FULL PAPER

Yttrium complexes incorporating the chelating diamides ${ArN(CH_2)_xNAr}^{2-}$ (Ar = C₆H₃-2,6-ⁱPr₂, x = 2, 3) and their unusual reaction with phenylsilane[†]

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Novel yttrium chelating diamide complexes [(Y{ArN(CH₂)_xNAr}(Z)(THF)_n)_y] (Z = I, CH(SiMe₃)₂, CH₂Ph, H, N(SiMe₃)₂, OC₆H₃-2,6-^tBu₂-4-Me; x = 2, 3; n = 1 or 2; y = 1 or 2) were made *via* salt metathesis of the potassium diamides (x = 3 (3), x = 2 (4)) and yttrium triiodide in THF (5, 10), followed by salt metathesis with the appropriate potassium salt (6–9, 11–13, 15) and further reaction with molecular hydrogen (14). 6 and 11 (Z = CH(SiMe₃)₂, x = 2, 3) underwent unprecedented exchange of yttrium for silicon on reaction with phenylsilane to yield (Si{ArN(CH₂)_xNAr}PhH) (x = 2 (16), 3) and (Si{CH(SiMe₃)₂}PhH₂).

Introduction

Since the pioneering work of Watson and Marks, considerable research activity has been directed towards the synthesis and characterisation of lanthanide and group 3 complexes that might offer *neutral*, isolable, co-catalyst free alternatives to the group 4 metallocene systems, which require activation by a highly Lewis acidic species, often methylaluminoxane (MAO), in order to polymerise olefins.¹

Most of the seminal work on lanthanide and group 3 complexes has relied on systems supported by permethylcyclopentadienyl ligands.² Lately, many research groups have studied complexes incorporating ligand systems free of this ubiquitous group, in an attempt to provide an alternative coordination environment for the metal centre that might affect the structure and reactivity of the complexes so-produced.³ Ligands incorporating nitrogen donor atoms are especially versatile, offering two valencies to the ligand framework that can be tailored to kinetically stabilise the metal centre. In addition the hard, anionic nitrogen atom is especially suited to the very hard, cationic lanthanide centre.⁴

We recently reported the synthesis and characterisation of yttrium iodide and bis(trimethylsilyl)methyl complexes supported by the chelating diamide $\{ArN(CH_2)_3NAr\}^{2-}$ (Ar = C_6H_3 -2,6-ⁱPr₂),⁵ previously reported by McConville and co-workers to effect 'living' polymerisation of α -olefins when the dimethyl titanium derivative is activated by B(C_6F_5)₃.⁶ A number of structurally similar lanthanide and group 3 chelating diamide complexes have been communicated by other groups, a representative sample of which includes [Y(NON){CH-(SiMe_3)_2}(THF)] (i),⁷ [Y(DADMB){CH(SiMe_3)_2}(THF)] (ii),⁸ [Y(P_2N_2)(CH_2SiMe_3)] (iii),⁹ [Y(NPN)(CH_2SiMe_3)(THF)] (iv),¹⁰ [Sc(BDPPyr)(CH_2SiMe_3)(THF)] (v)¹¹ and [Sc(N_2^{Mes}N_p)-(CH_2SiMe_3)(THF)] (vi)¹² (Fig. 1). Many other lanthanide and group 3 complexes supported by bi-, tri-, tetra- and polydentate amide ligands have been reported and are detailed in a series of excellent review articles.³

We report here the synthesis and characterisation of a number of yttrium complexes incorporating the chelating diamide $\{ArN(CH_2)_3NAr\}^{2-}$ (Ar = C₆H₃-2,6-ⁱPr₂), further to



Fig. 1 Selected group 3 complexes supported by chelating diamide ligands.

the work already communicated, as well as similar studies on the less sterically encompassing congener $\{ArN(CH_2)_2NAr\}^{2-}$ $(Ar = C_6H_3-2,6-iPr_2)$ that was anticipated to offer a somewhat different coordination environment at the metal centre, especially with respect to donor solvent coordination and reactivity towards olefinic monomers.

Results and discussion

Synthesis of potassium salts

We adopted a salt metathesis strategy in order to introduce the organic frameworks to the yttrium centre, in contrast to the σ -bond metathesis approach, using the tris-hydrocarbyl $[Y(CH_2SiMe_3)_3(THF)_2]^{13}$ or tris-amide $[Y\{N(SiMe_3)_2\}_3],^{14}$ preferred by a number of groups. It is now widely accepted that potassium reagents are more effective at introducing organic fragments to lanthanide centres than their lithium analogues. Potassium salts are much more reactive and the co-product in metathesis with lanthanide triiodides,¹⁵ potassium iodide, is insoluble in all common organic solvents and is usually too large to form an ate-complex with the lanthanide ion. Lithium reagents by comparison often require forcing conditions to react with the hard, Lewis-acidic lanthanides and give the metathesis products LiX (X = Cl, Br, I), which are extremely persistent as they have some solubility in organic solvents.¹⁶

The potassium reagents were prepared via transmetallation of the *in situ*-generated lithium complex with a stoichio-

[†] Electronic supplementary information (ESI) available: Molecular structure of [Y{ArN(CH₂)₃NAr}(OC₆H₃-2,6-Bu₂-4-Me)(THF)], selected region of the variable-temperature ¹H NMR spectrum of **6** in d_8 -toluene, tables of selected bond lengths (Å), angles (°), selected crystallographic data, full crystal data and structure refinements for 7–11 and 14–16, syntheses of YI₃, potassium menthoxide, 4 and 10–13. See http://www.rsc.org/suppdata/dt/b4/b400149d/

metric amount of potassium menthoxide¹⁷ rather than direct deprotonation of the parent diamine with potassium amide or hydride.¹⁸ The reaction solvent was chosen such that the potassium salt is insoluble, but the reagents and co-products all soluble, allowing purification by filtration and repeated washings with the reaction solvent. Reaction of $ArNH(CH_2)_{y}$ -NHAr (x = 3 (1), x = 2 (2)) with two equivalents of "BuLi in hexanes generated the lithium complex Li₂{ArN(CH₂),NAr}, which was used in situ to yield K_2 {ArN(CH₂)_xNAr} (x = 3 (3), x = 2 (4)) as a bright yellow, insoluble solid following addition of a slight excess of potassium menthoxide. The product was isolated in high yield from the lithium menthoxide solution by successive washings with hexanes in the glove box. Both 3 and 4 are moderately soluble in aromatic solvents and highly soluble in coordinating solvents such as diethyl ether or THF. ⁷Li NMR studies (d_6 -benzene– d_8 -THF) indicated only trace residual lithium-containing species.

Synthesis of yttrium complexes supported by {ArN(CH₂)₃NAr}²⁻

As we have previously communicated, reaction of 3 with a stoichiometric amount of YI₃ in THF overnight at room temperature resulted in a precipitate of insoluble potassium iodide; work-up yielded [Y{ArN(CH₂)₃NAr}I(THF)₂] 5 as a white, crystalline material in 18% yield after slow cooling of a toluene solution to -40 °C.5 The co-product, a sticky brown solid, is most likely a mixture of oligomeric species (addition of methanol precipitates some white solid. thought to be $\{Y(OMe)_{2}\}$. and the free diamine 1). The previously reported structure of 5 gives an early indication of the steric bulk of the diamide ${ArN(CH_2)_3NAr}^{2-}$ when compared with other known structures such as $[Y{C_5H_3(SiMe_3)_2}_2I(THF)]$; the latter structure incorporates only one THF unit whilst 5 includes two, strongly suggesting that the diamide is less sterically encumbering than two $\{C_5Me_5\}^-$ or $\{C_5H_3(SiMe_3)_2\}^-$ units.¹⁹ The ¹H NMR and ¹³C{¹H} NMR spectra offer singly and sharply resolved peaks for 5 alongside trace amounts of 1, which was retained during the recrystallisation and could not be removed by washing with pentane. Complex 5 provides an ideal route into yttrium complexes supported by the diamide $\{ArN(CH_2)_3NAr\}^{2-}$; salt metathesis with appropriate potassium salts yields a range of hydrocarbyl, amide and oxide derivatives of 5, as shown in Scheme 1.

Ar N ArTHF THF KR, Toluene, 20 °C Ar N ArPentane work-up THF R $R = CH(SiMe_3)_2, N(SiMe_3)_2,$ $KR', 20 °C OC_6H_2-2,6^{1}Bu-4-Me$ THF or Diethyl Ether Ar N Ar $R' = CH_2C_6H_5$ THF R' THF Scheme 1

As we stated in our earlier communication the reaction of **5** with an equimolar amount of KCH(SiMe₃)₂ in benzene or toluene at room temperature with overnight stirring and extraction into pentane yields [Y{ArN(CH₂)₃NAr}{CH(SiMe₃)₂}-(THF)] **6** as a colourless, crystalline material after slow cooling to $-42 \,^{\circ}C$.⁵ We also reported the molecular structure of **6**, which shows the expected loss of one THF unit concomitant with the exchange of iodide for the much bulkier bis(trimethyl-silyl)methyl ligand. The stoichiometry further confirms the notion that the diamide {ArN(CH₂)₃NAr}²⁻ is not as sterically bulky as two permethylcyclopentadienyl units; **6** has a coordinated THF moiety whilst [YCp*₂CH(SiMe₃)₂], isolated

under similar conditions, is base-free.²⁰ The relatively low yttrium coordination number in **6** and the proximal silylmethyl groups lead to the possibility of agostic interactions between yttrium and the latter in the solid state (as are found in the structure of $[NdCp*_2CH(SiMe_3)_2]^{21}$ for instance). However, the coordinated THF is likely to prevent any such interactions and indeed no distortion of silylmethyl groups towards the metal centre is found in this case, furthermore the sum of angles about C(1) is only 344.76°.

In d_6 -benzene solution the yttrium-bound methine carbon of 6 gives rise to a doublet at δ 36.5 ppm (${}^{1}J_{YC}$ = 35 Hz) in the ¹³C{¹H} NMR spectrum, whilst the attached protons display a corresponding doublet at δ –1.09 ppm (² J_{YH} = 2.2 Hz) in the ¹H NMR spectrum. The ⁸⁹Y chemical shift is δ 801 ppm (d_{5} -benzene– d_8 -THF).²² These chemical shift values are very different to those of the electron-rich permethylcyclopentadienylsupported complex [YCp*₂CH(SiMe₃)₂] (δ_c: 25.2 ppm, 37.0 Hz; $\delta_{\rm H}$: -0.10 ppm, 2.3 Hz; $\delta_{\rm Y}$: 79 ppm), but similar to those in compounds incorporating the harder, more electronegative nitrogen-based co-ligands, such as [Y(DADMB){CH(SiMe_3)2}-(THF)] ($\delta_{\rm C}$: 39.4 ppm, 35.6 Hz; $\delta_{\rm H}$: -0.94 ppm, 2.1 Hz),⁸ $[Y{PhC(NSiMe_3)_2}_2{CH(SiMe_3)_2}] (\delta_C: 43.5 \text{ ppm}, 30.0 \text{ Hz}; \delta_H:$ -0.94 ppm, 1.8 Hz; $\delta_{\rm Y}$: 721 ppm)²³ and [Y{Me₂Si(NCMe₃)- $(O^{t}Bu)_{2}$ {CH(SiMe₃)₂}] (δ_{C} : 33.8 ppm, 30.0 Hz; δ_{H} : -1.05 ppm, 2.0 Hz and -1.45 ppm, 1.5 Hz at -10 °C; $\delta_{\rm Y}$ 645 ppm).²⁴

The δ 1.0–4.0 ppm region of the ¹H NMR spectrum of 6, which unlike 5 has a prochiral yttrium centre, is broad and poorly resolved in both d_6 -benzene and d_8 -toluene at room temperature; the resonances arising from the diastereotopic isopropylmethyl groups in particular coalesce to give a single, broad signal (which is coincident with the peak arising from the THF β -protons). These inequivalent groups resolve as four poorly defined doublets below -35 °C (a poorly resolved triplet, due to the THF β -protons, can also be seen).²⁵ Elevation of the temperature to 50 °C did not significantly change the appearance of the spectrum compared to that at 20 °C. Thus the motion of these diastereotopic ligand groups is sufficiently rapid on the NMR timescale at room temperature for a single, averaged signal to be observed, as the temperature is lowered ligand movement becomes less energetic and these inequivalent functional groups are resolved separately.

When three drops of d_8 -THF were added to a d_6 -benzene solution of **6**, the ¹H NMR spectrum became sharply resolved with no evidence of the inequivalence noted above (Fig. 2). The



Fig. 2 Selected region of the ¹H NMR spectrum of 6 in d_6 -benzene alone (above) and with three drops of d_8 -THF (below).

appearance of free THF in this spectrum indicates that the d_8 -THF added rapidly exchanged for the coordinated THF and, since it is in vast excess, accounts for the majority of the coordinated THF (and thus has the effect of masking any exchange processes attributable to the labile THF co-ligand). It is also possible that an extra equivalent of THF not seen in the X-ray molecular structure becomes coordinated under these conditions, which changes the symmetry about the yttrium centre and thus removes the inequivalence of the diamide functional groups, giving the simpler ¹H NMR spectrum observed. Experiments with olefins (*vide infra*) would be expected to give further insight into the extent of THF association and dissociation in solution.

The synthesis of a less sterically hindered hydrocarbyl, formulated as the bis-THF adduct (Y{ArN(CH₂)₃NAr}(CH₂SiMe₃)- $(THF)_2$), was effected on a small scale in d_6 -benzene by reaction of 5 with KCH₂SiMe₃ and confirmed unequivocally by a characteristic doublet at δ -0.6 ppm (²J_{YH} = 3.0 Hz) for the yttrium-bound hydrocarbyl unit. However, all attempts to repeat this reaction on a preparative scale resulted in the formation of a complex mixture of this compound and others, most likely to be thermal decomposition products (tetramethylsilane was noted in the ¹H NMR spectrum). Whilst recrystallisation of this crude mixture from pentane at low temperature resulted in the deposition of colourless crystals from which the stoichiometry of the product could be confirmed by X-ray crystallography, it was not possible to isolate a pure sample for further analysis. Such problems with the (trimethylsilyl)methyl ligand have been encountered by other research groups, for example Schrock and co-workers, when reporting their yttrium complexes supported by the tridentate 'NON' ligand, noted that [Y(NON){CH(SiMe₃)₂}(THF)] was much more stable in vacuo than [Y(NON){CH₂SiMe₃}(THF)₂].⁷

It was also possible to synthesise another bis-THF solvated complex [Y{ArN(CH₂)₃NAr}(CH₂C₆H₅)(THF)₂], 7, by reaction of **5** with KCH₂C₆H₅ in THF or diethyl ether. The molecular structure (Fig. 3) confirms the presence of two THF ligands at the five-coordinate yttrium centre and establishes **7** as a relatively rare example of a structurally characterised yttrium benzyl complex; the only other examples known are [Y(CH₂C₆H₅)₂(TMEDA)(μ -Br)₂Li(TMEDA)],²⁶ [Y(Cp*)₂-(CH₂C₆H₅)₂(TMEDA)(μ -Br)₂Li(TMEDA)],²⁶ [Y(Cp*)₂-(CH₂C₆H₅)(THF)],²⁷ [Y{PhC(NSiMe₃)N(CH₂)₂NMe₂}₂(CH₂-Ph)₂Li] and [Y{PhC(NSiMe₃)N(CH₂)₃NMe₂}₂(CH₂Ph)].²⁸ The Y–C bond distance in **7** (2.458(4) Å) is very similar to those reported for the above compounds (2.440(6)–2.490(8) Å) whilst the coordinated THF units prevent any close approach of



the *ipso*-carbon (Y–C(28)–C(29) bond angle = $121.2(3)^{\circ}$), in contrast to the previously reported cerium complex $[Ce(Cp^*)_2(CH_2C_6H_5)]$, in which the benzyl ligand coordinates in an η^3 -mode.²⁹ The Y–N bond lengths in 7 are significantly longer than those in 5 or 6 (by 0.045 Å in the case of Y-N(1) from 5), whilst the bite-angle of the ligand (N(1)-Y-N(2)) is compressed by 1.47° from that in 5 and by 4.87° from 6, presumably due to the different electronic requirements of the co-ligand in the first instance and its steric bulk in the second. As with 5 and 6, and typically for transition metal and lanthanide amides, the nitrogen centres in 7 are planar (sum of angles at $(N1) = 359.9^\circ$, $(N2) = 359.1^\circ$), indicating sp² hybridisation, with the lone pair in the remaining p orbital, presumably in coordination with the yttrium centre.30 It is worth noting that the homoleptic lanthanide bis(trimethylsilyl)amides have an unusual pyramidal rather than trigonal planar lanthanide centre.³¹ The Y-THF separations are again within the range of 2.35-2.45 Å typical of THF-solvated yttrium complexes.32

The ¹H NMR spectrum of 7 (d_6 -benzene) shows a doublet due to coupling between yttrium and the two α -methylene protons of the benzyl co-ligand ($\delta_{\rm H} 2.29 \text{ ppm}$, ${}^2J_{\rm YH} = 4 \text{ Hz}$); corresponding resonances were seen in the ${}^{13}\text{C}{}^{1}\text{H}$ NMR spectrum ($\delta_{\rm C} 50.6 \text{ ppm}$, ${}^1J_{\rm YC} = 38 \text{ Hz}$, d_6 -benzene) and the ${}^{89}\text{Y}$ NMR spectrum ($\delta_{\rm Y} 608 \text{ ppm}$, d_6 -benzene– d_8 -THF). The ${}^{89}\text{Y}$ chemical shift value is, as discussed for 6, typical of cyclopentadienyl-free yttrium complexes within the broad chemical shift range typical of this nucleus. The other resonances due to 7 are resolved in the ¹H and ${}^{13}\text{C}{}^{1}\text{H}$ NMR spectra with much greater clarity than seen for the mono-THF solvated hydrocarbyl 6 (and the mono-THF solvated silylamide 8, vide infra), the mirror plane that bisects 7 through the achiral yttrium centre leading to single resonances with their associated couplings for all functional groups.

Despite repeated attempts it was not possible to isolate 7 in more than 10–15% yield. Furthermore, NMR studies of even crystalline samples of 7 revealed some contamination with small amounts of the diamine 1 and other unidentifiable by-products. The elemental analysis consistently registered a value some 3% too low in carbon content, also suggestive of a certain amount of decomposition at room temperature.

Although not appropriate for olefin polymerisation studies, heteroleptic lanthanide and group 3 amide complexes represent excellent synthetic targets for polar monomer polymerisation as well as offering interesting comparisons with the hitherto reported hydrocarbyls. Reaction of 5 with KN(SiMe₃)₂ in toluene gave a crystalline sample of [Y{ArN(CH₂)₃NAr}-{N(SiMe₃)₂}(THF)] 8 in about 40% yield. X-Ray crystallography confirmed the presence of a single THF unit at the four-coordinate yttrium centre (Fig. 4). Both the diamide (sum of angles at $(N1) = 360^\circ$, $(N2) = 359.4^\circ$) and the silylamide (sum of angles at $(N3) = 359.7^{\circ}$ nitrogen centres are planar, indicating the expected sp² hybridisation in each case. The lone pair at each nitrogen resides in the remaining p orbital and is presumably in coordination with the yttrium centre and in the case of N(3) the vacant silicon d orbitals as well. The Y-N(1) and Y-N(2) bond lengths are 0.084 and 0.079 Å respectively, shorter than the Y-N(3) bonds, but essentially the same as those in 7, due to this competition for lone-pair donation between silicon and yttrium that occurs at N(3) but not at the more basic, non-silylamide centres N(1) and N(2). The $Y-N(SiMe_{3})_{2}$ bond length of 2.272(3) Å is essentially the same as those in the homoleptic complex $[Y{N(SiMe_3)_2}_3]^{33}$ (2.224(6) Å) and in the heteroleptic complexes $[YCp_{2}^{*}(SiMe_{3})_{2}]^{20}$ (two independent molecules in the unit cell; Y(1)-N(1) 2.274(5) Å, Y(2)–N(2) 2.253(5) Å) and $[Y(C_5Me_4Et)_2-{NSiMe_3}_2]^{34}$ (2.276(3) Å). As for **6**, the relatively low yttrium coordination number and the proximal silylmethyl groups lead to the possibility of agostic interactions between these functionalities in the solid state. For example, the permethyl-





Fig. 4 ORTEP representation of the molecular structure of 8. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y–N(1) 2.188(4), Y–N(2) 2.194(3), Y–N(3) 2.272(3), Y–O 2.320(3); N(1)–Y–N(2) 95.43(14), N(1)–Y–N(3) 127.00(16), N(2)–Y–N(3) 126.24(13), N(1)–Y–O 104.09(15). Selected crystallographic data: crystal system: monoclinic, space group: $P2_1$ (no. 4), a = 11.0609(4), b = 17.1207(6), c = 11.3288(4) Å, $\beta = 106.524(2)^\circ$, U = 2056.74(13) Å³, Z = 2.

cyclopentadienyl complex [YCp*₂{N(SiMe₃)₂}] has an essentially planar Y–N–C–H unit that exhibits particularly prominent γ -hydrogen agostic interactions with the yttrium centre. There is a silylmethyl group aligned in a similar fashion in the structure of **8**, occupying the otherwise most vacant area of the coordination sphere. Although there is no evidence for γ -hydrogen agostic interactions in this case, this particular silylmethyl group in **8** nevertheless describes a slightly more acute angle than the others incorporating nitrogen–silicon bonds in this structure (N(3)–Si(1)–C(28) 109.7(2)°, Av. 113.1(3)°), indicative of a certain amount of non-classical interaction in the solid state.

The symmetry about yttrium in 8 is very similar to that in 6. In both cases the yttrium centre is prochiral, however the room-temperature ¹H NMR spectrum of 8 is similar to the lowtemperature spectrum of 6, indicating that 8 has considerably more structural rigidity in solution, due to delocalisation of the silylamide nitrogen lone pair towards the yttrium centre, which restricts the motion of the silylamide groups and in turn those of the diamide co-ligand. The diastereotopic isopropylmethyl groups in 8 resolve as two broad singlets and one (higher intensity) broad singlet in the room-temperature ¹H NMR spectrum; the corresponding region of the ¹³C{¹H} NMR spectrum also exhibits the appropriate four signals for these methyl groups. The inequivalent bridging methylene protons of the ligand backbone also resolve separately. Heating the sample of 8 to 40 °C yields a ¹H NMR spectrum very similar to the roomtemperature spectrum of 6, more rapid rotation causing the resonances arising from the diastereotopic isopropylmethyl groups in particular to coalesce; further heating to 60 and then 80 °C gives progressively better resolved spectra, but is accompanied by some decomposition after a few minutes at 80 °C, noted by the appearance of bis(trimethysilyl)amine in the spectrum.³⁵ Despite the apparent intractability of much of the ligand region in these spectra, ¹H-¹³C COSY NMR spectroscopy made it possible to assign each of the broad resonances in the room-temperature ¹H NMR spectrum to one or more particular functional groups (details are given in the Experimental section). Excess d_8 -THF added to the sample of 8 rapidly exchanges with the original THF, chaging the symmetry of the complex in the same manner discussed above for 6. Heating this sample to 50 °C made little difference to the appearance of its ¹H NMR spectrum.

Despite repeated attempts, the preparation of the highly sterically congested complex [Y{ArN(CH₂)₃NAr}(OAr*)(THF)] (OAr* = OC_6H_2 -2,6-^tBu₂-4-Me) resulted in the deposition of both colourless crystals of the target compound and other unidentified white solids. The presence of the target compound in this mixture and its stoichiometry were confirmed by X-ray diffraction studies of a carefully selected single crystal, however microanalysis revealed that this does not represent the bulk composition of the sample, the carbon content in particular being some ten percent too low.³⁶ ¹H and ¹³C{¹H} NMR studies also indicated the presence of both the target compound and other unidentifiable species.

The most active lanthanide complexes towards olefin polymerisation incorporate hydride co-ligands, those which adopt the rare terminal hydride bonding mode being more active than the more common hydride-bridged species.¹ Unfortunately, despite promising initial studies involving the reaction of **6** with molecular hydrogen in d_{12} -cyclohexane, it was not possible to synthesise a hydride supported by the diamide {ArN(CH₂)₃-NAr}²⁻ on a preparative scale, the reaction repeatedly yielding instead a pale yellow, highly viscous oil that did not show any yttrium hydride resonances in the ¹H NMR spectrum.

We commented in our earlier communication that the unreactivity of **6** towards olefins is most likely caused by the presence of coordinated THF. Consequently, we attempted to synthesise complexes of the form $(Y{ArN(CH_2)_3NAr}I)$ by reacting YI₃ with **3** in poorly coordinating solvents such as 'BuOMe or toluene.

'BuOMe is a more weakly basic solvent than THF yet still offers reasonable solubility towards ionic systems such as **3**. Reaction between stoichiometric amounts of YI₃ and **3** in 'BuOMe yielded exclusively the bis(ligand) ate-complex [Y{ArN(CH₂)₃NAr}₂K(PhMe)] **9** (Scheme 2) rather than the target complex. This complex **9** can be isolated under 'rational' conditions in 28% yield by adding two equivalents of **3** to a slurry of YI₃ in 'BuOMe or in 15% yield if the reaction is carried out in THF (no THF is retained after work-up).



Such an arrangement of ligands is revealing about the steric nature of the diamide $\{ArN(CH_2)_3NAr\}^{2-}$. Until the recent work of Evans *et al.* it was thought that tris(permethylcyclopentadienyl) complexes of lanthanide metals, particularly the smaller late lanthanides and yttrium, could not be made.³⁷ Indeed they cannot be made by simple salt metathesis of the lanthanide trichlorides with LiCp* even under forcing conditions, suggesting once again that the diamide $\{ArN(CH_2)_3-NAr\}^{2-}$ is considerably less sterically demanding than two permethylcyclopentadienyl units.

The molecular structure of **9** (Fig. 5) shows that the four nitrogen atoms are distributed in a slightly distorted tetrahedral array ³⁸ about each four-coordinate yttrium centre and confirms the exclusion of any ethereal solvent molecules. The Y–N bond lengths are slightly longer than those in the less sterically congested heteroleptic complexes, by 0.095 Å in the case of Y–N(1) (5) and Y–N(2) (9). There is a little variation in the Y–N bond distances within the structure of **9** itself; the Y–N(1) distance is the shortest (2.213(4) Å), but the discrepancies are small. The sum of angles at each nitrogen centre is also very similar; the greatest discrepancy from a planar arrangement is at N(4) (358.3°), the other centres are essentially planar (N(1): 359.1°, N(2): 359.8°, N(3): 360.0°). These planar geometries and similar Y–N bond lengths suggest that the lone pair at each



Fig. 5 ORTEP representations of the molecular structure of 9: a single unit (top) and the one-dimensional thread within the solid (below). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y–N(1) 2.213(4), Y–N(2) 2.265(4), Y–N(3) 2.246(4), Y–N(4) 2.246(4); N(1)–Y–N(2) 92.80(16), N(1)–Y–N(3) 117.20(16), N(1)–Y–N(4) 121.81(15). Selected crystallographic data: crystal system: monoclinic, space group: $P2_1/c$ (no. 14), a = 12.2379(2), b = 13.0294(2), c = 36.6872(6) Å, $\beta = 98.851(1)^\circ$, U = 5780.2(2) Å³, Z = 4.

nitrogen interacts with the yttrium centre, yielding a formally 16-electron centre. The potassium counter-ion sits in a pocket defined by two diamide aryl groups from separate yttrium anions and a molecule of toluene; this structure is repeated in one dimension throughout the lattice (Fig. 5).

There are two heteroleptic lanthanide anions incorporating amide and cyclopentadienyl ligands that display non-planar nitrogen centres. The bis(ligand) ate-complex $[(Y_{(C_5Me_4)})$ -SiMe₂NCH₂CH₂OMe₂)Li] reported by Okuda and co-workers for instance has a sum of nitrogen bond angles of 350.7(3) and 351.3(3)°, offering nitrogen centres somewhere in between planar and tetrahedral.³⁹ The similar bis(amide) anion $[LnCp_2(NPh_2)_2]^-$ (Ln = Y, Ln, Ce, Eu, Gd, Ho) offers structural features more consistent with one formally sp² and one sp³ centre, with an asymmetry in the Ln-N bond length across the series,40 however both of these lanthanide centres have 18 electrons given the above configuration. The observation of such a mixed hybridisation was rationalised by Lauher and Hoffmann for the MCp₂X₂ unit by invoking a single empty a₁ orbital at the metal centre into which only one lone pair of electrons can be accommodated.⁴¹ In the case of 9 there are fewer bonding electrons (two per amide nitrogen rather than the six offered by the cyclopentadienyl anion) thus allowing accommodation of all the non-bonding lone pair electrons into empty metal orbitals via sp² hybridisation at each nitrogen.

There are two distinct sets of ligand peaks of different integral values in the ¹H NMR spectrum. One set was assigned to **9** and are all slightly broadened due to the motion of the potassium cation within the coordination environment of the bis-ligand anion partially, but not completely, equalising the chemical shift of these protons. The other group, consisting of sharp resonances of lower intensity slightly upfield from those due to **9**, was attributed to **1**, formed during the reaction in reproducibly similar proportions, which explains to an extent the low yield of **9**.

Recent work in our laboratory has shown that lanthanide complexes can be prepared by the reaction of the lanthanide triiodide and an appropriate potassium salt in toluene.⁴² In this case, a stoichiometric mixture of YI₃ and **3** in toluene was heated to reflux for three days and yielded a mixture of highly toluene soluble products, a small proportion of which was recovered as a yellow powder from a highly concentrated solution at -45 °C. ¹H NMR studies revealed the presence of **9** and a compound that may be tentatively formulated as the base-free yttrium complex (Y{ArN(CH₂)₃NAr}I), however the poor yield and mixed nature of the products precluded any meaningful microanalysis.

Synthesis of yttrium complexes supported by {ArN(CH₂)₂NAr}²⁻

We were discouraged by a lack of success with preliminary studies of yttrium complexes incorporating a more sterically demanding diamide $\{ArN(CH_2)_4NAr\}^{2-}$ and consequently turned to the less sterically demanding diamide $\{ArN(CH_2)_2-NAr\}^{2-}$ in an attempt to discover whether the shortened bridge between the two aniline centres would have an effect on the structure and reactivity of the complexes so-produced. In doing so, we carried out an identical set of reactions to those detailed above and found strikingly similar behaviour in most cases, although some of the structures and reactivities towards small molecules were different.

The reaction of **4** with a stoichiometric amount of YI_3 in THF overnight at room temperature resulted in a precipitate of insoluble potassium iodide; work-up gave [{Y{ArN(CH₂)₂-NAr}I(THF)₂}₂] **10** as a white, crystalline material in 57% yield after slow cooling of a toluene solution to -42 °C. The yield is much higher than for **5**, presumably because the shorter, less flexible backbone disfavours any further reactions at the yttrium centre, in particular bis-chelation, which yield unwanted co-products.

An X-ray structure determination of 10 confirmed the inclusion of two THF units per yttrium centre (Fig. 6). It is interesting to note that 10 adopts a dimeric structure in the solid state, whilst 5 is monomeric, yielding in the case of 10 six-coordinate yttrium centres. These observations are consistent with the reduced steric demand of the two-carbon backbone and a more open coordination environment around the metal centre and give an early indication of the steric properties of this diamide.



Fig. 6 ORTEP representation of the molecular structure of **10** (only one of the two independent units shown). Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1b)–N(1b) 2.212(10), Y(1b)–N(2b) 2.198(11), Y(1b)–O(1b) 2.417(9), Y(1b)–O(2b) 2.394(8), Y(1b)–I(1b) 3.122(2), Y(1b)–I(1b_2) 3.232(2); N(1b)–Y(1b)–N(1b) 78.7(4), I(1b)–Y(1b)–1(1b_2) 76.67(4), Y(1b)–I(1b)–Y(1b_2) 103.33(4). Selected crystallographic data: crystal system: triclinic, space group: $P\overline{1}$ (no. 2), a = 12.2250(4), b = 14.2440(4), c = 25.3516(9) Å, a = 78.418(1), $\beta = 80.205(1)$, $\gamma = 85.201(2)^{\circ}$, U = 4256.0(2) Å³, Z = 2.

The structure of **10** consists of two independent units (only one is shown in the diagram for clarity) and two-and-a-half units of toluene (not shown either). Each yttrium centre has a highly distorted octahedral arrangement of ligands: the axial THF and amide centres O(1b) and N(2b) describe an angle of 167.8(3)° whilst the 'inner' equatorial angles described by I(1b)–Y(1b)–I(1b_2) and O(2b)–Y(1b)–N(1b) are 78.7(4) and 97.3(3)°, respectively. The only other dimeric yttrium iodide known in the literature is the highly unusual halide-bridged cation $[Y_2(\mu-I)(NPPh_3)_4(THF)_4]^+I_3^{-}\cdot(THF)_{6.5}$.⁴³ The Y–I bond lengths in **10** (3.112(2) and 3.239(2) Å) are shorter than in this cation (3.2732(11) and 3.3011(13) Å). As expected, the bridging Y–I bonds in both of these complexes are longer than the terminal Y–I bond in **5** (2.997(2) Å).

Complex 10 is much more sparingly soluble in aromatic hydrocarbons than 5; both are highly soluble in ethers. A d_6 -benzene solution of 10 shows peaks for both 10 and the highly soluble diamine 2. The ¹H NMR spectrum is somewhat deceptive; 2 is only present in trace amounts but appears to be a major component due to its much higher solubility. Removal of the d_6 -benzene and addition of a further quantity of the same solvent yields a spectrum with a much smaller amount of impurity and some concomitant loss of 10. Further washings are impractical due to loss of 10, however washing with pentane fails to remove 2.

In solution 10 may be dimeric, monomeric or an equilibrium mixture of the two. Unfortunately the low solubility of 10 in aromatic solvents prevented a study of its molecular weight in solution via the depression of the freezing point of benzene. Instead, NMR experiments were used to determine the degree of aggregation in solution. Variable-temperature studies showed that in the 20 to 60 °C range the degree of aggregation does not change since the appearance of the spectrum remains reasonably constant. The low solubility of 10 in aromatic solvents precluded any meaningful low-temperature NMR studies. Addition of five drops of d_8 -THF to a d_6 -benzene solution of 10 vastly increases its solubility, thus increasing the intensity of these peaks with respect to those of the highly soluble trace impurity 2. However, since the chemical shift values are not changed significantly by the addition of THF, a strong Lewis base that would be expected to cleave the weak iodide bridge, 10 is probably a monomer in both aromatic and ethereal solvents

The resonances assigned to 2 in these ¹H NMR spectra are different to those appearing when 2 alone is examined in the same solvent. Furthermore, the appearance of the THF peaks in the spectrum of 10 changes as the impurity is removed by successive washings with d_6 -benzene. In fact 2 behaves as a chelating diamine, analogous to TMEDA, displacing THF from the yttrium centres to yield a complex formulated as $(Y{ArN(CH_2)_2NAr}I{ArNH(CH_2)_2NHAr}(THF)_x)$. The coordination of 2 to the yttrium centre locks its conformation such that the couplings between the amine protons and those in the methylene bridge are resolved the ¹H NMR spectra, where as the high degree of motional freedom on the NMR timescale experienced by the diamine 2 alone leads to a well resolved singlet for these protons. When a slight excess of {YCl₃- $(THF)_{3,5}$ is suspended in a d_6 -benzene solution of 2 the chemical shifts of the resonances arising from 2 change markedly, demonstrating that 2 can also chelate around yttrium trichloride in preference to THF, although the peaks are too broad for coupling between the amine proton and those in the methylene bridge to be seen in this case.

Reaction of **10** with KCH(SiMe₃)₂ in toluene for 3 h leads to a deposit of insoluble potassium iodide; work-up with pentane and recrystallisation at low-temperature gives [Y{ArN-(CH₂)₂NAr}{CH(SiMe₃)₂}(THF)] **11** in about 50% yield. At first glance the molecular structure (Fig. 7) is quite similar to that of the congeneric species **6**. However, the N(1)–Y–N(2) bond angle in **11** is $80.32(12)^{\circ}$ as opposed to $97.79(9)^{\circ}$ in **6**,





Fig. 7 ORTEP representation of the molecular structure of **11**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y–N(1) 2.149(3), Y–N(2) 2.180(3), Y–C(27) 2.434(4), Y–O 2.327(3); N(1)–Y–N(2) 80.32(12), N(1)–Y–C(27) 117.26(13), N(2)–Y–C(27) 127.08(13), O(1)–Y–C(27) 113.29(12). Selected crystallographic data: crystal system: monoclinic, space group: $P2_1/n$ (no. 14), a = 12.5573(2), b = 17.9434(3), c = 19.4501(3) Å, $\beta = 99.444(1)^\circ$, U = 4323.1(1) Å³, Z = 4.

yielding a substantially more exposed yttrium centre as a direct result of the narrower bite of the chelate in this five-membered ring system. The THF unit is rotated about 90° away from its position in **6**, whilst the yttrium amide bonding in **11** is more asymmetric than in **6** (**11**: 2.149(3), 2.180(3) Å; **6**: 2.170(5), 2.175(5) Å). The average Y–N bond length is slightly shorter in **11** (**11**: 2.165(3) Å, **6**: 2.173(3) Å), as is the average Y–THF contact (**11**: 2.327(3) Å, **6**: 2.339(2) Å).

The ¹H NMR spectrum of **11** (d_6 -benzene) is similar to that obtained for 6, with overlapping peaks in the δ 3.5–4.0 ppm region and a broad multiplet at δ 1.3 ppm as well as an upfield doublet at δ -0.95 ppm (² J_{YH} = 2.3 Hz). The ¹³C{¹H} NMR spectrum (d_6 -benzene) is clean and diagnostic, featuring all of the expected peaks, with a doublet corresponding to the bis-(trimethylsilyl)methyl *a*-carbon at δ 36.7 ppm (¹ J_{YC} = 37 Hz). The chemical shift values and coupling constants in both the ¹H and ¹³C{¹H} NMR spectra for this functionality are very similar in both 6 and 11 (6: δ –1.09 ppm, ${}^{2}J_{YH}$ = 2.2 Hz; δ 36.5 ppm, ${}^{1}J_{YC} = 35$ Hz). Additionally, excess d_{8} -THF sharpens the diamide region of the ¹H NMR spectrum of 11, in the same manner and for the same series of reasons discussed and demonstrated for 6. The ⁸⁹Y chemical shift (d_6 -benzene- d_8 -THF) for 11 is δ 606 ppm, somewhat different from that observed for the three-carbon-backboned congener 6 (δ 801 ppm). This surprising result shows that the electronic environments of the two yttrium centres are slightly different and is indicative of the different extent to which the excess d_8 -THF added to each sample is coordinated, again symptomatic of the more open coordination sphere at yttrium in 11, but must be qualified by the large chemical shift range seen for the ⁸⁹Y nucleus (vide supra).

Complex 10 also reacts with KCH₂SiMe₃ in benzene or toluene to give, in low yield, a complex mixture including a species formulated as the thermally sensitive hydrocarbyl (Y{ArN(CH₂)₂NAr}(CH₂SiMe₃)(THF)₂). A diagnostic doublet for the yttrium hydrocarbyl protons is found in the ¹H NMR spectrum (d_6 -benzene– d_8 -THF) at δ –0.41 ppm (² J_{YH} = 3.4 Hz), shifted slightly downfield from that offered by the earlier compound (δ –0.60 ppm) but of a very similar coupling value. The remainder of the spectrum and the ¹³C{¹H} NMR spectrum contain major resonances due to the hydrocarbyl along with a number of unassigned peaks; the yttrium-bound silylmethylene resonance could not be located in the ¹³C{¹H} NMR spectrum. The ⁸⁹Y chemical shift is δ 656 ppm, similar to that for 11 (δ 606 ppm), but again shifted from that seen for 6 (δ 801 ppm).

Unfortunately, the presence of aforementioned unidentified species that could not be separated from the hydrocarbyl and its high thermal sensitivity precluded any further characterisation and confirm the problems associated with this co-ligand.

Further derivatives of 10 were made by reaction with KCH₂Ph in THF or diethyl ether to give [Y{ArN(CH₂)₂-NAr}(CH₂C₆H₅)(THF)₂] 12 and with KN(SiMe₃)₂ to yield $[Y{ArN(CH_2)_2NAr}{N(SiMe_3)_2}(THF)]$ 13. Both can be recovered from pentane as microcrystalline solids at low temperature in moderate to good yields. In a similar manner to the synthesis of 10, but in contrast to 11, a small amount of the free diamine 2 co-crystallises with 12 and 13, the presence of which can be diagnosed by its characteristic resonances in the ¹H NMR spectrum. The high pentane solubility of **12** and **13** prevents the separation of these components; the proportion of 2 in the samples can be determined as a quarter and an eighth, respectively, by integration of the ¹H NMR spectra. Apart from the presence of this diamine the ¹H NMR spectra of 12 and 13 are very similar to those of the more sterically encumbered complexes 7 and 8. There are four sets of benzylic resonances in the ¹H NMR spectrum of 12, three in the aromatic region and one around δ 2 ppm with all associated couplings well resolved (7: δ 2.29 ppm, ${}^{2}J_{\rm YH}$ = 3.44 Hz, **12**: δ 2.39 ppm, 2.09 Hz). The remainder of this spectrum and the ¹³C{¹H} NMR spectrum both include the expected resonances at good resolution, indicating rapid rotation of the diamide functional groups on the NMR timescale and coordinative saturation of the yttrium centre. The ¹H NMR spectrum of 13 is broad and poorly defined, the isopropyl methine, methylene bridge and THF *a*-proton resonances appear together as a broad signal at δ 3.84 ppm whilst the diastereotopic isopropyl methyl groups gave a single, broad peak at δ 1.41 ppm. Addition of d_8 -THF to the sample resolves the peaks singly and sharply for reasons detailed in the discussion of 8. Despite repeated attempts it was not possible to grow X-ray quality crystals of either 12 or 13, however the compositions were confirmed by microanalysis.

In contrast to the system supported by the more sterically encompassing chelating diamide $\{ArN(CH_2)_3NAr\}^{2-}$ it was possible to make a hydride complex supported by the ligand $\{ArN(CH_2)_2NAr\}^{2-}$ via σ -bond metathesis of *in situ* generated 11 with molecular hydrogen. The colour of the reaction mixture changed slightly from the pale, watery yellow of 11 to a yellowish green over the 3 day reaction period, but there was no deposition of solids. The hydride 14 was recovered from the pentane solution at low temperature as a white, microcrystalline solid in 9% yield.

Although most of the sample was microcrystalline, a single crystal suitable for X-ray diffraction studies was isolated from a concentrated sample of 14 at low temperature. The molecular structure shows the highly unusual incorporation of superstoichiometric equivalents of molecular hydrogen that appear to have added across one of the yttrium amide bonds at two of the three yttrium centres to give [Y₃{ArNH(CH₂)₂NAr}₂- $\{ArN(CH_2)_2NAr\}(\mu-H)_3(\mu_3-H)_2(THF)\}$, in which all three yttrium centres are different and there is an unusual mixture of bridging and face-capping hydrides (Fig. 8). Three hydrides are included in bridging positions at alternate apices of a hexagon also defined by the positions of the three yttrium centres with the remaining two capping opposite faces of the hexagon. There is considerable asymmetry about the face-capping hydrides H(4x) and H(5x), with the Y–H bond lengths varying from 1.94(12) to 2.39(8) Å. The bond lengths for the other three hydrides (H(1x)–H(3x)) range from 1.98(6) to 2.18(6) Å.

A mixture of bridging and face-capping hydrides is unusual but by no means unprecedented in lanthanide chemistry. The first trimetallic lanthanide hydrides were reported by Evans *et al.*, who synthesised [$\{\text{ErCp}_2(\mu-H)\}_3(\mu_3-Cl)$][Li(THF)₄] and [$\{\text{LuCp}_2(\mu-H)\}_3(\mu_3-H)$][Li(THF)₄]⁴⁴ and the analogous yttrium complex [$\{\text{YCp}_2(\mu-H)\}_3(\mu_3-H)$][Li(THF)₄].⁴⁵ Evans *et al.* later reported two different coordination modes for the yttrium



Fig. 8 ORTEP representation of the molecular structure of $[Y_3{ArNH(CH_2)_2NAr}_{2}{ArN(CH_2)_2NAr}(\mu-H)_3(\mu_3-H)_2(THF)]$ **14** (above) and of the central hydride core only (below). Thermal ellipsoids are drawn at the 20% probability level. Non-hydride hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1)–N(1) 2.184(7), Y(2)–N(4) 2.218(6), Y(2)–N(3) 2.589(7), Y(2)–O 2.375(5), Y(1)–H(1x) 2.18(6), Y(1)–H(4x) 2.30(8); N(1)–Y(1)–N(2) 81.4(2), H(1x)–Y(1)–H(3x) 122(2), H(4x)–Y(1)–H(5x) 49(3). Selected crystallographic data: crystal system: monoclinic, space group: $P2_1/c$ (no. 14), a = 25.4497(7), b = 14.2389(3), c = 25.1449(5) Å, $\beta = 105.140(1)^\circ$, U = 8795.6(4) Å³, Z = 4.

hydride [Y(C₅H₃-1,3-Me₂)₂H] determined by the crystallisation solvent.⁴⁶

Complex 14 is highly soluble in aromatic and ethereal solvents. The ¹H NMR spectrum of [Y₃{ArNH(CH₂)₂NAr}₂- ${ArN(CH_2)_2NAr}(\mu-H)_3(\mu_3-H)_2(THF)]$ should contain five complicated multiplets in the hydride region since all three yttrium centres are different, rendering their associated hydrides inequivalent, whilst even the face-capping hydrides are different due to the absence of any mirror planes in the molecule. In a similar manner, $[{YCp_2(\mu-H)}_3(\mu_3-H)][Li(THF)_4]$ has two complicated multiplets at δ 0.75 and -1.03 ppm in a 3 : 1 ratio, due to coupling between the inequivalent protons and the yttrium centres. However, in d_6 -benzene solution at 20 °C a single, slightly broadened triplet is found in a typical region for yttrium hydrides with hard, electronegative co-ligands (δ 5.91 ppm, ${}^{1}J_{YH} = 28$ Hz) whilst at 60 °C the same triplet is observed, slightly shifted upfield and at much better resolution (δ 5.74 ppm, ${}^{1}J_{YH}$ = 28 Hz). Conversely at 8 °C only a very broad singlet can be seen at δ 6.06 ppm. These values are similar to the dimeric yttrium bis(benzamidinate) and bis(N,O-bis(tertbutyl)(alkoxydimethysilyl)amide) hydrides, recently reported by Teuben and co-workers (δ 8.28 ppm, ${}^{1}J_{\rm YH} = 28$ Hz and δ 6.80 ppm, ${}^{1}J_{\rm YH}$ = 31 Hz, respectively) and are much further downfield than those arising from the previously reported cyclopentadienyl-supported complexes.^{23,24} An NOE experiment on a d_6 -benzene solution of 14, irradiating at the frequency of the yttrium hydride at 60 °C in an attempt to see whether other hydride resonances exist under the complicated ligand region, produced a small enhancement at δ 4.14 ppm (7.9%); selective irradiation at this frequency collapsed a peak in the isopropylmethyl region (δ 1.36 ppm). The remainder

of the spectrum clearly has peaks attributable to the diamide functional groups and THF but is generally broad and poorly resolved. ⁸⁹Y NMR spectroscopy also revealed just one resonance, at δ 453 ppm (50 °C, ¹J_{YH} coupling was not resolved).

Although the environment at the hydride centre of 14 varies slightly with temperature in solution, the basis of structure remains that of doubly-bridging hydrides between two or more equivalent yttrium centres throughout the temperature range studied, suggesting the formulation $[{Y}{ArN(CH_2)_2NAr}]$ - $(\mu$ -H)(THF)}, for 14, inconsistent with that obtained by X-ray crystallography. The broadening of the signals at room temperature compared to the higher temperature studies can be attributed to fluxional processes within the coordination sphere, such as the motion of THF or the associated isopropylmethyl proton in close proximity to the hydrides, which are slow on the NMR timescale at room temperature but more rapid at elevated temperatures. The complex does not revert to this simple dimeric form elucidated by NMR studies in solution from the more unusual mixed amido-amine structure [Y₃{ArNH- $(CH_2)_2NAr$ { $ArN(CH_2)_2NAr$ } $(\mu$ -H)₃ $(\mu_3$ -H)₂(THF)] found by X-ray crystallography, since no molecular hydrogen is seen in the ¹H NMR spectrum. Neither does it revert to a 'bridgingonly' form of the hexagonal trimer described above, as the three yttrium centres are still inequivalent, and would therefore give rise to a much more complicated ¹H NMR spectrum than that observed. Microanalysis is consistent with both the form of the hydride observed in solution and that seen in the solid state.47 It must be concluded that the very interesting and unusual structure determined by X-ray crystallography only represents a minor component of the mixture, which is predominantly the more conventional hydride $[{Y}{ArN(CH_2)_2NAr}(\mu-H) (THF)_{x}].^{48}$

In further contrast to the other diamide, it was possible to isolate a pure sample of the phenoxide complex [Y{ArN- $(CH_2)_2NAr$ }(OAr*)(THF)] **15** from pentane following the reaction of **10** with KOAr*(THF) in toluene. Crystals suitable for X-ray diffraction studies were grown from a highly concentrated pentane solution at low temperature. The molecular structure (Fig. 9) confirms the inclusion of a single THF unit per yttrium centre; the structure itself is a distorted tetrahedron. The N(1)–Y–N(2) bond angle is narrower in **15** than in the more sterically encompassing congener [Y{ArN(CH₂)₃-NAr}(OAr*)(THF)]³⁶ (82.53(15)° as opposed to 95.87(14)°), consistent with the differences in angles found in the analogous pairs of iodide and bis(trimethysilyl)methyl complexes. The



Fig. 9 ORTEP representation of the molecular structure of **15**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y–N(1) 2.173(4), Y–N(2) 2.168(4), Y–O(1) 2.066(4), Y–O(2) 2.319(4); N(1)–Y–N(2) 82.53(15), N(1)–Y–O(1) 126.86(16), N(1)–Y–O(2) 107.70(16), O(1)–Y–O(2) 98.99(15). Selected crystallographic data: crystal system: monoclinic, space group: $P2_1/n$ (no. 14), a = 10.2131(3), b = 23.5543(6), c = 18.5374(7) Å, $\beta = 101.190(1)^\circ$, U = 4374.6(2) Å³, Z = 4.

Y–O bond length (2.066(4) Å) is very similar to that in $[Y{ArN(CH_2)_3NAr}(OAr^*)(THF)]$ (2.092(3) Å) and in the homoleptic, base free complex $[Y(OAr)_3]^{49}$ (OAr = OC_6H_3 -2,6-'Bu₂) (2.00(1) Å). It is also close to the values reported for the heteroleptic complexes $[YCp^*{CH(SiMe_3)_2}(OAr^*)]^{50}$ (2.090(3) Å) and $[Y{PhC(NSiMe_3)_2}(OAr^*)]^{51}$ (2.0750(19) Å). The Y–N and Y–THF separations are essentially the same as those in earlier complexes reported herein.

In a similar manner to many of the other yttrium compounds reported herein, the room-temperature ¹H NMR spectrum of **15**, which again has a prochiral yttrium centre, has poorly resolved, overlapping diamide and co-ligand resonances in the δ 1.0–4.0 ppm region of the spectrum. Heating to 70 °C results in coalesence of the three peaks, two of much lower intensity, assigned to the 'Bu protons, and also gives better resolution of the resonances arising from the diamide ligands due to averaging of the chemical environments on the NMR timescale; the THF peak is shifted downfield upon heating such that it overlaps slightly with the sharpened isopropyl methine resonance.

Reaction of 6 and 11 with phenylsilane

Lanthanide hydrocarbyl and hydride complexes have been shown to be active towards both silane dehydrogenative coupling⁵² and olefin hydrosilylation.⁵³ Voskoboynikov *et al.* later reported the systematic synthesis of a number of lanthanide hydrides *via* the reaction of the hydrocarbyls with various organosilicon, -germanium and -tin hydrides.⁵⁴ Hydrosilylation catalysis has since been extensively studied by Tilley *et al.*, in particular using chelating bis(silylamido)-supported yttrium complexes.⁵⁵ Phenylsilane was chosen in this context to attempt to effect the synthesis of yttrium hydride complexes incorporating both of the diamide ligands reported on herein.

Both 6 and 11 reacted with a slight excess of phenylsilane in d_6 -benzene with complete consumption of the yttrium hydrocarbyl; 11 took over five days at room temperature to react completely whilst 6 required heating to 75 °C in order to do so (Scheme 3). During both reactions, the pale yellow solutions gradually turned a very dark orange. Neither 6 nor 11 reacted with the more sterically hindered diphenylsilane under the same conditions. Since reactions between lanthanide complexes and phenylsilane involve a sigma-bond metathesis mechanism, the difference in the N(1)-Y-N(2) bond angle and perhaps the way in which THF is coordinated in solution between 6 and 11 must be enough to change the reactive surface at yttrium. It turns out that instead of yielding either of the expected metathesis products (being an yttrium hydride or an yttrium phenyl) the reaction produces silicon-based hydrocarbyl and diamide complexes via the highly unusual substitution of yttrium for silicon.



The ¹H and ¹³C{¹H} NMR spectra of the *in situ* reaction of **6** with phenylsilane contain a great number of peaks and therefore very little diagnostic information. By comparison, the ¹H, ¹³C{¹H}, ²⁹Si and ²⁹Si{¹H} NMR spectra of the analogous *in situ* reaction of **11** are clear and easily interpretable. None of these spectra reveal any yttrium-coupled resonances. The ²⁹Si DEPT NMR spectrum has a doublet at δ –16.95 ppm (¹J_{SIH} = 220.5 Hz), a triplet at δ –34.75 ppm (¹J_{SIH} = 193.8 Hz) and a

quartet at δ -60.13 ppm (${}^{1}J_{\text{SiH}}$ = 200.7 Hz), which all resolve as singlets in the ${}^{29}\text{Si}\{{}^{1}\text{H}\}$ NMR spectrum. The quartet is clearly associated with excess PhSiH₃; the other resonances correspond to the highly soluble oils [Si{ArN(CH₂)₂NAr}PhH] **16** and Si{CH(SiMe₃)₂}PhH₂. These resonances are similar to those observed by Schmidbaur and co-workers in their extensive studies on the structure and reactivity of silylamines.⁵⁶ In both the reactions of **6** and of **11**, EI mass spectrometry of small aliquots taken from the NMR solutions revealed the existence of two products in which the ligands {CH(SiMe₃)₂}⁻ and {ArN(CH₂)_xNAr}²⁻ (*x* = 2, 3) had separately been transferred to silicon, *i.e.* to give Si{CH(SiMe₃)₂H₂Ph and Si{ArN(CH₂)_xNAr}HPh. The latter is the highest molecular weight peak in both spectra. All of these assignments have been confirmed by high resolution EI mass spectroscopy.

The reaction of 11 with phenylsilane was repeated on a preparative scale in an attempt to separate the silicon-containing products. This reaction was much slower, presumably due to greater dilution (about half an equivalent of 11 remained after five days), however over a 10-day period the reaction mixture changed from yellow to dark orange. Removal of all volatiles from the solution phase yielded a dark brown oil showing a ¹H NMR spectrum that was very similar to that of the earlier in situ studies. The coloured component is insoluble in pentane and can be removed by successive washings but displays only a broad ¹H NMR spectrum (d_6 -benzene) offering no diagnostic information. The pentane fraction yielded a very pale yellow, viscous oil, containing only Si{CH(SiMe₃)₂}H₂Ph and 16. Sublimation of this oily mixture (110 °C, 2×10^{-5} mbar) gave 16 as a colourless, viscous oil with concomitant decomposition of Si{CH(SiMe₃)₂}H₂Ph.

The ¹H NMR spectrum of **16** (d_6 -benzene) has four doublets and two septets (${}^2J_{HH} = 6.84$ Hz), corresponding to four diastereotopic isopropylmethyl protons and their associated methine protons, in the δ 0.7–1.5 and δ 3.7–4.0 ppm regions of the ¹H NMR spectrum, respectively (Fig. 10). Two other multiplets were found in the δ 3.3–3.6 ppm region of the ¹H NMR spectrum of **16**, arising from the inequivalent backbone methylene protons. Spin saturation transfer experiments indicated that the isopropylmethyl protons exchange on the NMR timescale at room temperature. The coupled silane protons (δ 4.67 ppm, ${}^{3}J_{HH} = 3.57$ Hz) and bis(trimethylsilyl)methine proton (δ –0.53 ppm, ${}^{3}J_{HH} = 3.57$ Hz) in Si{CH-(SiMe₃)₂}H₂Ph are resolved cleanly in the ¹H NMR spectrum of the mixture of the two silicon-containing products, along with a singlet (δ 0.12 ppm) corresponding to the associated



Fig. 10 Selected region of the ¹H NMR spectrum of Si{CH- $(SiMe_3)_2$ }H₂Ph and 16 in d_6 -benzene.

silylmethyls. The inequivalence seen in the ¹H NMR spectrum arises, in an analogous manner to 6 and 8, from the prochiral silicon centre, however the absence of a THF moiety that is labile on the NMR timescale accounts for the clearer spectral resolution in the case of 16.

X-Ray quality crystals were grown from a highly concentrated d_6 -benzene solution at room temperature thus allowing final confirmation of the structure of 16. The molecular structure (Fig. 11) clearly reveals the two equivalent sets of four diastereotopic isopropylmethyl groups that give rise to the four different resonances in the ¹H NMR spectrum. The fourcoordinate silicon centre has a tetrahedral distribution of ligands, whilst the two amine centres are essentially planar, with slightly more distortion towards a tetrahedral arrangement at N(2) than N(1) (sum of angles at N(1) = $359.22(12)^\circ$, at N(2) = 356.03(12)°). Such geometry, invoking sp² hybridisation, has already been discussed at length for early transition metal amides and silylamides in this work and is also very common in metal-free silylamine chemistry. Schmidbaur and co-workers have noted the difference between the tetrahedral geometry found at the non-silvlated analogues of the planar trisilylamines such as [N(SiH₂Ph)₃] and [N(SiH₂Ph)(SiMe₃)₂] and mono-silylamines, such as [N(SiH2Ph)(CH2Ph)2], [N{SiH2-2,4,6-^tBu₃)].⁵⁶ The Si–H bond length in **16** is 1.382(0.015) Å, very similar to those in [N(SiH₂Ph)₃] (1.36(2), 1.35(2) Å), whilst the Si-N contacts of 1.7098(13) Å (Si-N(1)) and 1.7196(13) Å (Si–N(2)) are within the range of 1.70–1.75 Å found in the above silylamines.



Fig. 11 ORTEP representation of the molecular structure of 16. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–N(1) 1.7098(13), Si–N(2) 1.7196(13), Si–H(1) 1.382(0.015), Si–C(27) 1.8557(16); N(1)–Si–N(2) 93.59(6), N(1)–Si–H(1) 110.7(0.6), N(2)–Si–H(1) 117.7(0.6), C(27)–Si–H(1) 103.7(0.6). Selected crystallographic data: crystal system: monoclinic, space group: $P2_1/n$ (no. 14), a = 16.7778(3), b = 9.6378(1), c = 19.7477(3) Å, $\beta = 109.171(1)^\circ$, U = 3016.14(8) Å³, Z = 4.

Facile intermolecular ligand redistribution, a consequence of the large size and predominantly ionic bonding mode of lanthanide centres, has been employed in the synthesis of lanthanide mixed amido–chloro complexes.⁵⁷ However the exchange of a lanthanide centre for a main group non-metal is highly unusual and unexpected, especially for a chelating dianionic fragment.

Ethene and 1-hexene studies

Two equivalents of 1-hexene failed to react with a solution of any of the hydrocarbyl complexes in d_{o} -benzene after 72 h at room temperature. Addition of a further six equivalents of 1-hexene likewise failed to induce any reaction. Elevation of the temperature in these experiments generally resulted in thermal decomposition, although the bis(trimethylsilyl)methyl and benzyl complexes were surprisingly thermally robust under these conditions. In all cases the THF unit blocks the active site for olefin insertion; the steric bulk of the various co-ligands also accounts for their unreactivity. Repeating these experiments with an atmosphere of ethene on a preparative scale failed to yield any insoluble poly(ethene). There is some evidence that the THF ligand is labile; in all complexes THF exchanges for d_8 -THF when a large excess of the latter is present and the various chemical shift values arising from the THF co-ligands show a small temperature dependency. However, were there to be a significant base free 'resting state' in these equilibria, olefin insertion would presumably take place. It was not possible to activate these complexes towards olefin polymerisation by the addition of the strong Lewis acid B(C₆F₅)₃, which might be expected to scavenge THF. This reagent instead caused immediate degradation of the complexes.

By comparison the hydride complex 14, formulated in solution as $[{Y{ArN(CH_2)_2NAr}(\mu-H)(THF)}],$ does react with 1-hexene and ethene in aromatic hydrocarbons. Addition of three equivalents of 1-hexene to a d_6 -benzene solution of 14 gave rapid loss of the characteristic pale green colour, to give a yellow solution, with concomitant loss of the hydride peak in the ¹H NMR spectrum. Integration of this spectrum revealed that approximately one equivalent of 1-hexene had been consumed; heating to 60 °C did not induce further monomer consumption.58 Unfortunately, the complicated nature of the resultant ¹H NMR spectrum precluded any further in situ characterisation of the reaction products and, despite repeated attempts, it was not possible to isolate and characterise any of these products on a preparative scale either, owing to their very high solubility in pentane even at low temperatures. A toluene solution of 14 also reacted with ethene (1.5 bar, 20 °C) with rapid loss of the characteristic pale green colour, this time to yield a colourless solution. After stirring for about 30 min at room temperature a very small amount of highly floculant, fibrous solid was deposited. Stirring for a further 30 min at room temperature gave a little more solid, however an additional 5 h stirring did not give a significantly increased amount of solid and it was not possible to isolate and characterise a measurable amount of this product.

Summary

Salt metathesis using first yttrium triiodide and the appropriate potassium diamide, followed by further metathesis with potassium hydrocarbyl, amide and phenoxide salts, provides a reliable synthetic route into a range of yttrium complexes incorporating the chelating diamides $\{ArN(CH_2)_xNAr\}^{2-}$ (x = 2, 3). These chelating diamides are not as sterically encompassing as the ubiquitous permethylcyclopentadienyl ligand, leading to THF coordination or, in the absence of THF, atecomplex formation. The bis(trimethylsilyl)methyl yttrium chelating diamide complexes react with phenylsilane to yield unprecedented ligand exchange products. In common with many non-cyclopentadienyl lanthanide complexes the compounds reported herein show at best very slight reactivity towards olefins, however studies involving polar monomers such as methyl methacrylate, rac-lactide and ε -caprolactone have shown encouraging results and will be disclosed in due course.

Experimental

General considerations

All inorganic experimental procedures were carried out by means of standard high-vacuum Schlenk-line techniques, under an atmosphere of dry nitrogen or catalytically dried and deoxygenated argon, or under catalytically dried and deoxygenated nitrogen in an MBraun or a Miller-Howe glove box. Glassware was dried in an oven at 120 °C, flame-dried *in vacuo* and repeatedly purged with an inert gas (dry argon or nitrogen) and evacuated prior to use. Celite 545 filter aid was flame dried *in vacuo* and filter cannulae equipped with Whatman[®] 25 mm glass microfibre filters were dried in an oven at 120 °C prior to use.

Reagents and materials

High purity nitrogen, argon, hydrogen and ethene gases were used as supplied by BOC Gases. Toluene was dried by heating to reflux over sodium, THF was heated to reflux over potassium and hexanes and pentane were heated to reflux over sodiumpotassium alloy. Solvents were stored in an ampoule containing a potassium mirror in all cases apart from THF, which was stored over activated 4 Å molecular sieves. All solvents were degassed prior to use. All deuterated solvents were purchased from Goss Chemicals and were dried over potassium (d_6 benzene, d_{12} -cyclohexane, d_8 -THF) or sodium (d_8 -toluene) then vacuum transferred into ampoules and stored under nitrogen prior to use. Yttrium chips, potassium metal, 1,3-dibromopropane, 1,8-diaminonaphthalene, sodium trifluoroacetate and mercury(II) iodide were purchased from Aldrich and used as supplied. 2,6-Diisopropylaniline was purchased from Aldrich, stirred over decolourising charcoal overnight and filtered; zinc powder was added and the mixture distilled to yield the pure material as a clear, colourless, mobile oil (55 °C, 0.1 mbar). ⁿBuLi (2.5 M solution in hexanes) was purchased from Acros Organics and used as supplied. KN(SiMe₃)₂ was purchased from Fluka and recrystallised from toluene prior to use. KCH-(SiMe₃)₂ was prepared via transmetallation of LiCH(SiMe₃)₂ with potassium menthoxide. KCH₂SiMe₃ was prepared via transmetallation of LiCH₂SiMe₃ with potassium menthoxide. ArNH(CH₂)₃NHAr,⁶ ArNH(CH₃)NHAr,⁵⁹ KCH₂C₆H₅, LiCH(SiMe₃)₂ and LiCH₂SiMe₃ were prepared according to literature preparations.

Analytical techniques

¹H, ¹³C{¹H} and ⁷Li NMR spectra were recorded on a Bruker Spectrospin AG 300DPX spectrometer operating at 300.13 MHz for ¹H measurements, 75.47 MHz for ¹³C measurements and 116.64 MHz for ⁷Li measurements and on a Bruker Spectrospin AG 500AMX spectrometer operating at 500.13 MHz for ¹H measurements. ²⁹Si and ⁸⁹Y NMR spectra were recorded on a Bruker Spectrospin AG 500AMX spectrometer. ¹³C and ¹H NMR spectra are referenced relative to the carbon or residual proton chemical shifts of the internal deuterated solvent set using external SiMe₄ for ¹H NMR and ¹³C{¹H} NMR. ²⁹Si spectra were referenced to external SiMe₄ and ⁸⁹Y to external YCl₃ in D₂O. Spectra were recorded at 20 °C unless indicated otherwise.

Elemental analyses were carried out by Mikroanalytisches Labor Pascher of Remagen-Bandorf, Germany (3–7) and The University of North London (8–15). Extensive ligand absorptions in the regions of the spectrum in which yttrium organometallic functionalities generally come into resonance precluded any meaningful IR studies.

Single crystal X-ray structural determinations were carried out on a KappaCCD diffractometer. All structures were solved by direct methods (SHELXS-86)⁶⁰ and refined (SHELXS-97)⁶¹ against all F^2 data. Structures are drawn in the text throughout as ORTEP representations derived from imported data (ORTEP23 for windows).⁶² EI-TOF mass spectroscopy was carried out on a VG autospec Fisons instrument (electron ionisation at 70 eV).

CCDC reference numbers 228144–228152.

See http://www.rsc.org/suppdata/dt/b4/b400149d/ for crystallographic data in CIF or other electronic format.

Syntheses

K₂{ArN(CH₂)₃NAr} 3. "BuLi (6.94 mL, 17.34 mmol, 2.5 M solution in hexanes) was added dropwise over 15 min with

stirring to a solution of **1** (3.42 g, 8.67 mmol, previously dissolved in 40 : 60 petroleum ether and dried over anhydrous Na₂SO₄) in 80 mL hexanes at -78 °C, then stirred for a further 2 h at room temperature. Potassium menthoxide (38.8 mL, 17.34 mmol, 0.447 M solution in heptane) was added dropwise over 15 min with stirring to the resultant pale yellow solution at -45 °C, which deposited a bright yellow precipitate. The resultant bright yellow suspension was stirred overnight at room temperature, poured onto a glass frit in the glove box, washed with hexanes (3 × 40 mL), dried on the frit for 2.5 h and collected as a bright yellow powder (3.314 g, 7.06 mmol, 81%).

Characterising data for **3**: ¹H NMR (d_6 -benzene): broad and poorly resolved; (d_6 -benzene with 3 drops d_8 -THF): δ 6.85 (s (br), 4H, C₆ H_3 (C₃H₇)₂), 6.10 (m (br), 2H, C₆ H_3 (C₃H₇)₂), 3.68 (m (br), 8H, CH(CH₃)₂, NCH₂CH₂CH₂N), 1.98 (s (br), 2H, NCH₂CH₂CH₂N), 1.31 (s (br), 24H, CH(CH₃)₂); ¹³C{¹H} NMR (d_6 -benzene with 3 drops d_8 -THF): δ 141.2, 132.9, 124.4, 123.9 (C_6 H₃(C₃H₇)₂), 51.4 (NCH₂CH₂CH₂N), 27.8 (CH(CH₃)₂), 24.5, 24.2 (CH(CH₃)₂, NCH₂CH₂CH₂N), ⁷Li NMR (d_6 -benzene): no resonances observed; ⁷Li NMR (d_6 -benzene with 3 drops d_8 -THF): δ 2.19, 1.09 (both sharp and of low intensity); elemental analysis: calc.: C: 68.88, H: 8.56, N: 5.95; found: C: 69.90, H: 9.17, N: 5.69%.

 K_2 {ArN(CH₂)₂NAr} 4. Complex 4 was prepared in an analogous fashion to 3; full synthetic details can be found in the ESI. †

[Y{ArN(CH₂)₃NAr}I(THF)₂] 5. YI₃ (1.000 g, 2.13 mmol) and 3 (1.000 g, 2.13 mmol) were slurried in THF (55 mL, 0 °C). The resultant yellow suspension, on stirring, rapidly turned to a white suspension, which was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue dried *in vacuo* for 1 h. Toluene (50 mL) was added and the suspension filtered to yield a clear, pale yellow solution. The solvent volume was reduced to 20 mL and the solution cooled to -45 °C over three days to yield 5 as colourless crystals (0.294 g, 0.391 mmol, 18%); a small amount of 1 was retained.

Characterising data for **5**: ¹H NMR (d_6 -benzene): δ 7.00–7.20 (m, residual protons from d_6 -benzene, $C_6H_3(C_3H_7)_2$), 4.17 (sept, 4H, $CH(CH_3)_2$), 3.74 (t, 4H, $NCH_2CH_2CH_2N$), 3.35 (sept, $CH(CH_3)_2$ 1), 3.25 (s, 8H, THF), 3.05 (m, 2.5H, $NCH_2-CH_2CH_2N$; $NCH_2CH_2CH_2N$, NH, 1), 1.41 (d, 24H, $CH-(CH_3)_2$), 1.20 (d, 2.5H, $CH(CH_3)_2$ 1), 0.98 (s, 8H, THF); ¹³C{¹H} NMR (d_6 -benzene): δ 145.7, 143.8, 142.5, 124.2, 123.7, 123.4, 122.9 ($C_6H_3(C_3H_7)_2$), 80.9 (low intensity), 70.1 (THF), 59.3 ($NCH_2CH_2CH_2N$), 50.5 ($NCH_2CH_2CH_2N$ 1), 33.2 ($NCH_2CH_2CH_2N$), 32.4 ($NCH_2CH_2CH_2N$ 1), 27.9 ($CH-(CH_3)_2$), 26.8, 25.1 (low intensity), 24.5 (THF), 24.3 ($CH(CH_3)_2$); elemental analysis: calc.: C: 55.85, H: 7.50, N: 3.72; found: C: 55.25, H: 7.50, N: 3.71%.

[Y{ArN(CH₂)₃NAr}{CH(SiMe₃)₂}(THF)] 6. 5 (0.200 g, 0.260 mmol) and KCH(SiMe₃)₂ (0.053 g, 0.260 mmol) were dissolved in toluene (40 mL, 0 °C). The resultant pale yellow suspension was stirred overnight at room temperature. The solvent was removed under reduced pressure from the resultant pale yellow suspension and the residue dried *in vacuo* for 1 h. Pentane (30 mL) was added and the suspension filtered to yield a clear, pale yellow solution. The solution was cooled to -45 °C overnight to yield 6 as colourless crystals (0.042 g, 0.059 mmol, 22%).

Characterising data for **6**: ¹H NMR (d_6 -benzene): broad and poorly resolved; ¹H NMR (d_6 -benzene with 3 drops d_8 -THF): δ 7.20 (m, 6H, C₆ H_3 (C₃ H_7)₂), 3.77 (sept, 4H, CH(CH₃)₂), 3.58 (m, 8H, NCH₂CH₂CH₂N and THF), 2.33 (m, 2H, NCH₂CH₂-CH₂N), 1.42 (m, 28H, CH(CH₃)₂ and THF), 0.06 (s, 18H, Si Me_3), -1.09 (d, ² J_{YH} = 2.2 Hz, 1H, YCH(SiMe₃)₂); ¹³C{¹H} NMR (d_6 -benzene with 3 drops d_8 -THF): δ 151.8, 145.2, 142.9, 124.6, 124.3, 124.1 (C_6H_3 (C₃ H_7)₂), 68.1 (THF), 60.0 (NCH₂- CH₂CH₂N), 50.1 (NCH₂CH₂CH₂N 1), 36.5 (d, ${}^{1}J_{YC} = 35$ Hz, YCH(SiMe₃)₂), 34.6 (NCH₂CH₂CH₂N), 28.6 (CH(CH₃)₂), 25.9 (THF), 24.3 (CH(CH₃)₂), 5.0 (CH(SiMe₃)₂); ⁸⁹Y NMR (d_{6} -benzene with 3 drops d_{8} -THF): δ 801 ppm; elemental analysis: calc.: C: 64.01, H: 9.47, N: 3.93; found: C: 63.89, H: 9.11, N: 4.29%.

[Y{ArN(CH₂)₃NAr}(CH₂C₆H₅)(THF)₂] 7. YI₃ (0.408 g, 0.869 mmol) and 3 (0.408 g, 0.869 mmol) were slurried in THF (40 mL, 0 °C). The resultant yellow suspension, on stirring, rapidly turned to a white suspension, which was stirred overnight at room temperature. A deep red solution of KCH₂C₆H₅ (0.113 g, 0.869 mmol) in THF (20 mL) was added to the white suspension at 0 °C. The resultant deep red suspension rapidly changed to an off-white suspension, which was warmed to room temperature and stirred for 3 h. The solvent was removed under reduced pressure and the residue dried in vacuo for 1.5 h. Pentane (30 mL) was added and the yellow suspension stirred for 2 h and then filtered to yield a clear, very pale yellow solution. The solvent volume was reduced to 10 mL and the product recovered as a pale yellow microcrystalline solid (0.085 g, 0.119 mmol, 14%). Crystals suitable for X-ray diffraction studies were grown from a highly concentrated pentane solution at 4 °C.

Characterising data for 7: ¹H NMR (d_6 -benzene): δ 7.00–7.30 (m, residual protons from d_6 -benzene, $C_6H_3(C_3H_7)_2$), 6.96 (m, 2H, *m*-CH₂ C_6H_5), 6.77 (d, 2H, *o*-CH₂ C_6H_5), 6.51 (t, 1H, *p*-CH₂ C_6H_5), 4.00 (sept, 4H, CH(CH₃)₂), 3.68 (t, 4H, NCH₂-CH₂CH₂N), 3.12 (m, 10H, THF), 2.64 (m (br), 2H, NCH₂-CH₂CH₂N), 2.29 (d, ² J_{YH} = 4 Hz, 2H, YCH₂ C_6H_5), 1.35 (d, 24H, CH(CH₃)₂), 1.00 (m, 10H, THF); ¹³C{¹H} NMR (d_6 -benzene): δ 154.3, 154.1, 146.0, 129.5, 123.7, 122.9, 116.7 ($C_6H_3(C_3H_7)_2$, CH₂ C_6H_5), 69.4 (THF), 59.8 (NCH₂CH₂-CH₂N), 50.6 (d, ¹ J_{Y-C} = 38 Hz, YCH₂ C_6H_5), 34.5 (NCH₂CH₂-CH₂N), 28.0 (CH(CH₃)₂), 25.1 (THF), 22.7 (CH(CH₃)₂); ⁸⁹Y NMR (d_6 -benzene): δ 608 ppm; elemental analysis: calc.: C: 70.07, H: 9.24, N: 3.89; found: C: 67.75, 67.54, H: 8.77, 8.69, N: 4.41, 4.42%.

[Y{ArN(CH₂)₃NAr}{N(SiMe₃)₂(THF)] 8. 5 (0.200 g, 0.266 mmol) and KN(SiMe₃)₂ (0.053 g, 0.266 mmol) were dissolved in toluene (50 mL, 0 °C). The resultant yellow suspension was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue dried *in vacuo* for 1 h. Pentane (40 mL) was added, and the suspension filtered to yield a clear, pale yellow solution. The solvent volume was reduced to 20 mL and the solution cooled to -45 °C to yield the product as colourless crystals (0.082 g, 0.115 mmol, 43%).

Characterising data for 8: ¹H NMR (d_6 -benzene): δ 7.00–7.30 (m, residual protons from d_6 -benzene, $C_6H_3(C_3H_7)_2$), 3.85 (m (br), 8H: 4H, THF; 2H, CH(CH₃)₂; 2H, NCH₂CH₂CH₂CH₂N), 3.47 (m (br), 4H: 2H, CH(CH₃)₂; 2H, NCH₂CH₂CH₂N), 2.31 (m (br), 2H, NCH₂CH₂CH₂N), 1.60, 1.50 and 1.32 (s (br) 24H, CH(CH₃)₂) 1.21 (m, 4H, THF), 0.04 (s, 18H, Si(CH₃)₂); ¹³C{¹H} (d_6 -benzene): δ 153.1, 145.2, 144.4, 144.0, 142.7, 124.0, 123.8, 123.5 ($C_6H_3(C_3H_7)_2$), 72.3 (THF), 59.8 (NCH₂CH₂-CH₂N), 34.6 (NCH₂CH₂CH₂N), 28.9, 28.3 (CH(CH₃)₂); 21.0, 24.5, 24.3 (CH(CH₃)₂), 25.1 (THF), 4.9 (N(SiMe_3)₂); elemental analysis: calc.: C: 62.24, H: 9.32, N: 5.88; found: C: 61.63, 61.82 H: 8.95, 8.98 N: 5.68, 5.72%.

[Y{ArN(CH₂)₃NAr}₂K(PhMe)] 9. YI₃ (0.250 g, 0.531 mmol) and 3 (0.500 g, 1.063 mmol) were slurried in 'BuOMe (50 mL, 0 °C). The resultant yellow–green suspension was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure from the pale yellow–grey suspension so-produced and the residue dried *in vacuo* at 40 °C for 1 h. Toluene (50 mL) was added and the suspension filtered to yield a clear, pale yellow solution. The solvent volume was reduced to 25 mL and the sample cooled to 4 °C to yield 9 as pale yellow crystals (0.150 g, 0.149 mmol, 28%). A directly analogous procedure carried out in THF yields **9** as pale yellow crystals (0.081 g, 0.08 mmol, 15%).

Characterising data for **9**: ¹H NMR (d_6 -benzene): δ 7.08, 6.89, 6.65 (m, $C_6H_3(C_3H_7)_2$, PhMe), 3.88 (s (br), 4H, CH-(CH₃)₂), 3.70 (s (br), 4H, $NCH_2CH_2CH_2N$), 3.47 (s (br), unidentified), 3.37 (sept, 4H, $CH(CH_3)_2$ 1), 3.01 (m, 6H, $NCH_2CH_2CH_2N$, NH 1), 2.62 (s, 2H, $NCH_2CH_2CH_2N$), 2.10 (s, PhMe), 1.75 (m, 2H, $NCH_2CH_2CH_2N$ 1), 1.24 (m, 48H, CH(CH₃)₂, CH(CH₃)₂ 1); ¹³C{¹H} (d_6 -benzene): δ 157.5, 146.2, 144.0, 142.7, 125.6, 124.4, 124.0, 123.8, 120.8 ($C_6H_3(C_3H_7)_2$, PhMe), 58.5 ($NCH_2CH_2CH_2N$), 50.8 ($NCH_2CH_2CH_2N$ 1), 36.1 ($NCH_2CH_2CH_2N$), 32.7 ($NCH_2CH_2CH_2N$ 1), 28.3 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$ 1), 24.7 ($CH(CH_3)_2$), 24.5 ($CH(CH_3)_2$ 1); elemental analysis: calc.: C: 72.87, H: 8.82, N: 5.57; found: C: 72.69, 72.62 H: 8.67, 8.73 N: 5.46, 5.42%.

[{Y{ArN(CH₂)₂NAr}I(THF)₂}₂] 10, [Y{ArN(CH₂)₂NAr}-{CH(SiMe₃)₂}(THF)] 11, [Y{ArN(CH₂)₂NAr}(CH₂C₆H₅)-(THF)₂] 12, [Y{ArN(CH₂)₂NAr}{N(SiMe₃)₂}(THF)] 13. Complexes 10, 11, 12 and 13 were prepared in analogous fashion to 5, 6, 7 and 8 respectively; full synthetic details can be found in the ESI.†

[{Y{ArN(CH₂)₂NAr}(μ -H)(THF)}₂] with trace amounts of [Y₃{ArNH(CH₂)₂NAr}₂{ArN(CH₂)₂NAr}(μ -H)₃(μ -H)₂(THF)] 14. 10 (0.200 g, 0.117 mmol) and KCH(SiMe₃)₂ (0.053 g, 0.260 mmol) were dissolved in toluene (40 mL, 0 °C). The resultant yellow suspension was stirred for 3 h at room temperature. The solvent was removed under reduced pressure from the resultant pale yellow suspension and the residue dried *in vacuo* for 1 h. Pentane (30 mL) was added, and the suspension filtered to yield a clear, pale yellow solution, which was repeatedly frozen, degassed and thawed before being exposed to an atmosphere of H₂ (1.5 bar, -210 °C) and stirred for 3 days at room temperature. The resultant pale, watery-green suspension was cooled to -45 °C overnight to yield 14 as a colourless microcrystalline solid (0.035 g, 0.0236 mmol, 9% yield), which co-crystallises with a small amount of 2.

Characterising data for 14: ¹H NMR (d_6 -benzene): ⁶³ δ 6.80– 7.45 (m, residual protons from d_6 -benzene, $C_6H_3(C_3H_7)_2$), 5.75 (t, ¹ $J_{YH} = 27$ Hz, YHY), 4.06 (sept, CH(CH₃)₂), 3.96 (s, N(CH₂)₂N)), 3.54 (s (br), THF), 3.40 (m, N(CH₂)₂N **2**, NH **2**), 3.07 (m, 0.7H, CH(CH₃)₂ **2**), 1.00–1.80 (m (br), THF, CH(CH₃)₂, other peaks), 0.53 (s (br), unassigned); ¹³C{¹H} NMR (d_6 -benzene): δ 155.5, 145.0, 144.2, 142.5, 124.3, 123.8, 123.3, 123.2, 122.4, 121.4, 120.8 ($C_6H_3(C_3H_7)_2$), 69.7 (THF), 60.5, 60.2 (N(CH₂)₂N), 34.2, 28.8 (unassigned, low intensity), 28.2, 27.8 (low intensity; CH(CH₃)₂), 25.9, 25.5 (CH(CH₃)₂), 14.0 (unassigned); ⁸⁹Y NMR (d_6 -benzene, 323 K): δ 453 (s (br)); elemental analysis: calc.: C: 66.47, H: 8.78, N: 5.67; found: C: 66.59, 66.71, H: 8.58, 8.64, N: 5.25, 5.42%.

[Y{ArN(CH₂)₂NAr}(OAr*)(THF)] (OAr* = OC_6H_2 -2,6^{-t}Bu₂-4-Me) 15. 10 (0.200 g, 0.117 mmol) and KOAr* (0.061 g, 0.234 mmol) were dissolved in toluene (40 mL, 0 °C). The resultant very pale yellow suspension was stirred overnight at room temperature. The solvent was removed under reduced pressure from the pale yellow suspension so-produced and the residue dried *in vacuo* for 2 h. Pentane (50 mL) was added, and the resultant pale yellow suspension filtered to yield a clear, pale yellow solution. The solvent volume was reduced to 10 mL and the solution was cooled to -45 °C to yield the product as colourless crystals (0.020 g, 0.026 mmol, 23% yield), which co-crystallises with approximately a quarter of an equivalent of 2.

Characterising data for 15: ¹H NMR (d_6 -benzene): δ 7.00– 7.30 (m, residual protons from d_6 -benzene, $C_6H_3(C_3H_7)_2$), 3.97 (m (br), 8H, $CH(CH_3)_2$, $N(CH_2)_2N$), 3.66 (s, 4H, THF), 3.44 (m, 2.1H, $CH(CH_3)_2$ **2**, NH **2**), 3.07 (m, 1.6H, $N(CH_2)_2N$ **2**), 2.23 (s, 3H, C₆H₂^tBu₂Me), 1.37 (d, 8.4H, CH(CH₃)₂ **2**), 1.29 (m, 72H, CH(CH₃)₂, C₆H₂^tBu₂Me), 1.17 (s, 4H, THF), ¹³C{¹H} NMR (d_{c} -benzene): δ 159.4, 152.8, 144.8, 143.8, 142.9, 137.0, 125.6, 124.5, 124.0, 123.4, 123.1 (C_{6} H₃(C₃H₇)₂, C_{6} H₂ 'Bu₂Me), 71.6 (THF), 58.8 (N(CH₂)₂N), 52.6 (N(CH₂)₂N **2**), 34.4, 31.0 (C_{6} H₂^tBu₂Me), 28.5 (CH(CH₃)₂), 28.1 (CH(CH₃)₂ **2**), 25.0 (CH(CH₃)₂), 25.8 (m, THF), 24.4, (CH(CH₃)₂ **2**); elemental analysis: calc.: C: 71.22, H: 9.16, N: 3.69; found: C: 70.93, 71.06, H: 9.36, 9.24, N: 3.49, 3.58%.

Reaction of 6 with phenylsilane (NMR scale)

Complex 6 (0.010 g, 0.014 mmol) and PhSiH₃ (3 μ L, 2.6 mg, 0.024 mmol) were added to d_6 -benzene (0.5 mL) to yield a watery yellow solution that was left at room temperature for seven days; ¹H NMR spectra taken at regular intervals, all of which indicated that no reaction had taken place. The colour did not change over the course of the week; no solid was deposited. The reaction mixture was heated to 70 °C for two days, during which time the colour darkened markedly, yielding a brown solution.

Characterising data: ¹H NMR: (d_6 -benzene): no diagnostic information; EI mass spectrometry (high resolution): calc. for [Si{ArN(CH₂)₃NAr}PhH]: m/z 498.343028, found: 498.339447 and calc. for {Si{CH(SiMe₃)₂}PhH₂}: 266.134236, Found: 266.134790.

Reaction of 11 with phenylsilane (NMR scale)

Complex 11 (0.010 g, 0.014 mmol) and PhSiH₃ (3 μ L, 2.6 mg, 0.024 mmol) were added to d_6 -benzene to yield a watery yellow solution, which was left at room temperature for three days; ¹H NMR spectra taken at regular intervals. The colour deepened markedly from a pale yellow to deep orange over the course of the reaction.

Reaction of 11 with phenylsilane (preparative scale)

Complex 11 (0.200 g, 0.117 mmol) and KCH(SiMe₃)₂ (0.046 g, 0.234 mmol) were dissolved in toluene (50 mL, 0 °C). The resultant pale yellow suspension was stirred for 3 h at room temperature, the solvent removed under reduced pressure and the residue dried *in vacuo* for 1 h. Pentane (50 mL) was added, and the suspension filtered to yield a clear, pale yellow solution. PhSiH₃ (3 μ L, 2.6 mg, 0.024 mmol) was added *via* microlitre syringe and the mixture allowed to stand at room temperature for 7 days, during which time the colour darkened markedly to deep orange and a very small amount of microcrystalline solid was deposited. The supernatant was separated from the solid, the volatiles removed under reduced pressure and the resultant orange oil dried *in vacuo*.

Characterising data for [Si{ArN(CH₂)₂NAr}PhH] **16**: ¹H NMR (d_6 -benzene): δ 7.65 (m, 2H, SiC₆ H_5), 7.00–7.15 (m, residual protons from d_6 -benzene, C₆ H_3 (C₃H₇)₂, SiC₆ H_5), 5.55 (s, 1H, SiH), 3.91, 3.78 (sept, 4H, CH(CH₃)₂), 3.68, 3.41 (m, 4H, N(CH₂)₂N), 0.73, 1.27, 1.37, 1.44 (d, 24H, CH(CH₃)₂); ¹³C{¹H} NMR (d_6 -benzene): δ 149.3, 148.6, 139.7, 136.1, 135.6, 130.6, 126.9, 124.4, 124.3 (SiC₆H₅, C₆H₃(C₃H₇)₂), 54.1 (N(CH₂)₂N), 28.7, 28.1 (CH(CH₃)₂), 25.8, 25.6, 25.0, 24.5 (CH(CH₃)₂); ²⁹Si DEPT NMR (d_6 -benzene): δ -16.95 (d, ¹J_{SIH} = 220.5 Hz); Accurate mass EI mass spectrometry: calc.: m/z484.327378, found: 484.328691.

Characterising data for mixture of $[Si{ArN(CH_2)_2NAr}-PhH]$ **16** and $\{Si{CH(SiMe_3)_2}PhH_2\}$: ¹H NMR (d_6 -benzene): all above peaks plus δ 7.55 (m, 1H, SiC₆H₅), 4.67 (d, 2H, ${}^3J_{HH} =$ 3.57 Hz, SiH₂), 0.12 (s, 18H, SiCH(SiMe_3)₂), -0.53 (t, ${}^3J_{HH} =$ 3.57 Hz, 1H, SiCH(SiMe_3)₂); ¹³C{¹H} NMR (d_6 -benzene): all above peaks plus δ 34.4, 22.7, 14.2, (unassigned) 1.8, 1.4 (SiCH(SiMe_3)₂), -2.4 (SiCH(SiMe_3)₂; ²⁹Si NMR (d_6 -benzene): above peak plus δ -34.75 (t, ${}^1J_{SiH} =$ 193.8 Hz); EI mass spectrometry: m/z 484 (37%, {Si{ArN(CH₂)_2NAr}PhH}⁺), 266 (10%, {Si{CH(SiMe_3)_2}PhH_2}⁺).

1-Hexene. In a typical experiment 10 µmol precatalyst and 30–40 µmol 1-hexene were dissolved in d_6 -benzene and the ¹H NMR spectra taken periodically to ascertain the extent of the reaction

Ethene. In a typical NMR-scale experiment a d_6 -benzene solution of 10 µmol precatalyst was repeatedly frozen, degassed and thawed before being exposed to an atmosphere of ethene (1.5 bar, 20 °C). ¹H NMR spectra were taken periodically to ascertain the extent of the reaction. In a typical preparativescale experiment a toluene solution (30 mL) of 25 µmol precatalyst was repeatedly frozen, degassed and thawed before being exposed to an atmosphere of ethene (1.5 bar, 20 °C) and stirred at room temperature.

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