A Tri-σ-aryl Vanadium(III) Derivative: Structural Determination of Trimesitylvanadium(III)–Tetrahydrofuran

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The reaction of $[VCl_3(thf)_3]$ with MesMgBr (Mes = 2,4,6-$Me_3C_6H_2$; thf = tetrahydrofuran) in thf led to the isolation of $[VMes_3(thf)]$ as blue crystals; an *X*-ray crystal structure determination showed that it contained monomeric pseudotetrahedral vanadium(III) ($\mu_{eff.}$ 2.73 μ_B at 298 K) binding a thf molecule and three mesityl ligands, with the V–C bond distances ranging from 2.099(6) to 2.116(7) Å.

Despite being of fundamental importance, the isolation of stable alkyls and aryls of vanadium has only recently been investigated.[1] Recent advances in the understanding of the chemistry of metal–carbon σ-bonds and the use of sterically demanding alkyl and aryl ligands has led to the isolation of some thermally stable compounds.[1] Nevertheless, homoleptic alkyl and aryl derivatives of vanadium are rather rare species, for the oxidation state +2 and +3.[1—3] However, the use of the mesityl ligand has allowed the isolation of homoleptic aryl compounds which were believed to be unstable.[4] There is still some confusion over the nature of even apparently well characterized vanadium(II) and vanadium(III) species because their very high sensitivity to oxygen and moisture prevents spectroscopic and, particularly, structural investigation. The V–C σ-bond has attracted particular attention for many years, because of its role in catalytic processes, but structural information is sparse.

We now report the determination of the structure of trimesitylvanadium(III)–tetrahydrofuran, obtained by the reported procedure.[3] Arylation of $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) was performed at −40 °C using MesMgBr (Mes = 2,4,6-$Me_3C_6H_2$). The magnesium salt was precipitated by addition of dioxane, and the resulting blue solution gave on standing at −20 °C deep blue crystals of $[VMes_3(thf)]$ (**1**) (yield >50%) [reaction (1)]. Complex (**1**) is thermally stable up to 100 °C, but very sensitive to air. Its magnetic moment of 2.73 μ_B at 298 K is that expected for a vanadium(III) derivative. Its structure was elucidated by *X*-ray analysis.

$$[VCl_3(thf)_3] + MesMgBr \xrightarrow[-thf]{-MgClBr} \underset{(\mathbf{1})}{[VMes_3(thf)]} \qquad (1)$$

$$Mes = 2,4,6\text{-}Me_3C_6H_2$$

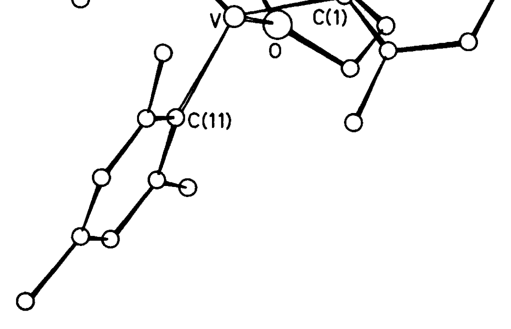

Figure 1. Projection of the structure of $[VMes_3(thf)]$. Bond distances (Å): V–C(1), 2.116(7); V–C(11), 2.099(6); V–C(21), 2.113(7); V–O, 2.069(4). Bond angles (°): C(21)–V–O, 108.9(2); C(11)–V–O, 111.0(3); C(11)–V–C(21), 107.2(3); C(1)–V–O, 90.8(2); C(1)–V–C(21), 118.5(3); C(1)–V–C(11), 119.0(3).

Crystal data: $C_{31}H_{41}OV$; *M* = 480.6, monoclinic, space group $P2_1/c$ (from systematic absences), *a* = 8.472(2), *b* = 14.273(4), *c* = 22.385(6) Å, β = 97.64(3)°; *U* = 2683(1) $Å^3$, *Z* = 4, D_c = 1.19 g cm^{-3}; *F*(000) = 1032, λ(Mo-K_α) = 0.71069

Å, $\mu(\text{Mo-}K_\alpha)$ = 3.76 cm^{-1}. The structure was solved by the heavy-atom method and refined by full-matrix least-squares anisotropically for nonhydrogen atoms. All the hydrogen atoms were located from a difference Fourier map and introduced as fixed contributors in the final refinement (U_{iso} = 0.100 $Å^2$). For 1959 unique observed structure amplitudes [$I>3\sigma(I)$, no absorption corrections] collected at room temperature on a Philips PW 1100 diffractometer in the range $5<2\theta<48°$ the current R is 0.057.†

The structure of (**1**) consists of the monomeric unit shown in Figure 1. Vanadium(III) is pseudotetrahedrally co-ordinated by a thf molecule and three σ-bonded mesityl ligands. The three V–C bond distances are similar, ranging from 2.099(6) to 2.116(7) Å. They compare well with those found in $[\text{Mes}_4\text{V}]$[5] (2.071—2.095 Å), while they are significantly shorter than those found in the bridging aryl vanadium(II) derivatives $\text{V}_2(\text{dmp})_4\cdot2\text{thf}$ [dmp = 2,6-dimethoxyphenyl; 2.143(8) and 2.134(8) Å][6] and $\text{V}_2(\text{tmp})_4\cdot2\text{thf}$ [tmp = 2,4,6-trimethoxyphenyl; 2.203(5) and 2.204(5) Å],[7] and in some vanadocene derivatives.[8] As a consequence of the steric hindrance, the methyl carbon atoms are significantly out of the plane of the phenyl rings, by 0.023—0.165 Å.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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