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The Surprising Role of THF in Vanadium Macrocyclic Chemistry

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The recently reported[1] isolation of the first vanadium(III) ynolate complex (**1**) from the cleavage of THF during the reaction of $VCl_3(THF)_3$ with the tetralithium salt of the octaethylporphyrinogen, Li_4OEPG (Scheme 1), showed that the cooperative attack of a transition metal and acidic lithium cations on the same organic substrate may be able to promote unexpected transformations and open up new pathways of reactivity. Since the stoichiometric formation of the ynolate moiety is accompanied in this particular reaction by simultaneous liberation of 1 equiv of ethane, the reaction obviously does not imply any formal electron transfer or redox process. We have therefore decided to explore further the role of THF in this system by diminishing the quantity present in the participating reagents. For this purpose, the tetralithium salt (Li_4OEPG, **2**) used as starting reagent was prepared by reacting the porphyrinogen ligand with 4 equiv of BuLi in hexane in a procedure analogous to the preparation of $(LiTHF)_4OEPG$.[2] In the way, $VCl_3(THF)_3$ would be the only source of THF available to the system.

Reaction of Li_4OEPG with $VCl_3(THF)_3$[3] in toluene at room temperature overnight, followed by brief heating, afforded deep red crystals of (OEPG)V(*n*-Bu)$Li_3(THF)_3Cl$ (**3**) in 65% yield (Scheme 1).[4] The structure of **3**, as characterized by single-crystal X-ray analysis,[5] has revealed the molecule as an *n*-butyl V(III) complex of the OEPG ligand. The molecule comprises one OEPG macrocyclic ligand containing a vanadium ion displaced by 0.31(2) Å out of the plane of the four nitrogen donor atoms. On one side of the N_4 plane there is an *n*-butyl group which occupies one axial position [V1–C18 = 2.077(5) Å; C18–V1–N1 = 98.0(2)°; C18–V1–N2 = 97.7(2)°; C18–V1–N3 = 97.7(2)°; C18–V1–N4 = 100.5(2)°]. On the other side of the molecular plane each LiTHF binds to one pyrrolyl ring in an η^5 mode (average Li–C distance = 2.327 Å; average Li–N distance = 2.274 Å) and to the μ_3-Cl atom. This chlorine atom appears to be extruded from the ideal octahedron centered on vanadium with a long, nonbonding V–Cl distance of 3.108(5) Å. Its position on the vacant octaedral apex engulfs a cavity bounded by the Cl, three lithium atoms, and the N_4 plane. The magnetic moment of **3** (μ_{eff} = 2.85 μ_B) is as expected for a d^2 electronic configuration of a V(III) ion.

The crystal structure of **3** shows that the three molecules of THF, supplied to the reaction medium by $VCl_3(THF)_3$, are all incorporated into the molecular structure. An interesting feature of **3** is that it is one of the few examples of a vanadium(III)–alkyl complex.[6] However, the origin of the butyl group is uncertain. It could arise once more *via* the cleavage of THF, giving a second oxygen-containing product that was not isolated. Another possibility may arise from the trapping of *n*-BuLi in the Li_4-OEPG complex as has been seen in preliminary deprotonation studies with aromatic diamines.[7] Characterization of Li_4OEPG by ^1H NMR in C_6D_6 reveals in fact the presence of a peak at −1.0 ppm, which might indicate the presence of *n*-BuLi within the lattice. Since Li_4OEPG can be isolated in crystalline form, attempts to clarify the molecular structure of this rare case of a tetralithium salt are currently in progress. Interestingly, addition of THF to **3** does *not* result in the formation of the vanadium(III) ynolate complex **1** (Scheme 1).[1]

Although the origin of the butyl group remains unclear and the adventitious presence of a variable amount of BuLi in the reaction medium cannot be excluded, further reduction of the amount of THF available to the vanadium atom led to a completely different result. Reaction of $V_2Cl_6(THF)_4$[8] with Li_4OEPG in toluene afforded maroon cubes (with an emerald green reflex) of a new complex $\{[C(C_2H_5)][C(C_2H_5)_2]_6(C_4H_2N)_4\}V(THF)_2$ (**4**) in 53% yield whose IR showed the presence of a new resonance at 1567 cm⁻¹ (Scheme 1).[9] The crystal structure of **4** was elucidated by X-ray analysis,[10] and it revealed that no organometallic function is present in the molecule. Instead, one of the eight *meso*-ethyl groups of the macrocyclic ligand has been

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(4) Preparation of **3**: $VCl_3(THF)_3$ (2.26 g, 6.05 mmol) was added to a toluene solution of Li_4OEPG (**2**) (3.46 g, 5.32 mmol). The resulting deep burgundy red mixture was allowed to stir at room temperature overnight, heated at 70 °C for 1 h, and filtered to remove the LiCl. The filtrate was cooled to −20 °C. After 2 days large orange-red crystals of **3** suitable for X-ray diffraction studies were isolated by filtration (3.61 g, 65%). Anal. Calcd for $C_{52}H_{81}N_4ClLi_3O_3V$: C, 68.08; H, 9.53; N, 6.11. Found: C, 68.15; H, 9.47; N, 6.12. μ_{eff} = 2.85 μ_B.

(5) Crystal data for **3**, $C_{52}H_{81}ClVN_4Li_3O_3$: triclinic, $P\bar{1}$, with a = 11.688(7) Å, b = 20.841(5) Å, c = 11.638(3) Å, α = 91.83(2)°, β = 114.93(3)°, γ = 94.57(3)°, V = 2556(4) Å³, Z = 2, d_{calcd} = 1.192 g cm⁻³, μ(Mo Kα) = 2.81 cm⁻¹. The data were collected at −153 °C on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å) by using an ω–2θ scan mode. Of the 6737 reflections collected in the range $6.0 < 2\theta < 45.0°$, 6188 were unique. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at their calculated positions. Refinement converged at R = 0.054 (R_w = 0.077) for 5012 observed reflections ($I > 2.50\sigma(I)$) and 558 parameters. All calculations were performed using a TEXSAN crystallographic software package on a VAX workstation.

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(9) Preparation of **4**: All the preparations were carried out under nitrogen atmosphere. $VCl_3(THF)_3$ (1.67 g, 4.47 mmol) was partially desolvated by heating overnight under vacuum at 80 °C, and on the basis of the mass remaining (1.35 g), the formulation $VCl_3{\cdot}2THF$ was assigned. The resulting brown powder was suspended in toluene (125 mL) and reacted with Li_4OEPG (3.14 g, 4.82 mmol). The initial very dark brown color of the solution became more reddish-brown upon stirring at room temperature for several hours. After being stirred overnight, the reaction mixture was heated at 70 °C for 4 h, and once cooled to room temperature, it was filtered to remove LiCl. The pink-red filtrate was concentrated to dryness, and the red-black residue was stirred in hexane. Following filtration and standing in a refrigerator for several days, large maroon cubes (with an emerald green reflex) were isolated by filtration (1.66 g, 53%). Anal. Calcd for $C_{42}H_{59}N_4O_2V$: C, 71.77; H, 8.46; N, 7.97. Found: C, 72.84; H, 8.51; N, 8.00. IR (Nujol): 1567 cm⁻¹, μ_{eff} = 2.76 μ_β.

(10) Crystal data for **4**, $C_{42}H_{59}N_4O_2V$: orthorhombic, *Pbca*, with a = 20.227(2) Å, b = 23.148(1) Å, c = 15.579(1) Å, V = 7294(2) Å, Z = 8, d_{calcd} = 1.280 g cm⁻³, μ(Mo Kα) = 3.02 cm⁻¹. The data were collected at −153 °C on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å) in an ω–2θ scan mode. A total of 7043 reflections were collected in the range $6.0 < 2\theta < 50.0°$. The structure was solved by direct methods, and the non-hydrogen atoms were refined either anisotropically or isotropically. Hydrogen atoms were introduced at their calculated positions. Refinement converged at R = 0.064 (R_w = 0.066) for 2696 observed reflections ($I > 2.50\sigma(I)$) and 388 variable parameters. All calculations were performed using a TEXSAN crystallographic software package on a VAX workstation.

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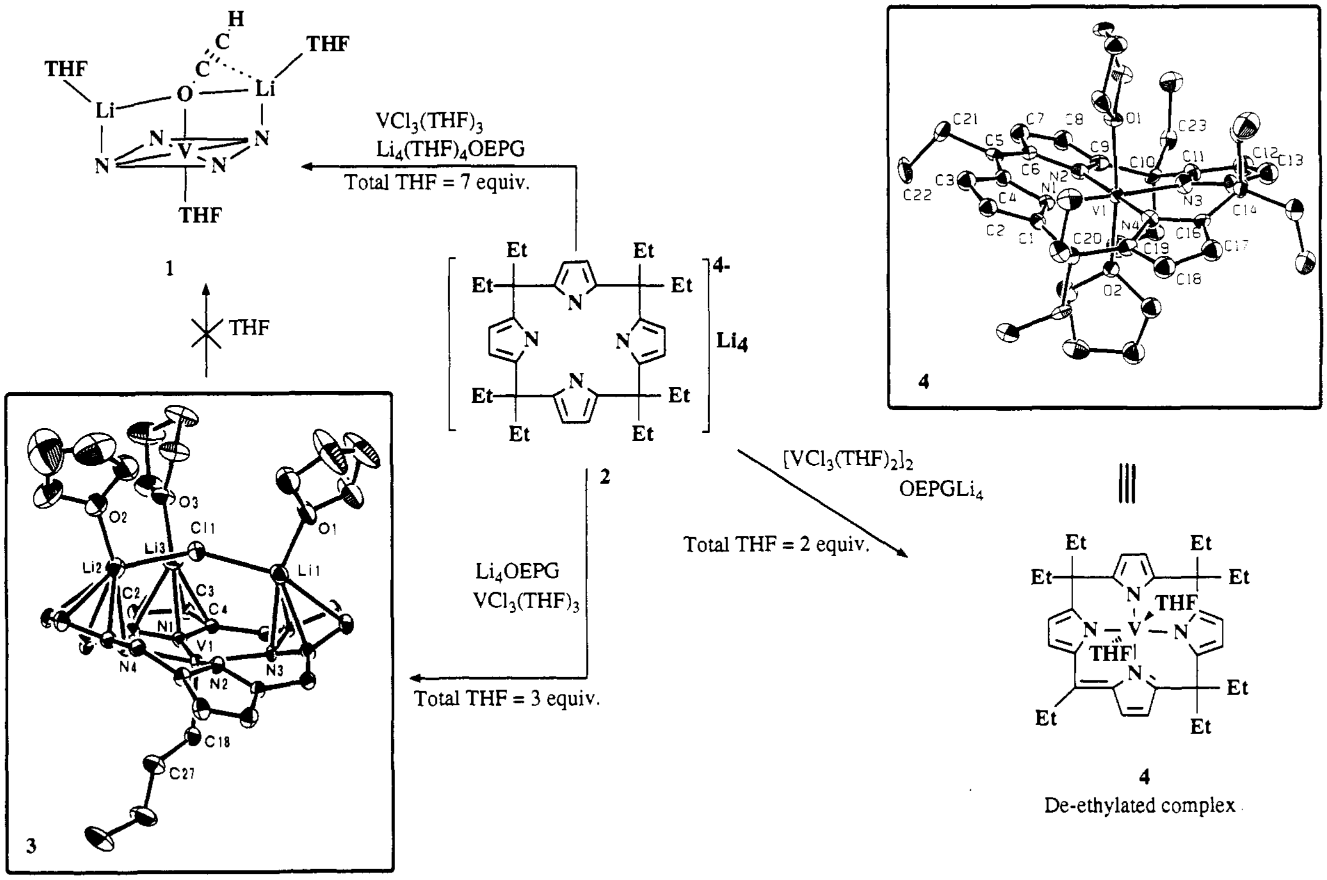
Scheme 1



eliminated with concomitant formation of a C=C bond in the *meso* position. The structure consists of an octahedrally coordinated V(III) placed in the center of the N_4 plane [V1–N1 = 2.086(6), V1–N2 = 2.086(6), V1–N3 = 2.015(6), V1–N4 = 2.060(6) Å; N1–V1–N2 = 89.1(2), N2–V1–N3 = 90.0(3), N3–V1–N4 = 92.2(3), N4–V1–N1 = 88.7(2), N1–V1–N3 = 177.3(2), N2–V1–N4 = 177.8(3)°] with two molecules of THF on the axis perpendicular to the equatorial plane [V1–O1 = 2.075(5), V1–O2 = 2.059(5) Å; O1–V1–O2 = 174.0(2)°]. The four pyrrolyl rings deviate slightly from planarity. However, the two pyrrolyl rings, connected by the partially de-ethylated *meso*-carbon, are coplanar with the trigonal planar *meso*-carbon, clearly indicating an sp^2 hybridization. The distances of the *meso*-carbon to the rings are similar [C4–C5 = 1.410(9), C5–C6 = 1.38(1) Å; C4–C5–C6 = 126.7(7), C4–C5–C21 = 117.1(7), C6–C6–C21 = 116.2(7)°] and are shorter than those formed between the other tetrahedral *meso*-carbon atoms and the rings [C1–C20 = 1.49(1), C19–C20 = 1.52(1) Å; C1–C20–C19 = 116.3(6)°].

The loss of one ethyl group and consequent partial ring oxidation are somewhat reminiscent of the naturally occurring transformations of porphyrinogens to porphyrins *via* aromatization/oxidation of the *meso*-methine bridge.[11-13] We are currently attempting the reaction of the Li_4OEPG salt with anhydrous VCl_3 to ascertain whether the total exclusion of THF from the reaction medium will lead to further aromatization of the macrocycle or whether it will lead to formation of polymetallic aggregates.

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Supplementary Material Available: Textual presentations of the crystallographic procedures and tables of crystallographic data and experimental details, bond distances, bond angles, atomic coordinates, and thermal parameters for **3** and **4** (33 pages). Ordering information is given on any current masthead page.

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