Dihydrogen reducing $[V\{\eta^2\text{-C(Mes)=NBu}^t\}_3]$ and making a Diamagnetic Divanadium(IV) Complex Containing a Vanadium–Vanadium Single Bond

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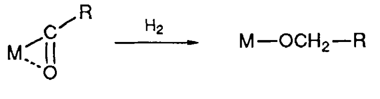
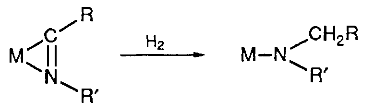
The vanadium complex $[V\{\eta^2\text{-C(Mes)=NBu}^t\}_3]$ **1** reacts at −30 °C with dihydrogen to form $[\{\eta^2\text{-C(Mes)=NBu}^t\}V(\text{MesCH}_2\text{NBu}^t)_2]$ **2**, thermally rearranging to a divanadium(IV) complex containing a vanadium–vanadium single bond (Mes = 2,4,6-$Me_3C_6H_2$).

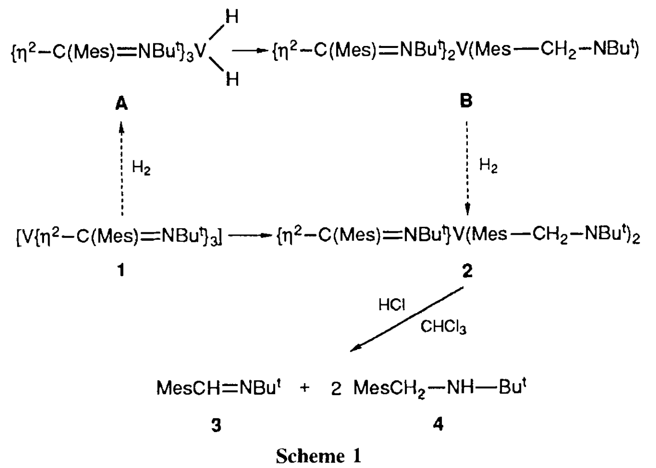
The reduction of the acyl functionality to the corresponding alkoxo group by the action of dihydrogen [eqn. (1)] is a key step in the catalytic reduction of carbon monoxide to hydrocarbons and alcohols.[1] Reaction (1), however, has not been observed in stoichiometric organometallic chemistry.[1,2] This paper deals with the very similar reduction of an $M\{\eta^2\text{-C(R)=R}'\}$ functionality by dihydrogen under very mild conditions [eqn. (2)].

Complex **1**, $[V\{\eta^2\text{-C(Mes)=NBu}^t\}_3]$[3] (Mes ≡ 2,4,6-$Me_3C_6H_2$) reacts rapidly with H_2 at 243 K, absorbing two moles of H_2 per mole of **1** and forming **2** in a good yield, as a red crystalline solid (μ_{eff} = 2.77 μ_B at 291 K).† Complex **2** is thermally very labile, but can be characterized at temperatures lower than 253 K. Analytical and spectroscopic data, in addition to the products formed by controlled hydrolysis in $CHCl_3$ **3**† and **4**† have been found in a 1 : 2 molar ratio) agree with the proposed formula (see Scheme 1). Reaction **2**, carried out using D_2 gave the deuteriated form of **2** which, upon hydrolysis, produced $\text{MesCD}_2\text{-NHBu}^t$ **5**.†

Such a result rules out the other possible reduction product of **1**, *i.e.* $[\{\eta^2\text{-C(Mes)=NBu}^t\}V(\eta^2\text{-CHMes-NHBu}^t)_2]$. Therefore the reduction of the **1** occurs as sketched in reaction (2).


(1)


(2)



$\{\eta^2\text{-C(Mes)=NBu}^t\}_3V(H)_2 \longrightarrow \{\eta^2\text{-C(Mes)=NBu}^t\}_2V(\text{Mes—CH}_2\text{-NBu}^t)$

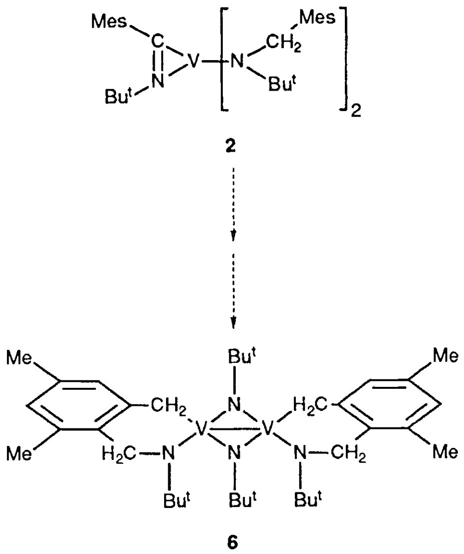
$[V\{\eta^2\text{-C(Mes)=NBu}^t\}_3] \longrightarrow \{\eta^2\text{-C(Mes)=NBu}^t\}V(\text{Mes—CH}_2\text{-NBu}^t)_2$

$\text{MesCH=NBu}^t + 2\ \text{MesCH}_2\text{—NH—Bu}^t$

Scheme 1

The proposed oxidative addition of H_2 to **1** (see **A** and **B** in Scheme 1) is not only a plausible step in the reduction of the $M\{\eta^2\text{-C(R)=NR}'\}$ functionality, but is largely justified by the chemistry of **1**, which undergoes very easily one- and two-electron oxidative additions with other reagents.[4] Complex **2** undergoes a thermal rearrangement at room temperature in tetrahydrofuran (thf) from which complex **6** was obtained as black crystals†‡§ after recrystallization from n-hexane (Scheme 2).

Such a thermal rearrangement is a quite complex reaction requiring aliphatic C–H and N–C bond cleavages. The rather low yield of **6** and its stoichiometry imply the formation of other by-products in the transformation of **2**. Not only the genesis, but also the structure of **6**, determined by an X-ray analysis,§ is quite unusual. The two pseudo-tetrahedral vanadium(IV) atoms (Fig. 1) are joined by two bridging amido



Scheme 2

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† All the compounds have spectroscopic and analytical data in agreement with their assigned structures.

‡ ^1H NMR data of **6**: (δ, $CD_3C_6D_5$, 200 MHz): 1.18 (s, 9 H, Bu^t), 1.57 (s, 9 H, Bu^t), 2.25 (s, 3 H, Me), 2.61 (s, 3 H, Me), 2.25 (s, 2 H, V-CH_2), 4.92 (s, 2 H, N-CH_2), 6.47 (s, 1 H, Ph) and 6.84 (s, 1 H, Ph).

§ *Crystal data*: Complex **6**, $C_{36}H_{60}N_4V_2$, M = 650.8, monoclinic, space group $P2_1/c$, a = 10.049(1), b = 20.675(2), c = 18.107(2) Å, β = 102.30(1)°, U = 3675.6(7) Å^3, Z = 4, D_c = 1.176 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 5.19 cm^{-1}, crystal dimensions 0.31 × 0.40 × 0.45 mm. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and refined by full-matrix least-squares. For 2870 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range 6° < 2θ < 46° the R value is 0.042. All the hydrogen atoms were located from difference maps and introduced as fixed contributors in the final stage of refinement. All calculations were carried out using 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.

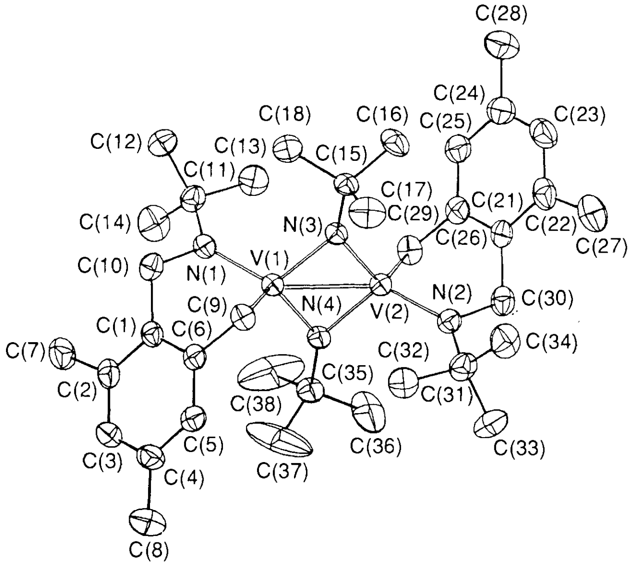

Fig. 1. An ORTEP view of complex **6**. Bond distances (Å): V(1)-V(2), 2.460(1); V(1)-N(1), 1.870(4); V(1)-N(3), 1.846(4); V(1)-N(4), 1.873(4); V(1)-C(9), 2.043(5); V(2)-N(2), 1.856(5); V(2)-N(3), 1.866(4); V(2)-N(4), 1.841(4); V(2)-C(29), 2.054(5).

groups, the additional bidentate ligand being an alkyl-amido derivative forming a metallacycle. One of the most remarkable properties of **6** is its diamagnetism.‡ This can derive either from a d^1–d^1 metal–metal bond or from a very strong antiferromagnetic coupling assisted by the amido bridges, but the very short V–V distance [2.460(1) Å][5,6] strongly supports a metal–metal single bond.

The easy reduction of an organometallic functionality bonded to vanadium(III) using H_2 and under very mild conditions opens a number of possibilities for designing vanadium complexes to be used in dinitrogen reduction.

We thank the Fondation Herbette and the Fonds National Suisse de la Recherche Scientifique (Grant. No. 20-28470-90) for financial support.

Received, 7th November 1990; Com. 0/05010E

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