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Yttrium iodide and bis(trimethylsilyl)methyl complexes of the chelating diamide $[ArN(CH_2)_3NAr]^{2-}$ (Ar = 2,6-$^iPr_2C_6H_3$)†

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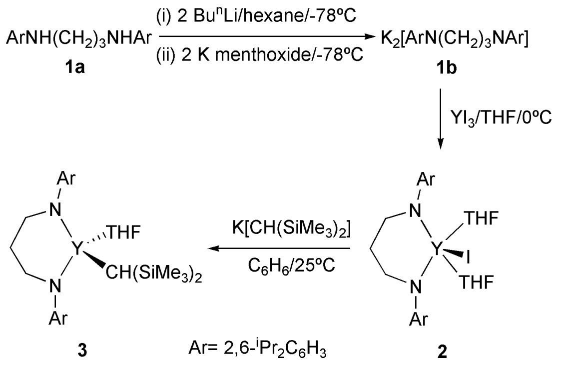
Yttrium triiodide reacts with the potassium salt $K_2[ArN(CH_2)_3NAr]$ (Ar = 2,6-$^iPr_2C_6H_3$) to yield a mono-iodide complex and, by further reaction with $K[CH(SiMe_3)_2]$, the corresponding alkyl complex, which have both been characterised by NMR spectroscopy and X-ray crystallography.

In recent years there has been increasing interest in the area of Group III and lanthanide complexes,[1] and in particular their application as neutral, single component alternatives to the ubiquitous Kaminsky metallocenes that catalyse the polymerisation of olefins.[2] There has also been a concerted effort towards the design and deployment of novel, cyclopentadienyl-free ligands.[3] Much of this work has focussed on nitrogen-based ligands,[4] including benzamidinate[5] and alkoxysilylamido[6] systems. McConville and co-workers have reported that Group IV complexes of the aryl diamine $ArNH(CH_2)_3NHAr$ (**1a**)[7] facilitate the polymerisation of α-olefins under 'living' conditions, *e.g.* when the dimethyl-titanium derivative $[Ti\{ArN(CH_2)_3NAr\}Me_2]$ is activated with $B(C_6F_5)_3$ at room temperature.[8] Herein we report the synthesis and characterisation of the complexes $[Y\{ArN(CH_2)_3NAr\}I(THF)_2]$ (**2**) and $[Y\{ArN(CH_2)_3NAr\}R(THF)]$ (**3**; R = $CH(SiMe_3)_2$) resulting from the reaction of YI_3 with the previously unreported potassium salt $K_2[ArN(CH_2)_3NAr]$ (**1b**) in THF, and of the resultant complex **2** with KR in benzene, respectively.

Exclusion of lithium salts is a key factor in lanthanide chemistry, preventing the formation of ate-complexes and the incorporation of lithium iodide; lithium reagents are also often not reactive enough to effect metathesis on hard, Lewis-acidic species such as the lanthanides.[9] Thus the reaction of $Li_2[ArN(CH_2)_3NAr]$ (generated *in situ* from the reaction of **1a** with two equivalents of Bu^{n}Li in hexanes at −78 °C) with two equivalents of potassium menthoxide[10] afforded **1b** as a bright yellow, insoluble solid (see Scheme 1). This solid was isolated in 88% yield from the lithium menthoxide solution by successive washings with hexanes in the glove box. No $Li_2[ArN(CH_2)_3NAr]$ or lithium menthoxide are retained in the product, elucidated by the absence of any signal in the ^7Li NMR spectrum when examined in d$_6$-benzene.



Scheme 1

Reaction of **1b** with a stoichiometric amount of yttrium triiodide in THF overnight at room temperature resulted in a precipitate of insoluble potassium iodide; work-up yielded **2** as a white, crystalline material in 20% yield after slow cooling of a toluene solution to −45 °C (see Scheme 1). X-Ray structure determination of **2**‡ confirmed the inclusion of two THF units in the complex, which adopts an axially-elongated square-based pyramidal geometry (Fig. 1). The angles between the apical iodine and the four basal oxygen and nitrogen atoms vary from 96.69(12)° (O(1)–Y–I) and 99.35(12)° (O(2)–Y–I) to 106.74(13)° (N(2)–Y–I) and 113.12(13)° (N(1)–Y–I). There is a corresponding variation in the N–Y–O angles, at 87.98(16)° (N(1)–Y–O(1)) and 89.59(17)° (N(2)–Y–O(2)). The Y–N bond lengths of 2.170(5) Å (Y–N(1)) and 2.175(5) Å (Y–N(2)) respectively are amongst the shortest known; the majority of the published distances for yttrium-amides lie between 2.20 and 2.30 Å.[11] Most of these reported distances are found within complexes incorporating the more weakly basic silyl-amide functionality $N(SiMe_3)_2$ and its variants, and accord with a higher electron density at the metal centre. The Y–O bond distances of 2.420(4) Å (Y–O(1)) and 2.368(4) Å (Y–O(2)) are within the published range of 2.35–2.45 Å for yttrium complexes containing THF.[11]

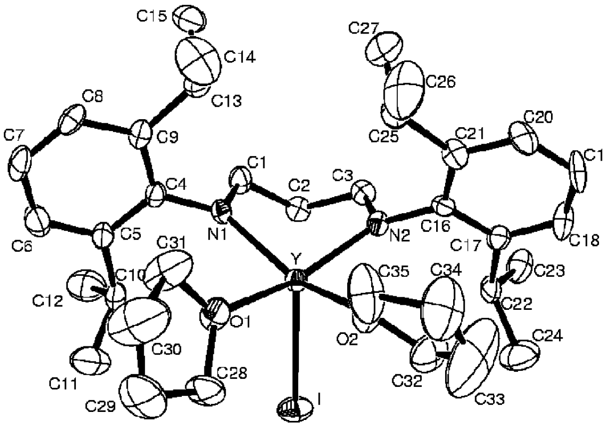


Fig. 1 Structure of $[Y\{ArN(CH_2)_3NAr\}I(THF)_2]$ (**2**).

The minor asymmetry within the crystal structure is lost in solution as all ligand and THF peaks are resolved singly and sharply with their expected coupling patterns in the ^1H NMR spectrum in d$_6$-benzene. Those corresponding to the bound THF were found at δ 0.98 and δ 3.25 ppm, shifted upfield from free THF; however, when the spectrum was recorded in d$_8$-THF these upfield peaks were lost and only those attributable to free protonated and partially-deuterated THF were observed.

No reaction occurs when **2** is mixed with an equimolar amount of KR (R = $CH(SiMe_3)_2$) in THF. However, the desired salt metathesis reaction proceeds in benzene at room temperature with overnight stirring and extraction into pentane to

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† Electronic supplementary information (ESI) available: synthesis and characterisation details. See http://www.rsc.org/suppdata/dt/b2/b203757b/

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yield **3** as a colourless, crystalline material after slow cooling to −45 °C (see Scheme 1). The X-ray crystal structure of **3** shows the expected loss of one THF unit concomitant with the exchange of iodine for the much bulkier bis(trimethylsilyl)-methyl ligand (Fig. 2). The coordinated atoms are distributed in an approximately tetrahedral fashion about the yttrium centre, with the steric bulk of the alkyl and amide substituents forcing an increase in the C(1)–Y–N(1) and C(1)–Y–N(2) bond angles from an ideal 109° to 121.90(10)° and 118.61(10)° respectively. The Y–N bond lengths are essentially identical to those in **2**, being 2.178(2) Å (Y–N(1)) and 2.168(3) Å (Y–N(2)). The bite angle of the diamide is considerably larger in **3** than in **2**, being 97.79(9)° as opposed to 94.39(18)°, due to the exchange of the iodide for the bulky alkyl group. The Y–C bond length of 2.432(3) Å is longer than that seen in the tris-alkyl [$Y\{CH(SiMe_3)_2\}_3$] (2.357(7) Å)[12] and is comparable to the distance of 2.468(7) Å observed in [$YCp^*_2\{CH(SiMe_3)_2\}$].[13]

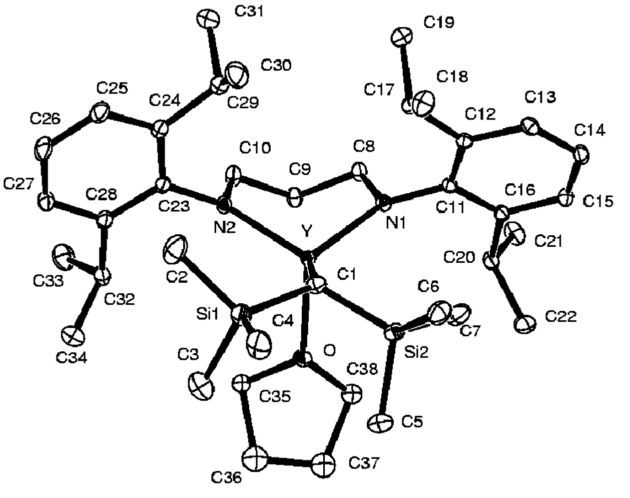

Fig. 2 Structure of [$Y\{ArN(CH_2)_3NAr\}R(THF)$] (**3**; $R = CH(SiMe_3)_2$).

The methine carbon of **3** displays a doublet at δ 36.5 ppm ($^1J_{YC}$ = 35 Hz) in the $^{13}C\{^1H\}$ NMR spectrum (d_6-benzene), whilst the attached protons display a corresponding doublet at δ −1.09 ppm in the ^1H NMR spectrum; the small value of $^2J_{YH}$ (2.2 Hz) in the latter mitigates against any agostic interaction, presumably due to the presence of coordinated THF (*vide infra*). The amide ligand region of the ^1H NMR spectrum in both d_8-toluene and d_6-benzene is broad and poorly resolved at room temperature. The broad signal at δ 1.4 ppm, assigned to both the THF *meta*-methylene and ^iPr-methyl resonances, resolves to four distinct doublets and a triplet at −30 °C in d_8-toluene, consistent with the solid state structure in which there are two equivalent sets of four diastereotopic methyl groups. Elevation of the temperature to 50 °C did not significantly change the appearance of the room temperature spectrum.

Addition of two equivalents of 1-hexene to a solution of **3** in d_6-benzene at room temperature failed to afford the insertion product [$Y\{ArN(CH_2)_3NAr\}\{(CH_2)_6CH(SiMe_3)_2\}(THF)$], or any other complex after 72 hours at room temperature, as elucidated by ^1H NMR.[11] Addition of a further six equivalents of 1-hexene failed to induce any reaction. Elevation of the temperature of this mixture by ten-degree increments to 70 °C over a period of several days did not result in any reaction between **3** and 1-hexene, and proceeded with only slight thermal decomposition of **3**; **3** finally underwent 50% thermal decomposition after 72 h at 80 °C. Such inactivity towards the polymerisation of 1-hexene suggests that, despite its tendency to exchange when a large excess of d_8-THF is present (as shown by the addition of three drops of d_8-THF to a solution of **3** in d_6-benzene), the THF unit remains within the coordination sphere of the complex under normal conditions and blocks the 'active site'. Further work is currently underway to synthesise base-free analogues of these compounds.

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Notes and references

‡ Crystal data for **2**. $M = 752.6$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.031(5)$, $b = 21.883(7)$, $c = 18.653(7)$ Å, $\beta = 98.93(4)°$, $V = 3642(3)$ Å^3, $Z = 4$, $\mu = 2.48$ mm^{-1}, $R_1 = 0.0358$. Data were collected on an Enraf-Nonius CAD4 instrument at 173 K for $2 < \theta > 23°$ with $\lambda = 0.71073$ Å. The structure was solved by direct methods and refined against all F^2 values using SHELXL-97.[14]

For **3**. $M = 713.03$, monoclinic, space group $P2_1/c$ (no. 14), $a = 19.2377(4)$, $b = 11.8507(2)$, $c = 17.8432(3)$ Å, $\beta = 90.028(1)°$, $V = 4067.9(1)$ Å^3, $Z = 4$, $\mu = 1.52$ mm^{-1}, $R_1 = 0.065$. Data were collected on a KappaCCD instrument at 173 K for $4.13 < \theta > 25.06°$ with $\lambda = 0.71073$ Å. The structure was solved by direct methods and refined against all F^2 values using SHELXL-97.[14] CCDC reference numbers 184124 and 184125. See http://www.rsc.org/suppdata/dt/b2/b203757b/ for crystallographic data in CIF or other electronic format.

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