Preparation and Reactivity of the First Yttrium Porphyrinogen Complex

Jayne Jubb,[a] **Sandro Gambarotta,***[a] **Robbert Duchateau**[b] **and Jan H. Teuben***[b]

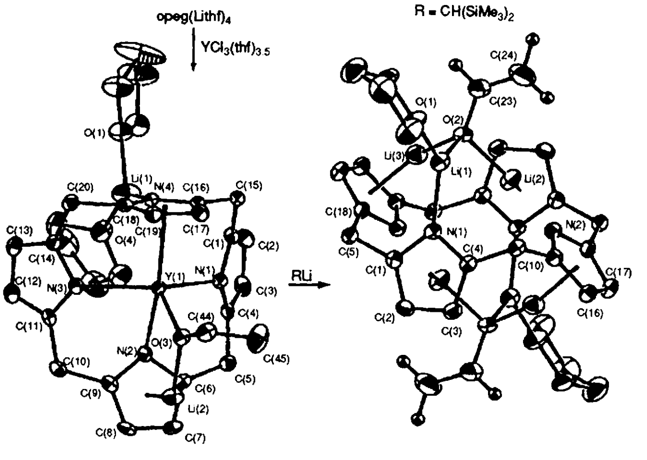
[a] *Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5*

[b] *Groningen Centre for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

Reaction of $Li_4(thf)_4(oepg)$ (oepg = octaethylporphyrinogen with $YCl_3(thf)_{3.5}$ affords the first yttrium porphyrinogen complex $[Li(thf)_2][(oepg)Y(\mu\text{-}OEt)Li(thf)]$ **1** *via* intermediate cleavage of thf, subsequent reaction with alkyl and hydride sources leads to the formation of the demetallated dienolate salt of the macrocycle $[(oepg)(thfLi)_4][(thf)LiOCH{=}CH_2]_2$ **2**.

The organometallic chemistry of yttrium has been based largely around compounds using cyclopentadienyl species as supporting ligands.[1] In particular, studies in this field have been encouraged by the discovery that bis(pentamethylcyclopentadienyl) systems such as $(C_5Me_5)_2Y\text{-}R$ [R = H, $CH(SiMe_3)_2$] are involved in a number of important processes such as catalytic oligomerization of terminal alkynes,[2] C–H σ-bond metathesis,[3] insertion reactions[4a,b] and olefin polymerization.[4c,d] Recently, there has been new impetus towards the search for alternative ligands in an attempt to extend yttrium chemistry beyond the traditional realm of yttrocene complexes. The results obtained were rather encouraging in this direction, having shown that these complexes work as precursors for the catalytic dimerization of terminal alkynes[5] and cyclometallation reactions.[6]

Among the possible alternatives, polydentate macrocyclic ligands[7] are of particular interest due to their well-known potential for the stabilization of alkyl and hydride functions. In addition, the steric hindrance at the metal centre may be fine-tuned *via* the selection of appropriate ligand substituents, and optical activity may be introduced into the complex. Owing to the large ionic radius of yttrium and the lanthanides, these ligands may also give rise to the assembly of multidecker structures.[8] In spite of these promising features, only a few examples of macrocyclic yttrium complexes have been reported, *viz* only those using phthalocyanines and porphyrins.[9] Chemical reactivity studies are available only in the case of the octaethylporphyrin (oep) complexes $(oep)Y[OC_6H_3(Bu^t)_2]$, $(oep)Y(\mu\text{-}Me)_2Li(OEt_2)$, $(oep)Y(\mu\text{-}OMe)_2AlMe_2$ and $(oep)Y[CH(SiMe_3)_2]$.[10]



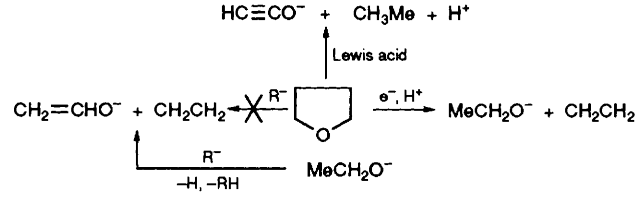
Scheme 1 Selected values of bond distances (Å) and angles (°). Ethyl groups have been omitted for clarity. Complex **1**: Y(1)–N(1) = 2.340(3); Y(1)–N(2) = 2.369(3); Y(1)–N(3) = 2.337(3); Y(1)–N(4) = 2.547(3); Y(1)–O(3) = 2.144(2); Y(1)–C(16) = 2.663(3); Y(1)–C(17) = 2.808(3); Y(1)–C(18) = 2.663(3); Y(1)–C(19) = 2.806(3); Li(1)–N(4) = 2.020(7); O(3)–C(44) = 1.416(4); C(44)–C(45) = 1.497(5); N(1)–Y(1)–N(3) = 136.3(1); N(1)–Y(1)–N(2) = 79.41(9); N(2)–Y(1)–N(3) = 79.86(9); N(1)–Y(1)–O(3) = 107.04(9); N(3)–Y(1)–O(3) = 109.21(9); O(3)–C(44)–C(45) = 112.1(3). Complex **2**: N(1)–Li(1) = 1.953(4); O(2)–Li(1) = 1.903(4); O(2)–Li(2) = 1.960(4); N(2)–Li(2) = 2.023(4); O(2)–Li(3) = 1.832(4); O(2)–C(23) = 1.358(3); C(23)–C(24) = 1.339(4); O(2)–C(23)–C(24) = 124.2(3); O(2)–C(23)–H(26) = 113(2); C(23)–C(24)–H(30) = 120(2); O(1)–Li(1)–O(2) = 120.3(2); N(1)–Li(1)–O(1) = 127.3(2); N(1)–Li(1)–O(2) = 110.8(2); Li(1)–O(2)–Li(2) = 107.2(2); Li(1)–O(2)–Li(3) = 100.4(2); Li(2)–O(2)–Li(3) = 92.9(2).

Recent success in the use of the porphyrin-precursor octaethylporphyrinogen (oepg) for investigating low- and medium-valent vanadium and samarium chemistry,[11] spurred us on towards attempting the preparation of some yttrium complexes. Herein, we report the synthesis, characterization and chemical behaviour of the novel yttrium macrocycle $[Li(thf)_2][(oepg)Y(\mu\text{-}OEt)Li(thf)]$ **1** obtained *via* the cleavage of thf.

The reaction of the tetralithium salt[11,12] of oepg $[Li_4(thf)_4oepg]$ with $YCl_3(thf)_{3.5}$ in thf proceeded at room temp. leading to the formation of **1** which was isolated as a white crystalline solid (70% yield) after extraction with either diethyl ether, hexane or pentane (Scheme 1).† The ^1H NMR spectrum showed two signals at δ 3.80 (quartet) and 1.17 (triplet) not attributable to the oepg ethyl groups. Following the elucidation of its molecular structure by single crystal X-ray diffraction analysis,‡ the presence of an ethoxide moiety bridging the yttrium metal centre and one lithium cation accounted for these resonances; the quartet being due to the CH_2O and the triplet to the Me of the ethoxide. In addition to the satisfactory refinement of the thermal parameters, the X-ray structure showed the expected C–C and C–O bond distances and angles [C(44)–C(45) = 1.497(5); O(3)–C(44) = 1.416(4) Å; O(3)–C(44)–C(45) = 112.1(3)°].

The presence of the ethoxide coordinated to the yttrium is believed to arise from the *in situ* cleavage of thf. Accordingly, a quantitative amount of ethylene was recovered from the reaction mixture. The alternative possibility that the ethoxide moiety arose from cleavage of diethyl ether during the extraction procedure was ruled out on the basis of the observation that the same product was formed when the purification step by extraction was carried out with pentane or hexane.

We have preliminarily explored the possibility of replacing the ethoxide group with the more synthetically useful alkyl and hydride substituents. Surprisingly, the reaction of **1** with either $LiCH(SiMe_3)_2$ or $LiBEt_3H$ led to the formation of a new species **2**§ which could be isolated as colourless crystals and whose X-ray fluorescence spectrum showed absence of yttrium (Scheme 1). In addition to the expected resonances for the oepg ligand, the ^1H NMR spectrum showed two doublets of doublets at δ 6.78 and 3.79. The chemical shift of these new resonances together with the presence of a band at 1583 cm^{-1} in the IR spectrum indicated the presence of an olefinic function in complex **2**. An X-ray crystal determination¶



Scheme 2

revealed **2** to be the demetallated dienolate salt of the macrocycle [oepg(Lithf)$_4$][(thf)LiOCH=CH$_2$]$_2$ **2** (Fig. 2). The enolate moiety is characterized by a C–C distance [C(23)–C(24) = 1.339(4) Å] which is shorter than in the ethoxide group of **1**, but slightly longer than expected for a C=C double bond. All the H atom positions were located and refined in the positions expected for sp^2 carbon atoms [O(2)–C(23)–C(24) = 124.2(3)°]. The fate of yttrium during the formation of **2** is unclear. However, new yttrium alkyl species are likely to be formed since two new resonances at δ −0.4 and −1.7 were observed in the ^{1}H NMR spectrum of the reaction mixture.

We have previously observed that thf will fragment in the presence of the vanadium–oepg macrocyclic complex[11,12] leading to incorporation of the ynolate (–OC≡CH) fragment and concomitant elimination of ethane (Scheme 2), and without involving a redox process. In contrast, the cleavage of thf obtained in the case of the yttrium complex **1** formed the ethoxide group. The appearance of ethylene during the reaction was monitored by an NMR-tube experiment which showed the appearance of the signal at δ 5.25. We do not yet fully understand from whence the two electrons and the extra proton required for this rupture come. It is very likely that they are generated from this electronically flexible ligand,[12] since no redox chemistry has ever been reported for yttrium compounds. Even more surprising, the presence of the two rare lithium enolate moieties in **2** formed during the reaction of **1** with RLi may be ascribed to either the further cleavage of another molecule of thf within the complex (the reaction was performed in benzene) or to dehydrogenation of the ethoxy group attached to yttrium. The first pathway would require that either ethylene or ethane (neither of which were observed) would be formed together with R–H, which was actually recovered in stoichiometric amount. The second pathway requires that the OEt group coordinated to yttrium is deprotonated by RLi on the α-CH$_2$ forming the LiOCH=CH$_2$ unit, after the further transfer of one hydride to the yttrium centre. The high reactivity of the intermediate yttrium hydride may easily account for complicated degradation pathways including demetallation of the porphyrinogen ring.

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Footnotes

† YCl$_3$(thf)$_{3.5}$ (2.50 g, 5.58 mmol) and Li$_4$(oepg)(thf)$_4$ (5.24 g, 6.14 mmol) were stirred in freshly distilled anhydrous thf (130 ml) at room temp. overnight. The resulting pale-pink solution was concentrated to dryness and the residue extracted with pentane (250 ml) overnight. The extract was then concentrated to about 50 ml and a white crystalline product was obtained (3.73 g, 76%) after leaving to stand at −20 °C overnight. Crystals suitable for X-ray diffraction analysis were obtained after recrystallization from pentane. ^{1}H NMR δ (C$_6$D$_6$): 6.47 (4H, br s, pyrrole), 6.23 (4H, br s, pyrrrole), 3.8 (2H, q, OCH_2CH$_3$), 3.2 (12H, m, thf), 2.2 (8H, br, CH_2CH$_3$), 2.1 (8H, br, CH_2CH$_3$), 1.28 (12H, m, thf), 1.17 (3H, t, OCH$_2$CH_3), 1.0 (12H, t, CH$_2$CH_3) and 0.89 (12H, t, CH$_2$CH_3). (Found: C, 66.51; H, 8.59; N, 6.17. Requires C, 66.66; H, 8.61; N, 6.22).

‡ *Crystal data* for **1**, C$_{50}$H$_{77}$O$_4$YN$_4$Li$_2$: M = 900.97, white cube, triclinic, $P\bar{1}$, a = 14.680(2), b = 15.617(2), c = 11.744(1) Å, α = 101.52(2), β = 112.03(1), γ = 87.85(2)°, V = 2443(1) Å^3, Z = 2, D_c = 1.224 g cm^{-3}, μ(Mo-Kα) = 12.43 cm^{-1}. The data were collected at −160 °C on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation (0.71609 Å) by using an ω-2θ scan mode. Of the 7336 reflections collected in the range $6.0 < 2\theta < 50.0°$, 6970 were unique. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located. Refinement converged at R = 0.040 (R_w = 0.046) for 5714 observed reflections [$I > 2.50\sigma(I)$] and 551 parameters.

§ **1** (2.30 g, 2.62 mmol) was dissolved in benzene (75 ml) and LiCH(SiMe$_3$)$_2$ (0.80 g, 4.81 mmol) was added. After stirring at room temp. overnight, the mixture was concentrated to about 30 ml and left to stand at 4 °C for 3 days affording cubic crystals of **2** (0.75 g, 35%) suitable for X-ray diffraction analysis. Complex **2** was also prepared by the overnight reaction of **1** (0.95 g, 1.08 mmol) with LiBEt$_3$H (1.1 ml, 1.08 mmol) in thf (30 ml) at room temp. After leaving to stand at −20 °C for 3 days, white diamond-shaped crystals of **2** were formed (0.35 g, 40%). ^{1}H NMR δ (C$_6$D$_6$) 6.78 (2H, dd, OCH=CH$_2$), 6.38 (8H, s, pyrrole), 3.79 (4H, dd, OCH=CH_2), 3.52 (8H, m, thf), 2.07 (16H, q, CH_2CH$_3$), 1.30 (8H, m, thf), 0.90 (2H, t, CH$_2$CH_3). (Found: C, 71.07; H, 8.66; N, 6.81. Requires C, 71.29, H, 8.72; N, 6.93.)

¶ *Crystal data* for **2**, C$_{48}$H$_{70}$O$_4$N$_4$Li$_6$: M = 808.76, triclinic, white cube, $P\bar{1}$, a = 11.5223(9), b = 11.774(1), c = 10.306(2) Å, α = 115.132(9), β = 104.99(1), γ = 69.54(1)°, V = 1175.9(6) Å^3, Z = 2, D_c = 1.142 g cm^{-3}, μ(Mo-Kα) = 0.65 cm^{-1}. The data were collected at −158 °C on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation (0.71609 Å) by using an ω-2θ scan mode. Of the 4355 reflections collected in the range $6.0 < 2\theta < 50.0°$, 4130 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 = 0.043 (R_w = 0.050) for 2722 observed reflections [$I > 2.50\sigma(I)$] and 293 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

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