X-Ray Crystallographic Determination of the Structure of Bis(methylcyclopentadienyl)ytterbium Tetrahydrofuranate and its Ready Formation by Four New Routes

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Summary $(MeC_5H_4)_2Yb\cdot OC_4H_8$, which is generated by reaction of MeC_5H_5 with YbC_6H_{10}, by H_2 reduction of $[(MeC_5H_4)_2YbMe]_2$, and by photolysis and thermolysis of $[(MeC_5H_4)_2YbMe]_2$, has a solid state structure consisting of chains of $(\mu\text{-}MeC_5H_4)(MeC_5H_4)Yb\,OC_4H_8$ repeating units related by a 2-fold screw axis and connected by one bridging cyclopentadienyl group per ytterbium

Although divalent organolanthanoid complexes have been known for many years,[1] solid state structural data on this class of organometallics have been elusive [2] We report here the first *X*-ray structure determination of a divalent organoytterbium complex, $(MeC_5H_4)_2Yb\,OC_4H_8$, (**1**), and describe four new syntheses of (**1**), equations (1)—(4), which demonstrate the importance of the divalent oxidation state to organoytterbium chemistry

$$YbC_6H_{10} + MeC_5H_5 \xrightarrow[25\ ^\circ C]{THF} \underset{(\mathbf{1'})}{(MeC_5H_4)_2Yb} \qquad (1)$$

$$[(MeC_5H_4)_2YbMe]_2 + H_2 \xrightarrow[50\ ^\circ C]{toluene} CH_4 + [(MeC_5H_4)_2YbH] \rightarrow (\mathbf{1'}) \qquad (2)$$

$$[(MeC_5H_4)_2YbMe]_2 \xrightarrow[toluene,\ 5\ ^\circ C]{h\nu} (\mathbf{1'}) \qquad (3)$$

$$[(MeC_5H_4)_2YbMe]_2 \xrightarrow[80\ ^\circ C]{pentane\text{–}Et_2O} (\mathbf{1'}) \qquad (4)$$

THF = tetrahydrofuran

We have previously reported[3] the synthesis of a series of hex-3-yne derivatives of the lanthanoids which constituted the first class of f-orbital element complexes known to function as homogeneous catalysts for the activation of molecular hydrogen Reactions (1) and (2) were examined to investigate the structure and catalytic activity of the ytterbium member of this class, YbC_6H_{10} In reaction (1), a dark brown THF solution of YbC_6H_{10} was treated with 1 equiv of MeC_5H_5 in an effort to obtain a crystalline, cyclopentadienyl-stabilized alkyne complex Removal of THF from the purple solution formed in this reaction left a green solid which was washed with toluene and recrystallized from THF by slowly diffusing pentane into the THF solution The yellow crystals obtained were characterized by i r , u v -visible, ^1H n m r [C_4D_8O δ 2 07(s) and 5 47(s)], and ^{13}C n m r (C_4D_8O, fully decoupled, ref to THF δ 15 3, 105 8, 107 5, and 116 8 p p m) spectroscopy and by *X*-ray crystallography and identified as (**1**)

A second reaction pathway to (**1**), reaction (2), was discovered while attempting the synthesis of a trivalent ytterbium hydride for comparison with the ytterbium hydrides presumably present in the catalytic hydrogenation reactions involving YbC_6H_{10} [3] An obvious route to lanthanoid hydrides based on alkali metal,[4] alkaline earth,[4] and actinoid[5] chemistry is hydrogenolysis of alkyl lanthanoid complexes, equation (5) Both H_2 and D_2 react with the orange $[(MeC_5H_4)_2YbMe]_2$[6] in toluene at 50 °C over a two week period to form the by-products expected from reaction (5), CH_4 and CH_3D, respectively The green precipitate isolated from the reaction mixture by filtration appeared to be an ytterbium hydride based on CH_3I decomposition reactions which generated CH_4 In further support of this hypothesis, the green precipitate generated *via* equation (2) using D_2, *i e* presumably $[(MeC_5H_4)_2YbD]$, reacted with CH_3I to form CH_3D Only 40—50% of the methane expected from pure $[(MeC_5H_4)_2YbH]$ was obtained, however, and further characterization suggested the green precipitate was a mixture which contained the hydride decomposition product (**1'**) The near i r -visible spectrum

$$L_xLn\text{–}R + H_2 \rightarrow L_xLn\text{–}H + RH \qquad (5)$$

contained absorptions characteristic of both Yb^{2+} and Yb^{3+}, and magnetic susceptibility measurements[7] varied from sample to sample yielding magnetic moments of 2—4 B.M., also consistent with a mixture of Yb^{2+} and Yb^{3+}. Since the toluene-soluble $[(MeC_5H_4)_2YbMe]_2$ cannot be present in the insoluble green precipitate, it appears that the trivalent component is an unstable ytterbium hydride which slowly decomposes to the divalent component, (**1′**). Recrystallization of the green precipitate by pentane diffusion into a THF solution forms crystals of (**1**).

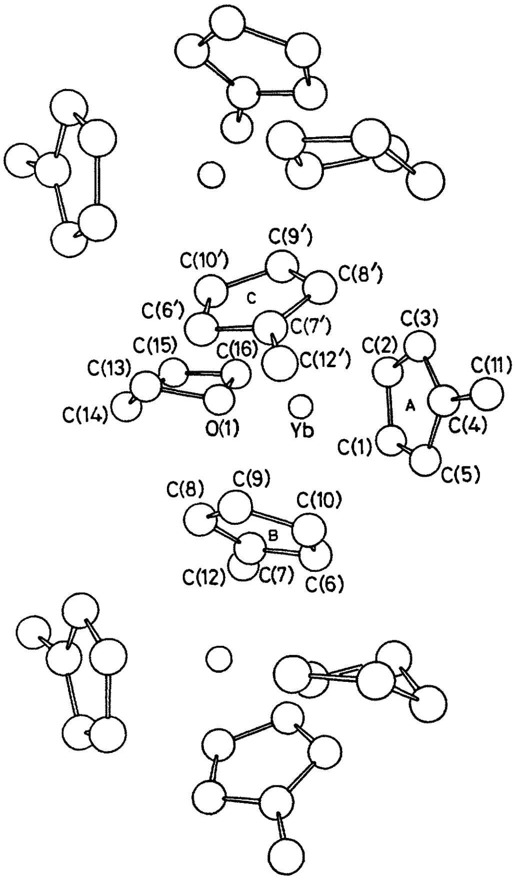

FIGURE. ORTEP plot of the structure of $(MeC_5H_4)_2Yb\cdot OC_4H_8$ with *b*-axis vertical. Bond distances to the Yb atom are C(1) 2·75(3), C(6) 2·91(3), C(6′) 2·94(3), C(2) 2·76(3), C(7) 2·94(3), C(7′) 2·94(3), C(3) 2·77(3), C(8) 2·93(3), C(8′) 2·84(3), C(4) 2·77(3), C(9) 2·89(3), C(9′) 2·79(3), C(5) 2·76(3), C(10) 2·88(3), C(10′) 2·85(3), O(1) 2·53(2) Å.†

The third synthesis of (**1**), reaction (3), was discovered as part of our investigation of the photochemistry of organolanthanoids. Overnight photolysis of $[(MeC_5H_4)_2YbMe]_2$ in toluene at 5 °C using a Hanovia 450 W mercury vapour lamp formed a green precipitate (25% conversion after 32 h) and methane. As in the other ytterbium reactions, recrystallization of the precipitate from THF–pentane yields crystals of (**1**).

It is also possible to convert $[(MeC_5H_4)_2YbMe]_2$ into (**1′**) thermally as shown in reaction (4). In toluene this reaction is slow, requiring several months even at 80 °C. The presence of diethyl ether facilitates the reaction, however, and conversions of 50% can be achieved in 8 h using a mixed pentane–ether solvent at 80 °C in a pressure vessel.

In contrast with samples of (**1**) obtained in the traditional way[1] by alkali metal reduction of $[(MeC_5H_4)_2YbCl]_2$, samples of (**1**) obtained *via* reactions (1)—(4) formed crystals suitable for *X*-ray diffraction studies.

Crystal data: monoclinic, space group $P2_1$, $a = 9{\cdot}055(1)$, $b = 8{\cdot}834(1)$, $c = 9{\cdot}809(2)$ Å, $\beta = 106{\cdot}79(1)°$, $U = 751{\cdot}21$ Å^3, $D_c = 1{\cdot}78$ g cm^{-3}, $Z = 2$. Intensity data were collected to $2\theta = 55°$ on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo-K_α radiation; 1820 reflections having $F_0 > 3\sigma(F_0)$. The structure was solved by Patterson and difference Fourier methods and refined to $R = 0{\cdot}048$ using rigid body refinement for the cyclopentadienyl groups and anisotropic thermal parameters for ytterbium. In the solid state, (**1**) forms chains oriented along the *b*-axis in which the repeating units, $(\mu\text{-}MeC_5H_4)(MeC_5H_4)Yb\cdot OC_4H_8$, are related by a two-fold screw axis and are connected by one bridging methylcyclopentadienyl group per ytterbium. The Figure shows a segment of one of the extended cyclopentadienyl ytterbium chains. This segment contains complete co-ordination environments for three ytterbium centres which are formally 10-co-ordinate. The three cyclopentadienyl rings surrounding each ytterbium, taken with the THF oxygen atom, comprise a distorted tetrahedron. The angles between the ytterbium ring-centroid vectors are A-ring–Yb–B-ring, 114·6, B–Yb–C, 118·0, and A–Yb–C, 116·8°. The average ytterbium–carbon distances in the terminal cyclopentadienyl A ring and the bridging B and C rings are 2·76, 2·91, and 2·87 Å, respectively. As expected, these distances are longer than those found in the trivalent ytterbium species, $[(MeC_5H_4)_2YbCl]_2$,[9] $[(C_5H_5)_2YbMe]_2$,[10] and $(C_5H_5)_2YbMe_2AlMe_2$,[11] which have ytterbium cyclopentadienyl carbon distances of 2·58, 2·61, and 2·66 Å, respectively.†

In the past, divalent organoytterbium complexes generally have been prepared using rather drastic conditions involving either alkali metal reduction or use of the elemental metal. Once formed, these species are reactive reducing agents owing to the stability of the trivalent state. The fact that (**1**) is generated in the four synthetic reactions described above demonstrates how easily divalent organoytterbium species can be obtained. Clearly, the accessibility of divalent species must be considered whenever organoytterbium syntheses and reactions

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† Further analysis of these distances by the method of Raymond (ref. 2), for example, is not appropriate at this stage owing to the limitations of the crystal. Despite the fact that complete data sets were collected on three separate crystals, we could not avoid some slight decomposition during data collection. When complete anisotropic refinement was attempted, several atoms exhibited non-positive definite values. In addition, there appears to be some disorder in the co-ordinated THF. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

are planned Moreover, these ready conversions of trivalent ytterbium complexes into reactive divalent species suggest considerable catalytic potential for ytterbium

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