Isolation and Characterization of a Vanadium Ethylidyne Complex. The Crystal Structure of $[(Cy_2N)_2V]_2Li(\mu^3\text{-}O)(\mu^2,\eta^1:\eta^1\text{-}CMe)$: an Unusual V_2LiO Cluster

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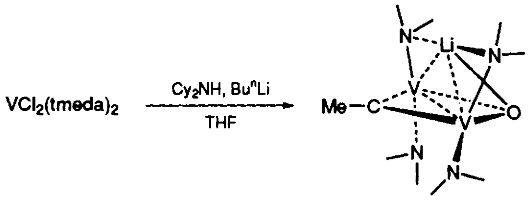
Reaction of $VCl_2(TMEDA)_2$ [TMEDA = *N,N,N′,N′*-tetramethylenediamine] with Cy_2NH [Cy = cyclohexyl] and Bu^nLi in tetrahydrofuran led to the formation of a complicated mixture of products from which a dinuclear ethylidyne complex $[(Cy_2N)_2V]_2(\mu^3,\eta^1\text{-}O)(\mu^2,\eta^1:\eta^1\text{-}CMe)$ **1** was isolated.

Interest in the chemistry of early transition metal alkylidenes and alkylidynes has been stimulated by a large number of remarkable transformations reported or expected for these species, which include olefin[1] and acetylene metathesis,[2] clusterification reactions,[3] olefin[4] and acetylene oligo- and poly-merization[5] and chemistry of metal–metal multiple bonds.[6] In addition, alkylidynes and carbene species are expected to play a fundamental role in important processes such as Fischer–Tropsch.[7] As a result of considerable synthetic efforts in this field, highly reactive alkylidene and alkylidynes functionalities are today widely documented in the chemistry of second and third row transition metals.[8] These species remain extremely rare only in the chemistry of titanium and vanadium since both Fischer- and Schrock-type carbenes are largely established in the chemistry of chromium.[9]

The coordination chemistry of divalent vanadium is characterized by a rather large collection of diverse compounds,[10] the absence of systematic development having probably been caused by the lack of suitable starting materials. The structures of V^{II} carboxylates,[11] aryloxides,[12] aryls,[13] thiolates[14] and amides[15] have in fact been reported only in the very recent literature. Very few examples of carbene complexes have been reported[16] and vanadium alkylidynes and vinylidenes remain unknown.

In this paper, we describe the isolation and the crystal structure of the first ethylidyne vanadium complex, obtained from the unexpected fragmentation of tetrahydrofuran (THF), probably promoted by a V^{II} amide complex.

The synthesis and characterization of the homoleptic V^{II} amide $(Cy_2N)_2V$, the dimeric structure of which has been postulated on the basis of analytical and magnetic results, has been described in a previous paper.[15] When the preparation was carried out using Cy_2NLi, prepared *in situ* from Cy_2NH and Bu^nLi in THF solution, small and variable amounts of different but homogeneous material could be isolated as deep-brown crystals from hexane after solvent replacement (Scheme 1).† While small, but reproducible differences were observed between the IR spectra of $[(Cy_2N)_2V]_2$ and of the new compound, the magnetic moments were rather comparable. Small but reproducible differences were also detected in the analytical results. We have now succeeded in growing a crystal of the new compound of a suitable size to undertake a crystal structure determination.‡ Although the data collection was hampered by the poor crystal scattering, the data were sufficient to demonstrate the chemical connectivity of a surprising vanadium-ethylidyne structure.



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Scheme 1

The crystal structure shows that the complex consists of a *nido* trigonal bipyramidal $V_2LiO(CMe)$ core. The basal plane of the distorted square pyramid is bound by two vanadium atoms, the oxygen, and the bridging carbon atom of the ethylidyne unit. The apical vertex is occupied by the lithium atom [V(1)–Li(1) = 2.51(2), V(2)–Li(1) = 2.58(2), Li(1)–O(1) = 2.33(2) Å]. The coordination geometry around each vanadium atom is distorted tetrahedral, the coordination polyhedron being defined by nitrogens of the two amido groups, the oxygen, and the bridging carbon of the ethylidyne unit. The two $(Cy_2N)_2V$ units are connected to each other and to the lithium atom by the μ^3-bonded oxygen atom [V(1)–O(1) = 1.809(6), V(2)–O(1) = 1.835(6) Å]. The $\mu^2,\eta^1:\eta^1$-CMe moiety, which bridges the two vanadium atoms [V(1)–C(48) = 1.79(1), V(2)–C(48) = 2.05(1) Å], is coplanar with the V(1)–V(2)–O(1) plane [dihedral angle between the V(1)–V(2)–O(1) and V(1)–V(2)–C(48)–C(49) planes = 176.6(8)°] and forms an almost linear array with the oxygen atom [O(1)–C(48)–C(49) = 166.5(9)°]. The rather long C–C distance of the ethylidyne moiety [C(48)–C(49) = 1.45(2) Å] compares well with those of other ethylidyne complexes.[17] The distorted trigonal planar geometry of the bridging carbon atom [V(1)–C(48)–C(49) = 149.5(9), V(2)–C(48)–C(49) = 123.5(8), V(1)–C(48)–V(2) = 86.8(4)°] together with the significant bending of the ethylidyne moiety towards one of the two vanadium atoms, might indicate that the two V–C bonds are not equivalent (double *vs.* single). More likely, this is caused by the steric interaction with the bulky cyclohexyl rings. The first of the two Cy_2N groups borne by each vanadium atom is terminally bonded [V(1)–N(1) = 1.915(8) Å] while the second bridges vanadium and lithium [V(1)–N(4) = 1.997(8), N(4)–Li(1) = 2.08(2) Å] and is probably responsible for the observed short V–Li distances [V(1)···Li(1) = 2.51(2), V(2)···Li(1) = 2.58(2) Å]. The very unusual coordination

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† A solution of Cy_2NH (1.6 g, 8.8 mmol) in THF (50 ml) was treated with Bu^nLi (6.0 ml, 1.4 mol dm^{-3}) at −80 °C. The resulting solution was allowed to warm up to room temp. The addition of $VCl_2(TMEDA)_2$[13b] (1.5 g, 4.4 mmol) turned red–brown. The resulting solution was evaporated to dryness and the residual solid redissolved in hexane. Deep-brown, moderately air-sensitive crystals of **1** (0.3 g, 0.34 mmol, 15%) separated upon standing 5 days at −30 °C. IR [Nujol, KBr, ν/cm^{-1}]: 1455(s), 1375(s), 1360(m), 1340(m), 1250(s), 1160(m), 1145(s), 1110(s), 1095(s), 1035(vs), 995(w), 970(s), 960(s), 815(s), 850(m), 805(w), 780(m), 760(s), 705(br), 670(s), 610(w), 580(m), 550(s), 510(m), 495(sh), 455(w), 430(w). [μ_{eff} = 2.35 μ_B].

‡ *Crystal data* for **1**: $C_{50}H_{91}N_4V_2LiO$, M = 873.12, triclinic $P\bar{1}$, a = 12.292(4), b = 20.258(2), c = 11.095(4) Å, α = 93.65(2), β = 112.15(2), γ = 94.04(2)°, V = 2540(1) $Å^3$, Z = 2, R = 0.097, R_w = 0.084, GOF = 3.06, for 524 parameters and 4128 out of 7588 unique reflections. Data were collected at room temp. for a brown crystal sealed in a glass capillary, using a Rigaku AFC5R diffractometer with graphite monochromated Cu-Kα radiation and 12 kW rotating-anode generator. Cell constants and orientation matrix were obtained from least-squares refinement of 25 reflections in the range 62.40 < 2θ < 75.78°. An empirical absorption correction (DIFABS) was applied to data. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were introduced at their calculated positions and not refined. Atom types were identified by satisfactory refinements and optimisation of thermal parameters. 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.

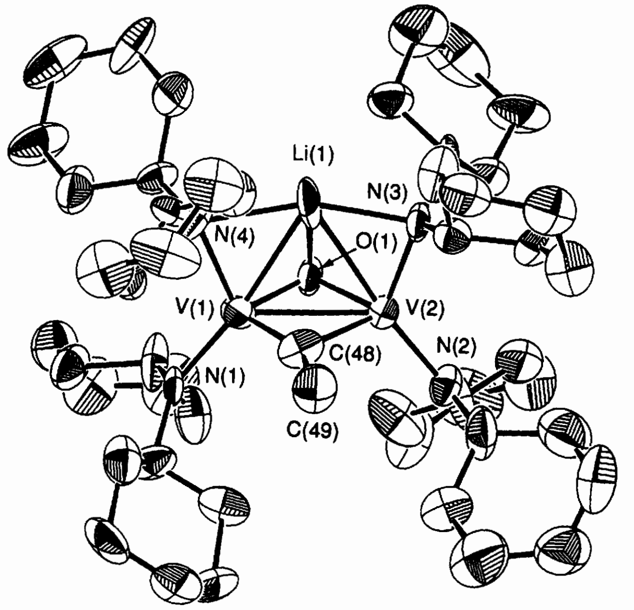

Fig. 1 ORTEP drawing of **1** showing the labelling scheme. Selected values of bond distances (Å) and angles (°): V(1)–Li(1) 2.51(2), V(2)–Li(1) 2.58(2), Li(1)–O(1) 2.33(2), V(1)–O(1) 1.809(6), V(2)–O(1) 1.835(6), V(1)–C(48) 1.79(1), V(2)–C(48) = 2.05(1), C(48)–C(49) 1.45(2), V(1)–N(1) 1.915(8), V(2)–N(2) 1.861(8), V(2)–N(3) 1.971(8), V(1)–N(4) 1.997(8), N(4)–Li(1) 2.04(2), V(1)···Li(1) 2.51(2), V(2)···Li(1) 2.58(2), C(48)···Li(1) 2.663(9), V(1)–V(2) 2.640(2), V(1)–C(48)–C(49) 149.5(9), V(2)–C(48)–C(49) 123.5(8), V(1)–C(48)–V(2) 86.8(4), O(1)–C(48)–C(49) 166.5(9), O(1)–Li(1)–N(4) 85.4(8), N(3)–Li(1)–N(4) 160.0(9), V(1)–O(1)–V(2) 92.9(3), N(1)–V(1)–N(4) 121.1(3), N(2)–V(2)–N(3) 121.8(3), O(1)–V(1)–C(48)–C(49) 4.0(2).

geometry of the lithium cation [O(1)–Li(1)–N(4) = 85.4(8); N(3)–Li(1)–N(4) = 160.0(9)°] is likely also caused by the considerable steric hindrance provided by the four cyclohexyl rings, which all have the characteristic 'chair' conformation.

The rather short V–V distance [V(1)–V(2) = 2.640(2) Å] may indicate a degree of metal–metal interaction. However, the magnetic moment (μ_{eff} = 2.35 μ_B) is only slightly lower than that expected for a dinuclear V^{IV} species without direct V–V bonding.

The crystal structure of complex **1** provides the first example of a vanadium complex with a bridging ethylidyne function. The serendipitous formation of the ethylidyne moiety can be explained only by assuming that fragmentation of a molecule of THF has occurred at some step of the reaction. This hypothesis is further supported by the presence of lithium and oxygen in the molecular frame. We tentatively suggest that complex **1** is formed by some highly reactive V^{II} intermediate species, either able to react with THF or to act as a scavenger of reactive fragments produced by collateral reaction of Bu^nLi with THF. No appreciable reaction was observed when a solution of the isolated homoleptic $[(Cy_2N)_2V]_2$ was refluxed in THF. Complex **1** was also not formed when $VCl_2(TMEDA)_2$ was reacted with Cy_2NLi previously prepared and isolated from Et_2O or hexane solutions.

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