PREPARATION AND REACTIVITY OF THE FIRST YTTRIUM PORPHYRINOGEN COMPLEX
Jubb, Jayne; Gambarotta, Sandro; Duchateau, Robbert; Teuben, Jan H.

Published in:
Journal of the Chemical Society-Chemical Communications

DOI:
10.1039/c39940002641

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1994

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Preparation and Reactivity of the First Yttrium Porphyrinogen Complex

Jayne Jubb,* Sandro Gambarotta,* Robbert Duchateau‡ 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 Li₄(thf)₄(oepg) (oepg = octaethylporphyrinogen with YCl₃(thf)₃.₅ affords the first yttrium porphyrinogen complex [Li(thf)]₄(oepg)Y(µ-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]([thf]Li)[Li(thf)²]₃LiOCH=CH₂ 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 these complexes work as precursors for the catalytic dimerization of terminal alkynes, 2 C-H σ-bond metathesis, 3 insertion reactions 4 and olefin polymerization. 5,6,7 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 chemistry. 8 In spite of these promising features, only a few examples of macrocyclic yttrium complexes have been reported, viz only those using phthalocyanines and porphyrinogens. 9 Chemical reaction studies are available only in the case of the octaethylporphyrin (oep) complexes (oep)Y[OC₆H₃-µ-OEt]₂, (oep)Y(µ-Me₂)₂[AlMe₂]₃ and (oep)Y[CH(SiMe₃)]₂. 10

Recent success in the use of the porphyrin-precur sor 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)]₄([oepg]Y(µ-OEt)Li(thf)) 1 obtained via the cleavage of thf.

The reaction of the tetrалithium salt 11,12 of oepg [Li-thf]oepg with YCl₃(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). 13 The 'H NMR spectrum showed two signals at 6 5.80 (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 unit bridging the yttrium metal centre and one lithium cation accounted for these resonances; the quartet being due to the CH₂O 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) = 1.416(4); O(3)-C(44)-C(45) = 112.1(3)].

13C NMR showed absence 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 alky and hydride substituents. Surprisingly, the reaction of 1 with either LiCH(SiMe₃)₂ or LiBE₃H 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 'H NMR spectrum showed two doublets of doublets at 6 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 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) = 2.336(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: Li(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(3); 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(2) = 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).
revealed 2 to be the demetallated dienolate salt of the macrocycle [oepg(Li(thf))][thf]LiOCH₂CH₃]. 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 sp² 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 no redox chemistry has ever been reported for yttrium compounds. Even more surprising, the presence of the two C(24) = 1.339(4) Å which is shorter than in the ethoxide group of 2642 and concomitant elimination of ethane (Scheme 2), an unexpected result. 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, 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 the ethoxy group attached to yttrium. The first pathway would require that either ethylene or ethane (neither of which were detected) were formed during the reaction. The second pathway requires that the OEt group coordinated to yttrium is deprotonated by RLi on the α-CH₃ forming the LiOCH₂CH₃ 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.

We are grateful to the NSERC (Canada) and to Shell Research B.V. (Amsterdam) for financial support. The RSC is gratefully acknowledged for a J. W. T. Jones Travelling Fellowship (to J. J.).

Received, 25th August 1994; Com. 4/05220J

Footnotes
† YCl₃(thf)₃.5 (2.50 g, 5.58 mmol) and Li₄(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-

References