Synthesis, Structures and Reactions of Ytterbium(II) Alkyls†

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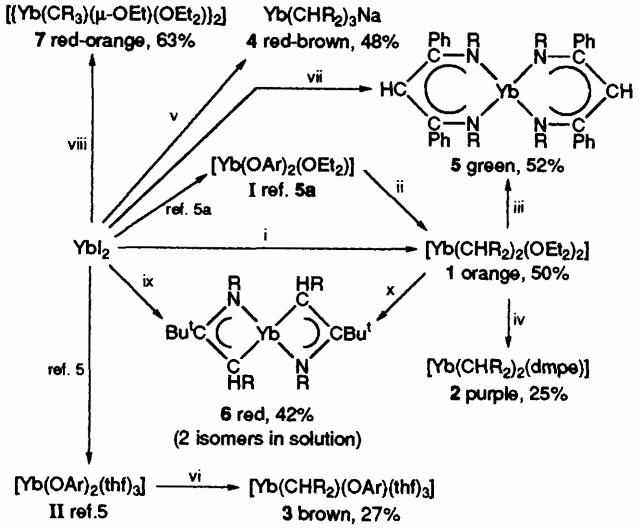
Treatment of $\mathrm{YbI_2}$ with 2 $\mathrm{NaCHR_2}$ gave $[\mathrm{Yb(CHR_2)_2(OEt_2)_2}]$ **1** in $\mathrm{Et_2O}$, but $\mathrm{Yb(CHR_2)_3Na}$ in n-$\mathrm{C_6H_{14}}$ {**1** was also obtained from 2 $\mathrm{KCHR_2}$ and $[\mathrm{Yb(OAr)_2(OEt_2)_2}]$}, while $\mathrm{YbI_2}$ and 2 $\mathrm{KCR_3}$ in $\mathrm{Et_2O}$ gave $[\{\mathrm{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)}\}_2]$ **7**; $[\mathrm{Yb(CHR_2)(OAr)(thf)_3}]$ was prepared from $[\mathrm{Yb(OAr)_2(thf)_3}]$ and $\mathrm{KCHR_2}$, and $[\mathrm{Yb\{N(R)C(Ph)C(H)C(Ph)NR\}_2}]$ or $[\mathrm{Yb\{N(R)C(Bu^t)CHR\}_2}]$ **6** from **1** + 4 PhCN or **1** + 2 $\mathrm{Bu^tCN}$ in $\mathrm{Et_2O}$, respectively; ^{171}Yb NMR spectral data confirmed the identity of each of the ytterbium(II) compounds, and single crystal X-ray results are presented for **6** and **7** (R = $\mathrm{SiMe_3}$, Ar = 2,6-$\mathrm{Bu^t_2}$-4-Me-$\mathrm{C_6H_2}$).

There has been much recent interest in the chemistry of lipophilic organic complexes of ytterbium(II), because of their high reactivity, potential as 1-electron reducing agents,[1] diamagnetism (being $\mathrm{f^{14}}$ complexes) and the use of ^{171}Yb (I = 1/2, 14.27% natural abundance) NMR spectroscopy[2] as a probe for their structures and reactivity. Mononuclear lanthanide(II) complexes bearing only monohapto ligands are currently restricted to those having $\mathrm{\bar{N}R_2}$, $\mathrm{\bar{O}Ar'}$, $\mathrm{\bar{O}CBu^t_3}$, $\mathrm{\bar{S}Ar''}$, $\mathrm{\bar{S}eSiR_3}$, $\mathrm{\bar{T}eSiR_3}$ or $\mathrm{\bar{S}n(CH_2Bu^t)_3}$ ligands [R = $\mathrm{SiMe_3}$, Ar′ = 2,6-$\mathrm{Bu^t}$-4-R′-$\mathrm{C_6H_2}$ (R′ = H, Me or $\mathrm{Bu^t}$), Ar″ = 2,4,6-$\mathrm{Bu^t_3}$-$\mathrm{C_6H_2}$.[3]

We report (Scheme 1) on (*a*) the synthesis of the ytterbium(II) bis(trimethylsilyl)methyl $[\mathrm{Yb(CHR_2)_2(OEt_2)_2}]$ **1**, $[\mathrm{Yb(CHR_2)_2(dmpe)_2}]$ **2** and $[\mathrm{Yb(CHR_2)(OAr)(thf)_3}]$ **3** and the binuclear mixed metal alkyl $\mathrm{Yb(CHR_2)_3Na}$ **4**; (*b*) the conversion of **1** into the β-diketinimate $[\mathrm{Yb\{N(R)C(Ph)C(H)C(Ph)NR\}_2}]$ **5** or the 1-aza-allyl $[\mathrm{Yb\{N(R)C(Bu^t)CHR\}_2}]$ **6**; and (*c*) the alkylytterbium(II) ethoxide $[\{\mathrm{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)}\}_2]$ **7** (dmpe = $\mathrm{Me_2PCH_2CH_2PMe_2}$). Compounds **5** and **6** were also obtained from 2$\mathrm{K\{N(R)C(Ph)C(H)C(Ph)NR\}}$[4a] or 2 $\mathrm{K\{N(R)C(H)CHR\}}$[4b] and $\mathrm{YbI_2}$, respectively. Compounds **1**–**7** have been characterised by microanalysis, NMR spectroscopy,‡ and for **6** (Fig. 1) and **7** (Fig. 2) single crystal X-ray diffraction.¶

Although X-ray quality crystals of the $\mathrm{Yb^{II}}$ bis(trimethylsilyl)methyls **1**, **2** and **3** were not obtained, their formulations are consistent with (i) analytical data, (ii) NMR spectra, especially the ^{171}Yb signal being a triplet for **1** and a doublet for **3**, due to $^2J_{^{171}\mathrm{Yb}-^1\mathrm{H}}$,‡ and (iii) the derivatisation of **1**. As for (ii) (^{171}Yb–^{1}H coupling had not previously been reported), the $^2J_{^{171}\mathrm{Yb}-^1\mathrm{H}}$ and reduced (^2k) spin–spin coupling constant may be compared with such data for other $^2J_{^x\mathrm{M}-^1\mathrm{H}}$ couples (obtained for $\mathrm{MPr^n}_n$):[7] $^2J_{^x\mathrm{M}-^1\mathrm{H}}$ [^2k (^{x}M–^{1}H)(x10^{19}



Scheme 1 *Reagents and conditions* (*ca*. 25 °C, unless otherwise stated; yields refer to crystalline products): i, 2 $\mathrm{NaCHR_2}$, $\mathrm{Et_2O}$, 24 h; ii, 2 $\mathrm{KCHR_2}$, $\mathrm{Et_2O}$, −30 °C, 1/2 h (with **3** as coproduct); iii, 4 PhCN, $\mathrm{Et_2O}$, 16 h; iv, dmpe, PhMe, −30 °C, 10 min; v, 3 $\mathrm{NaCHR_2}$, n-$\mathrm{C_6H_{14}}$, 48 h; vi, $\mathrm{KCHR_2}$, THF, −30 °C, 30 min; vii, 2 $\mathrm{K\{N(R)C(Ph)C(H)C(Ph)NR\}}$,[4a] $\mathrm{Et_2O}$, 48 h; viii, 2 $\mathrm{KCR_3}$, $\mathrm{Et_2O}$, 2 h; ix, 2 $\mathrm{K\{N(R)C(H)CHR\}}$,[4b] $\mathrm{Et_2O}$, 24 h; x, 2 $\mathrm{Bu^tCN}$, $\mathrm{Et_2O}$, 48 h

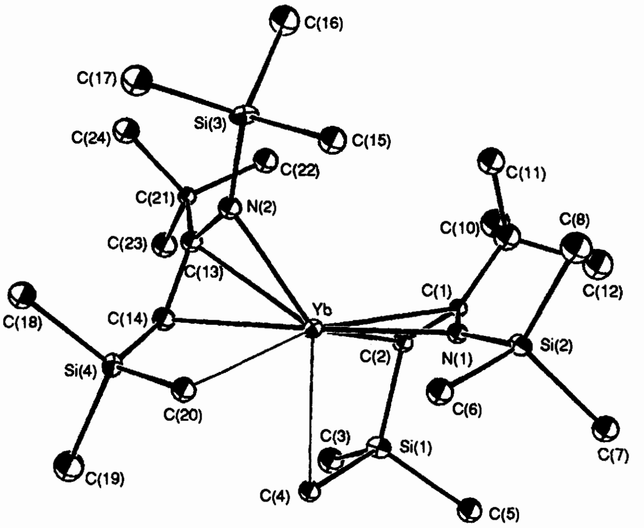


Fig. 1 The X-ray structure and atom labelling scheme for $[\mathrm{Yb\{N(R)C(Bu^t)CHR\}_2}]$ **6**. Selected bond lengths (Å) (data for molecule 'B' in parentheses): Yb–N(1) 2.326(14) [2.35(2)], Yb–C(1) 2.78(2) [2.73(2)], Yb–C(2) 2.68(2) [2.70(2)], C(1)–C(9) 1.53(3) [1.50(3)], C(2)–Si(1) 1.86(2) [1.87(2)], N(1)–Si(2) 1.69(2) [1.68(2)]; Yb–N(2) 2.344(12) [2.350(13)], Yb–C(13) 2.66(2) [2.68(2)], Yb–C(14) 2.63(2) [2.67(2)], Yb···C(4) 2.84(2) [2.81(2)], Yb···C(20) 2.90(2) [2.92(2)].

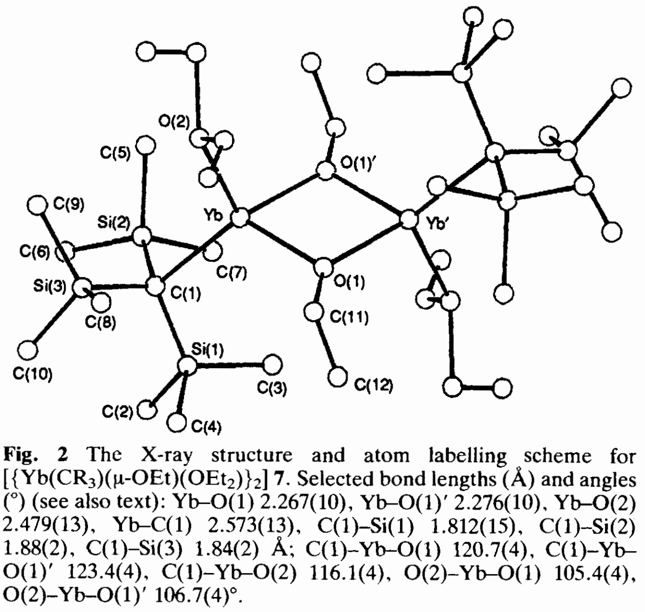


Fig. 2 The X-ray structure and atom labelling scheme for $[\{\mathrm{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)}\}_2]$ **7**. Selected bond lengths (Å) and angles (°) (see also text): Yb–O(1) 2.267(10), Yb–O(1)′ 2.276(10), Yb–O(2) 2.479(13), Yb–C(1) 2.573(13), C(1)–Si(1) 1.812(15), C(1)–Si(2) 1.88(2), C(1)–Si(3) 1.84(2) Å; C(1)–Yb–O(1) 120.7(4), C(1)–Yb–O(1)′ 123.4(4), C(1)–Yb–O(2) 116.1(4), O(2)–Yb–O(1) 105.4(4), O(2)–Yb–O(1)′ 106.7(4)°.

$NA^{-2}m^3$): ^xM = ^{171}Yb 30 [14.1], ^{113}Cd 52 [20.7], ^{119}Sn 49 [10.9], ^{199}Hg 95 [44.2] and ^{207}Pb 40 [15.8]. Regarding (iii), the conversion of the dialkyl **1** into the β-diketinimate **5** or 1-aza-allyl **6** parallels the reactions of $LiCHR_2$ with 2 PhCN or Bu^tCN to give $[Li\{N(R)C(Ph)C(H)C(Ph)NR\}]_2$[4a] or $[Li\{N(R)C(H)CHR\}]_2$,[4b] respectively.

Crystalline **6** is a monomer, the *rac*- rather than the *meso*-diastereoisomer, Fig. 1; there are two independent molecules (A and B) in the unit cell, of essentially the same geometry. The ytterbium atom is bound in an η^3-fashion to the two 1-aza-allyl ligands with average bond distances: Yb–N 2.34, Yb–C (2-position) 2.68 and Yb–C (3-position) 2.70 Å. Additionally, there is a close agostic intramolecular contact between Yb and one of the methyls of the $SiMe_3$ group attached to C-3 at an average distance of 2.86 Å. In benzene solution, NMR spectra show the presence of two isomers, possibly the *rac*- and *meso*-diastereoisomers (C-3 of the 1-aza-allyl ligand is a chiral centre).

Complex **4**, $Yb(CHR_2)_3Na$, was obtained from YbI_2 and either 2 or 3 equiv. of $NaCHR_2$ in hexane; in the former case, the YbI_2 was not completely consumed. The formulation of **4** is consistent with analytical data; it may be structurally similar to that of its isoelectronic X-ray-characterised amide $[Yb(NR_2)(\mu\text{-}NR_2)_2Na]$.[8]

A further unexpected reaction was that between YbI_2 and 2 equiv. of KCR_3 in Et_2O at ambient temperature, which yielded $[\{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)\}_2]$ **7**; using 1 equiv. of KCR_3 under the same conditions also gave **7** rather than the expected Grignard-like product. The ethoxo ligand in **7** must have arisen from ether cleavage by KCR_3, $Yb(CR_3)_2$, YbI_2 or $Yb(CR_3)I$. It is well known that dialkyl ethers are cleaved by strong Lewis acids, such as BCl_3;[9] the isolation of the coproduct(s) in the $YbI_2/KCHR_2/Et_2O$ reaction should prove informative. Subsequently, our colleagues (who are experts in CR_3 chemistry) have prepared and X-ray-characterised $[Yb(CR_3)_2]$ (from YbI_2 + 2 KCR_3 in C_6H_6) and $[\{Yb(CR_3)(\mu\text{-}I)(OEt_2)\}_2]$ {from $[Yb(CR_3)_2]$ and an excess of MeI or ICH_2CH_2I in Et_2O}, and shown that $[Yb(CR_3)_2]$ reacts with Et_2O to yield **7**.[10]

Crystalline **7** is a centrosymmetric dimer, Fig. 2, with each Yb atom in a distorted tetrahedral environment. The central YbOYbO ring is planar, as in $[\{Yb(OAr)(\mu\text{-}OAr)\}_2]$ **I**, but unlike that in $[\{Yb(NR_2)(\mu\text{-}OCBu^t_3)\}_2]$ **III**;[3c] the Yb-OEt bond lengths in **7** [*av.* 2.27(1) Å] are comparable to those for Yb–OAr_{br} in **I** [*av.* 2.28(2) Å] and Yb–O in **III** [*av.* 2.31(1) Å]; the endocyclic angles are: O–Yb–O 78.0(4) in **7**, $79.6(6)_{av.}$ in **I**, and 84.1(7)° in **III**, and Yb–O–Yb 102.0(4) in **7**, $100.4(7)_{av.}$ in **I** and 93.3(2)° in **III**.

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Footnotes

† No reprints available.

‡ *Selected spectroscopic data* [^1H NMR at 360.1 MHz, $^{13}C\{^1H\}$ NMR at 62.9 MHz, $^{29}Si\{^1H\}$ NMR at 49.7 MHz, ^{31}P NMR at 101.2 MHz and $^{171}Yb\{^1H\}$ NMR at 87.5 MHz]. **1** (293 K, $[^2H_6]$benzene): ^1H δ 0.34 ($SiMe_3$, s), −1.55 (CH, s), 0.95 and 3.36 (Et_2O, br); $^{13}C\{^1H\}$ 6.15 ($SiMe_3$), 27.34 (*C*H), 14.11 and 64.64 (Et_2O); $^{29}Si\{^1H\}$ −7.80; $^{171}Yb\{^1H\}$ 1035 (triplet), $^2J_{^{171}Yb-^1H}$ 30 Hz (at 295 K). **2** (293 K, $[^2H_8]$toluene): $^{13}C\{^1H\}$ 5.6 ($SiMe_3$), 13.3 [$(Me_2PCH_2)_2$], 27.6 [$(Me_2PCH_2)_2$]; $^{171}Yb\{^1H\}$ δ 1231 ($W_{1/2}$ = 260 Hz); ^{31}P δ −42.6. **3** (293 K, $[^2H_8]$toluene): $^{171}Yb\{^1H\}$ δ 725 (doublet), $^2J_{^{171}Yb-^1H}$ = 30 Hz. **4** (at 293 K, in $[^2H_6]$benzene): ^1H δ 0.29 ($SiMe_3$, s), −1.78 (CH, s); $^{29}Si\{^1H\}$ δ 0.08. **5** (at 293 K, in $[^2H_8]$toluene): ^1H δ 0.13 ($SiMe_3$, s), 5.46 (C*H*, s), 7.00, 7.45 and 7.02 (Phenyl, m); $^{13}C\{^1H\}$ 2.71 ($SiMe_3$), 104.84 (*C*H), 172.74 (Ph*C*N), 148.10, 128.05, 127.60 and 127.14 (Phenyl); $^{29}Si\{^1H\}$ −4.81; $^{171}Yb\{^1H\}$ 870.37. **6** (at 298 K, in $[^2H_6]$benzene): ^1H δ 0.26 and 0.33 ($SiMe_3$, d), 1.21 (CMe_3, d), 3.84 (C*H*, d); $^{13}C\{^1H\}$ 1.09 and 4.60 ($SiMe_3$, d), 30.49 (C*Me*$_3$, d), 41.22 (*C*Me_3, d), 80.0 (*C*H, d, $^1J_{C-Yb}$ 0.32 Hz), 192.5 (Bu^t*C*N, d); $^{171}Yb\{^1H\}$ 829.57 and 820.04. **7**: ^1H (at 298 K, in $[^2H_5]$pyridine) δ 0.11 ($SiMe_3$, s), 1.10 and 3.33 (Et_2O), 1.58 and 3.36 (μ-Et); $^{29}Si\{^1H\}$ (in $[^2H_6]$benzene + Et_2O) −11.22; $^{171}Yb\{^1H\}$ (in $[^2H_6]$benzene + Et_2O) 763.6.

¶ *Cystal data* for **6**, $C_{24}H_{56}N_2Si_4Yb$. M = 658.1, monoclinic, space group $P2_1/c$ (No. 14), a = 19.890(6), b = 16.259(4), c = 23.095(5) Å, β = 114.90(2)°, U = 6774 Å^3, $F(000)$ = 2720; Z = 8, D_c = 1.29 g cm^{-3}, μ(Mo-Kα) = 29.0 cm^{-1}, T = 173 K, specimen 0.3 × 0.3 × 0.3 mm^3, 8629 unique reflections for $2 < \theta < 22°$, 4612 reflections with $[|F^2| > 2\sigma(F^2)]$ used in the refinement; R = 0.066, R_w = 0.067, S = 1.3. H atoms fixed. For **7**, $C_{32}H_{84}O_4Si_6Yb_2$, M = 1047.6, monoclinic, space group $P2_1/n$ (non-standard No. 14), a = 9.358(8), b = 16.069(11), c = 16.547(12) Å, β = 91.12(6)°, U = 2487.6 Å^3, $F(000)$ = 1064; Z = 2, D_c = 1.40 g cm^{-3}, μ(Mo-Kα) = 38.9 cm^{-1}, T = 293 K, specimen 0.3 × 0.3 × 0.2 mm^3, 4551 unique reflections for $2 < \theta < 25°$, 2655 reflections with $[|F^2| > 2\,\sigma(F^2)]$ used in the refinement; R = 0.072, R_w = 0.080, S = 2.1. H atoms fixed.

Enraf-Nonius CAD-4 diffractometer, λ (Mo-Kα) 0.71069 Å, empirical absorption corrections, full-matrix least-squares, refinement with non-hydrogen atoms anisotropic, $w = 1/\sigma^2(F)$, heavy atom methods.

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