Octaethylporphyrin*–Yttrium–Methyl Chemistry: Preparation and Selective Activation of Dioxygen by (oep)Y(μ-Me)$_2$AlMe$_2$

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The octaethylporphyrinyttrium complex (oep)Y(μ-Me)$_2$AlMe$_2$, prepared *via* (oep)YOC$_6$H$_3$Bu$^t{}_2$ and (oep)Y(μ-Me)$_2$Li(OEt$_2$), is selectively oxidised by O$_2$ to afford (oep)Y(μ-OMe)$_2$AlMe$_2$.

The recent growth in organolanthanide chemistry has primarily focused on complexes stabilised by the bis(pentamethylcyclopentadienyl) ligand system. We have recently reported the use of the octaethylporphyrin dianion (oep) as a viable alternative ligand system.[1] The complexes (oep)MCH(SiMe$_3$)$_2$ **1** (M = Lu, Y) were shown[1] to undergo facile protonolysis with HX to give alkoxide, alkynyl and hydroxide species (oep)MX (X = OC$_6$H$_3$Bu$^t{}_2$, CCBu^t, OH).

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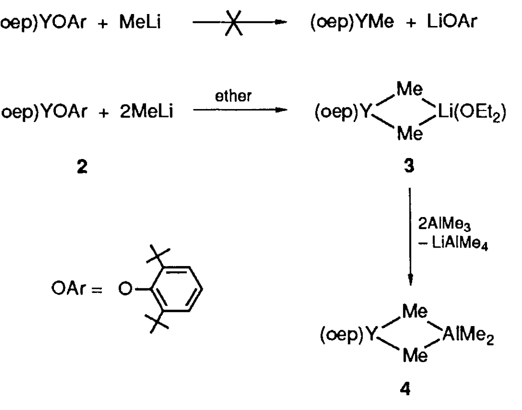
* oep represents the octaethylporphyrin dianion.

Attempts to prepare a catalytically active hydride were thwarted as (oep)MCH(SiMe$_3$)$_2$ is resistant to hydrogenolysis.[1] Methyl species M(C$_5$Me$_5$)$_2$Me (M = Sc,[2] Lu,[3] Y[3]) have an extensive reactivity including propene oligomerisation,[3b] methane transmetallation[2,3c] and β-methyl elimination.[3d]

This contribution focuses on the attempted preparation of (oep)MMe, and subsequent activation of O$_2$ by (oep)Y(μ-Me)$_2$AlMe$_2$. Reaction of (oep)YOC$_6$H$_3$Bu$^t{}_2$-2,6 **2**[1] with MeLi (2 equiv.)† in diethyl ether (−40 → 20 °C) afforded bright-red, diethyl ether-insoluble (oep)Y(μ-Me)$_2$Li(OEt$_2$) **3**, which can be best regarded as an adduct of putative (oep)YMe and MeLi·OEt$_2$. We have previously demonstrated[1] that (oep)MOC$_6$H$_3$Bu$^t{}_2$ (M = Lu, Y) reacts with LiCH(SiMe$_3$)$_2$ to afford **1**. To assist in accumulating evidence pertaining to methyl species, yttrium complexes were prepared to take advantage of the ^{89}Y (I = ½, 100% abundant) nucleus.

Coordinated MeLi can be readily removed by reaction of a suspension of **3** in hexane with AlMe$_3$ (2 equiv.)‡ to afford hexane-soluble, deep red (oep)Y(μ-Me)$_2$AlMe$_2$ **4**§ in excellent yield, which is readily separated from insoluble LiAlMe$_4$. The ethyl protons of the oep ligand in **4** are diastereotopic and give rise to an ABX$_3$ spin system with J_{AB} = 17 Hz, J_{AX} = J_{BX} = 7.6 Hz (simulated spectra). At −60 °C one peak for all aluminium methyls is observed at δ −8.96 ($^1J_{CH}$ 109 Hz) whilst the octaethylporphyrin resonances remain sharp. This lack of yttrium coupling or separate methyl resonances for the Y(μ-Me)$_2$AlMe$_2$ unit in the low-temperature ^{13}C NMR is in contrast to the related cyclopentadienyl analogues (C$_5$R$_5$)$_2$Y(μ-Me)$_2$AlMe$_2$ (R = H, Me).[4,5a] The significantly reduced $^1J_{CH}$ coupling for all AlMe$_4$ groups in **4** is also the mean of those found in static (C$_5$Me$_5$)$_2$Y(μ-Me)$_2$AlMe$_2$.[4c] In (C$_5$Me$_5$)$_2$Ln(μ-Me)$_2$MMe$_2$ the magnitude of C–H and Y–C coupling constants has been shown to be diagnostic[4a] of the coordination geometry of the methyl groups. A possible explanation is fast intramolecular exchange due to the open coordination environment afforded by the oep ligand, the agreement in the reduced J_{CH} being good evidence that the aluminium methyl groups remain bound (in a time-averaged manner) to yttrium. Such a proposal has precedent; the ^{1}H NMR spectra of (C$_5$R$_5$)$_2$Y(μ-Me)$_2$AlMe$_2$ at (R = H,[5a] 40 °C; R = Me,[4c] 75 °C) showed the (reversible) formation of a species having a single resonance for all aluminium methyl groups.

Variable-temperature ^{1}H and ^{13}C NMR indicate that **4** is monomeric, there being no indication of a temperature-dependent monomer–dimer equilibrium[4] as has been observed for the more sterically hindered bis(pentamethylcyclopentadienyl) analogues of **4**.[4] The sterically less hindered cyclopentadienyl species (C$_5$H$_5$)$_2$Ln(μ-Me)$_2$AlMe$_2$[5] exists only as monomers. An explanation is that a (μ-Me)$_2$AlMe$_2$ unit may be able to coordinate to a (C$_5$H$_5$)$_2$Ln or (oep)Y fragment without unfavourable steric interactions, whereas steric crowding presumably exerts a dominant influence when it is coordinated to a (C$_5$Me$_5$)$_2$Ln fragment. Their propensity for dimerisation will also be effected by the difference in electron density at yttrium in comparing (oep)Y and (C$_5$H$_5$)$_2$Y, with (C$_5$Me$_5$)Y.



Scheme 1

The hard electronegative octaethylporphyrin ligand has a clear influence on the reactivity of **4**. In contrast to the observed reactivity of (C$_5$R$_5$)$_2$Ln(μ-Me)$_2$AlMe$_2$,[4,5b] treatment of **4** with tetrahydrofuran (THF) or diethyl ether gives reversible adduct formation, without bridge splitting. Addition of C$_5$H$_5$N or 4-dimethylaminopyridine (1 equiv.) leads to decomposition.

Although dioxygen activation has been extensively studied for late transition metal complexes[6] and Wolczanski[7] has investigated the insertion of O$_2$ into the metal–methyl bond of (Bu$^t{}_3$CO)MMe$_2$ (M = Ti, Zr, Hf), the selective oxidation of lanthanide complexes by O$_2$ has not been previously observed, despite their intrinsic oxophilicity and frequently observed decomposition with oxygen.

(oep)Y(μ-Me)$_2$AlMe$_2$ **4** activates O$_2$ in a controlled manner to afford selectively (oep)Y(μ-OMe)$_2$AlMe$_2$ **5**.§ Addition of an excess of dry O$_2$ to a hexane solution of **4** results in its rapid and quantitative conversion to **5**. ^{1}H NMR monitoring shows **5** to be the only species formed.

$$\underset{\mathbf{4}}{\mathrm{(oep)Y(\mu\text{-}Me)_2AlMe_2}} + \mathrm{O_2} \rightarrow \underset{\mathbf{5}}{\mathrm{(oep)Y(\mu\text{-}OMe)_2AlMe_2}}$$

The bridging methoxy groups resonate at δ 0.76 (^{1}H NMR) and 46.9 (^{13}C NMR), whilst the terminal methyl groups resonate at δ −2.23 (^{1}H NMR) and −14.1 [full width at half maximum (fwhm) = 35 Hz] (^{13}C NMR), the magnitude of the shielding of the porphyrin ring being most noticeable in the upfield chemicals shifts in the ^{1}H NMR. The chemical shifts in the ^{1}H and ^{13}C NMR spectra (and elemental analysis) effectively rule out other possibilities such as (oep)Y(μ-Me)$_2$-Al(OMe)$_2$ or (oep)Y(μ-OMe)$_2$Al(OMe)$_2$.

An alkylperoxy species is a likely intermediate in this oxidation reaction; thus it was of considerable interest to prepare species of the type (oep)YOOR. Although (oep)YCH(SiMe$_3$)$_2$ **1** undergoes clean protonolysis,[1] reaction with anhydrous Bu^{t}OOH failed to yield an identifiable product, as did reaction of **1** with O$_2$.

Coordination to (oep)Y effectively mediates the oxidation of the Al–Me bonds in **5**. It is pertinent to note that oxidation of simple aluminium alkyls by O$_2$ is very fast and only the free radical chain oxidation of the last, less reactive Al–C bond in R–Al(OR)$_2$ has been studied.[8,9]

The octaethylporphyrin dianion has been shown to be an effective ligand system to stabilise yttrium methyl compounds, and is sufficiently robust to allow selective oxidation by O$_2$.

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† Reaction of **1** with MeLi (1 equiv.) leads to a 1 : 1 mixture of **2** and **3**. Although heavier alkali metals are less likely to form such adducts, reaction of **2** with solid KMe in hexane did not yield a tractable species.

‡ Reaction of **3** with AlMe$_3$ (1 equiv.) does not lead to (oep)YMe and LiAlMe$_4$, but to a 1 : 1 mixture of **3** and **4**.

§ *Spectroscopic data* for (oep)Y(μ-Me)$_2$AlMe$_2$ **4**; ^{1}H NMR (C$_7$D$_8$, 25 °C): δ 10.57 (CH), 4.04 (m, CH$_2$), 1.87 (t, Me), −3.72 (AlMe). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 147.7 (CH), 144.0 (CH), 100.9 (C), 20.3 (CH$_2$), 18.7 (Me), −8.0 (AlMe). ^{13}C NMR (C$_7$D$_8$, −60 °C): δ 146.3 (CH), 141.6 (CH), 99.7 (C), CH$_2$ and Me resonances obscured by solvent methyl resonance, −8.96 (q, 109 Hz, AlMe). (oep)Y(μ-OMe)$_2$AlMe$_2$ **5**; ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 10.49 (s, 4H, CH), 4.00 (m, 16H, CH$_2$), 1.85 (t, 24H, Me), 0.76 (s, 6H, OMe), −2.23 (s, 6H, AlMe). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 147.4 (CH), 142.52 (CH), 100.4 (C), 46.9 (OMe), 20.3 (CH$_2$), 18.8 (Me), −14.1 (fwhm = 35 Hz, AlMe).

Satisfactory elemental analysis was obtained for **3** (C,H, Al, Y) and **4** (C,H,N).

The chemistry of which is more comparable with their less sterically hindered, less electron-rich C_5H_5 counterparts[5,10] than with their C_5Me_5 analogues.[4]

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