Di- and Tri-valent Complexes of Ytterbium *via* Novel Metal Oxidation

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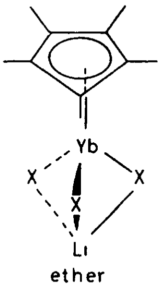
Summary Oxidation of Yb metal by iodopentamethylcyclopentadiene (IC_5Me_5) afforded $Li[Yb(C_5Me_5)I_3]$ and $Li[Yb(C_5Me_5)_2I_2]$ sequentially in the presence of LiI, analogous anionic chloride complexes, the new divalent complex $Yb(C_5Me_5)_2$, and methyl derivatives of both di- and tri-valent systems were obtained *via* metathetical reactions

Resurgence of interest in the organometallic chemistry of the lanthanides[1–4] has led us to synthesise a family of di- and tri-valent pentamethylcyclopentadienyl (η^5-C_5Me_5) derivatives of ytterbium, with a view towards developing reactivity patterns which interrelate these complexes Oxidation, reduction, and ligand substitution reactions are of particular interest, as are the formation and decomposition reactions of alkyl and, potentially, hydride complexes The preparation of organometallic compounds directly from bulk metal has been studied extensively for the main group metals and affords a route to organolanthanides [2,5]

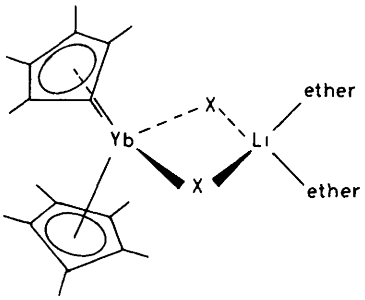
Reaction of Yb metal with pale yellow ether solutions of C_5Me_5I † and LiI for *ca* 15 hr afforded a complex of stoicheiometry $Li[Yb(C_5Me_5)I_3]$ $(ether)_2$ (**1**) in 30% isolated yield If stirred for a further 24 h, (**1**) was converted into $Li[Yb(C_5Me_5)_2I_2]$ $(ether)_2$, (**2**), which was isolated in *ca* 30% yield as purple crystals ‡ The structure of (**2**)§ and proposed structure for (**1**) are shown opposite

At either stage in the above reaction, Yb metal was recovered and the remaining Yb was present as YbI_2 (20—40%)

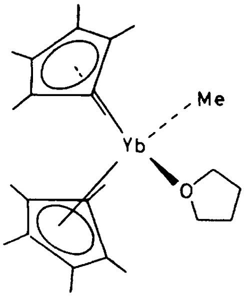
The formation of trivalent organometallic complexes under reducing conditions was initially surprising Presumably the first step in the reaction generated an $Yb^{II}(C_5Me_5)$ species Mechanistic aspects of the secondary



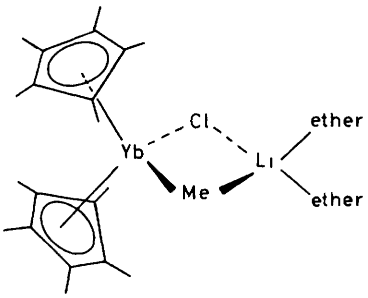
(1), X = I
(5), X = Cl



(2), X = I
(6), X = Cl
(9), X = Me



(7)



(8)

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† Generated *in situ* by slow, careful addition of I_2 to an ether solution of LiC_5Me_5 at −78 °C

‡ Characterizations of these and the following crystalline complexes were based on elemental analysis, estimation of weight % C_5Me_5 ligand, and in a number of cases by *X*-ray crystallography

§ Details of the structures of a related series including these complexes will be presented separately oxidation process, which may involve oxidation by C_5Me_5I, are under investigation since these may delineate the possible pathways using Yb^{II} as the reductant in synthetic organic chemistry.[6] An important point to note is that formation of anions may contribute to the oxidation process. The reaction described by equation (1),[6] *e.g.*, was kinetically

$$YbI_2{\cdot}THF_3 + IC_5Me_5 \rightarrow YbI_3{\cdot}THF_3 + C_5Me_5{\cdot} \tag{1}$$

slow. However, we observed that catalysis by trace amounts of I^- [as Li^+ or $NBu_4{}^+$ salts] led to clean, rapid oxidation presumably by inner sphere electron transfer from $YbI_3{}^-$. Similarly $Yb(C_5Me_5)I_2{}^-$ (*vide infra*) was rapidly oxidised as shown in equation (2).

$$Li[Yb(C_5Me_5)I_2] + IC_5Me_5 \rightarrow \underset{(\mathbf{1})}{Li[Yb(C_5Me_5)I_3]} + C_5Me_5{\cdot} \tag{2}$$

To examine further the reactivity of divalent ytterbium, the halide-free complex $Yb(C_5Me_5)_2$, (**3**), was synthesised. Complex (**3**) was isolated as bis ether adducts from diethyl ether, tetrahydrofuran (THF), or dimethoxyethane (DME) *via* the overall reaction sequence ¶ depicted by equations (3) and (4) and driven by precipitation of KBr. The Lewis

$$YbBr_2 + KC_5Me_5 \rightleftharpoons K[Yb(C_5Me_5)Br_2] \tag{3}$$

$$K[Yb(C_5Me_5)Br_2] + KC_5Me_5 \rightleftharpoons \underset{(\mathbf{3})}{Yb(C_5Me_5)_2} + 2\ KBr \tag{4}$$

acidity of (**3**) was demonstrated by reaction with LiI or MeLi, which produced $Li[Yb(C_5Me_5)I_2]$ and $Li[Yb(C_5Me_5)Me_2]$, respectively [analogous to the back reaction of equation (4)]. Ligands such as carbon monoxide, ethylene, and butadiene did not compete with THF as ligands for $Yb(C_5Me_5)_2$. Stoicheiometric oxidation of $Yb(C_5Me_5)_2(DME)$ with $[Fe(C_5H_5)_2]PF_6$ cleanly gave $[Yb(C_5Me_5)_2(DME)]PF_6$, (**4**) as purple crystals; oxidation with CH_2Cl_2 gave $Yb(C_5Me_5)_2Cl$.

Conventional substitution reactions of $YbCl_3$ with LiC_5Me_5 (one or two equiv., respectively) gave chloro anions (**5**) and (**6**)§ as the major products. Formation of anionic complexes such as (**2**) and (**6**) may be favoured as a result of the steric inability of the neutral $Yb(C_5Me_5)_2X$ ($X = I$, Cl) fragment to dimerise. Three methyl complexes were obtained upon reaction of (**6**) with MeLi. The neutral orange complex (**7**) was formed in THF below −20 °C, with one equiv. of MeLi. However the brown anion (**8**) was formed exclusively with the same reagents in ether. Two equivalents of MeLi with (**6**) gave the yellow dimethyl anion (**9**). Transformation of (**9**) to (**7**) occurred with one equiv. of $AlMe_3$ {which was thereby converted into $[AlMe_4]^-$}. Even with excess $AlMe_3$ (**9**) did not form alkyl-bridged complexes such as $Yb(C_5Me_5)_2Me_2AlMe_2$, unlike the less hindered cyclopentadienyl systems reported by Holton, *et al.*[7] Complex (**8**) was readily produced by ligand metathesis of (**6**) and (**9**) in diethyl ether or THF at 20 °C; differentiation of (**8**) from an equimolar mixture of (**6**) and (**9**) was established on the basis of the far i.r. spectra and the visible spectra in THF. The versatile halide-free reagent, (**4**), also afforded (**7**) or (**9**) with MeLi.

Preliminary attempts to isolate hydride complexes analogous to (**7**) and (**9**) by reaction of (**4**) with KH at 20 °C in DME led to formation of $Yb(C_5Me_5)_2DME$ with rapid hydrogen evolution. The reduced system was also cleanly obtained from reaction of (**4**) with neopentyl lithium at 20 °C.

These results demonstrate the substitution lability and Lewis-acid character of both Yb^{III} and Yb^{II} complexes. Chemical couples which effect Yb^{III}/Yb^{II} interchange of several organometallic complexes have also been demonstrated, as have the types of equilibria which could complicate reduction products from Yb^{III} complexes (particularly those containing halogen).

Added in proof: The red complex $Yb(C_5Me_5)_2THF_2$ was observed to lose one THF molecule when heated at 90 °C *in vacuo* to form the orange mono-THF complex $Yb(C_5Me_5)_2THF$. We have been informed recently by R. Andersen and D. Tilley (University of California, Berkeley) that they have also synthesized and obtained the molecular structure of the latter complex.

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¶ Although the reaction of 1,2-dibromoethane with Yb metal was reported (ref. 6) not to occur, we have observed rapid reaction in THF. $YbBr_2(THF)_2$ was isolated in 60—80% yield. $YbI_2(THF)_{3-4}$ and $YbI_2(CH_3CN)_5$ were also isolated as crystalline salts *via* the reported oxidation of Yb metal with 1,2-di-iodoethane.

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