

Figure 1. $WI_2(OCMe_3)_4$ molecule, with the atom-labeling scheme. The molecule has crystallographically imposed $4/m$ (C_{4h}) symmetry. Atoms are represented by ellipsoids of vibration at the 40% level.

Whether $W(OCMe_3)_6$ was an intermediate that decomposed to give $WO(OCMe_3)_4$ is unknown. It is also possible that $WO(OCMe_3)_4$ was formed by reaction with adventitious oxygen and/or water. In any event the challenge of preparing and identifying $W(OCMe_3)_6$ remains. The compound $WO(OCMe_3)_4$ is one we have isolated before in another way, and we shall report its structure and its chemical relationship to some other reactions of $W_2(OCMe_3)_6$ in a future publication.⁴

The structure of *trans*- $WI_2(OCMe_3)_4$ is shown in Figure 1. The molecule resides on a position of crystallographic $4/m$ or C_{4h} symmetry so that all angles around the tungsten atom are rigorously 90 or 180°, the two W–I distances are equal, and the four W–O distances are equal.

The $WI_2(OCMe_3)_4$ molecule is exceptionally interesting for several reasons. Perhaps most obvious is the fact that it is the only structurally characterized tungsten (or molybdenum) compound with the metal in oxidation state VI to contain metal to iodine bonds. The only adequately documented tungsten(VI) iodo compound in the literature appears to be WO_2I_2 , first reported in 1966.^{7,8} Since the structure is unknown beyond the statement that it is "a strongly disordered layer structure with a monoclinic unit cell", it is not certain whether there are discrete W–I bonds in this compound. It can be sublimed (but, to avoid decomposition to WO_2I , in the presence of excess I_2) so that some kind of molecule containing one or more W–I bonds does presumably exist. Obviously the dearth of iodo and bromo compounds of W^{VI} is attributable to the fact that there is normally an incompatibility between the oxidizing character of the metal in such a high formal oxidation state and the easy oxidizability of I[−] or iodine covalently bonded. What, then, allows *trans*- $WI_2(OCMe_3)_4$ to be stable?

It would appear that we have here a very striking example of the fact that alkoxide groups can be strong π donors to the metal atoms to which they nominally form single bonds. Strong π donation from the oxygen atoms would moderate the oxidizing power of the metal atom so that iodide ions in proximity to the $W(OCMe_3)_4^{2+}$ unit could simply form covalent bonds by sharing electrons rather than losing them altogether to form I_2 .

The structure of the $WI_2(OCMe_3)_4$ molecule provides direct evidence that strong $O \rightarrow W$ π bonding occurs. The W–O bond length, 1.840 (4) Å, is one of the shortest W–O or Mo–O "single" bond lengths yet reported.⁹ This must, of course, be in part due to the small radius of W^{VI} , but it also indicates considerable strengthening of the W–O bonds by π bonding. We note, further that the W–O–C angles are 160.5 (4)°, which provides another strong and independent indication that both

pairs of potential π electrons on each oxygen atom are being significantly donated to the metal atom.

The difference in the W–I and W–O bond lengths is 0.99 Å, whereas the difference between the commonly accepted single-bond covalent radii of the iodine and oxygen atoms is 0.67 Å. A large part of this "shortening" of the W–O bonds can be attributed to the strong $W \leftarrow O$ π interaction. Presumably in WO_2I_2 the oxygen atoms also donate π electron density over and above that needed to form $W=O$ bonds to the tungsten atom, and this also is a major factor in allowing the existence of a tungsten(VI) iodo compound.

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Registry No. $W_2(OCMe_3)_6$, 57125-20-9; *trans*- $WI_2(OCMe_3)_4$, 92543-30-1; I_2 , 7553-56-2; $WO(OCMe_3)_4(THF)$, 92543-29-8.

Supplementary Material Available: A more detailed account of the crystallographic work and tables of observed and calculated structure factors, anisotropic thermal parameters, and complete bond lengths and bond angles (8 pages). Ordering information is given on any current masthead page.

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A Novel Dinuclear Vanadium(II) Compound with Bridging Chlorine Atoms, Bridging Diphosphinomethane Ligands, and Bidentate Tetrahydroborate Ligands

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One of the major obstacles in developing the nonaqueous non-cyclopentadienyl chemistry of vanadium(II) has been the lack of soluble and easily prepared starting materials. At present the most readily available compound is a mixed vanadium–zinc complex $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$.^{1,2} While it can give rise to vanadium compounds that do not contain zinc atoms,³ sometimes molecules incorporating both vanadium and zinc are obtained.⁴

It has been reported recently⁵ that $LiBH_4$ can reduce vanadium in this V^{II} species to a +1 oxidation state, and in the presence of $PMePh_2$ an exotic, mixed V–Zn complex, $[V-(PMePh_2)_2H_2ZnBH_4]_2$ has been isolated. We have found that under similar conditions but in the presence of $Ph_2PCH_2PPh_2$ (dppm) a different reaction occurs, which affords a zinc free product. The use of dppm and $NaBH_4$ instead of $PMePh_2$ and $LiBH_4$, respectively, produces a complex of the formula $[V-(\mu-Cl)(\mu-dppm)BH_4]_2$. We consider this compound to be of unusual interest because it has, by virtue of its central $V(\mu-dppm)_2V$ frame, a potential for providing an entry into the chemistry of V^{II} dimers. At present no procedure for its isolation in a pure state is known, but we hope to solve that

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Table I. Crystallographic Data

| | |
|---|--|
| formula | $V_2Cl_3P_4C_{50}B_2H_{52}$ |
| fw | 971.28 |
| space group | <i>Pbca</i> |
| syst absences | $0kl$ ($k = 2n + 1$); $h0l$ ($l = 2n + 1$); $hk0$ ($h = 2n + 1$) |
| <i>a</i> , Å | 13.743 (4) |
| <i>b</i> , Å | 22.555 (5) |
| <i>c</i> , Å | 16.184 (2) |
| α , deg | 90.0 |
| β , deg | 90.0 |
| γ , deg | 90.0 |
| <i>V</i> , Å ³ | 5017 (3) |
| <i>Z</i> | 4 |
| <i>d</i> _{calcd} , g/cm ³ | 1.286 |
| cryst size, mm | 0.15 × 0.3 × 0.5 |
| μ (Mo K α), cm ⁻¹ | 6.250 |
| data colln instrum | Syntex P1 |
| radiation (monochromated in incident beam) | Mo K α ($\lambda = 0.71073$ Å) |
| orientation reflns range (2θ), deg | 15, 14.0 ≤ 2θ ≤ 36.1 |
| temp, °C | 22 |
| scan method | ω - 2θ |
| data colln range (2θ), deg | 4 ≤ 2θ ≤ 50 |
| no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$ | 1324; 1142 |
| no. of parameters refined | 167 |
| <i>R</i> ^a | 0.0595 |
| <i>R</i> _w ^b | 0.0774 |
| quality-of-fit indicator ^c | 1.649 |
| largest shift/esd, final cycle | 0.40 |
| largest peak, e/Å ³ | 0.7 |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w|F_o|$. ^c Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

problem and thus make available a valuable route to new vanadium chemistry in low oxidation state complexes. A particular goal is to find routes to compounds with multiple V-V bonds. It is noteworthy that this new compound represents the first example of a pair of group 5 transition atoms bridged by bis(diphenylphosphino)methane.

Experimental Section

All manipulations were carried out under an atmosphere of argon by using standard vacuum line techniques. $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$ was prepared according to the literature method.^{1,2}

Reaction of $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$ with $NaBH_4$. To a slurry of $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$ (0.81 g, 0.5 mmol) in 30 mL of THF were added dppm (0.77 g, 2 mmol) and $NaBH_4$ (0.11 g, 3 mmol). The mixture was stirred for 1 week, producing a dark green solution in which particles of white solid were suspended. Following filtration, the solvent was removed under vacuum. The black residue was redissolved in benzene (20 mL), producing a black-red solution. The benzene solution was filtered and hexane (50 mL) added, causing precipitation of a black solid (0.95 g). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into the benzene solution of the product. However the material so obtained was not homogeneous, and at least three components were observed: dark red crystals of $[V(\mu-Cl)(\mu-dppm)BH_4]_2$ (ca. 0.25 g, 26% yield) amorphous solid (probably a decomposition product, vide infra), and light green crystals shown to contain the initial $[V_2Cl_3(THF)_6]_2^+$ cation together with some unidentified monoanion, possibly $[M(BH_4)_3]^-$, where $M = V$ or Zn .

A complete identification of the green product by X-ray crystallography was precluded by severe difficulties associated with the presence of several badly disordered THF molecules. We tried to deal with this problem by collecting data at low temperature, but cooling to -45 °C or below resulted in disintegration of the crystals, probably due to a phase transition. No significant improvement in the structure refinement was observed with data collected at -42 °C.

Numerous attempts to isolate the red product in a pure state were unsuccessful. Different solvent mixtures involving toluene, benzene, THF, and hexane were employed, but no separation was accomplished.

Table II. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $[V(\mu-Cl)(\mu-dppm)BH_4]_2^a$

| atom | x | y | z | <i>B</i> , Å ² |
|-------|------------|-------------|-------------|---------------------------|
| V | 0.0004 (2) | 0.06424 (8) | -0.0351 (1) | 2.70 (4) |
| Cl | 0.0989 (3) | -0.0208 (1) | -0.0728 (2) | 3.16 (7) |
| P(1) | 0.1322 (3) | -0.0341 (1) | 0.1389 (2) | 2.68 (7) |
| P(2) | 0.1358 (3) | 0.0943 (1) | 0.0659 (2) | 2.87 (8) |
| B | 0.002 (2) | 0.1602 (7) | -0.086 (1) | 5.2 (5) |
| C(1) | 0.2078 (9) | 0.0292 (5) | 0.1025 (7) | 2.5 (3) |
| C(2) | 0.098 (1) | -0.0121 (5) | 0.2448 (8) | 3.7 (3)* |
| C(3) | 0.166 (1) | 0.0162 (5) | 0.2948 (8) | 3.7 (3)* |
| C(4) | 0.133 (1) | 0.0366 (6) | 0.3746 (8) | 4.7 (3)* |
| C(5) | 0.039 (1) | 0.0282 (6) | 0.3963 (9) | 5.0 (4)* |
| C(6) | -0.030 (1) | -0.0029 (6) | 0.3491 (9) | 5.6 (4)* |
| C(7) | 0.001 (1) | -0.0240 (5) | 0.2688 (8) | 4.4 (3)* |
| C(8) | 0.228 (1) | -0.0895 (5) | 0.1508 (7) | 2.7 (3)* |
| C(9) | 0.250 (1) | -0.1133 (6) | 0.2297 (7) | 4.1 (3)* |
| C(10) | 0.322 (1) | -0.1588 (6) | 0.2331 (9) | 5.2 (4)* |
| C(11) | 0.372 (1) | -0.1767 (6) | 0.1640 (8) | 4.7 (4)* |
| C(12) | 0.349 (1) | -0.1527 (6) | 0.0877 (8) | 4.7 (3)* |
| C(13) | 0.275 (1) | -0.1092 (6) | 0.0805 (8) | 3.9 (3)* |
| C(14) | 0.233 (1) | 0.1384 (5) | 0.0218 (7) | 3.2 (3)* |
| C(15) | 0.297 (1) | 0.1120 (6) | -0.0362 (8) | 4.0 (3)* |
| C(16) | 0.374 (1) | 0.1443 (7) | -0.0704 (9) | 5.7 (4)* |
| C(17) | 0.382 (1) | 0.2066 (7) | -0.053 (1) | 6.7 (5)* |
| C(18) | 0.317 (1) | 0.2319 (7) | 0.002 (1) | 6.6 (4)* |
| C(19) | 0.239 (1) | 0.1991 (6) | 0.0416 (9) | 5.3 (4)* |
| C(20) | 0.105 (1) | 0.1356 (5) | 0.1613 (8) | 3.7 (3)* |
| C(21) | 0.183 (1) | 0.1506 (6) | 0.2159 (9) | 5.0 (4)* |
| C(22) | 0.155 (1) | 0.1818 (7) | 0.293 (1) | 6.4 (4)* |
| C(23) | 0.055 (1) | 0.1939 (7) | 0.302 (1) | 6.4 (4)* |
| C(24) | -0.022 (1) | 0.1811 (7) | 0.249 (1) | 7.5 (5)* |
| C(25) | 0.007 (1) | 0.1492 (6) | 0.1729 (9) | 5.8 (4)* |
| H(1) | -0.054 (8) | 0.136 (4) | -0.036 (6) | 3 (3)* |
| H(2) | 0.046 (9) | 0.109 (5) | -0.110 (7) | 6 (3)* |
| H(3) | 0.05 (1) | 0.194 (5) | -0.043 (7) | 7 (4)* |
| H(4) | -0.037 (8) | 0.170 (4) | -0.131 (6) | 3 (3)* |

^a Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $1/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Furthermore, gas bubbles, probably associated with decomposition, were observed to evolve slowly from the solutions containing the product. When $LiBH_4$ was used instead of $NaBH_4$, the reaction was completed within several hours and apparently the same red product was obtained but the white contaminant was still present. The substitution of THF by CH_2Cl_2 , in which the starting material is soluble (in contrast to THF), does not affect the time required for the reaction or its outcome.

An EPR spectrum of the crude product showed one broad signal (*g* around 2.0) without hyperfine structure.

X-ray Crystallography. General procedures for data collection and structure refinement have been described previously.⁶ Basic information concerning the cell parameters and crystallographic analysis is summarized in Table I. Since the intensity of a selected reflection with χ about 90° varied less than 10% at different ψ angles, no correction for absorption was made. Corrections for Lorentz and polarization factors and loss of intensity due to decomposition (40%) were applied. Even large crystals of the complex did not diffract well, and few reflections with observable intensity were found for 2θ greater than 35°.

The structure was solved by direct methods using the program MULTAN 81. The positions of all non-hydrogen atoms were determined from a difference Fourier map. Full-matrix least-squares refinement, first with isotropic thermal parameters and then with anisotropic thermal parameters assigned to six atoms (see Table II), was carried out to convergence. Subsequent difference Fourier syntheses revealed the positions of hydrogen atoms in the BH_4 ligand. These hydrogen atoms, which are essential in defining the structure, were included in the refinement, which produced residuals shown in Table I. In view of the limitations on the data set, no attempt was made to include

(6) See, for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* 1979, 18, 3558.

Table III. Important Interatomic Distances and Angles for $[V(\mu\text{-Cl})(\mu\text{-dppm})\text{BH}_4]_2^a$

| Distances, Å | | | |
|--------------|------------|--------|-----------|
| V-V' | 3.112 (3) | V-H(1) | 1.78 (8) |
| Cl | 2.426 (3) | H(2) | 1.69 (10) |
| Cl' | 2.422 (3) | B-H(1) | 1.24 (9) |
| P(1) | 2.570 (4) | H(2) | 1.36 (10) |
| P(2) | 2.568 (4) | H(3) | 1.25 (11) |
| B | 2.314 (14) | H(4) | 0.94 (9) |

| Angles, deg | | | |
|-------------|-----------|-------------|----------|
| Cl-V-Cl' | 100.1 (1) | P(2)-V-H(1) | 94 (3) |
| P(1) | 91.3 (1) | H(2) | 92 (3) |
| P(2) | 88.0 (1) | H(1)-V-H(2) | 67 (4) |
| H(1) | 162 (3) | V-Cl-V' | 79.9 (1) |
| H(2) | 95 (4) | V-H(1)-B | 98 (5) |
| Cl'-V-P(1) | 88.0 (1) | V-H(2)-B | 98 (6) |
| P(2) | 93.2 (1) | H(1)-B-H(2) | 95 (6) |
| H(1) | 98 (3) | H(3) | 105 (6) |
| H(2) | 164 (4) | H(4) | 105 (8) |
| P(1)-V-P(2) | 178.7 (1) | H(2)-B-H(3) | 115 (7) |
| H(1) | 86 (3) | H(4) | 103 (7) |
| H(2) | 87 (3) | H(3)-B-H(4) | 128 (7) |

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

other relatively unimportant hydrogen atoms in the refinement.

A table of observed and calculated structure factors is available as supplementary material.

Results and Discussion

The final atomic parameters are listed in Table II. Important interatomic distances and angles are presented in Table III. Less important interatomic dimensions as well as a table of anisotropic thermal parameters are included in the supplementary material.

The molecule of $[V(\mu\text{-Cl})(\mu\text{-dppm})\text{BH}_4]_2$, which is represented by its ORTEP drawing in Figure 1, resides on a crystallographic inversion center. Formally, its geometry can be considered as an edge-sharing bioctahedron. The central core, $V_2Cl_2P_4(\text{BH}_4)_2$, has effectively D_{2h} symmetry. The chlorine bridges are symmetric, and all equivalent bonds in the coordination sphere have, within the limits of error, the same length. The B, H(1), and H(2) atoms deviate only slightly from coplanarity with the $V(\mu\text{-Cl})_2V'$ unit, since they are located 0.034, 0.090, and 0.129 Å, respectively, from the plane. The bridging C(1) carbon atom, which is puckered away from the V_2P_2 plane, and the phenyl groups are not positioned in accord with D_{2h} symmetry.

V-Cl distance is significantly shorter than in the confacial-bioctahedral $[V_2(\mu\text{-Cl})_3(\text{THF})_6]^+$ cation,² where it is 2.478 [3] Å. The V-V separation is equal to 3.112 (3) Å, which argues against any significant direct metal-metal interaction.

Although problems with the preparation have not yet allowed isolation of bulk samples of the pure compound, so that it has been impossible to carry out characterization by methods other than crystallography, the existence of this complex is of considerable importance. First of all, it shows that the mixed vanadium-zinc starting material can react in a nonredox manner with retention of a divanadium unit and without incorporation of zinc atoms into the product. Second, the compound has a potential for being a precursor to a variety of dinuclear vanadium species since bridging dppm ligands have shown a tendency to stabilize dimers against cleavage,⁷ although they do not always do so. Thus, we found that addition of excess pyridine to a post-reaction mixture containing $[V(\mu\text{-Cl})(\mu\text{-dppm})\text{BH}_4]_2$ precipitates monomeric $VCl_2(\text{py})_4$.⁸ This process has a noteworthy feature, namely

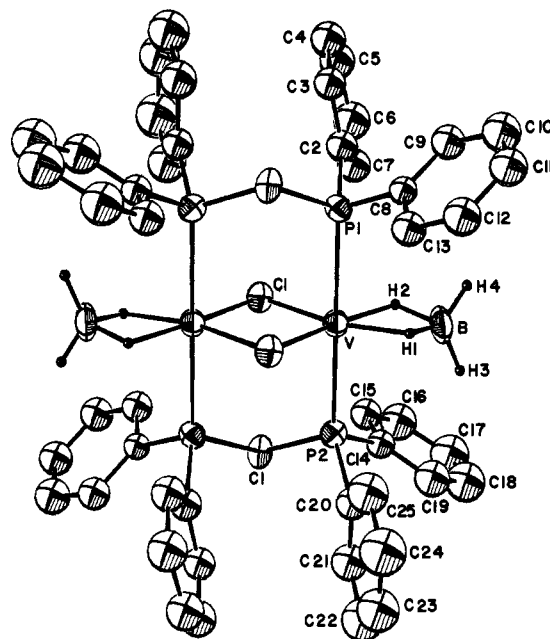


Figure 1. Molecular structure and atom-labeling scheme for $[V(\mu\text{-Cl})(\mu\text{-dppm})\text{BH}_4]_2$. The thermal ellipsoids are of 50% probability. Arbitrary radii have been assigned to the hydrogen atoms.

in spite of the complex composition of the mixture a pure product can be isolated readily (recrystallization from benzene by addition of hexane). Finally we point out that no dimeric vanadium complexes with diphosphines have been reported previously nor have any structural data concerning rare $V\text{-BH}_4$ species been available.^{9,10}

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Registry No. $[V(\mu\text{-Cl})(\mu\text{-dppm})\text{BH}_4]_2$, 92545-24-9; $[V_2Cl_3(\text{THF})_6]_2(\text{Zn}_2Cl_6)$, 89172-48-5; NaBH_4 , 16940-66-2.

Supplementary Material Available: Tables of observed and calculated structure factors, less important bond distances and angles, and anisotropic thermal parameters, B^2 's (9 pages). Ordering information is given on any current masthead page.

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Steric Factors Controlling the Formation of Allenyl- vs. Propargylcobaloxime Complexes

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Recent interest in our laboratories has focused on the reactions of low-valent-state transition-metal complexes with propargyl halides to form allenyl and/or propargyl transition-metal complexes. Such complexes have been proposed as highly reactive intermediates in the iron, cobalt, nickel, and copper salt catalyzed coupling reactions of Grignard reagents with propargyl halides to form substituted allenes.¹ It was

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