A Novel Reaction Mode of a η^2-Acyl Inserting into a C−C Bond: The Chemistry Associated with Vanadium(III) Bonded to a *meso*-Octaethyl Bis(pyridine)−Bis(pyrrole) Macrocycle

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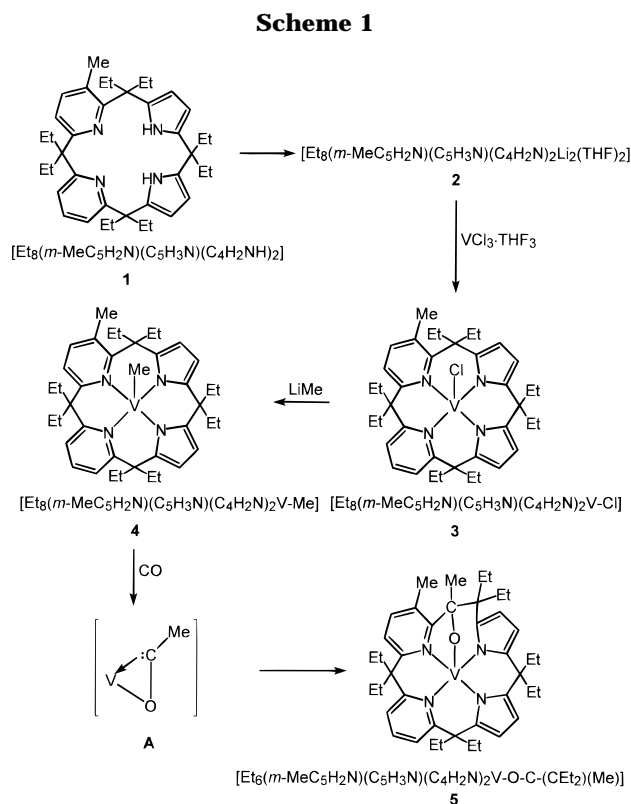*Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne, CH-1015 Lausanne, Switzerland*

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Summary: The doubly homologated meso-octaethylporphyrinogen 1, containing two pyridine and two pyrrole rings in cis arrangements, allowed the synthesis of highly reactive vanadium(III) organometallics, via the intermediacy of 2, [Et$_8$(m-MeC$_5$H$_2$N)(C$_5$H$_3$N)(C$_4$H$_2$N)$_2$-Li$_2$(THF)$_2$], and 3, [Et$_8$(m-MeC$_5$H$_2$N)(C$_5$H$_3$N)(C$_4$H$_2$N)$_2$V−Cl]. This latter complex has been converted to the corresponding [V−Me] derivative 4, [Et$_8$(m-MeC$_5$H$_2$N)-(C$_5$H$_3$N)(C$_4$H$_2$N)$_2$V−Me], which undergoes a facile carbonylation to 5, Et$_6$(m-MeC$_5$H$_2$N)(C$_5$H$_3$N)(C$_4$H$_2$N)$_2$V−OC(CEt$_2$)(Me)]. The intermediate η^2-acyl derivative thus found displayed an unusual carbenoid reactivity inserting into a C−C bond.

The organometallic chemistry developed inside a cavity can produce very reactive intermediates which display unprecedented reactivity, as a result of unavailable intermolecular pathways. Such a protecting metal environment can be provided by an appropriate macrocyclic ligand which should, however, contain at the same time reactive sites which act as a target for the organometallic functionality generated in the cavity. The macrocycle-based organometallic chemistry mentioned above has been greatly developed using the *meso*-octaethylporphyrinogen tetraanion[1] and led us to discover (i) the homologation of a macrocyclic ligand using carbon monoxide,[2] (ii) the intramolecular and intermolecular aliphatic C-H activation,[3] and (iii) the bifunctional carrying properties of polar organometallics.[1c,4] We report here the use of the unprecedented related bis-(pyrrole)−bis(pyridine) macrocycle **1**,[2b] which, though

Scheme 1

[Et$_8$(*m*-MeC$_5$H$_2$N)(C$_5$H$_3$N)(C$_4$H$_2$NH)$_2$]
1

[Et$_8$(*m*-MeC$_5$H$_2$N)(C$_5$H$_3$N)(C$_4$H$_2$N)$_2$Li$_2$(THF)$_2$]
2

[Et$_8$(*m*-MeC$_5$H$_2$N)(C$_5$H$_3$N)(C$_4$H$_2$N)$_2$V-Me]
4

[Et$_8$(*m*-MeC$_5$H$_2$N)(C$_5$H$_3$N)(C$_4$H$_2$N)$_2$V-Cl]
3

A

[Et$_6$(*m*-MeC$_5$H$_2$N)(C$_5$H$_3$N)(C$_4$H$_2$N)$_2$V-O-C-(CEt$_2$)(Me)]
5

being electronically very different from the parent *meso*-octaethylporphyrinogen, maintains some of its conformational characteristics. The organometallic derivatization of **1** has been performed (see Scheme 1) using vanadium(III).

The reference macrocycle **1** has been synthesized *via* the bis-homologation of the *meso*-octaethylporphyrinogen.[2b] Metalation with [VCl$_3$·THF$_3$] requires the preliminary formation of the lithium derivative **2**.[5] The alkylation of **3**[6] has been carried out in a conventional manner and gave the stable vanadium(III)−methyl derivative **4**,[5,7] which undergoes a quite facile carbonylation to give **5**.[8] The entire pathway has been structurally monitored *via* X-ray analysis on all compounds except **4**. We report here the structures of **3** and **5**,

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(5) See the Supporting Information.
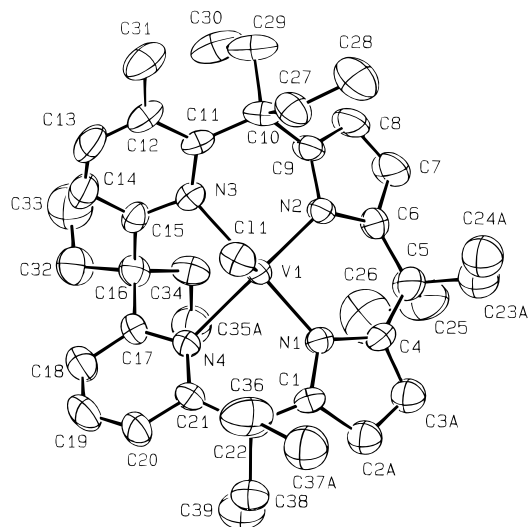
Figure 1. ORTEP view of complex **3**. Selected bond distances (Å) and angles (deg) are as follows: V1−Cl1, 2.230(2); V1−N1, 1.961(5); V1−N2, 1.953(6); V1−N3, 2.211-(6); V1−N4, 2.201(4); N3−V1−N4, 91.8(2); N2−V1−N4, 155.8(2); N2−V1−N3, 84.1(2); N1−V1−N4, 85.3(2); N1−V1−N3, 162.3(2); N1−V1−N2, 91.5(2). Disorder has been omitted for clarity.

which emphasize the major characteristics of a novel macrocycle having the *meso*-octaalkylporphyrinogen skeleton. The structure of **3** is shown in Figure 1[9] with some relevant structural parameters. The metal is displaced by 0.385(2) Å from the N₄ core, which shows significant tetrahedral distortions from planarity, the displacements from the mean plane ranging from −0.070(6) to 0.069(6) Å. The V−Cl line forms a dihedral angle of 11.5(1)° with the normal to the mean plane through the N₄ core. Complex **3** shows an irregular shape due to the twisting of the pyridine ring containing N3, which is tilted up with respect to the N₄ plane while the other three rings are tilted down. The conformation of the macrocycle leads two opposite methylene carbons to approach the chlorine ligand at close contacts of

(6) Procedure for **3**: VCl₃·3THF (9.90 g, 26.50 mmol) was added to a suspension of **2** (17.5 g, 26.4 mmol) in toluene (500 mL). The suspension was stirred overnight at room temperature to give a deep brown solution and solid precipitate, which was removed by filtration. The resulting solution was evaporated to dryness. The solid collected with *n*-hexane (400 mL) was microcrystalline. Toluene was then added until almost complete dissolution of the solid. Some undissolved solid was filtered. The solution was evaporated to dryness and the solid collected with *n*-hexane (75%). The solid recrystallized from toluene-hexane and gave deep yellow crystals for the X-ray analysis. Anal. Calcd for **3**, C₃₉H₅₂ClN₄V·0.5C₇H₈ (MW 734.5): C, 71.90; H, 7.90; N, 7.89. Found: C, 71.82; H, 8.27; N, 7.79. μ_{eff} = 2.93 μ_B at 297 K.

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(8) Procedure for **5**: A THF (30 mL) solution of **4** (1.60 g) was kept under carbon monoxide for 1 h at room temperature. The red solution turned deep brown. The THF was evaporated to dryness, and the residue, collected with *n*-hexane, crystallized (82%). Crystals suitable for the X-ray analysis were obtained from THF−hexane, and they contain crystallization solvents.[10] Anal. Calcd for C₄₁H₅₅N₄OV (MW 670): C, 73.43; H, 8.21; N, 8.36. Found: C, 73.56; H, 8.27; N, 8.00. μ_{eff} = 3.12 μ_B at 297 K.

(9) Crystal data for **3**: C₃₉H₅₂ClN₄V·0.5C₇H₈, monoclinic, space group *C*2/*c*, *a* = 21.601(2) Å, *b* = 11.063(1) Å, *c* = 33.028(3) Å, *β* = 97.16(2)°, *V* = 7831.2(13) Å³, *Z* = 8, ρ_{calcd} = 1.203 g cm⁻³, λ(Cu Kα) = 1.541 78 Å, μ(Cu Kα) = 30.17 cm⁻¹: crystal dimensions 0.19 × 0.40 × 0.72 mm. The structure was solved by the heavy-atom method and anisotropically refined for all the non-H atoms except for those affected by disorder. For 3389 unique observed reflections (*I* > 2σ(*I*)) collected at *T* = 295 K on a Siemens AED diffractometer (6 < 2θ < 140°) and corrected for absorption, the current *R* value is 0.068 (wR2 = 0.192). See the Supporting Information for more details.
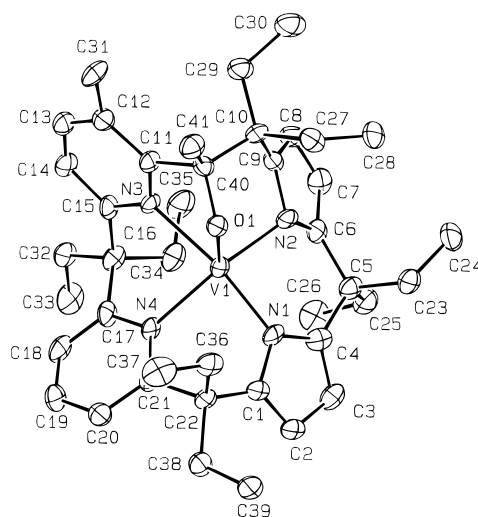
Figure 2. ORTEP view of complex **5**. Selected bond distances (Å) and angles (deg) are as follows: V1−O1, 1.827(4); V1−N1, 2.025(6); V1−N2, 1.991(5); V1−N3, 2.178-(6); V1−N4, 2.197(5); O1−C40, 1.423(8); C10−C40, 1.596-(10); C11−C40, 1.522(10); C40−C41, 1.522(11); N3−V1−N4, 83.3(2); N2−V1−N4, 146.1(2); N2−V1−N3, 96.7(3); N1−V1−N4, 82.4(2); N1−V1−N3, 156.6(2); N1−V1−N2, 85.1(3); V1−O1−C40, 116.9(4).
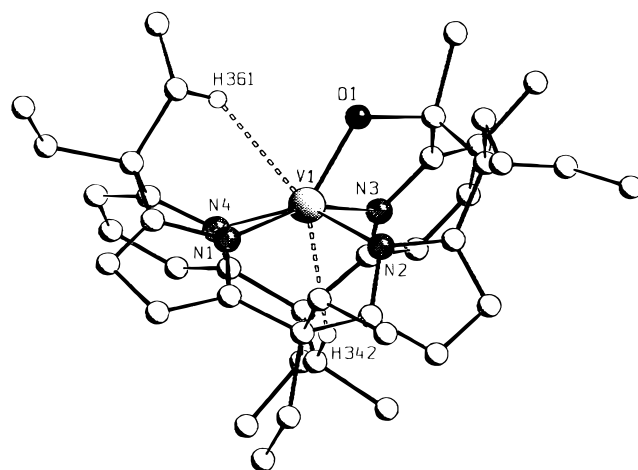
Figure 3. SCHAKAL side view of complex **5**, showing the aliphatic hydrogen−metal interactions.

3.476(9) Å for C27···Cl and 3.402(14) Å for C36···Cl. A close intramolecular contact involves the vanadium atom and the H341 hydrogen atom (located from a Fourier map) from the C34 methylene carbon (V···H, 2.24 Å; Cl−V−H341, 159°). This short-range metal··· hydrogen contact is particularly relevant in the context of the metal-assisted aliphatic C−H bond interaction, as has been observed in the porphyrinogen−zirconium chemistry.[3]

The same interesting metal···hydrogen contacts are seen in the structure of **5**, shown in Figure 2.[10] The bonding mode of the macrocycle is the same as that observed in complex **3**, as far as the inner core of nitrogen atoms is concerned. The V−O1 bond causes

(10) Crystal data for **5**: C₄₁H₅₅N₄OV·0.35C₆H₁₄·0.3C₄H₈O, monoclinic, space group *P*2₁/*n*, *a* = 11.700(4) Å, *b* = 17.698(6) Å, *c* = 18.557-(9) Å, *β* = 92.56(6)°, *V* = 3839(3) Å³, *Z* = 4, ρ_{calcd} = 1.250 g cm⁻³, λ(Cu Kα) = 1.541 78 Å, μ(Cu Kα) = 24.64 cm⁻¹, crystal dimensions 0.14 × 0.21 × 0.46 mm. For 3542 unique observed reflections (*I* > 2σ(*I*)) collected at *T* = 143 K on a Rigaku AFC6S diffractometer (6 < 2θ < 140°) and corrected for absorption, the current *R* value is 0.077 (wR2 = 0.191). See the Supporting Information for more details.

the formation of two puckered five- and six-membered chelate rings. The vanadium atom lies at 0.497(2) Å from the N_4 core, which shows remarkable tetrahedral distortions ranging from $-0.112(6)$ to $0.103(6)$ Å. The V$-$O1 line forms a dihedral angle of 31.6(2)° with the normal to the N_4 mean plane. Two hydrogen atoms from the *meso*-ethyl groups appear to complete the coordination sphere around vanadium: V$-$H342 = 2.48 Å; V$-$H361 = 2.48 Å; H361 is *cis* to the O1 oxygen atom (O1$-$V$-$H361 = 69°); H342 is on the opposite side. The dihedral angles formed by these lines with the normal to the N_4 mean plane are 38.1 and 10.3°, respectively.

The most important concern is related to the genesis of **5**, which is formally derived from a carbenoid insertion into a C-C bond, an unusual reactivity pathway for a η^2-acyl bonded to an early transition metal.[11] The reaction is interpreted mechanistically by invoking carbenium ion (the η^2-acyl functionality) attack on the α-carbon of the pyridine ring, followed by an alkyl migration.[12] We should emphasize, besides any mechanistic consideration, the potential of using **1** and **2** in early-transition-metal organometallic chemistry, for the generation of highly reactive species.

Supporting Information Available: Text giving synthetic procedures for **2**$-$**4** and detailed crystal data for **3** and **5** and ORTEP drawings (Figures S1 and S2) and tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for complexes **3** and **5** (18 pages). Ordering information is given on any current masthead page.

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