

Synthesis and thermal reactivity of organoscandium and yttrium complexes of sterically less bulky salicylaldiminato ligands†

David J. H. Emslie, Warren E. Piers* and Masood Parvez

Department of Chemistry, University of Calgary, 2500 University Drive, N. W, Calgary, Alberta, Canada, T2N 1N4. E-mail: wpiers@ucalgary.ca; Fax: 403 289 9488; Tel: 403 220 5746

Received 18th March 2003, Accepted 30th April 2003
First published as an Advance Article on the web 14th May 2003

Scandium and yttrium bis(ligand) mono(alkyl) complexes, of N-phenyl (L^1) N-2-isopropylphenyl (L^2) and N-mesityl (L^3) substituted *ortho-tert*-butylsalicylaldiminato ligands were prepared by alkane elimination from $[M(CH_2SiMe_2R)_3(THF)_2]$ ($R = Me, Ph$) and two equivalents of proteo ligand (HL). The resulting $[L_2M(THF)_n(CH_2SiMe_2R)]$ ($n = 0-2$, $L = L^1$ (**1**), L^2 (**2**), L^3 (**3**)) complexes are thermally unstable, decomposing rapidly between -20 and 20 °C. In order to gain insight in to ligand features necessary to impart thermal stability in early transition metal organometallic chemistry, the decomposition pathways of **1-3** have been investigated and compared with more sterically congested N-2,6-diisopropylphenyl substituted analogues. Compounds **1** and **2** decompose rapidly and cleanly at room temperature by 1,3-migration of the entire CH_2SiMe_2R group to the aldimine carbon. By contrast, L^3 mono(alkyls) **3** decompose cleanly by metallation of an *ortho*- $C_6H_2Me_3$ group. In the case of yttrium, the metallated alkyl undergoes subsequent 1,3-migration to the aldimine carbon, forming a five-membered C_4N -ring.

Introduction

Organoscandium and yttrium chemistry has been dominated by the bent metallocene or Cp-amido ligand environments,¹ but recent years have seen a surge of interest in alternative ancillaries.² While there is a huge variety of ligands to choose from, steric tunability, resistance to ligand redistribution or metallation and stability in the presence of reactive M–C or M–H bonds are among the requirements for an effective ancillary for supporting organogroup 3 metal chemistry. Therefore, despite the efforts of many groups, truly effective non-cyclopentadienyl ligand environments for the development of the organometallic chemistry of group 3 metals and the lanthanides are still rare.³

The salicylaldiminato ligand framework has a long history as an ancillary ligand in coordination and organometallic chemistry. Recently, bulky derivatives have been employed in the preparation of nickel(II),⁴ chromium(III),⁵ titanium(IV)⁶ and zirconium(IV)⁷ olefin polymerization catalysts and these ligands are therefore promising candidates for supporting organogroup 3 metal derivatives. Using a bulky N-2,6-diisopropylphenyl substituted salicylaldiminato ligand (L^4 , Chart 1) we prepared a range of both di(alkyl) and mono(alkyl) complexes, the latter

of which are remarkably thermally robust, decomposing cleanly (130 °C, 3 days) by metallation of an isopropyl group, followed by rapid 1,3-migration of the newly formed alkyl to the aldimine carbon.⁸ Bochmann and co-workers have employed the mesityl substituted ligand L^3 , among others, to prepare similar bis and mono ligand alkyl compounds of Sc and Y.⁹

It is clear from both our and Bochmann's work that the nature of the N substituent of the salicylaldiminato ligand has a profound effect on the behaviour of the resulting organoscandium and yttrium complexes of general formula $LMR_2(THF)_n$ and $L_2MR(THF)_n$. Although these derivatives are not particularly useful as single-site olefin polymerization catalysts, they do have potential in the polymerization of ϵ -caprolactone⁹ and as catalyst precursors for the hydroamination of C=C and C≡C bonds.¹⁰ The mono-ligand $LMR_2(THF)_n$ family is prone to ligand redistribution reactions and therefore we have focussed on the bis-ligand derivatives $L_2MR(THF)_n$. While the complexes employing bulky ligand L^4 are quite thermally stable, less sterically imposing ligands would be expected to lead to more reactive compounds; here we report the preparation and thermal stability of the bis-ligand Sc and Y complexes of the ligands L^1 , L^2 and L^3 . Along with metallation/migration deactivation pathways, we identify direct migration of the metal alkyl function to the imine carbon as being a significant thermal reactivity mode.

Results and discussion

Synthesis and characterization of $[(L^n)_2M(CH_2SiMe_2R)(THF)_n]$ complexes

The method of choice for preparing these compounds is alkane elimination using $M(CH_2SiMe_2R)_3(THF)_2$ ($R = CH_3, Ph$) and HL^n . The cleanest reactions occur when $R = Ph$ due to the superior stability and easier purification of this tris-alkyl starting material; however, in some instances the alkane by-product Me_3SiPh is difficult to remove from the product during work-up. In this case, use of the $R = CH_3$ tris-alkyl is preferred, since Me_4Si is easily dealt with due to its volatility.

Bis-ligand mono-alkyl scandium and yttrium complexes of the small N-phenyl substituted ligand (L^1) were thus generated cleanly *in situ* from $[M(CH_2SiMe_2Ph)_3(THF)_2]$ and 2 HL^1 in d_8 -toluene at -20 °C (Scheme 1). The scandium complex

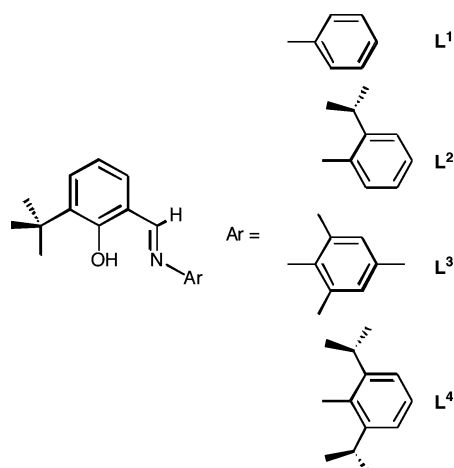
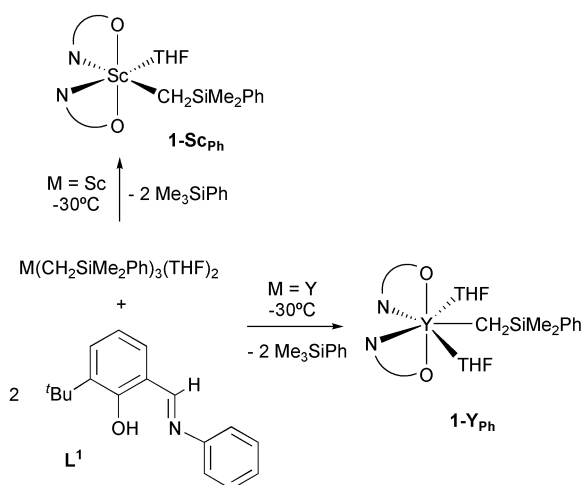


Chart 1

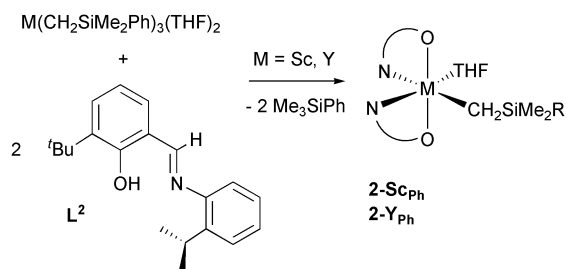
† Electronic supplementary information (ESI) available: Further experimental details. See <http://www.rsc.org/suppdata/dt/b3/b303097k/>



Scheme 1

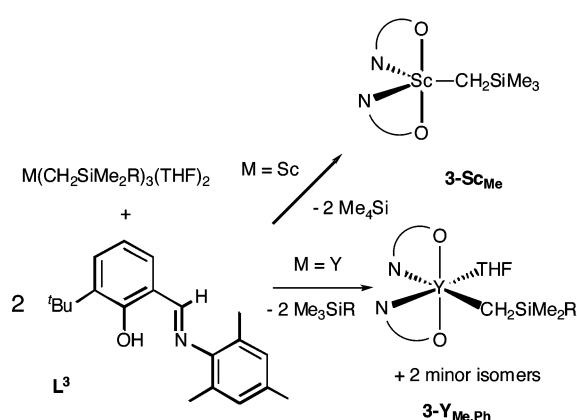
$[(L^1)_2Sc(CH_2SiMe_2Ph)(THF)]$ (**1-Sc_{Ph}**; the subscripted “Ph” in compound designations refers to the alkyl group substituent) shows inequivalent ligand environments by 1H and ^{13}C NMR at $-30^\circ C$, and is likely octahedral with *trans*-disposed phenoxy groups, and *cis* imines. This arrangement is also adopted by related trigonal bipyramidal complexes in order to minimise steric interactions between salicylaldiminato ligands.⁸ For the larger yttrium metal, the resulting complex $[(L^1)_2Y(CH_2SiMe_2Ph)(THF)_2]$ (**1-Y_{Ph}**) is seven coordinate with two THF ligands flanking the alkyl group. 1H NMR spectra of **1-Y_{Ph}** (-40 to $-80^\circ C$) show a single set of ligand and THF resonances, but diastereotopic YCH_2 and $SiMe_2Ph$ groups. These data are consistent with a single isomer, most likely of pentagonal bipyramidal geometry with the phenoxy groups occupying axial sites. Due to the thermal sensitivity of these compounds (*vide infra*), they were not isolated.

Reaction of $[M(CH_2SiMe_2Ph)_3(THF)_2]$ with two equivalents of the moderately more sterically encumbered HL^2 , incorporating an *ortho* isopropyl group, in *n*-hexane at or below $0^\circ C$ gave solutions of $[(L^2)_2M(CH_2SiMe_2Ph)(THF)]$ (**2-Sc_{Ph}**, **2-Y_{Ph}**, Scheme 2). While somewhat more thermally stable than the *N*-phenyl alkyls described above, concentration gave bright yellow oils for both compounds **2**, precluding satisfactory analytical data. However, their identity as mono-THF adducts of similar structure to **1-Sc_{Ph}** could be unambiguously assigned by 1H NMR in d_8 -toluene at $10^\circ C$. Thus, in the yttrium complexes, addition of each *N*-aryl isopropyl substituent prevents THF coordination, since the complexes of L^4 are THF free even for yttrium.



Scheme 2

Similar alkane elimination protocols lead to the *N*-mesityl substituted complexes $[(L^3)_2M(CH_2SiMe_2R)(THF)_n]$ ($M = Sc$, $R = Me$, $n = 0$, **3-Sc_{Me}**; $M = Y$, $R = Me$, Ph , $n = 1$ **3-Y_R**) which were isolated in good yield as yellow ($M = Sc$) or white ($M = Y$) solids (Scheme 3). Related mono(ligand), bis(alkyl) $[(L^3)_2M(CH_2SiMe_3)_2(THF)]$ ($M = Sc$, Y) complexes as well as $[(L^3)_3Y]$ were recently reported by Bochmann and co-workers.⁹ The scandium complex $[(L^3)_2Sc(CH_2SiMe_3)]$ (**3-Sc_{Me}**), which is stable for short periods of time in solution at room temperature,



Scheme 3

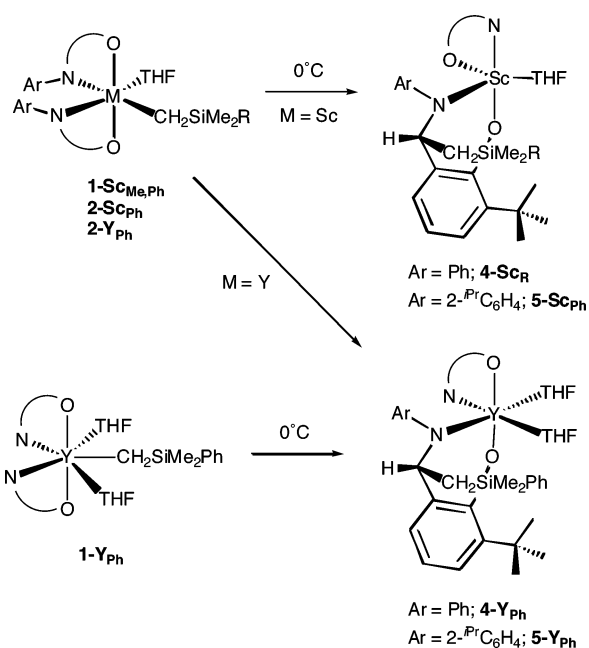
was isolated in 68% yield and characterised by elemental analysis and NMR spectroscopy. As with the *N*-2,6-diisopropylphenyl substituted analogue, $[(L^4)_2Sc(CH_2SiMe_3)]$,⁸ only a single isomer of **3-Sc_{Me}**, in which both salicylaldiminato ligands are equivalent, could be observed by NMR spectroscopy (-80 to $20^\circ C$). The O-donors likely occupy axial positions of a trigonal bipyramid, which is the preferred arrangement on the basis of steric and electronic factors.⁸

The yttrium complexes $[(L^3)_2Y(CH_2SiMe_2R)(THF)]$ (**3-Y_R**; $R = Me$, Ph) were prepared similarly but at $-20^\circ C$ due to lower thermal stability. The larger metal yttrium retains one molecule of THF, and d_8 -toluene solutions of **3-Y_R** clearly show the presence of three isomers at $-40^\circ C$; one major and two minor (96 : 2 : 2% for **3-Y_{Me}**, 92 : 6 : 2% for **3-Y_{Ph}**), which were investigated by 1H NMR, 2D-COSY and 2D-EXSY spectroscopy. All three isomers display a pair of resonances between -0.5 and -1.5 ppm for diastereotopic YCH_2 protons (dd, $^2J_{H,H}$ 12 Hz, $^2J_{H,Y}$ 2 Hz). The predominant species shows two $CH=NM$ s and six $C_6H_2Me_3$ signals due to inequivalent ligands which lack top-bottom symmetry, and is likely isostructural with **1-Sc_{Ph}**. Less information is available for the two minor isomers of **3-Y_R** since resonances other than the YCH_2 protons are obscured by those of the major isomer. We speculate that they are six-coordinate geometric isomers accessible *via* a transient five-coordinate intermediate. 2D-EXSY experiments show that the three isomers are in dynamic equilibrium, and since addition of 100 equivalents of d_8 -THF to solutions of **3-Y_{Me}** or **3-Y_{Ph}** did not change the ratio of isomers, none of the three solution species may be attributed to the five-coordinate, THF free complex.

Thermal reactivity of $[(L^n)_2M(CH_2SiMe_2R)(THF)_n]$ complexes

The alkyl compounds incorporating the less bulky ligands L^1 and L^2 decompose rapidly and cleanly at or below room temperature by 1,3-migration of the entire CH_2SiMe_2Ph group to the aldimine carbon (Scheme 4). For the least sterically protected *N*-Ph compounds, five-coordinate $[(L^1)-Sc\{('BuC_6H_3O)CH(CH_2SiMe_2Ph)NPh\}(THF)]$ (**4-Sc_{Ph}**) and octahedral $[(L^1)Y\{('BuC_6H_3O)CH(CH_2SiMe_2Ph)NPh\}(THF)_2]$ (**4-Y_{Ph}**) were obtained as analytically pure, brick-red solids from *in situ* generated toluene solutions of **1-M_{Ph}**. Both compounds are formed as a single diastereomer. The complexes were characterised by elemental analysis, NMR spectroscopy and in the case of **4-Y_{Ph}**, by X-ray crystallography. Additionally, the analogous scandium compound **4-Sc_{Me}**, formed by migration of a CH_2SiMe_3 group from *in situ* generated **1-Sc_{Me}**, was characterized crystallographically to show the structural features of compounds **4-Sc_R**.

In the solid state, the structure of **4-Sc_{Me}** (which contains three near identical molecules in the unit cell) is distorted trigonal bipyramidal, with the phenoxy group of the new amidoaryloxide ligand and the imine group of the intact



Scheme 4

salicylaldimine ligand in the axial sites (Fig. 1). In related $[(L^4)_2ScR]$ complexes,⁸ the axial positions are occupied by phenoxy groups, and the switch to an axial imine group in **4-Sc_{Me}** is most likely a result of the increased steric bulk and decreased planarity of the amidoaryloxide ligand relative to that of an intact salicylaldimine. In an effort to minimise steric interactions, the trigonal bipyramidal geometry of **4-Sc_{Me}** is quite distorted, with an angle of $165.20(8)^\circ$ between the two axial atoms (O12–Sc1–N11), and wedges as large as $142.49(7)^\circ$ (O13–Sc1–N12 between THF and the amido group) or as small as $101.33(7)^\circ$ (O11–Sc1–O13 between the phenoxy group of **L¹** and THF) in the equatorial plane. Similarly, the considerable

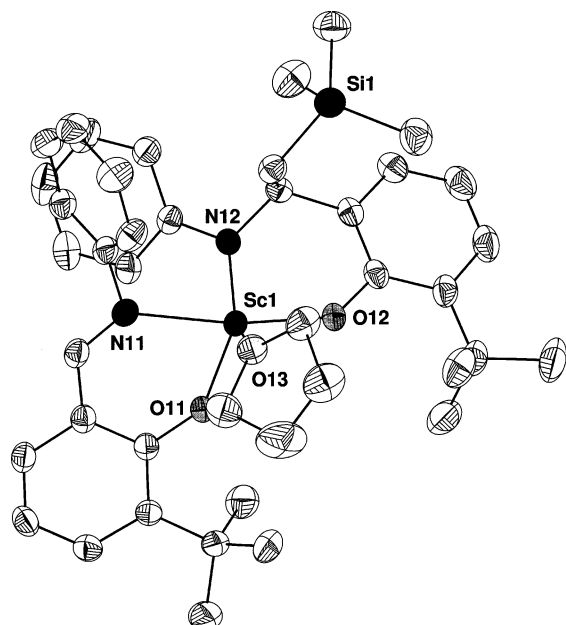


Fig. 1 Molecular structure of one of three very similar molecules of **4-Sc_{Me}** in the asymmetric unit (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles ($^\circ$) for the molecule shown: Sc(1)–O(11) 1.9549(16), Sc(1)–O(12) 1.9631(16), Sc(1)–N(12) 2.0798(19), Sc(1)–O(13) 2.2067(17), Sc(1)–N(11) 2.2880(19); O(12)–Sc(1)–N(11) $165.20(8)$, N(11)–Sc(1)–O(11) $82.28(7)$, N(11)–Sc(1)–N(12) $92.62(7)$, N(11)–Sc(1)–O(13) $83.24(7)$, O(12)–Sc(1)–O(11) $110.92(7)$, O(12)–Sc(1)–N(12) $87.78(7)$, O(12)–Sc(1)–O(13) $87.45(7)$, O(11)–Sc(1)–N(12) $115.08(7)$, N(12)–Sc(1)–O(13) $142.49(7)$, O(13)–Sc(1)–O(11) $101.33(7)$.

angle between the axial and equatorial phenoxy groups (O11–Sc1–O12 $110.92(7)^\circ$) arises in order to minimise steric interactions between *tert*-butyl groups.

1H - and ^{13}C NMR spectra of the six-coordinate yttrium complex, **4-Y_{Ph}**, show only one set of resonances for coordinated THF at room temperature. However, unlike **4-Sc_R** which exists as a single isomer in solution (-80 to $20^\circ C$), low-temperature 1H NMR spectra of **4-Y_{Ph}** are complicated by the presence of several isomers. Addition of d_8 -THF to solutions of **4-Y_{Ph}** in d_8 -toluene leads to the disappearance of signals for coordinated THF, indicating that the coordinated THF in **4-Y_{Ph}** is labile in solution. In the solid state, **4-Y_{Ph}** adopts a distorted octahedral geometry with the phenoxide groups *trans* to one another, and *cis*-disposed THF donors (Fig. 2).

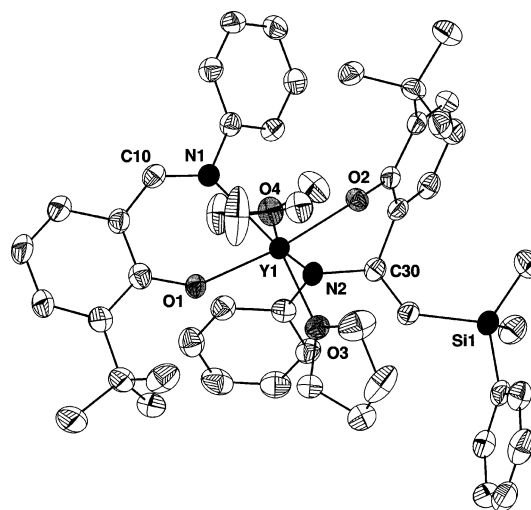


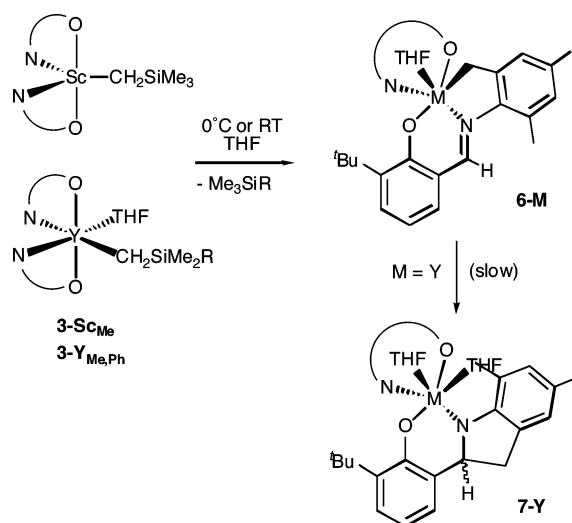
Fig. 2 Molecular structure of **4-Y_{Ph}** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles ($^\circ$): Y–O(1) 2.185(3), Y–O(2) 2.150(3), Y–O(3) 2.375(3), Y–O(4) 2.419(3), Y–N(1) 2.475(3), Y–N(2) 2.288(3), C(10)–N(1) 1.302(5), C(30)–N(2) 1.483(5); O(1)–Y–O(2) $167.91(11)$, O(3)–Y–N(1) $157.71(11)$, O(4)–Y–N(2) $164.16(11)$, O(1)–Y–N(1) $73.78(10)$, O(1)–Y–N(2) $109.99(11)$, O(1)–Y–O(3) $86.55(10)$, O(1)–Y–O(4) $85.64(10)$, O(2)–Y–N(1) $101.81(11)$, O(2)–Y–N(2) $81.70(11)$, O(2)–Y–O(3) $95.32(10)$, O(2)–Y–O(4) $82.86(10)$, N(1)–Y–N(2) $99.73(11)$, N(2)–Y–O(3) $96.75(11)$, O(3)–Y–O(4) $81.18(10)$, O(4)–Y–N(1) $86.86(11)$.

In an analogous fashion, the L^2 complexes **2-Sc_{Ph}** and **2-Y_{Ph}** decompose cleanly by nucleophilic attack of the entire CH_2SiMe_2Ph group on the aldimine carbon, albeit at a qualitatively slower rate than the L^1 derivatives (Scheme 4). The orange products, $[(L^2)M\{('BuC_6H_3O)CH(CH_2SiMe_2Ph)NC_6H_4^iPr-2\}-(THF)_n]$ ($M = Sc, 5-Sc_{Ph}, n = 1$ and $Y, 5-Y_{Ph}, n = 2$) are formed as a single diastereomer from *in situ* generated **2-M_{Ph}**, and were characterised by a range of 1D and 2D NMR spectroscopy. As with their precursors, the high solubility and tendency to form oils and retain solvent prevented isolation of **5-Sc_{Ph}** and **5-Y_{Ph}** as solids. The thermal instability of the **2-M_{Ph}** complexes lies in stark contrast to $[(L^4)_2M(CH_2SiMe_2Ph)]$ complexes⁸ which are indefinitely stable in toluene at $90^\circ C$, and decompose only after 3 days at $130^\circ C$ via metallation of one of the aryl isopropyl groups followed by 1,3-migration of the metallated carbon to the aldimine function. The superior thermal stability of the L^4 complexes highlight the importance of the 'N-2,6-dialkylaryl' motif in order to protect the aldimine carbon from intramolecular nucleophilic attack. Interestingly, during the course of this work, Bochmann and co-workers have reported $[(L^{Cy})_2-Y(CH_2SiMe_3)(THF)]$ ($L^{Cy} = N$ -cyclohexyl-*ortho-tert*-butyl-salicylaldiminato), which is stable in solution for several days at $60^\circ C$.⁹ The lack of alkyl group transfer in this compound may stem from the fact that this compound adopts a different geometry than the six- and seven-coordinate compounds **1** and **2**; the L^{Cy} complex contains equivalent ligand environments,

suggesting that the axial sites consist of the alkyl and THF ligands as indicated in the Bochmann paper.⁹

Thermal reactivity of $[(L^3)_2M(CH_2SiMe_2R)(THF)]$

In contrast to the L^1 and L^2 complexes, the L^3 mono(alkyls) $3-M_R$ decompose cleanly by metallation of an *ortho*- $C_6H_2Me_3$, rather than by a 1,3-migration of the alkyl group (CH_2SiMe_2R) to the aldimine carbon (Scheme 5). The products formed are Me_3SiR and bright-red $[(L^3)M\{('BuC_6H_3O)CH=NC_6H_2Me_2-CH_2\}(THF)]$ (**6-M**). The scandium compound was prepared from **3-Sc_{Ph}** at 25 °C in *n*-hexane (1 day), while **6-Y** was best prepared at 0 °C from *in situ* generated **3-Y_{Me}** in *n*-hexane (1 week). Both complexes give rise to five $C_6H_2Me_3$ or $C_6H_2Me_2-CH_2$ signals, two MCH_2 resonances and a single MCH_2 resonance in the 1H and ^{13}C NMR spectra at 25 °C. While decomposition of **3-Y_R** to **6-Y** is facile at 25 °C in hydrocarbon solution, this process is noticeably slower in the presence of excess THF, implying the intermediacy of five-coordinate, THF-free $[(L^3)_2Y(CH_2SiMe_2R)]$. Such a compound could not be detected in the NMR spectra of **3-Y_R**, but its existence is suggested by the equilibrium which exists between the three isomers of octahedral **3-Y_R** (*vide supra*).



Scheme 5

While **6-Sc** does not react further at room temperature, the newly formed alkyl group in **6-Y** undergoes 1,3-migration to the aldimine carbon, forming a C_4N -ring; brick-red $[(L^3)Y\{('BuC_6H_3O)CH=N-C_6H_2Me_2-CH_2\}(THF)_2]$ (**7-Y**) was isolated in reasonable yield as an approximate 3 : 1 mixture of diastereomers. This two-step process is related to the high-temperature decomposition of the L^4 scandium and yttrium compounds as described previously.⁸ The preference of L^3 for metallative rather than alkyl migratory decomposition pathways most likely stems from favourable formation of a five-membered metallacycle coupled with a more sterically protected aldimine carbon. Again, the presence of two *ortho*-substituents on the N-aryl moiety appears important in order to disfavor 1,3 transfer of the M-R group to the aldimine carbon prior to metallation.

Conclusions

Mono(alkyl) bis(ligand) complexes of scandium and yttrium have been prepared using three salicylaldiminato ligands of low to intermediate steric bulk. In contrast to previously reported N-2,6-diisopropylphenyl substituted analogues⁸ which are THF-free and indefinitely stable at 90 °C, compounds **1-3** retain 0–2 molecules of THF, and decompose at 0–25 °C. The N-phenyl and N-2-isopropylphenyl substituted compounds **1** and **2** decompose by 1,3-migration of the entire CH_2SiMe_2R

group to the aldimine carbon; both **4-Sc_{Me}** and **4-Y_{Ph}** have been studied by X-ray crystallography. By contrast, N-mesityl substituted compounds **3** decompose by metallation of an *ortho*- $C_6H_2Me_3$ group. In the case of yttrium, further chemistry ensues at room temperature; the newly formed alkyl group undergoes 1,3-migration to the aldimine carbon, forming a five-membered C_4N -ring. Similar reactivity is observed for the bulky N-2,6-diisopropylphenyl substituted analogue, which at 130 °C partakes in a related sequence of metallation followed by 1,3-migration, although in this case a six-membered C_5N ring is formed.⁸ The above study of thermal reactivity will aid in the design of future ligands for use in early transition metal organometallic chemistry.

Experimental

General procedures

These procedures have been described in detail elsewhere.^{8b} $ScCl_3(H_2O)_3$,¹¹ $YCl_3(THF)_3$,¹² $LiCH_2SiMe_2Ph$,^{8b} $[M(CH_2SiMe_2Ph)_3(THF)_2]$ ($M = Sc, Y$)^{8b} and *ortho-tert*-butylsalicylaldehyde¹³ were prepared by published methods. Anhydrous $ScCl_3(THF)_3$ was prepared from $ScCl_3(H_2O)_3$ and $SOCl_2$ in THF. Ligands HL^1 and HL^2 were prepared as described by Fujita and co-workers,⁷ while the preparation of HL^3 is described in the ESI.† Solutions of $[M(CH_2SiMe_2)_3(THF)_2]$ ($M = Sc, Y$) which are unstable above 0 °C, were prepared by a modification of the literature procedure (see experimental).¹⁴ Note: solid $[MCl_3(THF)_n]$ ($M = Sc, Y$) and $LiCH_2SiMe_2R$ ($R = Me, Ph$) start to react at room temperature (noticeable after ~30 s), so should be cooled to –78 °C very shortly after mixing. Elemental analyses were performed by Mrs Dorothy Fox or Ms Roxanna Simank of this department. A Fischer Scientific Ultrasonic FS-14 bath was used to sonicate reaction mixtures where indicated.

X-Ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on either a Rigaku AFC6S (University of Calgary) diffractometer.

CCDC reference numbers 206284 and 206285.

See <http://www.rsc.org/suppdata/dt/b3/b303097k/> for crystallographic data in CIF or other electronic format.

$[(L^1)_2Sc(CH_2SiMe_2Ph)(THF)]$ (**1-Sc_{Ph}**)

Generated *in situ*: A solution of HL^1 (16 mg, 62.8 μ mol) in d_8 -toluene (0.4 ml) was added to a solution of $[Sc(CH_2SiMe_2Ph)_3(THF)_2]$ (20 mg, 31.4 μ mol) in d_8 -toluene (0.2 ml) at –78 °C. The temperature was then raised to –20 °C for 1 h, which resulted in complete conversion to the product. 1H NMR (–30 °C, d_8 -toluene): δ 7.85 (d, 2H, J 7 Hz, Ph), 7.74, 7.63 {s, 2 \times 1H, $CH(NPh)$ }, 7.42–7.35 (m, 2H, Ph), 7.28–7.18 (m, 3H, Ph), 6.90–6.79 (m, 10H, Ph), 6.67–6.79 (m, 4H, Ph), 3.96, 3.79 (m, 2 \times 2H, coord. THF), 3.56 (m, 4H, free THF), 1.52, 1.35 (s, 2 \times 9H, CMe_3), 1.38 (br s, 4H, free THF), 1.18 (m, 4H, coord. THF), 0.37 (d, 1H, J 11 Hz, $ScCH_2$), 0.37, 0.34 (s, 2 \times 3H, $SiMe_2Ph$), 0.14 (d, 1H, J 11 Hz, $ScCH_2$). $^{13}C\{^1H\}$ NMR (–30 °C, d_8 -toluene): δ 170.88, 170.14 {s, $CH(NPh)$ }, 166.37, 164.76, 154.46, 152.62, 147.99, 140.31, 138.28, 123.97, 122.86 (s, 9 quaternary aromatic), 135.25, 134.37, 134.08, 133.34, 132.76, 128.79, 128.60, 127.51, 127.48, 126.14, 125.66, 123.33, 122.61, 115.79, 115.67 (s, 15 Ph), 71.51 (s, coord. THF), 67.86 (s, free THF), 35.35, 35.13 (s, 2 CMe_3), 29.63, 29.53 (s, 2 CMe_3), 29.53 ($ScCH_2$), 25.78 (s, free THF), 24.95 (coord. THF), 3.02, 2.73 (s, 2 $SiMe_2Ph$). Complexes $[(L^1)_2Y(CH_2SiMe_2Ph)(THF)]$ (**1-Y_{Ph}**), $[(L^2)_2Sc(CH_2SiMe_2Ph)(THF)]$ (**2-Sc_{Ph}**) and $[(L^2)_2Y(CH_2SiMe_2Ph)(THF)]$ (**2-Y_{Ph}**) were prepared similarly (see ESI†).

$[(L^3)_2Sc(CH_2SiMe_2Ph)]$ (**3-Sc_{Ph}**)

A solution of HL^3 (276 mg, 0.94 mmol) in *n*-hexane (4 ml) was added to $[Sc(CH_2SiMe_2Ph)_3(THF)_2]$ (300 mg, 0.47 mmol) in

n-hexane (20 ml) at -78°C . The mixture was then warmed to 0°C for 1 h, and the resulting orange solution evaporated to lower volume *in vacuo*. The slurry was sonicated, cooled to -78°C and filtered to collect a yellow solid. Yield 250 mg (68%). ^1H NMR (-20°C , d_8 -toluene): δ 7.67–7.64 (m, 2H, Ph), 7.62 {s, 2H, $\text{CH}(\text{NAr})$ }, 7.40 (dd, 2H, J 7, 2 Hz, Ph), 7.16–7.14 (m, 3H, Ph), 6.74 (s, 2H, Ph), 6.66 (dd, 2H, J 8, 2 Hz, Ph), 6.59 (t, 2H, J 8 Hz, Ph), 6.53 (s, 2H, Ph), 2.15 (s, 6H, $o\text{-C}_6\text{H}_2\text{Me}_3$), 2.14 (s, 6H, $o\text{-C}_6\text{H}_2\text{Me}_3$), 1.87 (s, 6H, $p\text{-C}_6\text{H}_2\text{Me}_3$), 1.18 (s, 18H, CMe_3), 1.07, 0.41 (d, $2 \times 1\text{H}$, $^2J_{\text{H,H}}$ 10 Hz, ScCH_2), 0.41, 0.25 (s, $2 \times 3\text{H}$, SiMe_2Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (-20°C , d_8 -toluene): δ 176.15 {s, $\text{CH}(\text{NAr})$ }, 167.30, 150.48, 146.48, 140.39, 135.79, 130.85, 130.55, 123.62 (s, 8 quaternary aromatic), 135.12, 134.98, 134.23, 130.67, 130.00, 128.12, 127.91, 117.08 (s, 8 Ph), 40.27 (weak s, ScCH_2) 35.53 (s, CMe_3), 30.23 (s, CMe_3), 21.18, 19.95 (s, $2 o\text{-C}_6\text{H}_2\text{Me}_3$), 19.66 (s, $p\text{-C}_6\text{H}_2\text{Me}_3$), 3.28, 2.94 (s, $2 \text{SiMe}_2\text{Ph}$). Anal. Calc. for $\text{C}_{49}\text{H}_{61}\text{N}_2\text{O}_2\text{SiSc}$: C, 75.16; H, 7.85; N, 3.58. Found: C, 75.20; H, 8.15; N, 3.54%. $[(\text{L}^3)_2\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ (**3-Y_{Me}**) and $[(\text{L}^3)_2\text{Y}(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{THF})]$ (**3-Y_{Ph}**) were prepared similarly from **HL³** and $[\text{Y}(\text{CH}_2\text{SiMe}_2\text{R})_3](\text{THF})_2$ in *n*-hexane at -20°C . Yields 69 and 75%, respectively (see ESI†).¹⁵

$[(\text{L}^1)\text{Sc}\{(\text{BuC}_6\text{H}_3\text{O})\text{CH}(\text{CH}_2\text{SiMe}_3)\text{NPh}\}(\text{THF})]$ **4-Sc_{Me}**

A mixture of $[\text{ScCl}_3(\text{THF})_3]$ (300 mg, 0.82 mmol) and $\text{LiCH}_2\text{SiMe}_3$ (231 mg, 2.45 mmol) in *n*-hexane (20 ml) was stirred for 2 h at 0°C and then filtered to give a colourless solution of $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$. After cooling to -78°C , a solution of **HL¹** (413 mg, 1.63 mmol) in *n*-hexane (4 ml) was added and the temperature raised to 0°C for 2 h and then RT for 16 h. The resulting bright red solution was evaporated to dryness *in vacuo* to give an oily red solid to which $\text{O}(\text{SiMe}_3)_2$ (10 ml) was added. The mixture was then sonicated and filtered to collect a brick-red solid which was washed with $\text{O}(\text{SiMe}_3)_2$ ($\times 2$) and dried *in vacuo*. Yield 303 mg (47%). Crystals of **4-Sc_{Me}** were grown by allowing a hot hexane solution of **4-Sc_{Me}** to cool to room temperature. ^1H NMR (C_6D_6): δ 7.90 {s, 1H, $\text{CH}(\text{NPh})$ }, 7.43 (dd, 1H, J 8, 2 Hz, Ph), 7.26 (dd, 1H, J 8, 2 Hz, Ph), 7.20–7.14 (m, 2H, Ph), 7.11 (dd, 1H, J 7, 1 Hz, Ph), 7.05–6.90 (m, 6H, Ph), 6.83 (d, 2H J 8 Hz, Ph), 6.71 (t, 1H, J 8 Hz, Ph), 6.70 (t, 1H, J 8 Hz, Ph), 6.62 (t, 1H, J 7 Hz, Ph), 4.66 (dd, 1H, $^3J_{\text{H,H}}$ 13, 3 Hz, CHCH_2), 3.58 (m, 4H, THF), 1.58 (s, 9H, CMe_3), 1.51 (dd, 1H, $^2J_{\text{H,H}}$ 12, $^3J_{\text{H,H}}$ 13 Hz, CHCH_2), 1.43 (s, 9H, CMe_3), 1.09 (dd, 1H, $^2J_{\text{H,H}}$ 12, $^3J_{\text{H,H}}$ 3 Hz, CHCH_2), 1.02 (m, 4H, THF), -0.07 (s, 9H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 171.03 {s, $\text{CH}(\text{NPh})$ }, 165.31, 161.72, 155.72, 151.58, 140.64, 137.39, 135.64, 124.10 (s, 8 quaternary aromatic), 134.84, 134.00, 129.97, 129.79, 127.82, 127.11, 125.64, 123.12, 117.94, 117.28, 114.90, 114.25 (s, 12 Ph), 71.68 (s, THF), 62.46 (s, CHCH_2), 35.68, 35.61 (s, 2CMe_3), 30.94, 29.94 (s, 2CMe_3), 26.01 (s, CHCH_2), 25.33 (s, THF), -0.65 (s, SiMe_3). Anal. Calc. for $\text{C}_{42}\text{H}_{55}\text{N}_2\text{O}_3\text{SiSc}\cdot\text{C}_3\text{H}_9\text{O}_{0.5}\text{Si}$: C, 68.40; H, 8.16; N, 3.54. Found: C, 68.06; H, 7.54; N, 3.79%. *Crystal data*: $\text{C}_{42}\text{H}_{55}\text{N}_2\text{O}_3\text{SiSc}$, $M = 708.93$, monoclinic, space group $P2_1/a$, $a = 16.67660(10)$, $b = 20.5525(2)$, $c = 35.7789(4)$ Å, $U = 12240.2(2)$ Å³, $T = 170(2)$ K, $Z = 12$, $\mu(\text{Mo-K}\alpha) = 0.25 \text{ mm}^{-1}$, 38126 reflections measured, 21153 unique ($R_{\text{int}} = 0.034$) which were used in calculations. The final $wR(F^2)$ was 0.119 (all data). $[(\text{L}^1)\text{Sc}\{(\text{BuC}_6\text{H}_3\text{O})\text{CH}(\text{CH}_2\text{SiMe}_2\text{Ph})\text{NPh}\}(\text{THF})]$, **4-Sc_{Ph}** and $[(\text{L}^1)\text{Y}\{(\text{BuC}_6\text{H}_3\text{O})\text{CH}(\text{CH}_2\text{SiMe}_2\text{Ph})\text{NPh}\}(\text{THF})_2]$, **4-Y_{Ph}**¹⁵ were prepared similarly in 84 and 62% yield, respectively (see ESI†). Crystals of **4-Y_{Ph}** $\cdot 0.5\text{C}_6\text{H}_5\text{Me}$ were grown by cooling a concentrated solution of **4-Y_{Ph}** in toluene to -35°C . *Crystal data*: $\text{C}_{51}\text{H}_{65}\text{N}_2\text{O}_4\text{SiY}\cdot\text{C}_{10}\text{H}_{12}$, $M = 1025.25$, monoclinic, space group $P2_1/c$, $a = 12.5136(2)$, $b = 24.7662(5)$, $c = 17.9392(4)$ Å, $U = 5556.23(19)$ Å³, $T = 170(2)$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.12 \text{ mm}^{-1}$, 18953 reflectons measured, 9653 unique ($R_{\text{int}} = 0.053$) which were used in calculations. The final $wR(F^2)$ was 0.153 (all data).

$[(\text{L}^2)\text{Sc}\{(\text{BuC}_6\text{H}_3\text{O})\text{CH}(\text{CH}_2\text{SiMe}_2\text{Ph})\text{NC}_6\text{H}_4\text{Pr-2}\}(\text{THF})]$, **5-Sc_{Ph}**

A solution of bright yellow $[(\text{L}^2)_2\text{Sc}(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{THF})]$ (**2-Sc_{Ph}**) in d_8 -toluene (0.6 ml) was generated as described above, and allowed to stand at room temperature for 5 days. The resulting orange solution of **5-Sc_{Ph}** was evaporated to dryness *in vacuo* to give a red–orange oil. The product was not isolated as a solid. ^1H NMR (C_6D_6): δ 7.83 {s, 1H, $\text{CH}(\text{NAr})$ }, 7.39 (m, 3H, Ph), 7.3–7.1 (m, 6H, Ph), 7.1–7.0 (m, 4H, Ph), 6.92 (d, 2H, J 7 Hz, Ph), 6.89 (td, 2H, J 8, 2 Hz, Ph), 6.63 (td, 2H, J 8, 2 Hz, Ph), 4.08 (dd, 1H, $^3J_{\text{H,H}}$ 12, 2 Hz, CHCH_2), 3.58 (s, 4H, THF), 3.14 (br septet, 2H, CHMe_2), 1.86 (dd, 1H, $^2J_{\text{H,H}}$ 13, $^3J_{\text{H,H}}$ 12 Hz, CHCH_2), 1.47, 1.26 (s, $2 \times 9\text{H}$, CMe_3), 1.32, 1.27, 1.16, 0.97 (d, $4 \times 3\text{H}$, J 7 Hz, CHMe_2), 1.38 (dd, 1H, $^2J_{\text{H,H}}$ 13, $^3J_{\text{H,H}}$ 2 Hz, CHCH_2), 1.04 (m, 4H, THF), -0.02 , -0.07 (s, $2 \times 3\text{H}$, SiMe_2Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 174.33 {s, $\text{CH}(\text{NAr})$ }, 166.92, 162.16, 153.80, 152.32, 141.01, 140.65, 140.04, 137.51, 137.09, 123.26, 121.15 (s, 11 quaternary aromatic), 134.88, 134.67, 134.01, 128.92, 128.69, 128.11, 127.70, 127.21, 127.09, 126.80, 126.75, 126.71, 125.96, 125.25, 116.95, 116.53 (s, 16 Ph), 71.79 (s, THF), 69.13 (s, CHCH_2), 35.80, 35.46 (s, 2CMe_3), 30.79, 29.91 (s, 2CMe_3), 29.11, 25.67, 25.62 (s, 3CHMe_2), 25.17 (s, THF), 24.71 (s, CHCH_2), -1.27 , -3.25 (s, $2 \text{SiMe}_2\text{Ph}$). $[(\text{L}^2)\text{Y}\{(\text{BuC}_6\text{H}_3\text{O})\text{CH}(\text{CH}_2\text{SiMe}_2\text{Ph})\text{NC}_6\text{H}_4\text{Pr-2}\}(\text{THF})_2]$, **5-Y_{Ph}** was prepared similarly (see ESI†).

$[(\text{L}^3)\text{Sc}\{(\text{BuC}_6\text{H}_3\text{O})\text{CH}=\text{NC}_6\text{H}_2\text{Me}_2\text{CH}_2\}(\text{THF})]$, **6-Sc**

A mixture of $[\text{ScCl}_3(\text{THF})_3]$ (300 mg, 0.82 mmol) and $\text{LiCH}_2\text{SiMe}_3$ (231 mg, 2.45 mmol) in *n*-hexane (20 ml) was stirred for 2 h at 0°C and then filtered to give a colourless solution of $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$. After cooling to -78°C , a solution of **HL³** (482 mg, 1.63 mmol) in *n*-hexane (4 ml) was added and the mixture stirred at room temperature for 14 h. The mixture was then cooled to -78°C and a flaky red solid collected by filtration and washed with cold *n*-hexane ($\times 1$). Yield 320 mg (56%). ^1H NMR (C_6D_6): δ 7.99, 7.62 {s, $2 \times 1\text{H}$, $\text{CH}(\text{NAr})$ }, 7.49 (dd, 1H, J 8, 2 Hz, Ph), 7.38 (dd, 1H, J 8, 2 Hz, Ph), 7.03 (dd, 1H, J 8, 2 Hz, Ph), 6.84 (s, 1H, $\text{C}_6\text{H}_2\text{Me}_3$), 6.82 (dd, 1H, J 8, 2 Hz, Ph), 6.71 (t, 1H, J 8 Hz, Ph), 6.64 (t, 1H, J 8 Hz, Ph), 6.47, 6.38, 6.30 (s, $3 \times 1\text{H}$, $\text{C}_6\text{H}_2\text{Me}_3$), 3.67 (m, 4H, THF), 2.22 (s, 3H, $\text{C}_6\text{H}_2\text{Me}_3$), 2.23, 2.17 (d, $2 \times 1\text{H}$, $^2J_{\text{H,H}}$ 12 Hz, ScCH_2), 2.07, 1.90 (s, $2 \times 3\text{H}$, $\text{C}_6\text{H}_2\text{Me}_3$), 1.88 (br s, 6H, $\text{C}_6\text{H}_2\text{Me}_3$), 1.63, 1.39 (s, $2 \times 9\text{H}$, CMe_3), 1.13 (m, 4H, THF). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 173.46, 164.66 {s, $2 \text{CH}(\text{NAr})$ }, 166.64, 163.69, 150.69, 148.75, 146.26, 139.85, 139.59, 135.62, 134.43, 130.85, 129.73, 126.60, 123.92, 123.80 (s, 14 quaternary aromatic), 134.76, 133.50, 132.83, 131.58, 129.51, 129.27, 127.48, 125.15, 116.70, 116.34 (s, 10 Ph), 70.75 (s, THF), 48.60 (weak s, ScCH_2), 35.74, 35.55 (s, 2CMe_3), 30.26, 30.15 (s, 2CMe_3), 25.40 (s, THF), 21.70, 21.26, 21.15 (s, $3 \text{C}_6\text{H}_2\text{Me}_3$), 19.37, 18.50 (br s, $2 \text{C}_6\text{H}_2\text{Me}_3$). Anal. Calc. for $\text{C}_{44}\text{H}_{55}\text{N}_2\text{O}_3\text{Sc}$: C, 74.97; H, 7.86; N, 3.97. Found: C, 75.26; H, 7.78; N, 3.92%.

$[(\text{L}^3)\text{Y}\{(\text{BuC}_6\text{H}_3\text{O})\text{CH}=\text{NC}_6\text{H}_2\text{Me}_2\text{CH}_2\}(\text{THF})]$, **6-Y**

A yellow slurry of $[(\text{L}^3)_2\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ (**3-Y_{Me}**) (160 mg, 0.19 mmol) in *n*-hexane (10 ml) was stirred for 1 week at 0°C . The resulting brick-red solution was evaporated to dryness *in vacuo*, dissolved in $\text{O}(\text{SiMe}_3)_2$ (10 ml), sonicated for 10–20 min until precipitation of a red solid, cooled to -45°C , and filtered to collect orange–red **6-Y**. Yield 71 mg (51%). ^1H NMR (d_8 -toluene): δ 8.02, 7.61 {s, $2 \times 1\text{H}$, $\text{CH}(\text{NAr})$ }, 7.44, 7.39, 7.05 (dd, $3 \times 1\text{H}$, J 8, 2 Hz, Ph), 6.79 (s, 1H, $\text{C}_6\text{H}_2\text{Me}_3$), 6.78 (dd, 1H, J 8, 2 Hz, Ph), 6.70, 6.58 (t, $2 \times 1\text{H}$, J 8 Hz, Ph), 6.43 (s, 2H, $\text{C}_6\text{H}_2\text{Me}_3$), 6.23 (s, 1H, $\text{C}_6\text{H}_2\text{Me}_3$), 3.62 (m, 4H, THF), 2.26 (s, 3H, $\text{C}_6\text{H}_2\text{Me}_3$), 2.13, 1.90 (s, $2 \times 3\text{H}$, $\text{C}_6\text{H}_2\text{Me}_3$), 1.86 (s, 6H, $\text{C}_6\text{H}_2\text{Me}_3$), 1.59, 1.45 (s, $2 \times 9\text{H}$, CMe_3), 1.18 (m, 4H, THF). YCH_2 signals not located. $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -toluene): δ 173.80, 165.54 {s, $2 \text{CH}(\text{NAr})$ }, 166.85, 163.85, 150.19, 148.03, 144.73,

139.71, 139.63, 134.78, 134.05, 129.60, 126.21, 123.40, 123.18 (s, 13 quaternary aromatic), 133.61, 133.19, 132.89, 130.84, 129.41, 125.95, 123.18, 116.03, 115.45 (s, 9 Ph), 70.25 (s, THF), 47.85 (d, $^1J_{\text{C,Y}}$ 32 Hz, YCH_2), 35.41, 35.37 (s, 2 CMe_3), 29.97, 29.90 (s, 2 CMe_3), 25.11 (s, THF), 21.45, 20.91, 20.70 (s, 3 $\text{C}_6\text{H}_2\text{Me}_3$), 18.55 (br s, 2 \times $\text{C}_6\text{H}_2\text{Me}_3$). Anal. Calc. for $\text{C}_{44}\text{H}_{55}\text{N}_2\text{O}_3\text{Y}$: C, 70.57; H, 7.40; N, 3.74. Found: C, 64.46; H, 6.91; N, 3.51%.¹⁵

$[(\text{L}^3)\text{Y}\{(\text{BuC}_6\text{H}_3\text{O})\text{CH}-\text{N}-\text{C}_6\text{H}_2\text{Me}_2-\text{CH}_2\}(\text{THF})_2]$, 7-Y

A solution of HL^3 (260 mg, 0.88 mmol) in *n*-hexane (4 ml) was added to $[\text{Y}(\text{CH}_2\text{SiMe}_2\text{Ph})_3(\text{THF})_2]$ (300 mg, 0.44 mmol) in *n*-hexane (20 ml) at -78°C . The solution was then stirred at 0°C for 2 h, and 25°C for 20 h before filtration and evacuation to dryness. The resulting orange-red oil was sonicated in $\text{O}(\text{SiMe}_3)_2$ (15 ml), cooled to -45°C , filtered, and washed with cold $\text{O}(\text{SiMe}_3)_2$ ($\times 2$) to leave an orange powder. Yield of 7-Y ($\sim 3:1$ mixture of diastereomers) 190 mg (52%). ^1H NMR (C_6D_6): δ 7.96 {s, 1H, major $\text{CH}(\text{NAr})$ }, 7.74 {s, 0.5H, minor $\text{CH}(\text{NAr})$ }, 7.50, 7.22, 7.08, 6.98 (d, $4 \times 1\text{H}$, J 8 Hz, major Ph), 7.48, 7.39, 7.18, 6.82 (d, $4 \times 0.5\text{H}$, J 8 Hz, minor Ph), 6.91 (s, 2H, major Ph), 6.91, 6.86 (t, $2 \times 0.5\text{H}$, J 8 Hz, minor Ph), 6.84, 6.60 (s, $2 \times 0.5\text{H}$, minor Ph), 6.83 (s, 1H, minor Ph), 6.83, 6.66 (t, $2 \times 1\text{H}$, J 8 Hz, major Ph), 6.72, 6.29 (s, $2 \times 1\text{H}$, major Ph), 4.37 (d, 1H, J 8 Hz, major CH), 4.21 (m, 1H, minor CH + minor CH_2), 3.66 (d, 1H, J 13 Hz, major CH_2), 3.59 (m, 12H, THF), 3.16 (dd, 1H, J 13, 8 Hz, major CH_2), 3.15 (0.5H, minor CH_2), 2.53 (br s, 6H, major $o\text{-C}_6\text{H}_2\text{Me}_3$), 2.23 (s, 3H, Me), 2.17 (s, 3H, Me), 2.04 (s, 4.5H, Me), 1.99 (s, 4.5H, Me), 1.71, 1.68 (s, $2 \times 4.5\text{H}$, minor CMe_3), 1.52 (s, 1.5H, minor Me), 1.52, 1.41 (s, $2 \times 9\text{H}$, major CMe_3), 1.20 (m, 12H, THF). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 174.49 {s, minor $\text{CH}(\text{NAr})$ }, 171.82 {s, major $\text{CH}(\text{NAr})$ }, 167.88, 163.67, 163.34, 155.69, 155.25, 151.64, 149.24, 139.85, 139.7, 137.96, 137.30, 136.84, 136.24, 135.35, 135.17, 135.09, 133.70, 127.53, 125.79, 123.82, 123.49 (s, 21 quaternary aromatic), 136.25 (minor), 136.16 (major), 133.56, 133.04 (major), 132.95 (minor), 130.64, 130.45, 129.5, 129.47 (major), 129.45 (minor), 128.00 (major), 126.60 (minor), 124.92 (minor), 124.21 (major), 115.89 (minor), 115.40 (major), 115.30 (minor), 115.24 (major) (s, 18 Ph), 75.21 (major CH), 74.58 (minor CH), 70.59 (s, THF), 48.69 (s, major CH_2), 40.02 (s, minor CH_2), 35.88, 35.81 (s, 2 minor CMe_3), 35.78, 35.66 (s, 2 major CMe_3), 30.95, 30.50 (s, 2 minor CMe_3), 30.63, 30.43 (s, 2 major CMe_3), 25.52 (s, THF), 23.38, 21.22, 21.21, 19.36 (s, 4 minor Me), 21.38, 21.05, 19.88(b), 19.22 (s, 4 major Me). Anal. Calc. for $\text{C}_{48}\text{H}_{63}\text{N}_2\text{O}_4\text{Y}$: C, 70.23; H, 7.74; N, 3.41. Found: C, 68.14; H, 7.68; N, 3.33%.¹⁵

Acknowledgements

This work was supported by NSERC in the form of a Discovery Grant and a Steacie Memorial Fellowship (2001-2003) to WEP. D. J. H. E. thanks the Alberta Ingenuity Fund for a Postdoctoral Associateship.

References

- W. E. Piers, P. J. Shapiro, E. E. Bunel and J. E. Bercaw, *Synlett*, 1990, 74-84; S. A. Cotton, *Polyhedron*, 1999, **18**, 1691; H. Butenschon, *Chem. Rev.*, 2000, **100**, 1527-1564; U. Siemeling, *Chem. Rev.*, 2000, **100**, 1495-1526; S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953-1976; G. A. Molander and J. A. C. Romero, *Chem. Rev.*, 2002, **102**, 2161-2185.
- W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233-234**, 131-155; F. T. Edlmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851-1896; N. Marques, A. Sella and J. Takats, *Chem. Rev.*, 2002, **102**, 2137-2159; Z. Hou and Y. Wakatsuki, *Coord. Chem. Rev.*, 2002, **231**, 1-22; X. Xie, *Coord. Chem. Rev.*, 2002, **231**, 23-46; V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283-316.
- P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood and W. Clegg, *Organometallics*, 2001, **20**, 2533-2544; L. K. Knight, W. E. Piers and R. McDonald, *Chem.-Eur. J.*, 2000, **6**, 4322-4326; L. W. M. Lee, W. E. Piers, M. R. J. Elsegood, W. Clegg and M. Parvez, *Organometallics*, 1999, **18**, 2947-2949; P. G. Hayes, W. E. Piers and R. McDonald, *J. Am. Chem. Soc.*, 2002, **124**, 2132-2133.
- C. M. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben and M. W. Day, *Organometallics*, 1998, **17**, 3149-3151.
- V. C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 1969-1971.
- J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojoh, N. Kashiwa and T. Fujita, *Angew. Chem., Int. Ed.*, 2001, **40**, 2918-2920; M. Mitani, J.-I. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S.-i. Kojoh, T. Matsugi, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327-3336; M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 7888-7889; P. D. Hustad, J. Tian and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 3614-3621; P. D. Hustad and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 11578-11579.
- S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsure, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847-6856.
- (a) D. J. H. Emslie, W. E. Piers and R. MacDonald, *J. Chem. Soc., Dalton Trans.*, 2002, 293-294; (b) D. J. H. Emslie, W. E. Piers, M. Parvez and R. MacDonald, *Organometallics*, 2002, **21**, 4226-4240.
- A. Lara-Sanchez, A. Rodriguez, D. L. Hughes, M. Schormann and M. Bochmann, *J. Organomet. Chem.*, 2002, **663**, 63-69.
- D. J. H. Emslie, H. A. Phillips, F. Lauterwasser, L. L. Schafer, W. E. Piers, unpublished results.
- Y. Hatakeyama, H. Kido, M. Harada, H. Tomiyasu and H. Fukutomi, *Inorg. Chem.*, 1988, **27**, 992-996.
- P. Sobota, H. Utiko and S. Szafert, *Inorg. Chem.*, 1994, **33**, 5203-5206.
- G. Casiraghi, G. Casnati, G. Puglia, G. Sartori and G. Terenghi, *J. Chem. Soc., Perkin Trans. I*, 1980, 1862-1865.
- M. F. Lappert and R. Pearce, *J. Chem. Soc., Chem. Commun.*, 1973, 126-127.
- Low% C elemental analyses for group 3 alkyls: G. C. Bazan, W. P. Schaefer and J. E. Bercaw, *Organometallics*, 1993, **12**, 2126-2130; J. Eppinger, M. Spiegler, W. Hieringer, W. A. Herrmann and R. Anwender, *J. Am. Chem. Soc.*, 2000, **122**, 3080-3096; P. W. Roesky, *Inorg. Chem.*, 1998, **37**, 4507-4511; D. M. Roitershtein, J. W. Ziller and W. J. Evans, *J. Am. Chem. Soc.*, 1998, **120**, 11342-11346.