Oxovanadium(V) and Oxovanadium(IV) Organometallic Compounds from Direct Oxidation of the corresponding Vanadium(III) Precursors: the X-Ray Structure of Tris-mesityl Oxovanadium(V)

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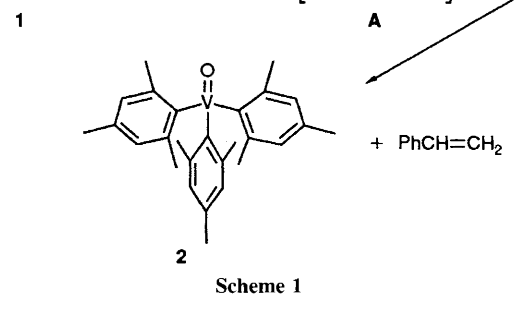
Organometallic derivatives of vanadium(III) VL^1_3(L^1 = Mes = 2,4,6-$Me_3C_6H_2$), VL^2_3[L^2 = η^2-C(Mes)=NBu^t], VL^3_3 [L^3 = O–C(Mes)=NPh] have been converted either by epoxides or dioxygen to the corresponding oxovanadium(V) and oxovanadium(IV) complexes.

The degradation of organometallic compounds by molecular oxygen is a well-known phenomenon.[1a] Nevertheless, little is known about the chemistry accompanying the reaction of homoleptic alkyl or aryl derivatives of transition metals with oxygen and oxygen transfer agents. In such a reaction dioxygen usually binds in a very preliminary stage to the metal and then is transferred to the organic functionality.[1b,c] The formation of an oxo compound derived from only oxidation of the metal is a very rare event.[2] In this context we report the oxidation of three different vanadium(III) organometallic compounds by expoxides and dioxygen.

The reaction of [V(Mes)$_3$(thf)], **1**[3] (Mes = 2,4,6-$Me_3C_6H_2$) in tetrahydrofuran (thf) at room temperature with styrene oxide produces *ca.* 83% of **2**,†‡ (Scheme 1) which was crystallised from n-hexane as an orange solid. The nature of the epoxide affects only the rate of the formation of **2**. Complex **2** is monomeric in benzene by cryoscopy and thermally very stable. The chemistry of **2** is quite similar to that of [VO(CH_2SiMe_3)$_3$] reported earlier and derived from a rather complex and undefined oxidation and hydrolysis of V(CH_2SiMe_3)$_4$.[4] Complex **2** was claimed to be derived from the air oxidation of **1**, but its nature has never been established.[5] Formation of **2** from the reaction with epoxides is



Scheme 1

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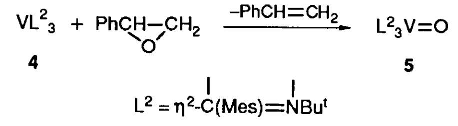
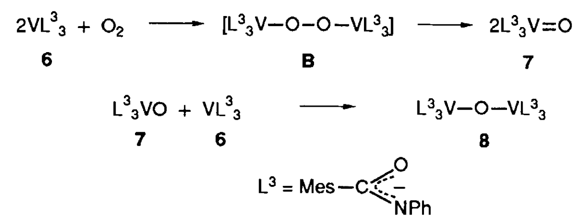
† Satisfactory analytical data have been obtained.

‡ ^{1}H NMR data: complex **2** (C_6D_6, 200 MHz); δ 1.98 (s, 3H, Me), 2.74 (s, 6H, Me), 6.42 (s, 2H, Mes); complex **5** (C_6D_6, 200 MHz), δ 1.30 (s, 9H, Bu^t), 2.23 (s, 3H, Me), 2.30 (bs, 6H, Me), 6.60 (s, 2H, Mes); complex **7** (C_6D_6, 200 MHz), δ 1.90 (s, 3H, Me), 2.45 (s, 6H, Me), 6.44 (s, 2H, Mes), 6.73 (t, 1H, Ph), 6.87 (t, 2H, Ph), 7.29 (d, 2H, Ph J_{HH} 7.4 Hz Ph).



Scheme 2



Scheme 3

just the reverse of what has been observed in the epoxidation of alkenes promoted by the M=O functionality,[1b,c] both reactions going through the same intermediate **A**. The structure of **2** was established by X-ray analysis§ and is shown in Fig. 1. This is a so far unique structure of a tetrahedral trisaryloxovanadium(v) with the most relevant structural parameters. Vanadium has a pseudo-tetrahedral coordination, with the *o*-methyl of the Mes residues protecting the metal centre. Organometallic derivatives of vanadium(v) are rare species,[6] since the alkyl or aryl residue is intrinsically a reducing agent for vanadium(v).

$$\underset{\mathbf{1}}{\mathrm{Mes_3V(thf)}} + \underset{\mathbf{2}}{\mathrm{OVMes_3}} \xrightarrow[-\mathrm{thf}]{\text{toluene}} \underset{\mathbf{3}}{\mathrm{Mes_3V\text{–}O\text{–}VMes_3}} \qquad (1)$$

Upon adding an equimolar amount of **1** to a toluene solution of **2** [eqn. (1)], complex **3**[†¶] was obtained (*ca.* 76%) as a red crystalline solid. It is paramagnetic, having a magnetic moment of 1.81 μ_B at 293 K per vanadium. Reactions producing a μ-oxo species from the corresponding terminal oxo complex have been reported for other metals, including vanadium,[1c,7,8] though they have never been observed in the organometallic chemistry of vanadium.

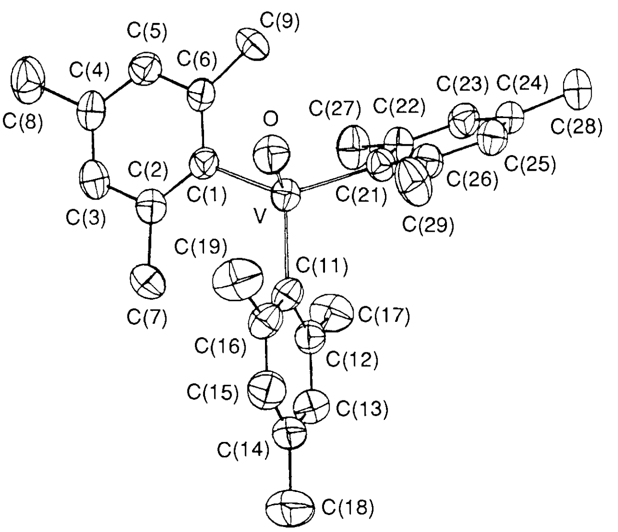


Fig. 1 An ORTEP drawing for complex **2**. Bond distances (Å) and angles (°): V–O 1.578(4), V–C(1) 2.078(4), V–C(11) 2.022(4), V–C(21), 2.079(3), C(11)–V–C(21) 108.5(2), C(1)–V–C(21) 122.3(2), C(1)–V–C(11) 116.3(2), O–V–C(21) 102.4(2), O–V–C(11) 105.0(2), O–V–C(1) 99.2(2).

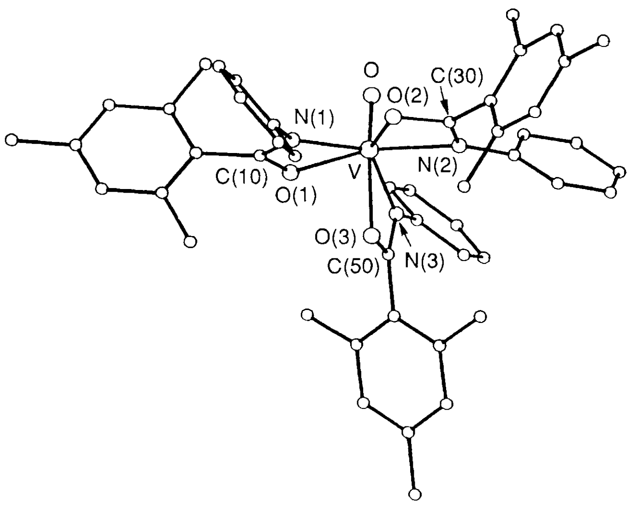


Fig. 2 A PLUTO drawing for complex **7**. Bond distances (Å) and angles (°): V–O 1.594(3), V–O(1) 2.152(3), V–N(1) 2.053(3), V–O(2) 2.011(3), V–N(2) 2.112(3), V–O(3) 2.197(3), V–N(3) 2.040(3), C(30)–V–C(50) 101.7(1), C(10)–V–C(50) 96.4(1), C(10)–V–C(30) 139.0(1), O(4)–V–C(10) 94.8(1), O(4)–V–C(30) 97.4(1), O(4)–V–C(50) 134.9(1).

The pseudo-trigonal planar tricoordinate complex **4**,[9] [V(η^2-C(Mes)=NBuᵗ)$_3$], undergoes oxidation by styrene oxide to give the corresponding oxovanadium(v) derivative, **5**, obtained as yellow crystals from n-hexane (*ca.* 75%) (Scheme 2).

Complex **5**[†‡¶] is diamagnetic and monomeric in benzene. The oxidation of **4** by O_2 is a more complex reaction, leading to insertion of oxygen into the V–C bond.[9] Unlike **2**, complex **5** does not react with its precursor **4**.

In the absence, as in complex **6**,[9] of an oxygen-sensitive vanadium–carbon bond, the oxidation of a vanadium(III) derivative was carried out with dioxygen in thf at room temperature (Scheme 3).

Complex **7**,[†‡] very likely formed from the O–O cleavage of a peroxo precursor **B**, was isolated after recrystallisation from n-hexane as red crystals (*ca.* 87%). Its characterisation includes X-ray analysis§ and the structure is shown in Fig. 2

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§ *Crystal data* for **2**: $C_{27}H_{33}OV$, $M = 424.5$, monoclinic, space group $P2_1/c$, $a = 18.254(2)$, $b = 15.960(2)$, $c = 8.200(1)$ Å, $\beta = 101.11(1)°$, $U = 2344.2(5)$ Å^3, $Z = 4$, $D_c = 1.203$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71069$ Å), μ(Mo-Kα) = 4.22 cm^{-1}; crystal dimensions 0.40 × 0.46 × 0.50 mm^3. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least-squares. For 1618 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 46°$, the R value is 0.051.

For **7**: $C_{48}H_{48}N_3O_4V$, $M = 781.9$, monoclinic, space group $P2_1/n$, $a = 12.242(1)$, $b = 33.707(3)$, $c = 10.330(1)$ Å, $\beta = 93.16(1)°$, $U = 4256.1(7)$ Å^3, $Z = 4$, $D_c = 1.220$ g cm^{-3}, Cu-Kα radiation ($\lambda = 1.54178$ Å), μ(Cu-Kα) = 23.09 cm^{-1}; crystal dimensions 0.42 × 0.48 × 0.52 mm^3. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least-squares. For 5130 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 140°$, the R value is 0.062.

For both compounds all the hydrogen atoms were located from difference maps and introduced as fixed contributors in the final stage of refinement. During the refinements constraints were applied to the bond distances and angles within the aromatic rings. All calculations were carried out using SHELX86 and SHELX76. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ The ν/cm^{-1} (V–O)(Nujol) are: 680 in complex **3** *vs.* 1029 in complex **2**; 700 in complex **8** *vs.* 976 in complex **7**; 946 in complex **5**. Complex **3** has an M_r of 853 (cryoscopy in benzene), calcd. 833.

with selected molecular parameters. Complex **7** is a monomer containing a seven coordinate vanadium(v). It reacts readily (Scheme 3) in thf with **6** giving, after addition of n-hexane, crystals of **8**†¶ (*ca.* 65%), a paramagnetic (μ_{eff} = 1.39 μ_B at 293 K) vanadium(IV) derivative. The sequence of reactions in Scheme 3, additionally supported by the absorption of one mole of O_2 per two metal atoms, has been variously suggested in vanadium chemistry,[1c] but never clearly established.

Received, 1st February 1991; Com. 1/00483B

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