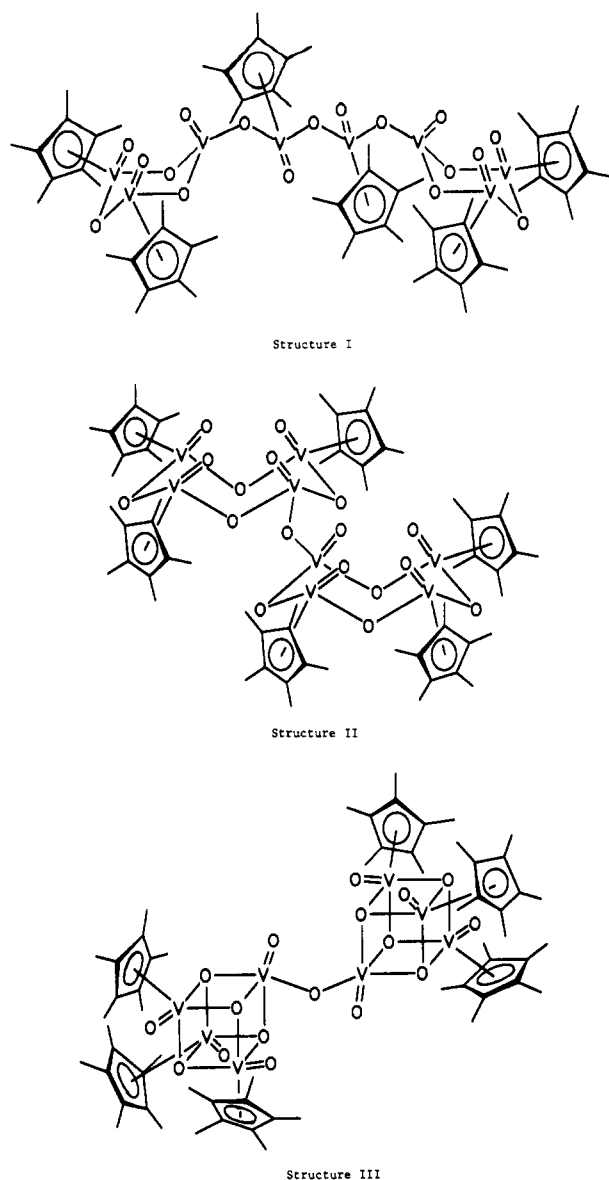
While there is no direct precedent for any of the structures I–III in Figure 6, several compounds contain the

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**Figure 6.** Proposed structures for  $(\eta\text{-C}_5\text{Me}_5)_6\text{V}_8\text{O}_{17}$  (5).

proposed units. A molybdenum cubane  $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{O})(\mu_3\text{-O})]_4$  analogous to that in III has been proposed.<sup>37</sup> An alternative structure for this compound is a  $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{O})(\mu\text{-O})]_4$  ring, as in II.<sup>38</sup> In  $[(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\mu\text{-O})_2\text{Mo}(\text{O})_2]_2$  there are tetranuclear rings with some molybdenum having  $\eta\text{-C}_5\text{H}_5$  and some only oxygen ligands.<sup>39</sup> In  $(\eta\text{-C}_5\text{H}_5)_{10}\text{V}_{12}\text{O}_{17}$  two  $[\text{V}_6(\mu_3\text{-O})_8]$  cuboctahedra are linked by an oxygen atom,<sup>6</sup> whereas in  $(\eta\text{-C}_5\text{Me}_5)_6\text{Mo}_8\text{O}_{16}$  two  $[(\eta\text{-C}_5\text{Me}_5)_3\text{Mo}_3(\mu\text{-O})_3(\mu_3\text{-O})_3\text{Mo}(\text{O})]$  units are linked by two oxygen atoms.<sup>40</sup>

### Experimental Section

**General Methods.** The starting material  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  (1) was prepared by the published procedure,<sup>41</sup> and  $(\eta\text{-C}_5\text{Me}_4\text{H})_2\text{V}$  and  $(\eta\text{-C}_5\text{Me}_4\text{Et})_2\text{V}$  were prepared analogously;<sup>42</sup>  $[(\eta\text{-C}_5\text{Me}_5)\text{V}(\text{O})(\mu\text{-O})]_3$  was prepared as described previously.<sup>8</sup> All other materials

were reagent grade. Solvents (toluene, hexane) were predried according to standard methods, stored under vacuum over MeLi, and distilled under vacuum. Infrared spectra were measured on a Perkin-Elmer 683 instrument, mass spectra on a KRATOS MS50 instrument, and NMR spectra on a Varian XL-200 multinuclear instrument.  $^{51}\text{V}$ - $^{17}\text{O}$  heteronuclear decoupling experiments were conducted at the University of Illinois on a General Electric GN 300 WB instrument equipped with a locally modified two coil probe. The inner coil was used for decoupling as well as observing vanadium. The outer coil was used for observing oxygen. Magnetic moments were determined by the Faraday method at 295 K with an Alpha Scientific magnet equipped with a Cahn electrobalance. Microanalyses (C, H, and Cl) were by Beller Laboratory, Göttingen, Germany; vanadium was determined by atomic absorption using a Perkin-Elmer 2380 spectrophotometer. Molecular weights by osmometry were obtained at the Mikroanalytisches Laboratorium, Engelskirchen, Germany.

The molecular orbital calculations on  $[(\eta\text{-C}_5\text{H}_5)\text{M}]_4(\mu\text{-O})_6$  were of the extended Hückel type using the programs of Hoffmann and co-workers.<sup>43</sup> Coefficients for C, H, and O were supplied in the program, those for vanadium from ref 44, and those for titanium from ref 45. The distances were taken from the structures of  $[(\eta\text{-C}_5\text{Me}_5)\text{M}]_4(\mu\text{-O})_6$  (M = Ti, V) but were averaged and idealized to produce the maximum symmetry. The values used were C-H = 0.96, C-C = 1.40, V-C = 2.35, V-O = 1.81, and V-V = 3.00 Å or Ti-C = 2.38, Ti-O = 1.836, and Ti-Ti = 3.225 Å.

**Reaction between  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  and  $\text{O}_2$ : Formation of  $[(\mu\text{-}\eta^3\text{-C}_5\text{Me}_5\text{O}_3)\text{V}(\text{O})]_2$ .** A solution of  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  (0.527 g, 1.64 mmol) in hexane (60 cm<sup>3</sup>) was incubated with  $\text{O}_2$  (3.28 mmol) at -30 °C. The pale burgundy solution quickly turned deep reddish brown and heat was evolved. After the solution was stirred at -30 °C for 12 h, the color of the solution was unchanged and no precipitate had formed. Upon evaporation to dryness, an oily reddish brown residue was obtained (0.615 g). The crude reaction product was redissolved in hexane (10 cm<sup>3</sup>) and purified by chromatography on controlled-pore glass beads (Sigma, Pg-240-200), under argon with hexane as the eluting agent. The column dimensions were 1.8-cm diameter by 26-cm length.

The first fraction was pale yellow. On evaporation of hexane in vacuo, colorless crystals were obtained. Yield: 0.140 g, 63%. These were characterized as  $(\text{C}_5\text{Me}_5)_2$ . Mass spectrum (EI, 70 eV, high resolution):  $m/e$  270.2336 (4); calcd for  $\text{C}_{20}\text{H}_{30}^+$ ,  $m/e$  270.2347.  $^1\text{H}$  NMR ( $^2\text{H}_8$ ,  $\text{C}_6\text{H}_5\text{CH}_3$  solution, 200 MHz): 1.10 (s, 6 H), 1.65 (s, 12 H), 1.72 ppm (s, 12 H).  $^{13}\text{C}$  NMR ( $^2\text{H}$   $\text{CHCl}_3$  solution, 50 MHz): 10.9, 12.5, 19.3 ppm ( $\text{C}_5(\text{CH}_3)_5$ ); 59.8, 133.2, 141.7 ppm ( $\text{C}_5(\text{CH}_3)_5$ ). Mp: 53–58 °C. The results are in reasonable agreement with the literature.<sup>12,13</sup> A sample prepared by the literature method melted at 52–55 °C.

The second fraction was ruby red. The volume of this fraction was reduced to 10 cm<sup>3</sup>, and it was then set aside at room temperature for several days. Red crystals of 3 formed. Yield, based on the NMR of the crude product: 0.082 g, 20%. The crystals were characterized as  $[(\mu\text{-}\eta^3\text{-C}_5\text{Me}_5\text{O}_3)\text{V}(\text{O})]_2$  (3). Mass spectrum (EI, 70 eV):  $m/e$  500; a table of the fragmentation pattern has been deposited previously.<sup>10</sup>  $^1\text{H}$  NMR ( $^2\text{H}_8$ ,  $\text{C}_6\text{H}_5\text{CH}_3$  solution, 200 MHz): 2.05 (s, 18 H), 2.12 ppm (s, 12 H).  $^{51}\text{V}$  NMR ( $\text{C}_6\text{H}_5\text{CH}_3$  solution, 52.5 MHz, relative to  $\text{VOCl}_3$ ): -672 ppm (s). Infrared spectrum (Nujol mull, KBr plates): 935 (m), 957 cm<sup>-1</sup> (sh),  $\nu(\text{V}=\text{O})$ . The identity of 3 was also established by X-ray crystallography.<sup>10</sup>

**Reaction of  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  with  $\text{O}_2$ : Formation of  $[(\eta\text{-C}_5\text{Me}_5)\text{V}]_4(\mu\text{-O})_6$  (4).** A solution of  $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$  (1.204 g, 3.75 mmol) in toluene (50 cm<sup>3</sup>) was incubated with  $\text{O}_2$  (2.81 mmol) at 22 °C for 48 h. The solution slowly turned deep green. The solvent was removed in vacuo, giving an oily green residue. Organic byproducts and unreacted starting material were removed under dynamic vacuum at 100 °C, leaving a dry black residue. From the residue, 4 was isolated in 50% yield by extraction with

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toluene. The identity of **4** was proven by comparison with an authentic sample prepared by the reaction between **1** and  $N_2O$  (see below).

**Reaction of  $(\eta-C_5Me_5)_2V$  with  $O_2$ : Formation of  $(\eta-C_5Me_5)_6V_8O_{17}$  (**5**).** A solution of  $(\eta-C_5Me_5)_2V$  (0.477 g, 1.49 mmol) in toluene (50 cm<sup>3</sup>) was incubated with  $O_2$  (2.98 mmol) at 22 °C for 72 h. The color of the solution quickly changed from burgundy to dark brown and eventually to olive green. The resultant mixture was filtered to remove a small quantity of solid. The filtrate was concentrated to 10 cm<sup>3</sup> in vacuum and then layered with hexane (20 cm<sup>3</sup>), giving a black precipitate. The precipitate was removed by filtration, washed with hexane (20 cm<sup>3</sup>), and dried in vacuo. Yield of **5**: 0.180 g, 65%. Anal. Calcd for  $C_{85}H_{90}V_8O_{17}$ : C, 48.3; H, 6.0; V, 27.4. Found: C 47.7; H, 5.9; V, 26.5. Molecular weight (by osmometry in  $C_6H_6$  solution): 1220; calcd, 1490. Infrared: 945 (sh), 960 (m), 975 (m) cm<sup>-1</sup> ( $\nu(V=O)$ ). <sup>1</sup>H NMR (<sup>2</sup>H<sub>6</sub>  $C_6H_6$  solution, 200 MHz): 2.11 ppm (s). <sup>13</sup>C NMR (<sup>2</sup>H<sub>1</sub>  $CHCl_3$  solution, 50 MHz): 129.5 ppm (s,  $C_5(CH_3)_5$ ), 11.7 ppm (s,  $C_5-(CH_3)_5$ ). <sup>51</sup>V NMR ( $C_6H_5CH_3$  solution, 52.5 MHz, relative to  $VOCl_3$ ): -481 (s, 2 V), -578 ppm (s, 6 V). Magnetic moment: 0  $\mu_B$  (295 K).

**Reaction of  $(\eta-C_5Me_5)V(CO)_4$  with  $O_2$ : Formation of  $(\eta-C_5Me_5)_6V_8O_{17}$  (**5**).** A solution of freshly sublimed  $(\eta-C_5Me_5)V(CO)_4$  (0.715 g, 2.40 mmol) in toluene (50 cm<sup>3</sup>) was incubated with  $O_2$  (2.40 mmol) at 22 °C for 96 h. The initially orange solution slowly became deep olive green. The solution was filtered to remove a small quantity of precipitate. The solvent was removed from the filtrate in vacuum and the residue recrystallized from toluene/hexane. Yield of **5**: 0.32 g, 71%. The product was identified as **5** by comparison of its NMR and infrared spectra with those of a sample prepared by oxidation of  $(\eta-C_5Me_5)_2V$  with  $O_2$  (see above).

**Reaction of  $(\eta-C_5Me_4H)_2V$  with  $O_2$ : Formation of  $(\eta-C_5Me_4H)_6V_8O_{17}$ .** A solution of  $(\eta-C_5Me_4H)_2V$  (0.560 g, 1.91 mmol) in hexane (50 cm<sup>3</sup>) was incubated with  $O_2$  (3.82 mmol) at 22 °C for 48 h. The initial violet burgundy solution turned brown and deposited a brown precipitate. The precipitate was removed by filtration, and the filtrate was reduced in volume until a yellow oil formed. This oil was identified as  $(C_5Me_4H)_2$  by mass and NMR spectroscopies. The brown precipitate was dissolved in toluene (50 cm<sup>3</sup>); on being stirred for 48 h, the solution became olive green. The volume of the solution was reduced to 25 cm<sup>3</sup> in vacuo, and then hexane (25 cm<sup>3</sup>) was layered onto it. A black precipitate formed. This was removed by filtration and dried in vacuum. Yield of  $(\eta-C_5Me_4H)_6V_8O_{17}$ : 0.25 g, 75%. Anal. Calcd for  $C_{54}H_{78}V_8O_{17}$ : C, 46.1; H, 5.5%. Found: C, 47.1; H, 5.7. <sup>1</sup>H NMR (<sup>2</sup>H<sub>6</sub>  $C_6H_6$  solution 200 MHz): 6.02 (s, 1 H,  $C_5(CH_3)_4H$ ), 2.32, 2.10 ppm (2 s, 12 H,  $C_5(CH_3)_4H$ ). <sup>13</sup>C NMR (<sup>2</sup>H  $CHCl_3$  solution, 50 MHz): 134.7, 128.8, 118.9 ppm ( $C_5(CH_3)_4H$ ); 13.9, 11.9 ppm ( $C_5(CH_3)_4H$ ). <sup>51</sup>V NMR ( $C_6H_5CH_3$  solution, 52.5 MHz, relative to  $VOCl_3$ ): -517 (s, 2 V), -592 ppm (s, 6 V). <sup>17</sup>O NMR (<sup>2</sup>H  $CHCl_3$  solution, 40.7 MHz, relative to  $H_2O$ ): 635 (s), 1153 (s), 1186 ppm (s). Infrared: 955 (m), 985 cm<sup>-1</sup> (m) ( $\nu(V=O)$ ). The compound was diamagnetic by the Evans NMR method. Mass spectrum (EI, 70 eV):  $m/e$  1082 ( $(C_5Me_4H)_4V_7O_{15} + H^+$ ), 948 ( $(C_5Me_4H)_3V_8O_{11} + H^+$ ), 921 ( $(C_5Me_4H)_2V_8O_{17} - H^+$ ), 916 ( $(C_5Me_4H)_3V_8O_9 + H^+$ ), 800 ( $(C_5Me_4H)V_8O_{17} - H^+$ ), 790 ( $(C_5Me_4H)_2V_7O_{12} - H^+$ ), 779 ( $(C_5Me_4H)_2V_8O_8 + H^+$ ), 733 ( $(C_5Me_4H)V_7O_{16} - H^+$ ), 657 ( $(C_5Me_4H)V_8O_8^+$ ), 641 ( $(C_5Me_4H)_2V_5O_9^+$ ), 625 ( $(C_5Me_4H)_2V_5O_8^+$ ), 603 ( $(C_5Me_4H)V_6O_{11}^+$ ), 592 ( $(C_5Me_4H)_2V_5O_6 - H^+$ ), 437 ( $(C_5Me_4H)V_4O_7^+$ ), 405 ( $(C_5Me_4H)V_4O_5^+$ ), 389 ( $(C_5Me_4H)V_4O_4^+$ ), 373 ( $(C_5Me_4H)V_4O_3^+$ ), 356 ( $(C_5Me_4H)V_4O_2 - H^+$ ).

**Reaction of  $(\eta-C_5Me_5)V_4(\mu-O)_6$  (**4**) with  $O_2$ : Formation of  $(\eta-C_5Me_5)_6V_8O_{17}$  (**5**).** A solution of  $(\eta-C_5Me_5)V_4(\mu-O)_6$  (0.400 g, 0.48 mmol) in toluene (40 cm<sup>3</sup>) was incubated with  $O_2$  (1.43 mmol) at 22 °C for 72 h. The initial green color of the solution of **4** turned immediately brown and then slowly olive green. The solution was filtered to remove a small amount of precipitate, the filtrate concentrated to 15 cm<sup>3</sup> in vacuum, and then hexane (20 cm<sup>3</sup>) layered onto it. A black precipitate of **5** formed. This was collected by filtration washed with hexane (20 cm<sup>3</sup>) and dried in vacuo. Yield: 0.26 g, 74%. The product **5** was shown by spectroscopy to be identical with that obtained by oxidation of **1** with  $O_2$  (see above).

**Reaction of  $(\eta-C_5Me_5)_2V$  with  $N_2O$ : Formation of  $[(\eta-C_5Me_5)V_4(\mu-O)_6]$  (**4**).** A solution of  $(\eta-C_5Me_5)_2V$  (0.657 g, 2.05 mmol) in toluene (60 cm<sup>3</sup>) was incubated with  $N_2O$  (4.10 mmol) at 22 °C for 72 h. The color of the solution changed from burgundy to green. The toluene was removed from the solution in vacuum and the residue sublimed under vacuum at 80 °C for 24 h. This procedure removed  $(C_5Me_5)_2$  as an oily solid on the probe, leaving a dark green residue. The residue was extracted with hexane (50 cm<sup>3</sup>). Concentration of the green solution to 20 cm<sup>3</sup> gave green crystals of **4**. Further extractions of the residue with hexane gave more product, for a total yield of 0.37 g (85%) of deep green **4**. Anal. Calcd for  $C_{40}H_{60}V_4O_6$ : C, 57.1; H, 7.1; V, 24.3. Found: C, 57.1; H, 7.2; V, 23.7. Mass spectrum (EI, 70 eV):  $m/e$  840; calcd for  $4^+$ ,  $m/e$  840. <sup>1</sup>H NMR (<sup>2</sup>H<sub>6</sub>  $C_6H_6$  solution, 200 MHz): 2.00 ppm (s). Infrared: 375 cm<sup>-1</sup> (m),  $\nu[V_4(\mu-O)_6]$ . Magnetic moment: 2.90  $\mu_B$  (Faraday method) 295 K; 2.15  $\mu_B$  (Evans method, independent of temperature between 213 and 295 K). Crystals of **4**, prepared as described, were also characterized by X-ray crystallography.<sup>11</sup>

**Reaction of  $(\eta-C_5Me_4H)_2V$  with  $N_2O$ : Formation of  $[(\eta-C_5Me_4H)V_4(\mu-O)_6]$ .** A solution of  $(\eta-C_5Me_4H)_2V$  (0.53 g, 1.81 mmol) in hexane (50 cm<sup>3</sup>) was incubated with  $N_2O$  (3.62 mmol) at 22 °C for 48 h. The resultant bright green solution was filtered and the solvent removed under vacuum. Sublimation of the residue under vacuum at 80 °C for 18 h gave pale yellow  $(C_5Me_4H)_2$  on the probe. This compound was identified by high-resolution mass spectroscopy (calcd for  $C_{18}H_{26}^+$ ,  $m/e$  242.2035; found,  $m/e$  242.2047 (**5**)) and <sup>1</sup>H NMR spectroscopy (<sup>2</sup>H<sub>6</sub>  $C_6H_6$  solution, 200 MHz): 1.09 (s, 6 H), 1.67 (s, 6 H), 1.769, 1.786, 1.794 (singlets, total 12 H), and 6.06 ppm (s, 2 H). After the sublimation a dark green residue remained. Extraction with toluene gave green  $[(\eta-C_5Me_4H)V_4(\mu-O)_6]$  in 85% yield. The very air-sensitive product was characterized by mass spectroscopy (EI, 70 eV): calcd for  $[(C_5Me_4H)V_4]O_6^+$ ,  $m/e$  784; found,  $m/e$  784. Infrared spectroscopy: 375 cm<sup>-1</sup> (m),  $\nu[V_4(\mu-O)_6]$ .

**Reaction of  $(\eta-C_5Me_4Et)_2V$  with  $N_2O$ : Formation of  $[(\eta-C_5Me_4Et)V_4(\mu-O)_6]$ .** A solution of  $(\eta-C_5Me_4Et)_2V$  (0.66 g, 1.90 mmol) in hexane (50 cm<sup>3</sup>) was incubated with  $N_2O$  (3.80 mmol) at 22 °C for 96 h. The solvent was removed under vacuum and the green residue sublimed under vacuum at 90 °C for 24 h. A pale yellow oil collected on the probe. This was characterized as  $(C_5Me_4Et)_2$  by mass spectroscopy (EI, 70 eV):  $m/e$  298; calcd for  $(C_5Me_4Et)_2$ ,  $m/e$  298. The green residue that remained was extracted with toluene, giving deep green  $[(\eta-C_5Me_4Et)V_4(\mu-O)_6]$  in 80% yield. The product was characterized by mass spectroscopy.

**Reaction of  $PMe_2Ph$  with  $[(\eta-C_5Me_5)V(O)(\mu-O)]_3$ : Formation of  $[(\eta-C_5Me_5)V_4(\mu-O)_6]$  (**4**).** To a solution of  $[(\eta-C_5Me_5)V(O)(\mu-O)]_3$  (0.96 g, 1.50 mmol) in tetrahydrofuran (200 cm<sup>3</sup>) was added  $PMe_2Ph$  (0.73 cm<sup>3</sup>, 4.40 mmol). The solution was stirred at room temperature for 48 h, during which time it changed from brown to dark green. The solution was filtered to remove a small amount of precipitate and then the solvent removed in vacuum to give a solution volume of circa 50 cm<sup>3</sup>. On being set aside for 2 weeks, the solution deposited crystals of **4**. Yield: 0.05 g, 5%. These were characterized by X-ray crystallography. Attempts to obtain higher yields of the product were unsuccessful due to the presence of oily  $PMe_2Ph$  and  $OPMe_2Ph$ .

**Reaction of  $[(\eta-C_5Me_5)V(O)(\mu-O)]_3$  with  $(\eta-C_5Me_5)_2V$ : Formation of  $[(\eta-C_5Me_5)V_4(\mu-O)_6]$  (**4**).** A solution of **1** (0.15 g, 0.46 mmol) in toluene (30 cm<sup>3</sup>) was added to a solution of  $[(\eta-C_5Me_5)V(O)(\mu-O)]_3$  (0.30 g, 0.46 mmol) in toluene (40 cm<sup>3</sup>) and the resultant brown solution stirred at room temperature for 48 h. The solution became deep green. The solvent was removed in vacuum and the residue sublimed at 90 °C for 24 h, giving  $(C_5Me_5)_2$  on the probe. Dissolution of the residue in toluene (25 cm<sup>3</sup>) and precipitation with hexane (30 cm<sup>3</sup>) gave **4** in 25% yield. The identity of **4** was established by spectroscopy and comparison with a sample prepared from the reaction between **1** and  $N_2O$  described above.

**Reaction of  $(\eta-C_5Me_5)_6V_8O_{17}$  (**5**) with  $SOCl_2$ : Formation of  $(\eta-C_5Me_5)VCl_2(O)$  (**2**).** To a solution of **5** (0.2 g, 0.13 mmol) in  $CH_2Cl_2$  (25 cm<sup>3</sup>) was added  $SOCl_2$  (0.105 g, 0.88 mmol). The solution was stirred at room temperature for 15 min, and then the solvent and excess  $SOCl_2$  were removed under vacuum. Extraction with ether (20 cm<sup>3</sup>) and evaporation of the extracts gave  $(\eta-C_5Me_5)VCl_2(O)$  (**2**) as a blue-green solid. Yield: 0.205 g,



0.75 mmol, 70% (based on vanadium). The product 2 was identified by mass, infrared, and NMR spectroscopies and comparison with an authentic sample.<sup>23</sup>

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## Synthesis of Group 6 (Aryloxy)carbyne and Phosponiocarbyne Complexes from Chlorocarbyne Precursors

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Displacement of chloride from the group 6 chlorocarbyne complexes  $\text{Tp}'(\text{CO})_2\text{M}\equiv\text{CCl}$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Tp}' = \text{HB}[\text{N}_2\text{C}_3\text{Me}_2\text{H}]_3$ ) with aryloxy anions produces the neutral (aryloxy)carbynes  $\text{Tp}'(\text{CO})_2\text{M}\equiv\text{COAr}$  ( $\text{Ar} = \text{Ph}, 4\text{-C}_6\text{H}_4\text{CH}_3, 4\text{-C}_6\text{H}_4\text{OCH}_3$ ). Tertiary phosphines ( $\text{PMe}_2\text{Ph}, \text{PPh}_3, \text{PCy}_3$ ) also displace chloride from the tungsten halocarbyne precursor to give the cationic phosponiocarbynes  $[\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CPR}_3][\text{PF}_6]$ . Complex 5a,  $[\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CPMe}_2\text{Ph}][\text{PF}_6]$ , crystallizes in the triclinic space group  $\text{P}\bar{1}$  with unit cell dimensions  $a = 10.897$  (3) Å,  $b = 11.631$  (3) Å,  $c = 13.939$  (4) Å,  $\alpha = 102.96$  (2)°,  $\beta = 108.79$  (2)°,  $\gamma = 94.59$  (2)°,  $Z = 2$ , 4954 observed data,  $R = 0.039$  and  $R_w = 0.070$ . Although no one-bond coupling between phosphorus and the carbyne carbon was observed for the  $\text{PMe}_2\text{Ph}$  or  $\text{PPh}_3$  products, the tricyclohexyl derivative displays a small phosphorus-carbon one-bond coupling constant ( $^1J_{\text{P-C}} = 15$  Hz) in its <sup>13</sup>C NMR spectrum. All complexes have been characterized by <sup>1</sup>H and <sup>13</sup>C NMR and IR spectroscopy and by elemental analysis.

### Introduction

The stability imparted by heteroatom substituents bearing lone-pair electrons in low-oxidation-state Fischer-type carbene complexes, which tempers the characteristic electrophilic behavior of these compounds, has been documented by more than two decades of organometallics research.<sup>1</sup> The role of the transition metal is crucial in dictating the reactivity pattern accessible to the carbene carbon atom. While  $(\text{CO})_5\text{W}=\text{CHPh}$ , a low-oxidation-state Fischer carbene complex, is electrophilic at carbon, the carbene carbon in  $\text{Cp}_2(\text{R})\text{Ta}=\text{CHPh}$ , a high-oxidation-state Schrock alkylidene complex, is nucleophilic.<sup>1d</sup> The field of transition-metal carbyne chemistry, although less mature, has likewise provided numerous synthetic, theoretical, structural, and reactivity studies into the nature of the transition-metal-carbon multiple bond.<sup>2</sup> The only previously reported oxycarbyne complexes are the siloxycarbyne intermediates in the reductive coupling of

Chart I

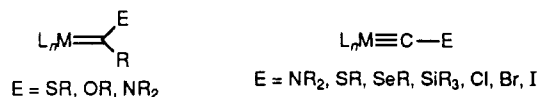
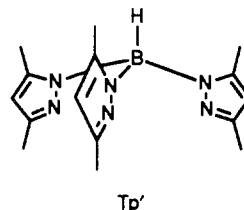
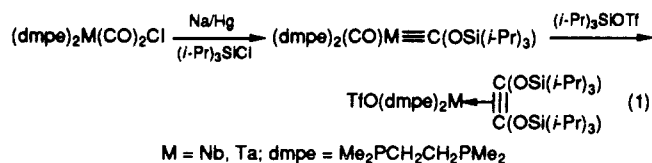


Chart II



$(\text{dmpe})_2\text{M}(\text{CO})_2\text{Cl}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) reported by Lippard et al. (eq 1).<sup>3</sup>



Substantive work has been devoted to carbyne complexes bearing other heteroatom substituents. Amino-carbynes comprise the majority of stable heteroatom-

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