Organometallic Complexes of Scandium and Yttrium Supported by a Bulky Salicylaldimine Ligand

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Organometallic derivatives of scandium and yttrium supported by a bulky salicylaldiminato ligand were prepared from the tris(alkyl) precursors $[M(CH_2SiMe_2R)_3(THF)_2]$ (M = Sc, **1-Sc$_R$**; M = Y, **1-Y$_R$**; R = CH_3, Ph) via alkane elimination. The new precursors **1-M$_{Ph}$** are convenient alternatives to the **1-M$_{Me}$** derivatives, due to their higher thermal stability and crystallinity; **1-Sc$_{Ph}$** has been characterized crystallographically. Reaction of these compounds with 1 equiv of protio ligand gives isolable mono(ligand) bis(alkyl) derivatives only for **1-Y**; for other derivatives **1-Sc**, mixtures were obtained. The products of the former reaction retain either two (**2-Y$_{Ph}$**) or one (**3-Y$_{Ph}$**) THF ligands; both of these compounds have been characterized crystallographically. In solution, both exhibit fluxional exchange between two geometric isomers which were characterized by variable-temperature NMR spectroscopy. Heating solutions of either compound leads to facile ligand redistribution. Reactions of tris(alkyls) **1** with 2 equiv of protio ligand gives the five-coordinate, THF-free bis(ligand) mono(alkyl) complexes **4-M$_R$**. These compounds are highly thermally stable, decomposing at temperatures above 140 °C via a pathway involving metalation of one of the N-aryl isopropyl methyl groups. The derivatives **4-Sc$_{Me}$** and **4-Y$_{Ph}$** have been structurally characterized, as well as the product of thermolysis of **4-Sc$_{Me}$**, the nonorganometallic four-coordinate complex **5-Sc**. Both **4-Sc$_{Me}$** and **4-Y$_{Ph}$** react slowly but cleanly with H_2. The former yields a product, **7-Sc**, derived from transfer of the in situ formed scandium hydride to the aldimine carbon of one of the ligands. The yttrium product, however, is the D_2-symmetric dimeric μ-hydride complex **6-Y**, characterized by spectroscopic and crystallographic methods. A survey of **6-Y**'s reactivity toward deuterated solvents, d_2-**6-Y**, ethylene, (trimethylsilyl)acetylene, $[HB(C_6F_5)_2]_2$, benzophenone, pyridine, and THF suggests that it does not dissociate into a monomeric hydride but reacts as a dimer. Nonetheless, products from the reactions of (trimethylsilyl)acetylene, $[HB(C_6F_5)_2]_2$, benzophenone, pyridine, and THF were isolated and characterized spectroscopically and, in the case of the product from the benzophenone reaction, crystallographically. Finally, reactions of mono(alkyls) **4-Sc$_{Me}$** and **4-Y$_{Ph}$** with a further 1 equiv of protio ligand gave nonorganometallic tris(ligand) coordination complexes, both of which were structurally and spectroscopically characterized. The scandium derivative **8-Sc** contained an O-bound κ^1-salicylaldiminato ligand, while for **8-Y**, containing the larger Y nucleus, all three ligands were chelating in the normal κ^2 bonding mode.

Introduction

While the early development of organoscandium and yttrium chemistry was dominated by the bis(cyclopentadienyl) bent-metallocene ligand environment,[1] recent years have seen a concerted effort by several groups to implement alternative ancillary ligand systems for organo group 3 metal chemistry.[2] In part, this stems from the fact that, although the metallocene framework is effective at stabilizing Lewis base free organometallic compounds, the two Cp donors use up two of the metal's three valences, limiting the number of more interesting reactive ligands to one. The development of suitable uninegative donors would allow for organometallic derivatives with two hydrocarbyl or hydrido ligands and expand the possibilities for new stoichiometric or catalytic chemistry at a group 3 metal center. The availability of well-defined group 3 complexes LMR_2 also provides an avenue into group 3 alkyl cations analogous to that for the group 4 metallocenium cations, which are so effective as olefin polymerization catalysts.[3] Thus, in addition to the opportunity to pose fundamental questions in the organometallic chemistry of the group

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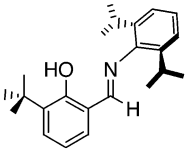
3 metals, there is also potential for breakthroughs on problems of considerable practical interest.

We have recently introduced the uninegative β-diketiminato ligand framework into organoscandium chemistry[4] and made significant inroads in the chemistry of organoscandium cations.[5] However, for reasons that are not yet entirely clear, we have been unable to enlist this ligand for use in analogous organoyttrium chemistry. In considering alternatives, we turned to a bulky salicylaldiminato ligand recently employed in nickel-based olefin polymerization catalysts by Grubbs et al.,[6] **I**. This general ligand family has also found recent



I

application in catalysts based on Cr(III)[7] and Ti(IV)[8] and in the Zr(IV)-based Mitsui catalysts.[9] Key design features of the specific ligand **I** include the ubiquitous 2,6-diisopropylaryl groups on the aldimine nitrogen to block space above and below the ligand plane and the bulky ortho *tert*-butyl group on the phenoxide portion of the ligand. The latter feature provides steric bulk which lies in the chelating plane of the ligand near the metal center.

Herein we describe the coordination chemistry of this ligand with both organoscandium and yttrium derivatives. While synthesis of a lanthanum salicylaldiminato complex has been described some time ago,[10] the compounds reported here are the first organometallic group 3 compounds supported by the salicylaldiminato ligand ancillary. We use an alkane elimination ligand attachment procedure and also describe some useful new scandium and yttrium tris(alkyl) derivatives for use as starting materials in such procedures. Part of this work has been communicated.[11]

Results and Discussion

Tris(alkyl) Complexes. Three main protocols exist for ligand attachment to group 3 metals: salt metathesis, alkane elimination,[12] and amine elimination.[13] Of these, alkane elimination conveniently provides organometallic derivatives directly and avoids the problems with salt occlusion that beset salt elimination routes. To date, the thermally unstable trialkyl complexes $[M(CH_2SiMe_3)_3(THF)_2]$[14] (M = Sc, **1-Sc$_{Me}$**; M = Y, **1-Y$_{Me}$**) are the most widely used starting materials for alkane elimination and are usually prepared in situ. However, use of more bulky CH_2SiMe_2Ph groups has allowed us to prepare the thermally more robust analogues $[M(CH_2SiMe_2Ph)_3(THF)_2]$ (M = Sc, **1-Sc$_{Ph}$**; M = Y, **1-Y$_{Ph}$**), which are isolable in excellent yields (Sc, 75%; Y, 87%) as crystalline solids. These tris(alkyls) are stable at 45 °C (24 h) in d_8-toluene, but after 24 h at 65 °C, decomposition resulted to give Me_3SiPh and an unidentified, insoluble brown precipitate.

These new tris(alkyl) complexes are amenable to large-scale synthesis (≥2 g) and may be stored indefinitely at −35 °C. Their availability allows for quick screening of reaction conditions via NMR-tube-scale experiments and for better control of reaction stoichiometry in preparatory-scale reactions. The $-CH_2SiMe_2Ph$ groups have also been found to impart higher stability to LMR_2 and L_2MR complexes and generally lead to lower solubility and increased crystallinity in the products. Disadvantages are that $LiCH_2SiMe_2Ph$ is not commercially available and the Me_3SiPh byproduct of alkane elimination reactions is less volatile than $SiMe_4$ (bp 170 vs 27 °C), although of similarly high solubility.

In toluene solution, complexes **1-M$_{Ph}$** exist as a single isomer (+40 to −80 °C) in which all three alkyl groups are equivalent, implying a trigonal-bipyramidal geometry with THF axially coordinated. The solid-state structure of the scandium complex **1-Sc$_{Me}$** is consistent with the solution data, showing a nearly regular trigonal bipyramid (O−Sc−O = 175.43(5)°, C(1)−Sc−C(10) = 119.23(8)°, C(10)−Sc−C(19) = 119.91(7)°, C(19)−Sc−C(1) = 120.86(8)°) with the equatorial alkyl groups arranged in a pinwheel array (Figure 1). The Sc−C bond lengths (2.248(2), 2.250(2), and 2.254(2) Å) are essentially identical and fall within the usual range for Sc−C bonds.,[4a,15−17] In contrast, the Sc−O bond lengths

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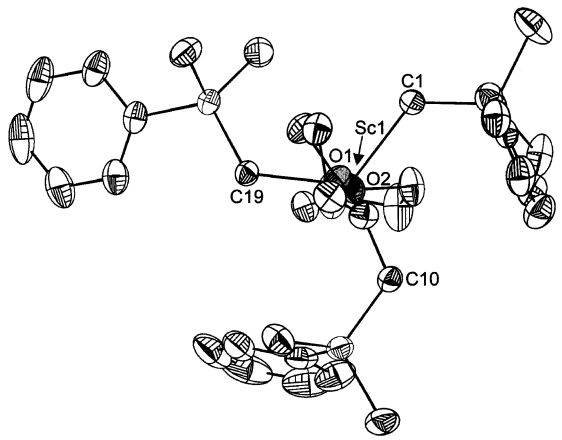


Figure 1. Molecular structure of **1-Sc$_{Ph}$** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Sc−C(1) = 2.248(2), Sc−C(10) = 2.254(2), Sc−C(19) = 2.2498(19), Sc−O(1) = 2.1966(14), Sc−O(2) = 2.2252-(14); O(1)−Sc-O(2) = 175.43(5), C(1)−Sc−C(10) = 119.23-(8) C(10)−Sc−C(19) = 119.91(7), C(19)−Sc−C(1) = 120.86-(8), O(1)−Sc−C(1) = 90.38(7), O(1)−Sc−C(10) = 90.68(7), O(1)−Sc−C(19) = 88.25(7), O(2)−Sc−C(1) = 90.80(7), O(2)−Sc−C(10) = 91.76(7), O(2)−Sc−C(19) = 87.19(6).

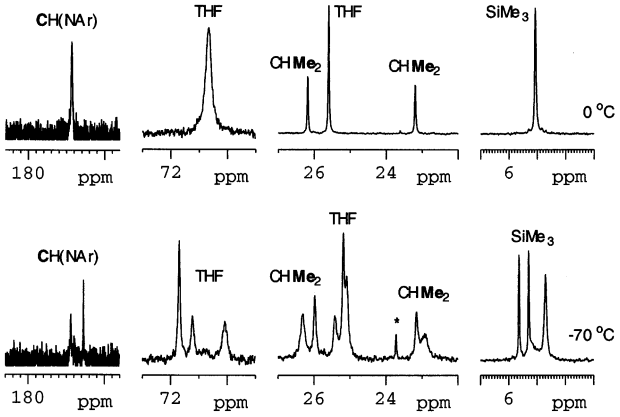
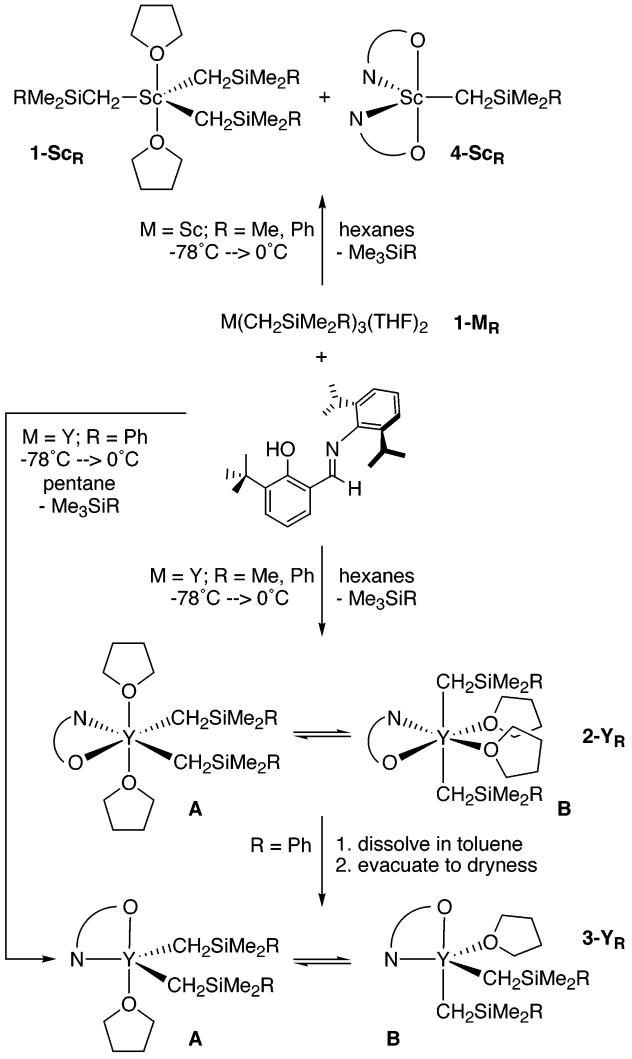


Figure 2. Selected regions of the 100 MHz ^{13}C NMR spectra of **2-Y$_{Ph}$** at 0 and −70 °C.

are different (Δ = 0.0244(14) Å) but fall within the range of reported Sc−O$_{THF}$ bond distances, 2.181(2)−2.228(5) Å.[4a,16,17]

Mono(ligand) Bis(alkyl) Complexes. Alkane elimination from the reactions of [Y(CH$_2$SiMe$_2$R)$_3$(THF)$_2$] (**1-Y$_R$**) with 1 equiv of the protio salicylaldimine ligand **I** proceeds in hexane at temperatures below 0 °C and results in precipitation of a pale yellow solid identified as the mono(ligand) bis(THF) stabilized dialkyl derivatives [LY(CH$_2$SiMe$_2$R)$_2$(THF)$_2$] (**2-Y$_R$**) (Scheme 1). The THF ligands in complex **2-Y$_{Ph}$** are more labile, and under slightly different reaction conditions the five-coordinate mono(THF) adduct [LY(CH$_2$SiMe$_2$Ph)$_2$(THF)]-(**3-Y$_{Ph}$**) was obtained. The complex **3-Y$_{Ph}$** was also formed by dissolution of **2-Y$_{Ph}$** in toluene, followed by evaporation to dryness; heating solid **2-Y$_{Ph}$** for 3 days at 40 °C under vacuum resulted in incomplete removal of THF (∼1.2 equiv remained) and some accompanying decomposition. The complexes **2-Y$_{Ph}$** and **3-Y$_{Ph}$** are thermally stable in solution at room temperature but undergo clean ligand redistribution upon heating to 60 °C to give the bis(ligand) complex [L$_2$Y(CH$_2$SiMe$_2$Ph)] (**4-Y$_{Ph}$**; see below), and Me$_3$SiPh (resulting from thermal decomposition of [Y(CH$_2$SiMe$_2$Ph)$_3$(THF)$_2$]), which were identified by ^{1}H NMR spectroscopy. The sterically less protected CH$_2$SiMe$_3$ complex **2-Y$_{Me}$** is not as stable and undergoes redistribution at room temperature.

Scheme 1



Attempts to form related mono(ligand) compounds of scandium by similar procedures gave mixtures containing mainly unreacted tris(alkyl) complex and bis(ligand) derivatives [L$_2$Sc(CH$_2$SiMe$_2$R)], along with small amounts of [LSc(CH$_2$SiMe$_2$R)$_2$(THF)$_x$]. The inaccessibility of bis-(alkyl) complexes of scandium with this donor is due either to rapid ligand redistribution or to competitive reaction of the mono(ligand) complex with a second equivalent of protio ligand **I**. This situation prevented isolation of the scandium dialkyls analogous to **3-Y$_R$**.

Due to the lability of the THF ligands, the six-coordinate organoyttrium complex **2-Y$_{Ph}$** shows time-averaged ^{1}H NMR spectra at 25−40 °C, but at lower temperatures the spectra resolve into a pattern consistent with the presence of two isomers in a 1:1 ratio. The low-temperature ^{13}C spectrum (Figure 2) clearly shows that, in one isomer, the two THF molecules are equivalent and the CH$_2$SiMe$_2$R groups are inequivalent (isomer **A**), while in the second isomer **B**, the situation is reversed. This is only consistent with the trans,cis isomers shown in Scheme 1, since any of the less

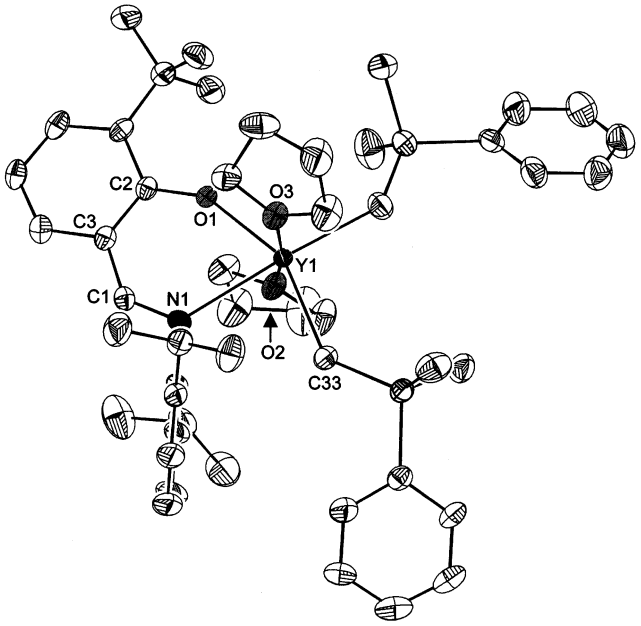


Figure 3. Molecular structure of **2-Y$_{Ph}$** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Y−C(24) = 2.430(6), Y−C(33) = 2.440(5), Y−O(1) = 2.166(3), Y−O(2) = 2.358(4), Y−O(3) = 2.363(4), Y−N(1) = 2.661(4); O(3)−Y−O(2) = 168.32(13), O(1)−Y−C(33) = 151.83(16), N(1)−Y−C(24) = 175.28(18), O(3)−Y−C(24) = 94.25(18), O(3)−Y−C(33) = 96.70(17), O(3)−Y−N(1) = 90.14(13), O(3)−Y−O(1) = 84.04(13), O(2)−Y−C(24) = 89.70(18), O(2)−Y−C(33) = 93.64(17), O(2)−Y−N(1) = 86.32(13), O(2)−Y−O(1) = 84.29(13), C(24)−Y−C(23) = 97.79(19), C(33)−Y−N(1) = 79.95(16), N(1)−Y−O(1) = 71.88(13), O(1)−Y−C(24) = 110.27(17).

symmetric cis,cis isomers would result in more complex spectra. Since both isomers are C_s symmetric, in the low-temperature ^{1}H NMR spectrum, each isomer gives rise to one C*H*Me$_2$ and two CH*Me*$_2$ signals. The solid-state structure of the cis-alkyl isomer of **2-Y$_{Ph}$** (isomer **A**, Figure 3) further supports this assignment. On the basis of the behavior of the mono(THF) compound **3-Y$_{Ph}$**, the interconversion of the isomers of six-coordinate **2-Y$_{Ph}$** most likely involves THF dissociation to transiently yield the fluxional five-coordinate compound.

Trigonal-bipyramidal **3-Y$_{Ph}$** also exists as a mixture of two isomers in solution, which are in rapid equilibrium at 0 °C but are in slow exchange at low temperature (Figure 4). Again, the CH_2SiMe_2Ph groups are inequivalent in one isomer and equivalent in the other. Of the possible trigonal-bipyramidal isomers, only **A** and **B** (Scheme 1) are likely, considering the preference of the salicylaldimine ligand to adopt bite angles of 70−80° and the preference for more electronegative donors to occupy axial sites of a trigonal bipyramid. Indeed, this assignment is supported by the solid-state structure of **3-Y$_{Ph}$**, isomer **A** (Figure 5).

In the structures of both **2-Y$_{Ph}$** and **3-Y$_{Ph}$**, the ligand bite angle is considerably less than 90° (71.88(13) and 73.89(5)°, respectively), resulting in distortion from ideal octahedral or trigonal-bipyramidal geometries. The Y−C bond lengths (2.440(5) and 2.30(6) Å for **2-Y$_{Ph}$** and 2.398(2) and 2.404(2) Å for **3-Y$_{Ph}$**) are similar to those of the previously reported dialkyl yttrium complexes.[18]

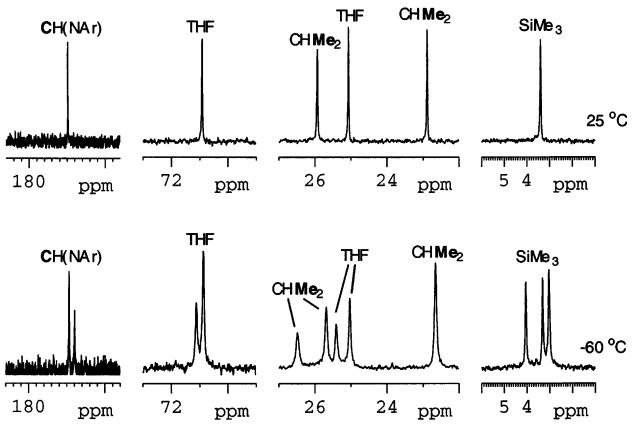


Figure 4. Selected regions of the 100 MHz ^{13}C NMR spectra of **3-Y$_{Ph}$** at 25 and −60 °C.

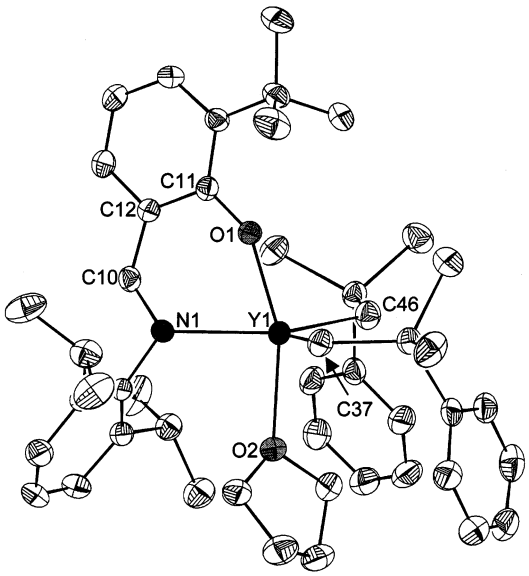


Figure 5. Molecular structure of **3-Y$_{Ph}$** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Y−C(24) = 2.404(2), Y−C(33) = 2.398(2), Y−O(1) = 2.1212(14), Y−O(2) = 2.3761(14), Y−N(1) = 2.4655(16); O(1)−Y−O(2) = 160.37(5), O(1)−Y−N(1) = 73.89(5), O(1)−Y−C(24) = 97.67(7), O(1)−Y−C(33) = 95.75(7), O(2)−Y−N(1) = 86.86(5), O(2)−Y−C(24) = 90.43(6), O(2)−Y−C(33) = 98.00(7), N(1)−Y−C(24) = 125.92(6), C(24)−Y−C(33) = 110.96(7), C(33)−Y−N(1) = 122.91(6).

Bis(ligand) Mono(alkyl) Complexes: Synthesis and Thermal Decomposition. Elimination of 2 equiv of Me_3SiR (R = Me, Ph) from **1-M$_R$** and **I** at room temperature gave the bright yellow, THF-free complexes [$L_2M(CH_2SiMe_2R)$] (M = Sc, R = Me, **4-Sc$_{Me}$**; M = Sc, R = Ph, **4-Sc$_{Ph}$**; M = Y, R = Ph, **4-Y$_{Ph}$**) in good yields (Scheme 2). The least sterically congested derivative combining CH_2SiMe_3 with yttrium could not be prepared in suitable purity due to competitive formation of the tris(ligand) complex [L_3Y], (**8-Y**, see below), even at low temperature. In contrast to the bis(alkyl) complexes **2-M$_R$** and **3-M$_R$**, there is no evidence for ligand

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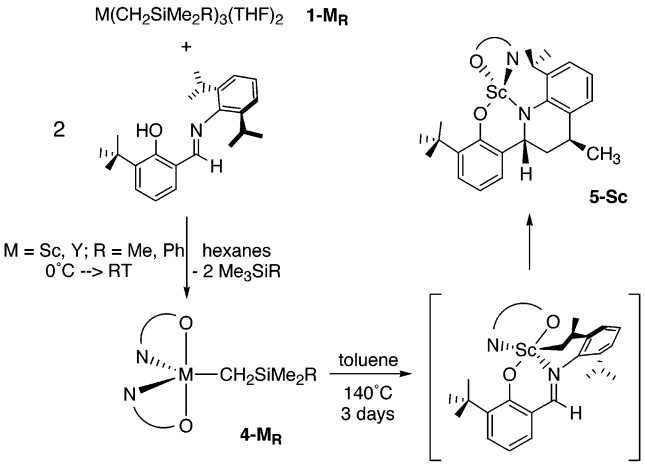
Scheme 2



redistribution processes stemming from the mono(alkyl) complexes **4-M$_R$**.

In solution, all three isolated [$L_2M(CH_2SiMe_2R)$] complexes exist as a single isomer (60 to −80 °C) in which both salicylaldimine ligands are equivalent. The geometry was established by the solid-state structures of both **4-Sc$_{Me}$** (Figure 6) and **4-Y$_{Ph}$**,[11] which are isostructural, although the yttrium complex is more distorted from ideal trigonal-bipyramidal geometry due to the decreased bite angle of the salicylaldimine ligand around the larger metal. Metrical data for the two complexes are given in Table 1. The M−N and M−O bond lengths are comparable to those of the related complexes, but the M−C bond lengths are at the shorter end of the scale for neutral group 3 mono(alkyl) complexes (Sc−C = 2.243(8)−2.271(7) Å[14−16,19] and Y−C = 2.35(1)−2.45(2) Å[18,20]), perhaps because of the relatively low coordination number in these compounds.

Complexes **4-M$_R$** are remarkably thermally stable in solution, decomposing slowly at 140 °C (total decomposition after 3 days). For scandium, this process occurs cleanly with loss of Me_3SiR to give the unusual brick red product **5-Sc** (Scheme 2), but for yttrium an analogous product, though detected in the ^{1}H NMR spectrum, undergoes further undefined chemistry. The ^{1}H NMR spectrum of **5-Sc** is consistent with a structure resulting from metalation of a ligand isopropyl methyl group to give the undetected intermediate shown in Scheme 2, followed by a 1,2-migration insertion of this newly formed alkyl group to the aldimine carbon. Connectivities were established using homodecoupling, 2D-COSY, and HMQC NMR experiments, and within the detection limits of ^{1}H NMR spectroscopy, the reaction is >97% diastereoselective, which is remarkable, as the product contains three stereocenters. An alternative decomposition pathway involving migration of the CH_2SiMe_2R group to the aldimine carbon was not observed for compounds **4-M$_R$**, even though this type of

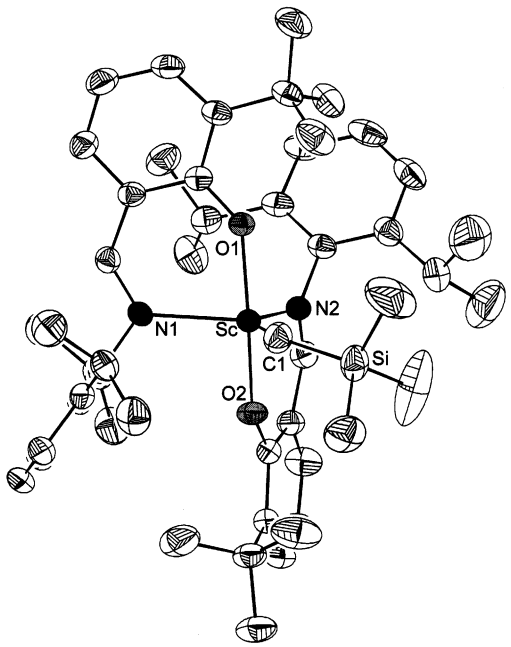


Figure 6. Molecular structure of **4-Sc$_{Me}$** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). See Table 1 for selected bond distances and angles.

reaction has precedence in organometallic complexes of aldimine based ligands.[21] Likely the two aryl isopropyl groups block the path of 1,2-migration insertion by protecting both faces of the imine C=N moiety (Figure 6).

Red crystals of **5-Sc** were characterized by X-ray crystallography (Figure 7). The structure exhibits distorted-tetrahedral geometry at scandium with one intact salicylaldimine ligand as well as the phenoxyamido ligand containing the newly formed C(40)−C(41) bond. The polycyclic nature of this ligand results in twisting of the isopropyl-substituted aryl group on N(2) directly toward O(1), distorting the O(1)−Sc−N(2) angle to 148.17(12)°. The relative stereochemistry in **5-Sc**, at Sc, C(40)),and C(42) is *RSR*/*SRS*.

Reactions of Compounds 4-M$_R$ with Hydrogen. The yttrium bis(ligand) complex **4-Y$_{Ph}$** reacts cleanly with H_2 (4 atm, 24 h, 25 °C) to give a 90% isolated yield of the bridging hydride dimer [$L_2Y(\mu\text{-}H)_2YL_2$] (**6-Y**; Scheme 3), which was characterized by both spectroscopy and X-ray crystallography. Complex **6-Y** is also formed, albeit less cleanly, from **4-Y$_{Ph}$** and H_3SiPh.[22]

In d_8-toluene solution, the dimeric nature of the hydride is demonstrated by the observation of a triplet at δ 7.54 ppm in the ^{1}H NMR spectrum ($^1J_{H,Y}$ = 32 Hz) for the bridging hydrides. The pattern of resonances for the ligands indicate that they are equivalent and the spectrum is invariant between +25 and −80 °C. Thus, complex **6-Y** exists as a single diastereomer, and although the NMR data are not able to distinguish

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4-Sc_{Me} and 4-Y_{Ph}

param	4-Sc_{Me}	4-Y_{Ph}	param	4-Sc_{Me}	4-Y_{Ph}
M−C(1)	2.196(2)	2.384(2)	O(1)−M−C(1)	97.34(7)	100.05(9)
M−O(1)	2.0013(13)	2.1473(13)	O(1)−M−N(1)	82.00(5)	77.30(5)
M−O(2)	2.0009(13)	2.1342(13)	O(1)−M−N(2)	88.47(5)	90.62(5)
M−N(1)	2.2450(15)	2.4238(16)	O(2)−M−C(1)	96.65(7)	99.23(7)
M−N(2)	2.3056(15)	2.4420(15)	O(2)−M−N(1)	96.11(6)	97.03(5)
O(1)−M−O(2)	165.90(5)	159.93(5)	O(2)−M−N(2)	79.96(5)	75.83(5)
C(1)−M−N(1)	105.01(5)	122.07(6)	M−C(1)−Si	132.94(12)	131.36(11)
C(1)−M−N(2)	137.60(7)	116.28(6)	N(1)−M−C(1)−Si	166.99(15)	17.54(18)
N(1)−M−N(2)	117.39(5)	121.58(5)	N(2)−M−C(1)−Si	−13.5(2)	−165.51(12)

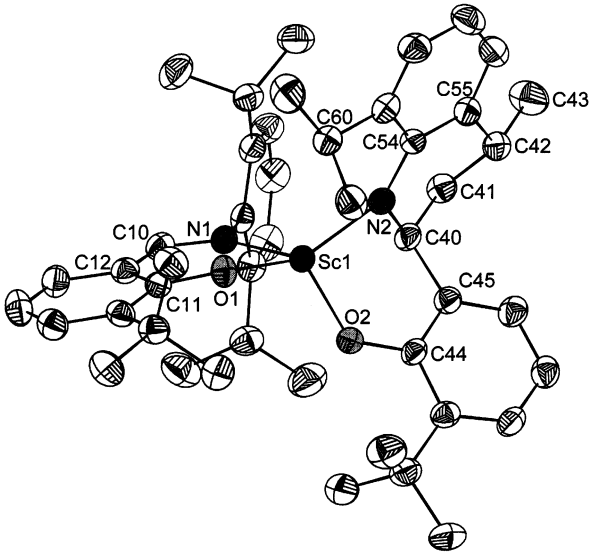
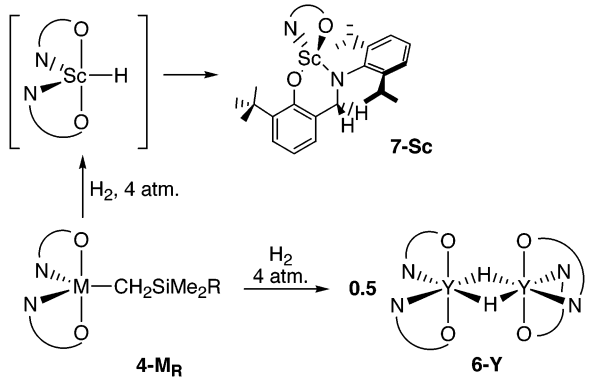


Figure 7. Molecular structure of **5-Sc** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Sc−O(1) = 1.985(3), Sc−O(2) = 1.920(3), Sc−N(1) = 2.204(3), Sc−N(2) = 2.0303(3), C(10)−N(1) = 1.293(5), C(40)−N(2) = 1.506(5), C(54)−N(2) = 1.391(5); O(1)−Sc−N(1) = 83.11(11), O(2)−Sc−N(2) = 92.48(12), O(1)−Sc−O(2) = 112.98(12), N(1)−Sc−N(2) = 105.50(13), O(1)−Sc−N(2) = 148.17(12), O(2)−Sc−N(1) = 112.05(12), N(1)−Sc−O(1)−C(11) = 20.2(4), Sc−O(1)−C(11)−C(12) = −22.1(5), O(1)−C(11)−C(12)−C(10) = 4.3(5), C(11)−C(12)−C(10)−N(1) = 7.2(9), C(12)−C(10)−N(1)−Sc = −3.8(6), C(10)−N(1)−Sc−O(1) = −5.9(3), N(2)−Sc−O(2)−C(44) = 1.5(3), Sc−O(2)−C(44)−C(45) = −22.0(5), O(2)−C(44)−C(45)−C(40) = −4.7(5), C(44)−C(45)−C(40)−N(2) = 60.6(5), C(45)−C(40)−N(2)−Sc = −76.5(3), C(40)−N(2)−Sc−O(2) = 41.7(2), C(54)−N(2)−C(40)−C(41) = −26.0(5), N(2)−C(40)−C(41)−C(42) = 53.6(4), C(40)−C(41)−C(42)−C(55) = −53.(4), C(41)−C(42)−C(55)−C(54) = 27.9(5), C(42)−C(55)−C(54)−N(2) = −1.6(6), C(55)−C(54)−N(2)−C(40) = 0.3(5).

between the D_2-symmetric *rac* and the C_{2h} *meso* isomer, the *rac* isomer is most likely favored on steric grounds. Exclusive dimerization of monomers with the same stereochemistry has been reported previously.[23] This assignment is supported by the X-ray crystal structure (Figure 8), which is a rare example of a structurally characterized non-cyclopentadienyl yttrium hydride.[22a,24] As shown in the view given in Figure 8b, the two O−Y−O vectors are rotated relative to each other by approximately 30−40° (O(3)−Y(2)−Y(1)−O(2) = 40.48(8)°; O(4)−Y(2)−Y(1)−O(1) = 29.95(8)°) in order to minimize unfavorable steric interactions between the opposing ligand ^{i}Pr and ^{t}Bu groups, which extend into the shared space above and below the bridging hydrides.

Scheme 3



The bridging hydrides were located from the difference map and were refined with isotropic thermal parameters. The Y−H distances of 2.11(3), 2.16(2), 2.25(3), and 2.17(3) Å are similar to those of other structurally characterized yttrium hydride complexes, the data for which are collected in Table 2. While all the yttrium hydrides listed in Table 2 are dimeric in the solid state, in solution, monomeric hydrides are accessible via dissociative cleavage of the dimer in some instances. For example, a monomer/dimer equilibrium has recently been investigated by Casey et al. using NMR line-broadening techniques and by mixing solutions of $[Cp^*_2Y(\mu\text{-H})]_2$ and $[Cp^*_2Y(\mu\text{-D})]_2$ at low temperature to observe the formation of $[Cp^*_2Y]_2(\mu\text{-H})(\mu\text{-D})$.[25] While this is the only hydride dimer for which quantitative information concerning dissociation is available, qualitative evidence for dissociation equilibria in other systems is apparent in H/D exchange phenomena (Table 2). Most Cp-donor-containing hydrides appear to undergo dissociation to some extent. In contrast, complex **6-Y** exhibits no evidence for dissociation under any conditions studied. In the ^{1}H NMR spectrum, a triplet is observed for the μ-H groups from 25 to −80 °C. Furthermore, when the bridging deuteride $[L_2Y(\mu\text{-D})]_2$ (d_2-**6-Y**) was synthesized and mixed with protio **6-Y** (1:1, C_6D_6 or C_7D_8), no formation of the $[L_2Y]_2(\mu\text{-H})(\mu\text{-D})$ isotopomer (*d*-**6-Y**) was observed even after 2 days at room temperature. The absence of any *d*-**6-Y** implies that dissociation into monomer is not kinetically significant in this system and that any reactivity of **6-Y** must occur through the dimer. In keeping with these

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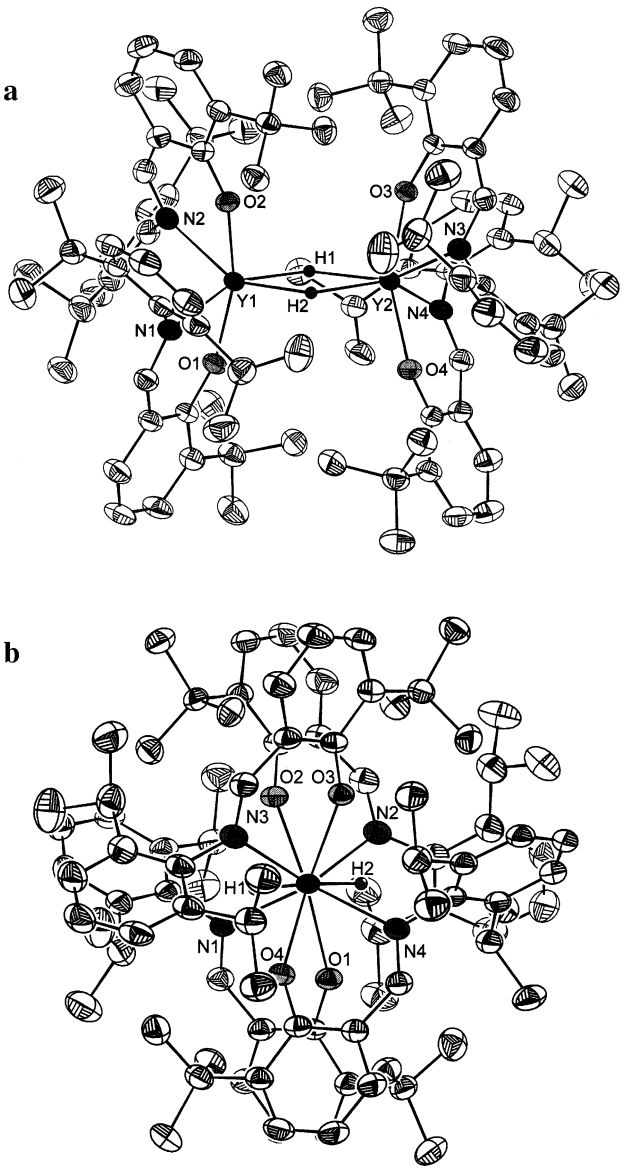

Figure 8. Two views of the molecular structure of **6-Y**·2(toluene) (toluene and hydrogen atoms other than H(1) and H(2) omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Y(1)−H(1) = 2.108(28), Y(1)−H(2) = 2.162(23), Y(2)−H(1) = 2.245(33), Y(2)−H(2) = 2.165(28), Y(1)···Y(2) = 3.634(1), H(1)···H(2) = 2.372(48), Y(1)−O(1) = 2.1511(19), Y(1)−O(2) = 2.1333(19), Y(2)−O(3) = 2.1468(19), Y(2)−O(4) = 2.1530(19), Y(1)−N(1) = 2.508(2), Y(1)−N(2) = 2.543(3), Y(2)−N(3) = 2.556(3), Y(2)−N(4) = 2.501(2); H(1)−Y(1)−H(2) = 67.49(118), H(1)−Y(2)−H(2) = 65.06(115), O(1)−Y(1)−O(2) = 162.75(8), N(1)−Y(1)−H(2) = 155.09(80), N(2)−Y(1)−H(1) = 151.16(84), O(3)−Y(2)−O(4) = 156.68(8), N(3)−Y(2)−H(2) = 152.72(82), N(4)−Y(2)−H(1) = 142.72(75), O(1)−Y(1)−Y(2)−O(4) = 29.95(8), O(2)−Y(1)−Y(2)−O(3) = 40.48(8), N(1)−Y(1)−Y(2)−N(3) = 55.8(1), N(2)−Y(1)−Y(2)−N(4) = 65.66(10).

observations, **6-Y** does not undergo H/D exchange via σ bond metathesis with deuterated NMR solvents either, as is often observed in the metallocene systems which dissociate readily into monomers.[24,25] In this regard, **6-Y** exhibits behavior similar to that of the related benzamidinato group 3 hydrides $[\{(PhC(NSiMe_3)_2)_2M(\mu\text{-}H)\}_2]$ (M = Sc,[26] Y[24]), which also do not undergo the H/D scrambling reactions in deuterated solvents. It has been suggested that the reactivity patterns of these benzamidinato complexes is a result of more ionic metal−ligand bonding, which contracts the orbitals at the electropositive metal centers. More polarized M−H bonds result in robust dimers for these compounds. This is reflected in the much lower field chemical shifts seen for the benzamidinato and the salicylaldiminato hydrides in comparison to those hydrides more susceptible to dissociation (Table 2). Likely, in the present salicylaldiminato complexes, the metal−ligand bonding also has a strong ionic component. The apparently high steric price paid by dimerization in this bis(salicylaldiminato) ligand environment and the observed lack of dissociation into monomeric hydrides in solution is difficult to reconcile but speaks to the high tendency of the polarized Y−H moiety to stabilize itself through dimerization.

Unlike the yttrium alkyls, the reactions of compounds **4-Sc$_R$** with H_2 (4 atm, 24 h, 25 °C) do not yield an isolable scandium hydride; rather, a product derived from a 1,3-migration of an incipient hydride to the aldimine carbon of the ligand is observed (Scheme 3). Evidently, for scandium, the smaller ionic radius precludes dimerization. However, the N-aryl isopropyl groups, while sufficient to block migration of a bulky alkyl group (vide supra), are not capable of preventing 1,3-hydride migration. In the solid state, **7-Sc** adopts a tetrahedral geometry (Figure 9) with similar Sc−O bond lengths of 1.9683(11) Å for the monoanionic ligand and 1.9475(11) Å for the dianionic ligand, while the Sc−N_{imine} and Sc−N_{amido} bond lengths of 2.1990(13) and 2.0108(13) Å, respectively, are quite different. This latter bond length is similar to those in other scandium amido complexes such as $[ScCl_2(THF)_2\{N(SiMe_3)_2\}]$, which has an Sc−$N_{amido}$ distance of 2.039(2) Å.[27]

Reactivity Survey of 6-Y. There are variations in the reactivity of group 3 and lanthanide μ-hydride complexes, which depend on the availability of monomeric hydride species, the presence or absence of coordinated solvent, and the steric bulk at the metal center. For example, $[Cp^*_2Y(\mu\text{-}H)]_2$,[22e] [*rac*-($C_5H_2$-2-$SiMe_3$-4-$CMe_3$)$_2$$SiMe_2$)$Y(\mu\text{-}H)]_2$,[28] and [*rac*-(BnBp)$Y(\mu\text{-}H)]_2$ (BnBp = (C_5H_2-2-$SiMe_3$-4-CMe_3)$_2$$Si(OC_{10}H_6)_2$)[23a] are active toward olefin polymerization, while $[(PhC(NSiMe_3)_2)_2Y(\mu\text{-}H)]_2$[24,29] and $[(Me_2Si(N^tBu)(O^tBu))_2Y(\mu\text{-}H)]_2$[30] show little or no activity. This qualitatively correlates with the H/D exchange reactivity discussed above, suggesting that for ethylene polymerization efficacy, dissociation into monomer is required. However, irrespective of olefin polymerization activity, most yttrium hydride complexes undergo hydroyttration chemistry with small molecules such as alkynes, carbonyl functions, and pyridines. The reactivity in this connection for **6-Y** is summarized in Scheme 4, and these observations are qualitatively consistent with the notion that the compound reacts as a dimer, rather than by

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Table 2. Comparison of Structurally Characterized Dimeric Yttrium Hydride Complexes

complex	Y−H bond lengths (Å)	δ(Y−H)[a]	dissoc	ref
6-Y	2.11(3), 2.16(2), 2.25(3), 2.17(3)	7.54	no	
[{PhC(NSiMe$_3$)$_2$}Y(μ-H)}$_2$]	2.19(3), 2.17(3), 2.11(3), 2.16(3)	8.28	no	23
[{(NN)Y(thf)(μ-H)}$_2$][b]	2.22(4), 2.27(4)	5.88	yes	22a
[{(BnBp)$_2$Y(μ-H)}$_2$][c]	2.235(2), 2.097(2), 2.4(1), 2.0(1)	5.97	yes	24a
[{(C$_5$H$_4$Me)$_2$Y(thf)(μ-H)}$_2$]	2.17(8), 2.19(8)	2.02		43b
[{(Me$_4$C$_5$SiMe$_2$N^{t}Bu)Y(thf)(μ-H)}$_2$]	2.48(4), 1.98(6), 2.39(4), 2.31(6)	5.50	yes	20a, 43c
[{(2,4,7-Me$_3$C$_9$H$_4$)$_2$Y(μ-H)}$_2$]	2.12(6), 2.09(4), 2.12(4), 2.14(7)	2.69	yes	43d
[{(C$_5$H$_3$Me$_2$)$_2$Y(thf)(μ-H)}$_2$]	2.27(6), 2.03(7)	2.82		43e
[{(C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$Y(μ-H)}$_2$][d]	2.02(6), 2.07(6) & 2.04(6), 2.15(6)	1.86		43f
[Cp*$_2$Y(μ-H)(μ-CH$_2$C$_5$Me$_4$)YCp*]	2.10(7), 2.14(7)	5.35[e]	yes	43g

[a] In ppm. [b] NN = bis(silylamido)biphenyl. [c] BnBp = (C$_5$H$_2$-2-SiMe$_3$-4-CMe$_3$)$_2$Si(OC$_{10}$H$_6$)$_2$. [d] Two crystallographically independent molecules in the unit cell. [e] Data given is for [Cp*$_2$Y(μ-H)]$_2$, taken from ref 25.

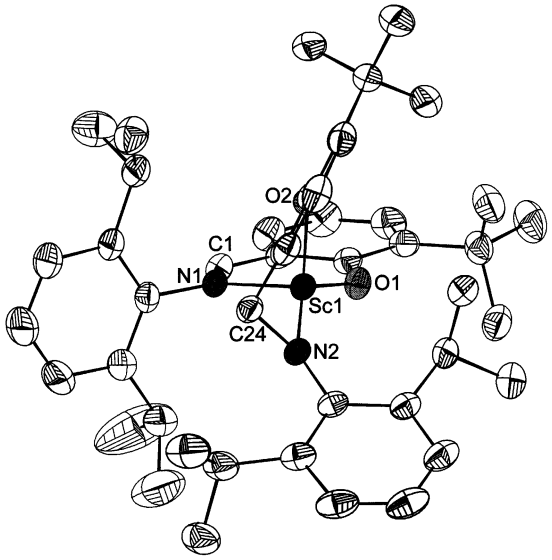

Figure 9. Molecular structure of **7-Sc**·0.5(hexane) (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Sc−O(1) = 1.9683(11), Sc−O(2) = 1.9475(11), Sc−N(1) = 2.1990(13), Sc−N(2) = 2.0108(13), Sc−C(24) = 2.6421(17), C(1)−N(1) = 1.294(2), C(24)−N(2) = 1.497(2); O(1)−Sc−N(1) = 84.58(7), O(2)−Sc−N(2) = 97.94(5), O(1)−Sc−O(2) = 112.20(5), N(1)−Sc−N(2) = 117.11(5), O(1)−Sc−N(2) = 134.64(5), O(2)−Sc−N(1) = 109.50(5), N(1)−Sc−O(1)−C(2) = 24.39(15), Sc−O(1)−C(2)−C(3) = −22.8(2), O(1)−C(2)−C(3)−C(1) = 1.9(3), C(2)−C(3)−C(1)−N(1) = 6.4(3), C(3)−C(1)−N(1)−Sc = 2.7(2), C(1)−N(1)−Sc−O(1) = −12.72(13), N(2)−Sc−O(2)−C(25) = 2.79(12), Sc−O(2)−C(25)−C(26) = −23.67(19), O(2)−C(25)−C(26)−C(24) = −3.8(2), C(25)−C(26)−C(24)−N(2) = 66.90(18), C(26)−C(24)−N(2)−Sc = −78.85(13), C(24)−N(2)−Sc−O(2) = 40.85(10).

an initial dissociative step to provide reactive monomer. For example, **6-Y** shows no polymerization activity under 1 atm of ethylene at room temperature and very low activity under 4 atm. Another reagent which would be expected to react rapidly with terminal M−H bonds but slowly with the dimeric structure of **6-Y** is the highly electrophilic borane [HB(C$_6$F$_5$)$_2$]$_2$. This borane itself readily dissociates into a monomer in aromatic hydrocarbon solution,[31] which rapidly complexes transition-metal hydrides to give robust hydridoborate M[(μ-H)$_2$B(C$_6$F$_5$)$_2$] complexes.[32] **6-Y** reacts extremely slowly (8 days at room temperature) with HB(C$_6$F$_5$)$_2$ to form [L$_2$Y(μ-H)$_2$B(C$_6$F$_5$)$_2$], the structure of which was confirmed by spectroscopy and via elemental analysis. The very slow reactions with ethylene and HB(C$_6$F$_5$)$_2$ are indicative of slow or nonexistent dissociation of **6-Y** into a reactive monomer.

Typically, organoyttrium hydrides catalyze the oligomerization of alkynes to give dimers (e.g. HRC═CH−C≡CR), trimers, or higher oligomers.[29,32a,33,34] Reaction of **6-Y** with excess HC≡CSiMe$_3$ at room temperature for 3 days gave the monomeric acetylide complex [L$_2$Y-(C≡CSiMe$_3$)]. The monomeric structure of the acetylide product is indicated by the observation of two doublets due to the alkynyl carbons in the ^{13}C NMR spectrum (δ 163.12 (d, $^1J_{C,Y}$ = 72 Hz, α-Y*C*≡CR) and δ 108.91 (d, $^2J_{C,Y}$ = 12.5 Hz, β-YC≡*C*R)). The ^{1}H NMR spectra indicate the presence (∼10%) of a second species, which may be a μ-acetylide dimer, since the majority of yttrium alkynyl complexes are dimeric in solution[29,35] unless stabilized by a coordinating base.[29,33,36,37] For the major monomeric acetylide species, ^{1}H NMR spectra indicate a trigonal-bipyramidal structure analogous to the structures of compounds **4-M$_R$**. The preference for a monomeric structure is a testament to the steric congestion at the metal center in the bis(salicylaldiminato) ligand environment. The concurrent production of vinyltrimethylsilane and the apparent absence of H$_2$ in sealed-NMR-tube experiments suggest that the first step in this process is alkyne insertion into Y−H rather than direct σ-bond metathesis between the C$_{sp^2}$−H bond of the alkyne and Y−H. The alkyne insertion could conceivably involve the dimer, producing an yttrium vinyl species that then undergoes σ-bond metathesis with another equivalent of alkyne.

The reactions of **6-Y** with a selection of Lewis bases also imply direct, slow reaction with the dimer to give

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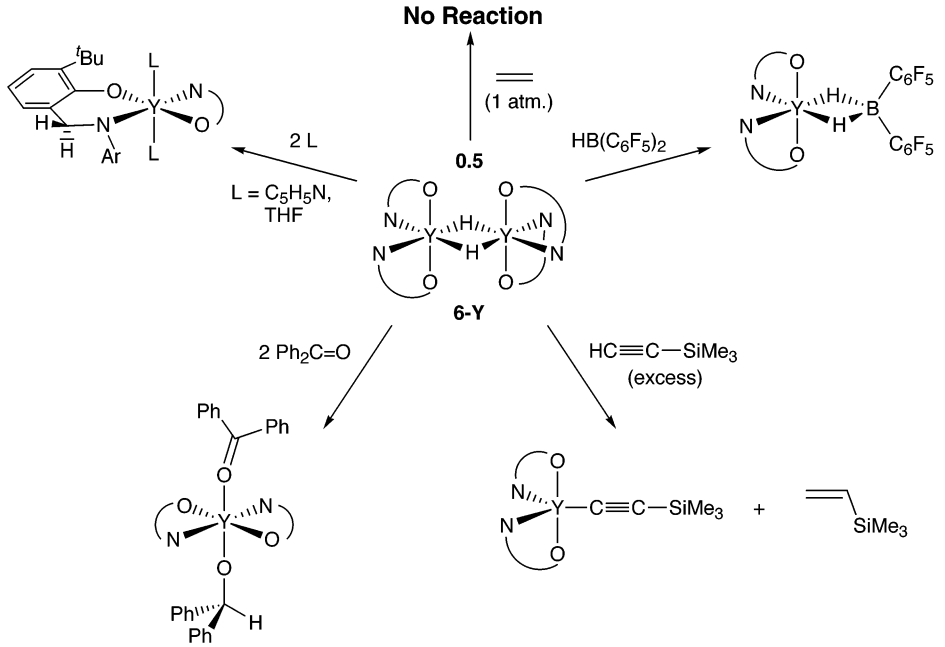
Scheme 4



a more reactive monomeric hydride species, which undergoes insertion or migration to the ligand aldimine carbon. In an example of the former pathway, reaction of **6-Y** with excess benzophenone gave a bright yellow solid which was identified as the bis(ligand) alkoxy ketone compound [*trans*-$L_2Y(OCHPh_2)(OCPh_2)$] by elemental analysis, NMR spectroscopy, and X-ray crystallography. The structure is shown in Figure 10, depicting the trans arrangement of both the alkoxide/ketone ligands and the salicylaldimine ancillaries. The Y−O(4) bond to the ketone is longer than the others in the molecule at 2.444(2) Å, in line with the dative nature of this bond. A comparison with the related complexes $Cp^*_2YCl(O{=}CPh_2)$,[38] $[Tb\{N(SiMe_3)_2\}_3(O{=}CPh_2)]$,[39] and $[DyCp_3(O{=}CPh_2)]$,[40] which are suitable for comparison due to the similar ionic radii of Y, Dy, and Tb (0.893, 0.908, and 0.923 Å, respectively[41]), reveals that the $M-O_{ketone}$ bond distances for these complexes are shorter (Y, 2.312(2) Å; Tb, 2.305(9) Å; Dy, 2.384(3) Å) than $Y-O_{ketone}$ in $[L_2Y(OCHPh_2)(OCPh_2)]$. This is reflective of the more severe steric environment in $[L_2Y(OCHPh_2)(OCPh_2)]$. For all four complexes, the M−O= C angle is approximately linear, ranging from 165.2 to 170.7°, as is common for ligation of carbonyl functions to d^0 metals.[42]

Reaction of **6-Y** with Lewis bases such as pyridine and THF give products in which 2 equiv of Lewis base is taken up, and the yttrium hydride is transferred to the aldimine carbon of one of the salicylaldimine ligands. Alternative outcomes such as simple coordination or activation of the ligated pyridine[22a,29,35c,36] or THF[22a,24,33,35c,43] are not operative in the present system, where 1,3-hydride migration to the ancillary ligand is more facile. Solution NMR data for these two compounds are consistent with the geometry shown in Scheme 4, although for the THF adduct, the lability of the Lewis base indicates somewhat more complicated behavior due to the accessibility of a fluxional five-coordinate species.

In summary, the reactivity patterns observed for yttrium hydride **6-Y** indicate that it does not dissociate into a monomeric hydride, resulting in sluggish reaction rates in relation to other systems for which dimer dissociation is more facile. Despite the high steric congestion associated with the bis(salicylaldimine) ligand environment in **6-Y**, it appears to react primarily as the dimer with typical small-molecule substrates, although in the absence of kinetic studies, very slow, rate-limiting dissociation into reactive monomers cannot be ruled out.

Tris(ligand) Complexes. A final aspect of the chemistry of the group 3 metals Sc and Y with the bulky salicylaldimine ligand employed here is the tendency to form nonorganometallic tris(ligand) coordination complexes L_3M. For yttrium, the third ligand is readily instituted via alkane elimination, necessitating care in the preparation of the derivatives **4-Y$_R$**; addition of another 1 equiv of **I** gives the tris(ligand) compound **8-Y** in high yield (Scheme 5). This octahedral complex exists as a single isomer in solution with all three ligands equivalent on the NMR time scale (25 to −80 °C), suggesting a facial coordination arrangement of the ligands. This has been confirmed by X-ray crystallography (Figure 11). The high steric requirements of

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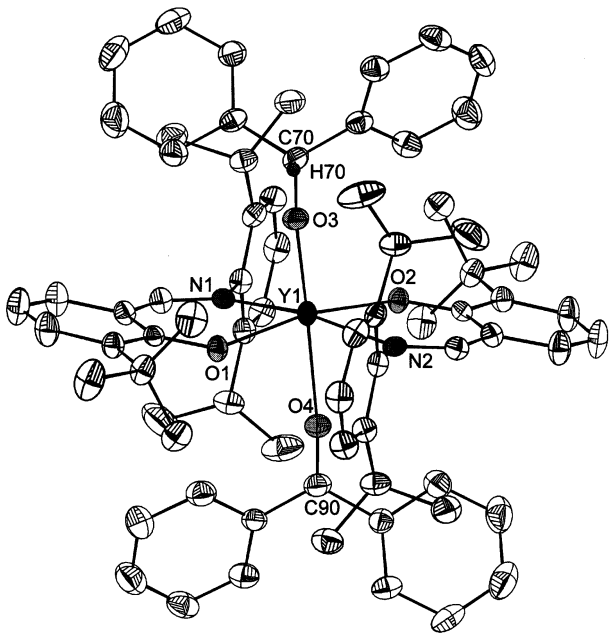
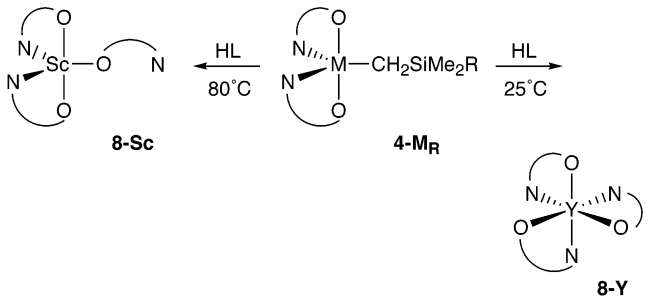


Figure 10. Molecular structure of $L_2Y(OCHPh_2)(O{=}CPh_2)$ (hydrogen atoms other than H(70) omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Y−O(1) = 2.160(2), Y−O(2) = 2.166(2), Y−O(3) = 2.067(2), Y−O(4) = 2.444(2), Y−N(1) = 2.509(3), Y−N(2) = 2.528(3), C(11)−O(1) = 1.316(4), C(41)−O(2) = 1.313(4), C(70)−O(3) = 1.404(4), C(90)−O(4) = 1.243(4); O(1)−Y−N(1) = 75.99(9), O(2)−Y−N(2) = 75.26(9), O(1)−Y−O(2) = 167.15(9), N(1)−Y−N(2) = 170.64(9), O(3)−Y−O(4) = 178.07(12), Y−O(4)−C(90) = 170.7(3), O(4)−C(90)−C(91) = 119.3(4), O(4)−C(90)−C(97) = 119.3(4), C(91)−C(90)−C(97) = 121.4(3), Y−O(3)−C(70) = 169.5(2), O(3)−C(70)−C(71) = 111.4(3), O(3)−C(70)−C(77) = 110.6(3), C(71)−C(70)−C(77) = 116.0(3).

Scheme 5



the ligand are reflected in the Y−N distances, which show that the imine moiety of one of the ligands is less tightly coordinated than the other two (Y−N(1) = 2.581(4) Å, Y−N(2) = 2.694(4) Å, and Y−N(3) = 2.603(4) Å). To compensate, the Y−O bond length of this same ligand (Y−O(2) = 2.107(3) Å) is slightly shorter than that of the other two ligands (Y−O(1) = 2.133(3) Å, Y−O(3) = 2.130(3) Å).

In contrast to the facile synthesis of **8-Y**, there was no reaction observed between **4-Sc$_{Me}$** and **I** at room temperature. Under forcing conditions, (80 °C for 4 days) a new product with a broad room-temperature ^{1}H NMR spectrum was formed. Investigation of this product by variable-temperature NMR spectroscopy gave a sharp spectrum at −20 °C, which was consistent with the presence of an approximately 1:1 mixture of two isomers

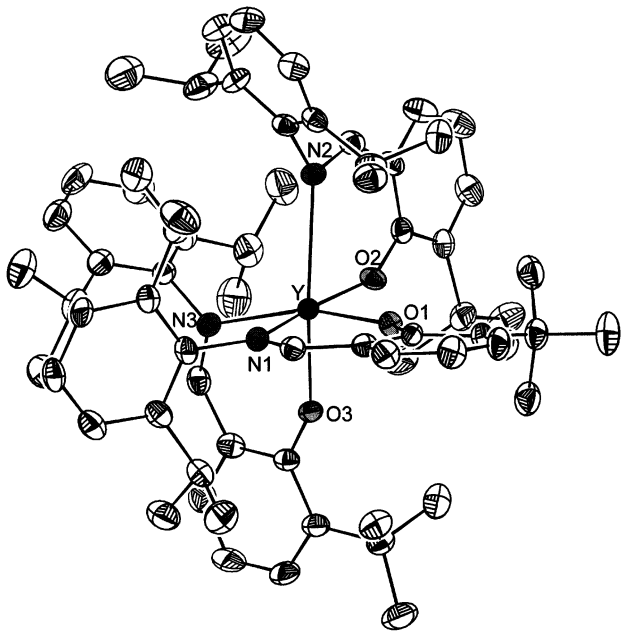


Figure 11. Molecular structure of **8-Y** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Y−O(1) = 2.133(3), Y−O(2) = 2.107(3), Y−O(3) = 2.130(3), Y−N(1) = 2.581(4), Y−N(2) = 2.694(4), Y−N(3) = 2.603(4); O(1)−Y−N(3) = 164.97(12), O(2)−Y−N(1) = 164.22(12), O(3)−Y−N(2) = 165.04(12), O(1)−Y−O(2) = 91.46(12), O(1)−Y−O(3) = 91.51(11), O(1)−Y−N(1) = 73.57(11), O(1)−Y−N(2) = 94.91(11), N(3)−Y−O(2) = 91.97(12), N(3)−Y−O(3) = 73.71(11), N(3)−Y−N(1) = 103.78(12), N(3)−Y−N(2) = 100.10(12), O(2)−Y−O(3) = 92.64(12), O(3)−Y−N(1) = 92.71(12), N(1)−Y−N(2) = 102.05(11), N(2)−Y−O(2) = 73.74(11).

in which none of the ligands are related by symmetry. Given the apparent tendency toward imine dissociation in **8-Y**, it seemed likely that the analogous scandium complex **8-Sc** might be a five-coordinate $[(\kappa^2\text{-L})_2(\kappa^1\text{-L})]$-Sc species in which the imine arm of the third ligand is completely dissociated. This species is a bulky phenoxy analogue of the alkyl complex **4-Sc$_{Me}$**, which exists as a single isomer with the alkyl group in an equatorial position. Therefore, a similar arrangement is expected for **8-Sc**, and it is likely that the two isomers seen in solution at low temperature result from hindered rotation of the bulky $\kappa^1(O)$-salicylaldimine group. 2-D COSY NMR experiments allow for assignment of the ^{1}H NMR spectrum of **8-Sc** at −20 °C and support this interpretation of the data. Finally, the X-ray crystal structure of **8-Sc** shows that the molecule is indeed trigonal bipyramidal with one ligand κ^1(O)-coordinated in an equatorial position and the noncoordinated imine group angled away from the metal center (Figure 12). The metrical data for this compound are unremarkable.

Conclusions

The organometallic chemistry of the group 3 metals scandium and yttrium as supported by a bulky salicylaldiminato ligand has been explored. Both mono- and bis(ligand) complexes of yttrium were prepared via alkane elimination protocols and characterized, while only the bis(ligand) derivatives of scandium were found to be chemically well-behaved enough for detailed study.

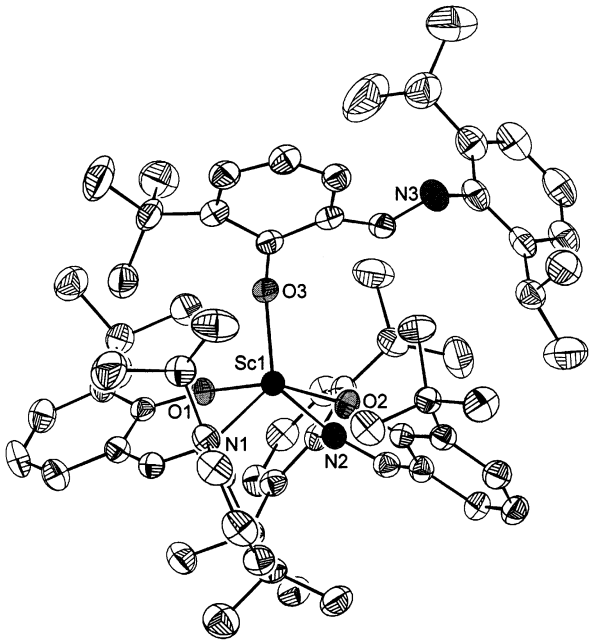


Figure 12. Molecular structure of one of the two crystallographically independent molecules of **8-Sc**·0.5(hexane) (hydrogen atoms and hexane omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg): Sc(1)−O(1) = 1.972(2), Sc(1)−O(2) = 1.998(2), Sc(1)−O(3) = 1.959(2), Sc(1)−N(1) = 2.257(2), Sc(1)−N(2) = 2.2.265(3); O(1)−Sc(1)−O(2) = 161.79(9), O(1)−Sc(1)−N(1) = 81.34(9), O(1)−Sc(1)−N(2) = 86.74(7), O(1)−Sc(1)−O(3) = 94.15(9), O(2)−Sc(1)−N(1) = 92.52(9), O(2)−Sc(1)−N(2) = 80.34(9), O(2)−Sc(1)−O(3) = 103.75(9), O(3)−Sc(1)−N(1) = 119.43(9), N(1)−Sc(1)−N(2) = 115.05(9), N(2)−Sc(1)−O(3) = 124.99(9).

Although this ancillary ligand provides an adequate level of steric stabilization for even the larger yttrium nucleus, these compounds show reactivity patterns with similarities to other noncyclopentadienyl organoscandium and yttrium complexes. For example, hydrogenolysis reactions of the alkyl derivatives **4-M$_R$** proceed slowly to give hydrides due to the electropositive nature of the metal centers. The putative monomeric hydride products of these reactions undergo either rapid hydride transfer to the aldimine carbon of one of the ancillary ligands (M = Sc) or effectively irreversible dimerization (M = Y). This behavior results in sluggish reactivity toward small molecules for **6-Y**. Finally, for the larger metal, facile formation of tris(ligand) coordination complexes is possible when excess ligand is present.

Experimental Section

General Procedures. All operations were performed under a purified argon atmosphere using glovebox or vacuum line techniques. Toluene, hexane, and THF solvents were dried and purified by passing through activated alumina and Q5 columns.[44] NMR spectra were recorded in dry, oxygen-free C_6D_6, unless otherwise noted. ^{1}H, ^{2}H, ^{13}C{^{1}H}, HMQC, DEPT, and COSY NMR experiments were performed on Bruker AC-200, AMX-300, and WH-400 or Varian 200 MHz spectrometers. Data are given in ppm relative to solvent signals for ^{1}H and ^{13}C spectra. 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. The ligand **I** was prepared by a literature procedure. Complexes **1-M$_{Me}$** were generated in situ from MCl_3·*n*THF and $LiCH_2SiMe_3$ (Sigma-Aldrich). $LiCH_2SiMe_2Ph$ was prepared via a modification of the previously reported literature procedure.[45] All other materials were obtained from Sigma-Aldrich and purified according to standard procedures. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on either a Bruker P4/RA/SMART 1000 CCD diffractometer (University of Alberta) or a Rigaku AFC6S diffractometer (University of Calgary). Details of the crystallographic data and data analysis are given in Table 3; full details can be found in the Supporting Information.

Synthesis of $LiCH_2SiMe_2Ph$. $Me_2PhSiCH_2Cl$ (7.8 g, 42 mmol) was added to a slurry of Li powder (0.5% Na; 880 mg, 127 mmol) in toluene (50 mL) at room temperature. The mixture was then stirred at 75 °C for 2−3 days before being filtered, and the residue was washed twice with toluene. The resulting orange solution was evaporated to dryness in vacuo, slurried in *n*-hexane (10 mL), sonicated, cooled to −78 °C, and filtered to collect a yellow-white solid which was washed with a small volume of cold *n*-hexane. The resulting cream white solid was dried in vacuo for 1 h. Yield: 4.6 g (59%). ^{1}H NMR (C_6D_6): δ 7.55−7.50 (m, 2H, Ph), 7.27−7.15 (m, 3H, Ph), 0.24 (s, 6H, $SiMe_2$), −2.42 (s, 2H, $LiCH_2$).

[Sc(CH$_2$SiMe$_2$Ph)$_3$(THF)$_2$] (1-Sc$_{Ph}$). A mixture of [$ScCl_3$(THF)$_3$] (1.00 g, 2.72 mmol) and $LiCH_2SiMe_2Ph$ (1.28 g, 8.16 mmol) in toluene (40 mL) was stirred for 6 h at 0 °C and then evaporated to dryness in vacuo. After addition of *n*-hexane (70 mL), the mixture was sonicated to break up the solid and filtered to give a clear solution. This was concentrated in vacuo (ca. 5 mL) and then cooled to −78 °C to precipitate a white solid which was collected by filtration. Yield: 1.29 g (75%). X-ray-quality crystals were grown by cooling an *n*-hexane solution to −40 °C. ^{1}H NMR (C_6D_6): δ 7.74 (dd, 6H, J = 7, 1 Hz, *o*-Ph), 7.27 (ddd, 6H, J = 7, 7, 1 Hz, *m*-Ph), 7.18 (tt, 3H, J = 7, 1 Hz, *p*-Ph), 3.77, 1.15 (m, 2 × 8H, THF), 0.44 (s, 18H, Si*Me*$_2$Ph), −0.11 (s, 6H, Sc−C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.34 (s, quaternary aromatic), 134.30, 128.47, 128.12 (s, 3 Ph), 71.75 (s, THF), 37.0 (broad s, Y−*C*H$_2$), 25.35 (s, THF), 3.18 (s, Si*Me*$_2$Ph). Anal. Calcd for $C_{35}H_{55}O_2Si_3Sc$: C, 65.99; H, 8.70. Found: C, 64.89; H, 8.80.

[Y(CH$_2$SiMe$_2$Ph)$_3$(THF)$_2$] (1-Y$_{Ph}$). A procedure identical with that described above using a mixture of [YCl_3(THF)$_{3.5}$] (1.00 g, 2.23 mmol) and $LiCH_2SiMe_2Ph$ (1.05 g, 6.70 mmol) was employed to yield 1.32 g (87%) of **1-Y$_{Ph}$**. ^{1}H NMR (C_6D_6): δ 7.74 (dd, 6H, J = 8, 1 Hz, *o*-Ph), 7.28 (ddd, 6H, J = 7, 7, 1 Hz, *m*-Ph), 7.18 (tt, 3H, J = 8, 1 Hz, *p*-Ph), 3.63, 1.11 (m, 2 × 8H, THF), 0.45 (s, 18H, Si*Me*$_2$Ph), −0.52 (d, 6H, $^2J_{H,Y}$ = 3 Hz, Y−C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.98 (s, quaternary aromatic), 134.27, 128.39, 128.16 (s, 3 Ph), 71.21 (s, THF), 31.97 (d, $^1J_{C,Y}$ = 35 Hz, Y−*C*H$_2$), 25.27 (s, THF), 3.54 (s, Si*Me*$_2$Ph). Anal. Calcd for $C_{35}H_{55}O_2Si_3Y$: C, 61.73; H, 7.08. Found: C, 58.26; H, 6.83.

[LY(CH$_2$SiMe$_3$)$_2$(THF)$_2$] (2-Y$_{Me}$). A mixture of [YCl_3(THF)$_{3.5}$] (0.84 g, 1.88 mmol) and $LiCH_2SiMe_3$ (0.53 g, 5.63 mmol) in *n*-hexane (30 mL) was stirred for 4 h at 0 °C and then filtered to give a colorless solution of [$Y(CH_2SiMe_3)_3$(THF)$_x$]. After the mixture was cooled to −78 °C, a solution of **I** (0.63 g, 1.88 mmol) in cold *n*-hexane (20 mL) was added and the temperature was raised to 0 °C for 30 min. The resulting yellow solid was collected by filtration and washed with *n*-hexane (×2). Yield: 0.92 g (66%). ^{1}H NMR (d_8-toluene, 25 °C): δ 7.94 (s, 1H, C*H*(NAr)), 7.44 (d, 1H, J = 7 Hz, Ph), 7.12−7.03 (m, 3H, Ph), 6.84 (d, 1H, J = 7 Hz, Ph), 6.57 (t, 1H, J = 7 Hz, Ph), 3.69 (s, 8H, THF), 2.94 (septet., 2H, C*H*Me$_2$), 1.67 (s, 9H, CMe_3), 1.34 (m, 8H, THF), 1.25, 0.94 (d, 2 × 6H, J = 6

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Table 3. Summary of Data Collection and Structure Refinement Details

	1-Sc$_{Ph}$	**2-Y$_{Ph}$**	**3-Y$_{Ph}$**	**4-Sc$_{Me}$**	**5-Sc**
formula	$C_{35}H_{55}O_2ScSi_3$	$C_{49}H_{72}NO_3Si_2Y$	$C_{45}H_{64}NO_2Si_2Y$	$C_{50}H_{71}N_2O_2ScSi$	$C_{46}H_{59}N_2O_2Sc$
fw	637.02	868.17	796.06	805.14	716.91
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
a, Å	16.9753(3)	22.7450(3)	21.5355(2)	11.9830(7)	11.2423
b, Å	13.0885(3)	9.8118(1)	11.0719(1)	17.6241(10)	20.2909
c, Å	17.0669(4)	23.0596(4)	37.1685(4)	22.7220(13)	18.3725
α, deg					
β, deg	94.012(1)	105.621(1)	93.6312	91.0259(11)	100.568(1)
γ, deg					
V, Å^3	3782.65(14)	4956.12(12)	8844.62	4797.9(5)	4119.98(19)
space group	*P*2$_1$/*c*	*P*2$_1$/*c*	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*
Z	4	4	8	4	4
d_{calcd}, mg m^{-3}	1.119	1.164	1.196	1.115	1.156
μ, mm^{-1}	0.32	1.26	1.41	0.216	0.217
R1	0.044	0.091	0.037	0.0468	0.079
wR2	0.094	0.207	0.082	0.1339	0.162
wR2 (all data)	0.111	0.221	0.091	0.211	0.153
GOF	1.03	1.15	1.01	1.029	1.00

	6-Y	**7-Sc**	$L_2Y(OCHPh_2)(O{=}CPh_2)$	**8-Y**	**8-Sc**
formula	$C_{106}H_{138}N_4O_4Y_2$	$C_{49}H_{68}N_2O_2Sc$	$C_{72}H_{81}N_2O_4Y$	$C_{69}H_{90}N_3O_3Y$	$C_{72}H_{97}N_3O_3Sc$
fw	1710.02	762.01	1127.30	1098.35	1075.94
cryst syst	triclinic	triclinic	triclinic	monoclinic	triclinic
a, Å	13.5187(1)	10.8442(2)	11.8539(2)	13.065(1)	13.1532(2)
b, Å	18.9396(2)	12.4440(2)	11.8956(2)	22.8064(18)	21.9728(3)
c, Å	20.8165(3)	18.4372(3)	13.2843(2)	21.3288(17)	23.6174(3)
α, deg	80.2648(4)	102.259(1)	105.608(1)	98.106(1)	
β, deg	78.9598(4)	99.938(1)	116.443(1)	106.4928(18)	91.425(1)
γ, deg	83.2781(7)	103.838(1)	101.171(1)	105.357(1)	
V, Å^3	5136.08(10)	2294.37(7)	1504.82(4)	6093.8(8)	6502.40(16)
space group	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$	*P*2$_1$/*n*	*P*$\bar{1}$
Z	2	2	1	4	4
d_{calcd}, mg m^{-3}	1.106	1.103	1.244	1.197	1.099
μ, mm^{-1}	1.17	0.20	1.020	1.005	0.16
R1	0.053	0.053	0.055	0.0664	0.072
wR2	0.138	0.130	0.119	0.1505	0.140
wR2 (all data)	0.147		0.122	0.182	
GOF	1.05	1.03	1.06	0.907	0.97

Hz, CH*Me*$_2$), 0.23 (s, 18H, SiMe$_3$), −0.54 (broad s, 4 H, YC*H*$_2$). ^{13}C{^{1}H} NMR (*d*$_8$-toluene, 0 °C): *δ* 174.28 (s, *C*H(NAr)), 166.88, 150.8 (b), 140.93, 140.31 (s, four quaternary aromatic), 135.71, 133.79, 126.94, 124.34 (s, 4 Ph), 123.05 (s, quaternary aromatic), 116.40 (s, Ph), 70.67 (s, THF), 35.91 (s, *C*Me$_3$), 32.0 (v weak s, Y*C*H$_2$), 30.59 (s, C*Me*$_3$), 28.92 (s, *C*HMe$_2$), 26.18 (s, CH*Me*$_2$), 25.60 (s, THF), 23.19 (s, CH*Me*$_2$), 5.06 (s, SiMe$_3$). Anal. Calcd for $C_{39}H_{68}NO_3SiY$: C, 62.96; H, 9.21; N, 1.88. Found: C, 60.32; H, 8.44; N, 2.03.

[LY(CH$_2$SiMe$_2$Ph)$_2$(THF)$_2$] (2-Y$_{Ph}$). A mixture of [Y(CH$_2$SiMe$_2$Ph)$_3$(THF)$_2$] (0.2 g, 0.29 mmol) and **I** (0.10 g, 0.29 mmol) in *n*-hexane (10 mL) was warmed from −78 to 0 °C over 1 h, stirred at 0 °C for an additional 1 h, cooled to −78 °C, and then filtered to collect a pale yellow solid which was washed with cold *n*-hexane (×2). Yield: 205 mg (80%). X-ray-quality crystals were grown by cooling a hexane solution to −35 °C. ^{1}H NMR (C$_6$D$_6$): *δ* 7.98 (s, 1H, C*H*(NAr)), 7.77 (d, 4H, *J* = 8 Hz, Ph), 7.48 (dd, 1H, *J* = 8, 2 Hz, Ph), 7.29−7.01 (m, 9H, Ph), 6.92 (dd, *J* = 8, 2 Hz, 1H, Ph), 6.64 (t, 1H, *J* = 8 Hz, Ph), 3.59 (broad s, 8H, THF), 2.85 (septet, 2H, *J* = 7 Hz, C*H*Me$_2$), 1.64 (s, 9 H, CMe$_3$), 1.22 (s, 8H, THF), 1.14, 0.86 (d, 2 × 6H, *J* = 7 Hz, CH*Me*$_2$), 0.47 (s, 12H, CH$_2$Si*Me*$_2$Ph), −0.35 (broad s, 4H, C*H*$_2$SiMe$_2$Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$): *δ* 174.50 (s, *C*H(NAr)), 166.83, 150.4, 147.74, 141.18, 140.65 (s, 5 quaternary aromatic), 135.55, 134.34, 134.04, 128.02, 127.93, 127.02, 124.45 (s, 7 Ph), 123.22 (s, quaternary aromatic), 116.73 (s, Ph), 70.37 (s, THF), 35.88 (s, *C*Me$_3$), 30.61 (s, C*Me*$_3$), 30.2 (v weak s, Y*C*H$_2$), 29.06 (s, *C*HMe$_2$), 26.03 (s, CH*Me*$_2$), 25.53 (THF), 23.09 (s, CH*Me*$_2$), 3.49 (s, Si*Me*$_2$Ph). Anal. Calcd for $C_{49}H_{72}NO_3Si_2Y$: C, 67.79; H, 8.36; N, 1.61. Found: C, 64.65; H, 8.07; N, 1.66.

[LY(CH$_2$SiMe$_2$Ph)$_2$(THF)] (3-Y$_{Ph}$). Method 1. A mixture of [Y(CH$_2$SiMe$_2$Ph)$_3$(THF)$_2$] (0.30 g, 0.44 mmol) and **I** (0.15 g, 0.44 mmol) in *n*-pentane (10 mL) was stirred at 0 °C for 2 h, cooled to −78 °C, and filtered to collect a pale yellow solid which was washed with cold *n*-pentane (×2). Yield: 0.24 g (68%).

Method 2. Solid **2-Y$_{Ph}$** (0.38 g, 0.44 mmol) was dissolved in toluene (10 mL) and then evaporated to dryness in vacuo (×2). The resulting solid was slurried in *n*-hexane, sonicated, cooled to −78 °C, and then filtered to collect a cream white solid which was washed with cold *n*-hexane (×1). Yield: 0.21 g (60%). X-ray-quality crystals were grown by cooling a hot hexane solution to −35 °C. ^{1}H NMR (C$_6$D$_6$): *δ* 7.94 (s, 1H, C*H*(NAr)), 7.78 (dd, 4H, *J* = 8, 2 Hz, Ph), 7.51 (dd, 1H, *J* = 8, 2 Hz, Ph), 7.21−7.13 (m, 8H, Ph), 6.99−6.92 (m, 4H, Ph), 6.68 (t, 1H, *J* = 8 Hz, Ph), 3.35 (broad s, 4H, THF), 2.78 (broad septet, 2H, *J* = 7 Hz, C*H*Me$_2$), 1.66 (s, 9 H, CMe$_3$), 1.10 (d, 6H, *J* = 7 Hz, CH*Me*$_2$), 1.00 (s, 4H, THF), 0.78 (d, 6H, *J* = 7 Hz, CH*Me*$_2$) 0.48 (s, 12H, CH$_2$Si*Me*$_2$Ph), −0.08 (broad s, 4H, C*H*$_2$SiMe$_2$Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$): *δ* 174.88 (s, *C*H(NAr)), 167.08, 148.61, 146.97, 141.53, 140.80 (s, 5 quaternary aromatic), 135.30, 134.63, 134.25, 128.69, 128.21, 127.35, 124.50 (s, 7 Ph), 123.16 (s, quaternary aromatic), 117.05 (s, Ph), 70.92 (s, THF), 35.91 (s, *C*Me$_3$), 32.30 (d, $^1J_{C,Y}$ = 42 Hz, *C*H$_2$SiMe$_2$Ph), 30.44 (s, C*Me*$_3$), 29.46 (s, *C*HMe$_2$), 25.94 (s, CH*Me*$_2$), 25.07 (THF), 22.89 (s, CH*Me*$_2$), 3.40 (s, CH$_2$Si*Me*$_2$Ph). Anal. Calcd for $C_{45}H_{64}NO_2Si_2Y$: C, 67.89; H, 8.10; N, 1.76. Found: C, 66.83; H, 8.09; N, 1.57.

[L$_2$Sc(CH$_2$SiMe$_3$)] (4-Sc$_{Me}$). A mixture of [ScCl$_3$(THF)$_3$] (0.3 g, 0.82 mmol) and LiCH$_2$SiMe$_3$ (0.23 g, 2.45 mmol) in *n*-hexane (30 mL) was stirred for 2 h at 0 °C and then filtered to give a colorless solution of [Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$]. After the mixture was cooled to −78 °C, a solution of **I** (0.55 g, 1.63 mmol) in *n*-hexane (20 mL) was added and the temperature was raised to 0 °C for 2 h and then to room temperature for 1 day. The

bright yellow solution was evaporated to dryness in vacuo to give a yellow oil, to which $O(SiMe_3)_2$ (5 mL) was added. After sonication, the mixture was cooled to −45 °C and the resulting bright yellow solid collected by filtration and washed with cold $O(SiMe_3)_2$ (×2). Yield: 0.47 g (72%). X-ray-quality crystals were grown by allowing a hot *n*-hexane solution to cool to room temperature. ^{1}H NMR (C_6D_6): δ 7.85 (s, 2H, C*H*(NAr)), 7.37 (dd, 2H, J = 8, 2 Hz, Ph), 7.14−7.01 (m, 4H, Ph), 6.91 (dd, 2H, J = 7, 2 Hz, Ph), 6.76 (dd, 2H, J = 8, 2 Hz, Ph), 6.53 (t, 2H, J = 8 Hz, Ph), 3.25, 2.67 (sept, 2 × 2H, J = 7 Hz, C*H*Me$_2$), 1.47 (d, 6H, J = 7 Hz, CH*Me*$_2$), 1.19 (s, 18H, C*Me*$_3$), 1.09 (d, 1H, $^2J_{H,H}$ = 10 Hz, ScC*H*$_2$), 0.96, 0.95, 0.69 (d, 3 × 6H, J = 7 Hz, CH*Me*$_2$), 0.24 (s, 9H, Si*Me*$_3$), 0.23 (d, 1H, $^2J_{H,H}$ = 10 Hz, Sc−C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 175.79 (s, *C*H(NAr)), 167.63, 150.81, 142.19, 141.15, 140.53 (s, 5 quaternary aromatic), 135.07, 134.95, 127.62, 125.35, 124.61 (s, 5 Ph), 123.15 (s, quaternary aromatic), 117.12 (s, Ph), 45.39 (weak s, Sc−*C*H$_2$), 35.57 (s, *C*Me$_3$), 30.57 (s, C*Me*$_3$), 30.22, 29.11 (s, 2 *C*HMe$_2$), 26.03, 25.66, 23.78, 22.49 (s, 4 CH*Me*$_2$), 4.27 (s, Si*Me*$_3$). Anal. Calcd for $C_{50}H_{71}N_2O_2SiSc$: C, 74.59; H, 8.89; N, 3.46. Found: C, 74.38; H, 9.04; N, 3.56.

[L$_2$Sc(CH$_2$SiMe$_2$Ph)]·$^1/_2$(hexane) (4-Sc$_{Ph}$). A solution of [Sc(CH$_2$SiMe$_2$Ph)$_3$(THF)$_2$] (0.3 g, 0.47 mmol) and **I** (0.32 g, 0.94 mmol) in *n*-hexane (20 mL) was stirred at 0 °C for 1 h and then at room temperature for 6 h. The mixture was then evaporated to lower volume in vacuo, sonicated, and cooled to −78 °C and the resulting pale yellow solid collected by filtration and washed with cold *n*-hexane (×2). Yield: 0.34 g (79%). ^{1}H NMR (C_6D_6): δ 7.86 (s, 2H, C*H*(NAr)), 7.76 (d, 2H, J = 5 Hz, Ph), 7.38 (d, 2H, J = 7 Hz, Ph), 7.15−7.02 (m, 7H, Ph), 6.91 (d, 2H, J = 7 Hz, Ph), 6.78 (d, 2H, J = 7 Hz, Ph), 6.56 (t, 2H, J = 8 Hz, Ph), 3.16, 2.69 (sept, 2 × 2H, J = 7 Hz, C*H*Me$_2$), 1.17 (d, 1H, $^2J_{H,H}$ = 10 Hz, Sc−C*H*$_2$), 1.36 (d, 6H, J = 7 Hz, CH*Me*$_2$), 1.23 (m, 4H, *n*-hexane), 1.13 (s, 18H, C*Me*$_3$), 0.97 (d, 6H, J = 7 Hz, CH*Me*$_2$), 0.89 (m, 3H, *n*-hexane), 0.88, 0.69 (d, 2 × 6H, J = 7 Hz, CH*Me*$_2$), 0.49 (d, 1H, $^2J_{H,H}$ = 10 Hz, ScC*H*$_2$), 0.43 (s, 6H, Si*Me*$_2$Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 175.83 (s, *C*H(NAr)), 167.58, 150.83, 146.38, 142.23, 141.09, 140.55 (s, 6 quaternary aromatic), 135.25, 135.03, 134.48, 128.11, 127.78, 127.66, 125.34, 124.59 (s, 8 Ph), 123.25 (s, quaternary aromatic), 117.25 (s, Ph), 40.97 (broad s, ScCH$_2$) 35.56 (s, *C*Me$_3$), 32.30 (s, *n*-hexane), 30.58 (s, C*Me*$_3$), 30.24, 29.14 (s, 2 *C*HMe$_2$), 26.05, 25.69, 23.74 (s, 3 CH*Me*$_2$), 23.39 (s, *n*-hexane), 22.48 (s, CH*Me*$_2$), 14.70 (s, *n*-hexane), 3.81, 2.76 (s, 2 Si*Me*$_2$-Ph). Anal. Calcd for $C_{58}H_{80}N_2O_2SiSc$: C, 76.53; H, 8.86; N, 3.08. Found: C, 76.27; H, 8.47; N, 2.98.

[L$_2$Y(CH$_2$SiMe$_2$Ph)] (4-Y$_{Ph}$). A solution of [Y(CH$_2$SiMe$_2$-Ph)$_3$(THF)$_2$] (0.2 g, 0.29 mmol) and **I** (0.2 g, 0.29 mmol) in *n*-pentane (30 mL) was stirred for 4 h at room temperature. The pale yellow solution was then concentrated in vacuo (ca.10 mL), sonicated, cooled to −78 °C, and filtered to collect a pale yellow solid which was washed with cold *n*-pentane (×2). Yield: 0.21 g (77%). X-ray-quality crystals were grown by slow cooling of a hot *n*-hexane solution to room temperature. ^{1}H NMR (C_6D_6): δ 7.82−7.79 (m, 4H, C*H*(NAr) & Ph), 7.38 (dd, 2H, J = 8, 2 Hz, Ph), 7.15−7.01 (m, 7H, Ph), 6.91 (dd, 2H, J = 6, 3 Hz, Ph), 6.76 (dd, 2H, J = 8, 2 Hz, Ph), 6.55 (t, 2H, J = 8 Hz, Ph), 3.00, 2.78 (sept, 2 × 2H, J = 7 Hz, C*H*Me$_2$), 1.33 (d, 6H, J = 7 Hz, CH*Me*$_2$), 1.17 (s, 18H, C*Me*$_3$), 1.00, 0.86, 0.81 (d, 3 × 6H, J = 7 Hz, CH*Me*$_2$), 0.50, 0.43 (s, 2 × 3H, Si*Me*$_2$Ph), 0.39, 0.06 (dd, 2 × 1H, $^2J_{H,H}$ = 11, $^2J_{H,Y}$ = 3.5 Hz, YC*H*$_2$). ^{13}C-{^{1}H} NMR (C_6D_6): δ 175.86 (s, *C*H(NAr)), 167.69, 167.66, 149.05, 146.71, 141.86, 140.96, 140.82 (s, 7 quaternary aromatic), 135.51, 134.82, 127.93, 125.16, 124.86 (s, 5 Ph), 123.41 (s, quaternary aromatic), 116.77 (s, Ph), 35.54 (s, *C*Me$_3$), 32.42 (d, $^1J_{C,Y}$ = 49 Hz, Y−*C*H$_2$), 30.32 (s, *C*HMe$_2$), 30.23 (s, C*Me*$_3$), 29.49 (s, *C*HMe$_2$), 26.00, 25.37, 23.98, 22.84 (s, 4 CH*Me*$_2$), 4.37, 3.05 (s, 2 Si*Me*$_2$Ph). Anal. Calcd for $C_{55}H_{73}N_2O_2SiY$: C, 72.50; H, 8.07; N, 3.07. Found: C, 72.12; H, 8.25; N, 3.12.

Thermolysis of 4-Sc$_M$: Preparation of 5-Sc. A bright yellow solution of **4-Sc$_{Me}$** (0.39 g, 0.48 mmol) in toluene (30 mL) was heated at 140 °C for 3 days. The resulting red solution was evaporated to dryness in vacuo to give an oil to which *n*-hexane (10 mL) was added. After sonication, the mixture was cooled to −78 °C and the resulting brick red solid collected by filtration and washed with cold *n*-hexane (×2). Yield: 0.18 g (52%). X-ray-quality crystals were grown by cooling a hot *n*-hexane solution of **5-Sc** to room temperature. ^{1}H NMR (C_6D_6): δ 7.83 (s, 1H, C*H*(NAr)), 7.45 (dd, 1H, J = 8, 2 Hz, Ph), 7.27 (dd, 1H, J = 8, 1 Hz, Ph), 7.20 (d, 2H, J = 7 Hz, Ph), 7.07 (d, 1H, J = 8 Hz, Ph), 7.00−6.95 (m, 3H, Ph), 6.82−6.95 (m, 3H, Ph), 6.61 (t, 1H, J = 8 Hz, Ph), 4.50 (dd, 1H, J = 4 Hz, H^a), 3.34 (quartet of dd, 1H, J = 5.5, 6, 12 Hz, H^d), 3.29, 2.74, 2.61 (sept, 3 × 1H, J = 7 Hz, C*H*Me$_2$), 2.15 (ddd, 1H, J = 14, 6, 1.5 Hz, H^b), 1.62, 1.59 (s, 2 × 9H, C*Me*$_3$), 1.48 (d, 6H, J = 7 Hz, CH*Me*$_2$), 1.29 (d, 3H, J = 5 Hz, CH^d*Me*^{a}), 0.97, 0.85, 0.83 (d, 3 × 3H, J = 7 Hz, CH*Me*$_2$), 0.80 (ddd, 1H, J = 14, 12, 4 Hz, H^c) 0.75 (d, 3H, J = 7 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 174.70 (s, *C*H(NAr)), 166.89, 164.08, 148.19, 145.83, 142.24, 141.91, 140.91, 136.14 (s, 8 quaternary aromatic), 135.60, 135.35 (s, 2 Ph), 132.89, 132.58 (s, 2 quaternary aromatic), 128.32, 125.95, 125.47, 124.87, 124.68 (s, 5 Ph), 124.28 (s, quaternary aromatic), 123.82 (s, Ph), 123.09 (s, quaternary aromatic), 122.61, 119.14, 118.19, 115.89 (s, 4 Ph), 53.39 (s, C^1H^a), 35.94 (s, *C*HMe$_2$), 35.77 (s, *C*Me$_3$), 35.47 (s, *C*Me$_3$), 32.83 (s, C^2H$_2$), 30.48, 30.04 (s, 2 C*Me*$_3$), 30.04, 29.68 (s, 2 *C*HMe$_2$), 27.42 (s, C^3H^{d}Me^a), 25.81 (*C*HMe$_2$), 25.81, 25.65 (s, 2 CH*Me*$_2$), 22.91 (s, C^{3}H^d*Me*^{a}), 22.86, 22.66, 21.82, 20.02 (s, 4 CH*Me*$_2$). Anal. Calcd for $C_{46}H_{59}N_2O_2Sc$: C, 77.06 H, 8.29; N, 3.91. Found: C, 76.55; H, 8.71; N, 3.77.

[L$_2$Y(μ-H)$_2$YL$_2$]·(hexane) (6-Y). A solution of **4-Y$_{Ph}$** (1.0 g, 1.10 mmol) in toluene (30 mL) was stirred under H_2 (4 atm) for 1 day at room temperature. The pale yellow solution was then evaporated to dryness in vacuo, *n*-hexane (ca.10 mL) was added, and the mixture was sonicated, cooled to −78 °C, and filtered to collect a pale yellow solid which was washed with cold *n*-hexane (×2). Yield: 0.79 g (90%). X-ray-quality crystals were grown by cooling a 1:1 toluene−*n*-heptane solution to −35 °C. ^{1}H NMR (C_6D_6): δ 8.14 (s, 4H, C*H*(NAr)), 7.54 (t, 2H, $^1J_{H,Y}$ = 32 Hz, μ-*H*), 7.27−7.11 (m, 8H, Ph), 7.09 (t, 4H, J = 8 Hz, Ph), 6.93 (d, 4H, J = 7 Hz, Ph), 6.85 (d, 4H, J = 7 Hz, Ph), 6.53 (t, 4H, J = 7 Hz, Ph), 3.25, 2.85 (sept, 2 × 4H, J = 6.5 Hz, C*H*Me$_2$), 1.42 (d, 12H, J = 7 Hz, CH*Me*$_2$), 1.22 (m, 8H, *n*-hexane), 1.13 (d, 12H, J = 7 Hz, CH*Me*$_2$), 1.07 (s, 36H, C*Me*$_3$), 0.91 (d, 12H, J = 7 Hz, CH*Me*$_2$), 0.88 (t, 6H, *n*-hexane), 0.58 (d, 12H, J = 7 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 176.68 (s, *C*H(NAr)), 166.98, 151.30, 142.44, 141.54, 140.58 (s, 5 quaternary aromatic), 135.59, 133.48, 127.07, 125.37, 123.81 (s, 5 Ph), 123.35 (s, quaternary aromatic), 116.46 (s, Ph), 35.22 (s, *C*Me$_3$), 32.30 (s, *n*-hexane), 30.13 (s, *C*HMe$_2$), 30.13 (s, C*Me*$_3$), 28.16 (s, *C*HMe$_2$), 27.61, 27.47, 25.84 (s, 3 CH*Me*$_2$), 23.39 (s, *n*-hexane), 21.72 (s, CH*Me*$_2$), 14.69 (s, *n*-hexane). Anal. Calcd for $C_{98}H_{136}N_4O_4Y_2$: C, 73.02; H, 8.50; N, 3.47. Found: C, 73.33; H, 8.23; N, 3.59.

[L$_2$Y(μ-D)$_2$YL$_2$]·(hexane) (*d*$_2$-6-Y). A procedure analogous to that described above using D_2 gave 132 mg (75%) of ***d*$_2$-6-Y**. ^{2}H NMR (C_6H_6): δ 7.59 (J_{YD} = 5 Hz). Anal. Calcd for $C_{98}H_{134}D_2N_4O_4Y_2$: C, 72.93; H/D, 8.62; N, 3.47. Found: C, 72.91; H/D, 8.75; N, 3.58.

Synthesis of 7-Sc. A solution of [L$_2$Sc(CH$_2$SiMe$_3$)] (0.30 g, 0.37 mmol) in toluene (20 mL) was stirred under H_2 (4 atm) for 1 day at room temperature. The resulting orange solution was evaporated to dryness in vacuo, $O(SiMe_3)_2$ (ca. 5 mL) was added, and the mixture was sonicated, cooled to −45 °C, and filtered to collect a bright yellow solid which was washed with cold $O(SiMe_3)_2$ (×2). Yield: 0.16 g (60%). X-ray-quality crystals of **7-Sc**·0.5(*n*-hexane) were grown by cooling an *n*-hexane solution to −35 °C. ^{1}H NMR (C_6D_6): δ 7.81 (s, 1H, C*H*(NAr)), 7.38 (dd, 1H, J = 8, 2 Hz, Ph), 7.25 (dd, 1H, J = 8, 2 Hz, Ph), 7.11 (d, 1H, J = 8 Hz, Ph), 7.08−6.99 (m, 5H, Ph), 6.76 (dt, 1H, J = 8, 2 Hz, Ph), 6.66 (t, 1H, J = 8 Hz, Ph), 6.55 (t, 1H, J = 8 Hz, Ph), 4.71 (d, 1H, $^2J_{H,H}$ 15 Hz, $^1J_{C,H} \approx$ 100 Hz, C^1*H*),

4.46 (d, 1H, $J_{H,H}$ = 15 Hz, $^1J_{C,H} \approx$ 110 Hz, C^1H), 3.43 (sept., 1H, J = 6 Hz, CHMe$_2$), 3.31 (sept, 2H, J = 7 Hz, CHMe$_2$), 2.78 (sept, 1H, J = 6 Hz, CHMe$_2$), 1.59, 1.45 (s, 2 × 9H, CMe_3), 1.28 (d, 6H, J = 7 Hz, CHMe_2), 1.24, 0.97 (d, 2 × 3H, J = 6 Hz, CHMe_2), 0.91 (d, 6H, J = 7 Hz, CHMe_2), 0.90, 0.88 (d, 2 × 3H, J = 6 Hz, CHMe_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 176.16 (s, CH(NAr)), 166.82, 162.74, 150.41, 145.34, 144.97, 142.05, 141.68, 141.01, 137.22 (s, 9 quaternary aromatic), 135.76, 135.35 (s, 2 Ph), 130.33 (s, quaternary aromatic), 128.54, 127.83, 126.72, 125.28, 125.07, 124.43 (s, 6 Ph), 122.94 (s, quaternary aromatic), 119.20, 118.51 (s, 2 Ph), 60.14 (s, C^1H$_2$), 35.83, 35.63 (s, 2 CMe$_3$), 30.52, 29.97 (s, 2 CMe_3), 29.97, 29.89, 29.42 (s, 3 CHMe$_2$), 25.82, 25.73, 25.37, 25.12, 23.79, 23.40 (s, 6 CHMe_2). Anal. Calcd for $C_{46}H_{61}N_2O_2Sc$: C, 76.85; H, 8.55; N, 3.90. Found: C, 77.30; H, 8.05; N, 3.87.

Reaction of 6-Y with HB(C$_6$F$_5$)$_2$. A solution of **6-Y** (40 mg, 2.48 × 10^{-5} mol) and HB(C$_6$F$_5$)$_2$ (17 mg, 4.96 × 10^{-5} mol) in toluene (3 mL) was stirred at room temperature for 8 days and then evaporated to dryness in vacuo. The resulting mixture was slurried with *n*-hexane, cooled to −78 °C, and filtered to collect a pale yellow solid which was dried in vacuo for 20 min; yield 20 mg (35%). ^{1}H NMR (d_8-toluene, 25 °C): 7.79 (d, 2H, J = 3 Hz, CH(NAr)), 7.17 (dd, 2H, J = 8, 2 Hz, Ph), 7.10−6.97 (m, 4H, Ph), 6.83, 6.63 (dd, 2 × 2H, J = 8, 2 Hz, Ph), 6.44 (t, 2H, J = 8 Hz, Ph), 3.36, 2.73 (sept., 2 × 2H, J = 7 Hz, CHMe$_2$), 3.04 (broad quartet, $^1J_{H,B}$ = 74 Hz, μ-H), 1.23 (broad s, 6H, hexane), 1.53, 1.12, 0.97 (d, 3 × 6H, J = 7 Hz, CHMe_2), 0.89 (t, J = 7 Hz, 6H, hexane), 0.70 (s, 18H, CMe_3), 0.60 (d, 6H, J = 7 Hz, CHMe_2). ^{19}F NMR (d_8-toluene, 20 °C): −132.6 (m, 2F, ortho-F), −158.8 (t, 1F, J = 20 Hz, para-F), −163.9 (m, 2F, meta-F). ^{13}C{^{1}H} NMR (d_8-toluene, 25 °C): δ 176.99 (s, CH(NAr)), 135.83, 135.77, 128.25, 125.67, 124.87, 118.39 (s, 6 Ph), 35.09 (s, CMe$_3$), 30.58, 30.05 (s, 2 × CHMe$_2$), 29.35 (s, CMe$_3$), 25.94, 25.54, 23.52, 22.72 (s, 4 × CHMe_2). ^{11}B NMR (d_8-toluene, 20 °C): −17.10 (t, $^1J_{B,H}$ = 74 Hz). Anal. Calcd for $C_{61}H_{69}F_{10}N_2O_2BY$: C, 63.60; H, 6.04; N, 2.43. Found: C, 63.03; H, 5.88; N, 2.54.

Reaction of 6-Y with HC≡CSiMe$_3$. To a solution of **6-Y** (100 mg, 6.55 × 10^{-5} mol) in toluene (10 mL) was added HC≡CSiMe$_3$ (0.2 mL, 1.42 mmol). After it was stirred at room temperature for 3 days, the yellow solution was evaporated to dryness in vacuo, and the resulting oily solid was dried in vacuo for 12 h. The product was then slurried in *n*-hexane (2 mL) and cooled to −35 °C, and the mother liquors were removed to give 43 mg of a yellow powder; yield 35 mg (33%). ^{1}H NMR of major isomer (d_8-toluene, −60 °C): δ 7.77 (d, 2H, J = 2 Hz, CH(NAr)), 7.33 (dd, 2H, J = 8, 2 Hz, Ph), 7.10−7.01 (m, 4H, Ph), 6.92 (broad d, 2H, J = 8 Hz, Ph), 6.80 (dd, 2H, J = 8, 2 Hz, Ph), 6.51 (t, 2H, J = 8 Hz, Ph), 3.12, 2.82 (sept, 2 × 2H, J = 7 Hz, CHMe$_2$), 1.54 (d, 6H, J = 7 Hz, CHMe_2), 1.14 (s, 18H, CMe_3), 1.04, 0.91, 0.75 (d, 3 × 6H, J = 7 Hz, CHMe_2), 0.25 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR of major isomer (d_8-toluene, 0 °C): δ 175.21 (s, CH(NAr)), 167.33 (s, quaternary aromatic), 163.13 (d, $^1J_{C,Y}$ = 72 Hz, YCCSiMe$_3$), 148.46, 141.83, 140.66, 140.58 (s, 4 quaternary aromatic), 134.91, 134.41, 127.36, 125.02, 124.45, 123.06 (s, 5 Ph), 123.06 (s, quaternary aromatic), 116.50 (s, Ph), 108.91 (d, $^2J_{C,Y}$ = 12 Hz, YCCSiMe$_3$), 35.22 (s, CMe$_3$), 29.74 (s, 2 × CMe_3), 30.05, 29.24 (s, 2 × CHMe$_2$), 27.47, 24.69, 24.35, 22.53 (s, 4 CHMe_2), 1.40 (s, SiMe$_3$). Anal. Calcd for $C_{51}H_{69}N_2O_2SiY$: C, 71.30; H, 8.09; N, 3.26. Found: C, 70.96; H, 7.51; N, 3.31.

Reaction of 6-Y with Benzophenone. A solution of **6-Y** (50 mg, 3.28 × 10^{-5} mol) and Ph$_2$CO (24 mg, 1.31 × 10^{-4} mol) in C_6H_6 (2 mL) was stirred at room temperature for 6 days and then evaporated to dryness. The resulting yellow oil was sonicated in *n*-hexane to give a yellow solid from which the near-colorless mother liquors were decanted. The solid was then washed an additional two times with *n*-hexane to give 34 mg of product (51% yield). ^{1}H NMR (d_8-toluene, 40 °C): δ 7.84 (s, 1H, CH(NAr)), 7.66 (broad s, 4H, Ph), 7.36 (m, 6H, Ph), 7.14−6.96 (m, 18H, Ph), 6.78 (d, 1H, J = 7 Hz, Ph), 6.52 (t, 3H, J = 7 Hz, Ph), 6.31 (s, 1H, OCHPh$_2$), 2.99, 2.90 (sept, 2 × 2H, J = 7 Hz, CHMe$_2$), 1.16 (broad s, 18H, CMe_3), 1.09, 1.02, 0.89, 0.82 (d, 3 × 6H, J = 6 Hz, CHMe_2). ^{13}C{^{1}H} NMR (d_8-toluene, 40 °C): δ 175.98 (s, CH(NAr)), 135.37, 134.16, 132.66 (b), 130.91 (b), 128.67, 128.40, 127.5 (b), 127.40, 126.47, 125.11, 124.81, 116.16 (s, 12 x Ph), 82.63 (s, OCHPh$_2$), 35.57 (s, 2 × CMe$_3$), 30.24 (s, 2 × CMe_3), 30.24, 29.50 (s, 2 × CHMe$_2$), 26.02, 24.91, 23.68, 23.00 (s, 4 × CHMe_2). Anal. Calcd for $C_{72}H_{81}N_2O_4Y$: C, 76.71; H, 7.24; N, 2.48. Found: C, 76.90; H, 7.44; N, 2.55.

Reaction of 6-Y with Pyridine. A solution of **6-Y** (100 mg, 6.55 × 10^{-5} mol) and pyridine (0.03 mL, 3.71 × 10^{-4} mol) in toluene (5 mL) was stirred at room temperature for 18 h and then evaporated to dryness in vacuo. The resulting orange solid was washed with *n*-pentane (×2) and dried in vacuo; yield 85 mg (70%). ^{1}H NMR (d_8-toluene, −60 °C): δ 8.89, 8.49 (d, 2 × 2H, J 5 Hz, *o*-NC$_5H_5$), 8.01 (s, 1H, CH(NAr)), 7.58, 7.46, 7.39 (d, 3 × 1H, J = 7.5 Hz, Ph), 7.22−6.94 (m, 6H, Ph), 6.92 (dd, 1H, J = 7.5 Hz, Ph), 6.80 (d, 1H, J 7.5 Hz, Ph), 6.61 (dd, 3H, J = 7.5, 7.5 Hz, Ph), 6.47 (t, 2H, J 7.5 Hz, *p*-NC$_5H_5$), 6.25, 6.01 (dd, 2 × 2H, J 7.5, 5 Hz, *m*-NC$_5H_5$), 4.79 (s, 2H, CH_2), 2.75, 2.37 (sept, 2 × 2H, J = 6 Hz, CHMe$_2$), 1.45, 1.37 (s, 2 × 9H, CMe_3), 1.27 (m, 6H, pentane), 1.17 (d, J = 6 Hz, CHMe$_2$), 0.94 (t, 6H, pentane), 0.70, 0.52, 050 (d, 3 × 6H, J = 6 Hz, CHMe_2). ^{13}C{^{1}H} NMR (d_8-toluene, 0 °C): δ 175.41 (s, CH(NAr)), 139.12, 136.16, 133.25, 129.58, 129.04, 128.65, 126.42, 125.77, 125.76, 125.05, 124.53, 123.48, 122.16, 116.63, 115.93 (s, 15 × Ph), 65.74 (s, CH$_2$), 35.43, 35.32 (s, 2 × CMe$_3$), 31.11, 30.44 (s, 2 × CMe_3), 28.69, 28.58 (s, 2 × CHMe$_2$), 27.55, 26.21, 23.00, 21.96 (s, 4 × CHMe_2). Anal. Calcd for $C_{61}H_{83}N_4O_2Y$: C, 73.76; H, 8.42; N, 5.64. Found: C, 74.23; H, 8.47; N, 5.60.

Reaction of 6-Y with THF. A solution of **6-Y** (80 mg, 4.34 × 10^{-5} mol) in toluene (2 mL) was layered with THF (∼0.5 mL) and allowed to stand for 3 days. The pale yellow mother liquors were then decanted, and the remaining yellow crystals were dried in vacuo for 10 min. Yield: 78 mg (72%). ^{1}H NMR (d_8-toluene, 100 °C): δ 8.02 (d, 1H, J = 2 Hz, CH(NAr)), 7.28 (dd, 1H, J = 8, 2 Hz, Ph), 7.15−6.92 (m, 7H, Ph), 6.86 (dd, 1H, J = 8 Hz, Ph), 6.53, 6.48 (t, 2 × 1H, J = 8 Hz, Ph), 4.35 (broad s, 2H CH$_2$), 3.74, 3.15 (sept, 2 × 2H, J = 7 Hz, CHMe$_2$), 3.61, 1.43 (m, 2 × 8H, THF), 1.32, 1.13 (d, 2 × 6H, J = 7 Hz, CHMe_2), 1.18 (d, 12H, J = 7 Hz, CHMe_2), 1.14, 1.07 (s, 2 × 9H, CMe_3). ^{13}C{^{1}H} NMR (d_8-toluene, 80 °C): δ 174.35 (s, CH(NAr)), 134.47, 133.11, 127.43, 126.50, 124.92, 123.96, 123.11, 122.71, 115.69, 115.15 (s, 10 Ph), 68.95 (broad s, THF), 63.08 (s, CH$_2$), 25.0 (broad s, THF), 34.66, 34.61 (s, 2 × CMe$_3$), 30.23, 29.25 (s, 2 × CMe_3), 29.66, 28.42 (s, 2 × CHMe$_2$), 25.01, 24.88, 22.84 (s, 3 CHMe_2). Anal. Calcd for $C_{68}H_{93}N_2O_4Y$: C, 71.50; H, 8.56; N, 3.09. Found: C, 71.58; H, 8.11; N, 2.67.

Synthesis of L$_3$Y (8-Y). A mixture of [YCl$_3$(THF)$_{3.5}$] (0.3 g, 0.67 mmol) and LiCH$_2$SiMe$_3$ (0.19 g, 2.01 mmol) in *n*-hexane (30 mL) was stirred for 2 h at 0 °C and then filtered to give a colorless solution of [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$]. After the mixture was cooled to −78 °C, a solution of **I** (0.68 g, 2.01 mmol) in *n*-hexane (20 mL) was added and the temperature was raised to 0 °C for 2 h and then to room temperature for 6 days. The mixture was then concentrated in vacuo (ca. 10 mL), sonicated, and cooled to −78 °C and the resulting pale yellow solid collected by filtration and washed with *n*-hexane (×2). Yield: 0.55 g (75%). X-ray-quality crystals were grown by allowing a hot toluene solution to cool to room temperature. ^{1}H NMR (C_6D_6): δ 7.88 (d, 3H, J = 1 Hz, CH(NAr)), 7.48 (dd, 3H, J = 8 Hz, J = 2 Hz, Ph), 7.04−6.98 (m, 9H, Ph), 6.75 (dd, 3H, J = 8 Hz, J = 2 Hz, Ph), 6.57 (t, 3H, J = 8 Hz, Ph), 3.67, 2.13 (sept, 2 × 3H, J = 7 Hz, CHMe$_2$), 1.54 (s, 27H, CMe_3), 0.95, 0.80, 0.66, 0.61 (d, 4 × 9H, J = 7 Hz, CHMe_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 177.97 (s, CH(NAr)), 166.91, 152.61, 143.53, 141.69, 140.27 (s, 5 quaternary aromatic), 136.35, 134.74, 127.45, 125.35, 125.19 (s, 5 Ph), 123.83 (s, quaternary aromatic), 116.44 (s, Ph), 36.15 (s, CMe$_3$), 32.07 (s, CMe_3), 29.27 (s, CHMe$_2$), 27.86 (s, CHMe_2), 27.77 (s, CHMe$_2$), 26.94, 23.81,

22.74 (s, 3 CH*Me*$_2$). Anal. Calcd for $C_{69}H_{90}N_3O_3Y$: C, 75.45; H, 8.26; N, 3.83. Found: C, 75.12; H, 8.24; N, 3.85.

Synthesis of [(κ^2-L)$_2$(κ^1-L)Sc] (8-Sc). A mixture of [Sc(CH$_2$SiMe$_3$)L$_2$] (**4-Sc$_{Me}$**; 0.2 g, 0.25 mmol) and **I** (84 mg, 0.25 mmol) in toluene (20 mL) was stirred for 4 days at 85 °C and then evaporated to dryness in vacuo. The resulting yellow oil was sonicated in *n*-pentane, cooled to −78 °C, and then filtered to collect a yellow solid, which was washed with cold *n*-pentane (×2); yield 149 mg (56%). X-ray-quality crystals of **8-Sc**·0.5(*n*-hexane) were grown by cooling a hot hexane solution to room temperature. ^{1}H NMR (d_8-toluene, −20 °C): δ 9.13, 8.77 (s, 2 × 1H, C*H*(NAr)), 8.46 (d, 1H, J = 7 Hz, Ph), 7.99, 7.81 (s, 2 × 1H, C*H*(NAr)), 7.73 (s, 2H, C*H*(NAr)), 7.38−7.33 (m, 4H, Ph), 7.26 (d, 1H, J = 7 Hz, Ph), 7.16−6.76 (m, 22H, Ph), 6.57−6.46 (m, 6H, Ph), 6.40 (t, 1H, J = 7 Hz, Ph), 6.12 (t, 1H, J = 8 Hz, Ph), 3.66, 3.32, 3.19, 3.06 (sept, 4 × 1H, J = 7 Hz, C*H*Me$_2$), 2.97 (m, 3H, C*H*Me$_2$), 2.82, 2.78 (sept, 2 × 1H, J = 7 Hz, C*H*Me$_2$), 2.73 (m, 3H, C*H*Me$_2$), 1.48 (d, 3H, J = 7 Hz, CH*Me*$_2$), 1.37, 1.33 (s, 2 × 9H, C*Me*$_3$), 1.32, 1.29, 1.23, 1.20, 1.16, 1.14, 1.10 (d, 7 × 3H, J = 7 Hz, CH*Me*$_2$), 1.10 (s, 9H, C*Me*$_3$), 1.08, 1.07 (d, 2 × 3H, J = 7 Hz, CH*Me*$_2$), 1.06 (12H, CH*Me*$_2$), 1.03 (s, 3H, J = 7 Hz, CH*Me*$_2$), 1.03 (s, 9H, C*Me*$_3$), 1.02, 1.00 (d, 2 × 3H, J = 7 Hz, CH*Me*$_2$), 0.94 (s, 9H, C*Me*$_3$), 0.93 (d, 3H, J = 7 Hz, CH*Me*$_2$), 0.91 (s, 9H, C*Me*$_3$), 0.81, 0.79 (d, 2 × 3H, J = 7 Hz, CH*Me*$_2$), 0.75 (6H, CH*Me*$_2$), 0.68, 0.51 (d, 2 × 3H, J = 7 Hz, CH*Me*$_2$). ^{13}C NMR (d_8-toluene, −20 °C): δ 177.24, 177.18, 177.00, 176.16 (s, 4 × *C*H(NAr)), 167.15, 166.78, 166.67, 165.64, 165.30 (s, 5 × quaternary aromatic), 158.96, 157.56 (s, 2 × *C*H(NAr)), 152.26, 152.22, 151.78, 151.17, 151.04, 148.41, 142.94, 142.30, 141.58, 141.45, 141.17, 141.13, 140.01, 139.92, 139.82, 139.50, 138.72, 138.66 (s, 18 × quaternary aromatic), 136.95 (s, Ph), 136.28 (s, quaternary aromatic), 136.20, 135.88, 135.85 (s, 3 × Ph), 135.84 (s, quaternary aromatic), 135.66, 135.58, 135.47 (s, 3 × Ph), 133.57 (s, quaternary aromatic), 130.19, 129.62, 129.13, 128.69, 128.08, 127.94, 127.74, 126.29, 125.65, 125.46, 125.42, 125.25, 125.09, 124.90, 124.70, 124.57 (s, 16 × Ph), 123.88 (s, quaternary aromatic), 123.71 (s, Ph), 123.52 (s, quaternary aromatic), 123.43 (s, Ph), 123.40 (s, quaternary aromatic), 123.33, 122, 81, 118.49, 117.93, 117.59, 117.51, 117.12 (s, 7 × Ph), 36.29, 36.03, 35.69, 35.59, 35.47 (s, 6 × *C*Me$_3$), 32.20, 31.94, 31.75, 31.33, 30.72, 30.67 (s, 6 × C*Me*$_3$), 30.44, 30.32, 30.06, 29.41, 29.29, 28.99, 28.98, 28.74, 28.36, 27.98 (s, 10 × *C*HMe$_2$), 26.46, 26.26, 26.25, 26.02, 25.85, 25.70, 25.64, 25.61, 24.90, 24.09, 23.83, 23.59, 23.51, 22.88, 22.74, 22.65, 22.52 (s, 17 × CH*Me*$_2$). Anal. Calcd for $C_{69}H_{90}N_3O_3Sc$: C, 78.60; H, 8.60; N, 3.99. Found: C, 78.04; H, 8.68; N, 3.74.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, and all bond distances and angles for the structurally characterized molecules presented here. This material is available free of charge via the Internet at http://pubs.acs.org.

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