

## Rare-Earth Metal Alkyl, Amido, and Cyclopentadienyl Complexes Supported by Imidazolin-2-iminato Ligands: Synthesis, Structural Characterization, and Catalytic Application<sup>†</sup>

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The rare earth metal dichlorides [(1)MCl<sub>2</sub>(THF)<sub>3</sub>] (**2a**, M = Sc; **2b**, M = Y; **2c**, M = Lu) and the gadolinium complex [(1)GdCl<sub>2</sub>(THF)<sub>2</sub>]·[LiCl(THF)<sub>2</sub>] (**2d**), containing the 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-iminato ligand **1**, proved to be versatile starting materials for the preparation of trimethylsilylmethyl (“neosilyl”) and bis(trimethylsilyl)amido complexes [(1)M(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>] (**3a–3d**) and [(1)M(HMDS)<sub>2</sub>(THF)] [**4a–4d**, HMDS = hexamethyldisilazide, N(SiMe<sub>3</sub>)<sub>2</sub>] and for the preparation of the benzyl complex [(1)Lu(CH<sub>2</sub>Ph)<sub>2</sub>(THF)<sub>2</sub>] (**5c**) by the reaction with LiCH<sub>2</sub>SiMe<sub>3</sub>, Na[N(SiMe<sub>3</sub>)<sub>2</sub>], and KCH<sub>2</sub>Ph, respectively. Treatment of **2a–2c** with KCp\* afforded the mono(pentamethylcyclopentadienyl) complexes [(1)Sc(Cp\*)Cl(THF)] (**6a**), [(1)Y(Cp\*)Cl(THF)<sub>2</sub>] (**6b**), and [(1)Lu(Cp\*)Cl(THF)] (**6c**). In contrast, the gadolinocene complex [(1)Gd(Cp\*)<sub>2</sub>(THF)] (**7**) was isolated from the reaction of **2d** with 2 equiv of KCp\*. The molecular structures of **3a–3d**, **4b**·THF, **4d**, **5c**, **6a**, **6c**, and **7**·THF were determined by X-ray diffraction analyses, revealing the presence of exceptionally short metal–nitrogen bonds. The neosilyl complexes **3b** and **3c** showed high catalytic activity in the intramolecular hydroamination of aminoalkenes and aminoalkynes and in the hydrosilylation of 1-hexene and 1-octene with PhSiH<sub>3</sub>.

### Introduction

Ever since the preparation of the first tris(cyclopentadienyl) rare earth metal complexes, [(η-C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>M], by Wilkinson and Birmingham in 1954,<sup>1</sup> the organometallic chemistry of the rare earth elements has been dominated by cyclopentadienyl ligands (Cp), or by ligands that may be regarded as Cp analogues.<sup>2–4</sup> As cyclopentadienides normally serve as prototypical ancillary ligands that stabilize a metal complex but do

not themselves participate in chemical transformations, these homoleptic Cp complexes do usually not display particularly interesting catalytic reactivity, and the interest in this class of compounds is mainly justified from a historic and structural point of view.<sup>5</sup> Accordingly, bis(cyclopentadienyl) complexes of the type [(Cp)<sub>2</sub>M(X)(L)<sub>n</sub>] (X = anionic ligand, L = neutral ligand) play a much more prominent role with regard to the application of rare earth metal complexes in homogeneous catalysis,<sup>6</sup> and in the past, numerous metallocene or lanthanocene complexes have been developed that were able to catalyze efficiently organic transformations such as the polymerization of olefins, dienes, acrylates, and alkynes<sup>7</sup> and the hydrogenation,<sup>8</sup> hydroamination,<sup>9</sup> hydrosilylation,<sup>10</sup> and hydroboration<sup>11</sup> of alkenes and alkynes.<sup>12</sup> In contrast, significantly less use has been made of mono(cyclopentadienyl) complexes of the type

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(1) (a) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 6210. (b) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42.

(2) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.

(3) Herrmann, W. A.; Anwander, R. *Top. Curr. Chem.* **1996**, *179*, 1.

(4) (a) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851. (b) Edelmann, F. T. *Angew. Chem.* **1995**, *107*, 2647. *Angew. Chem., Int. Ed.* **1995**, *34*, 2466. (c) Kempe, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 468.

(5) This statement needs to be specified in view of the unexpected preparation and unusual reactivity of tris(pentamethylcyclopentadienyl) lanthanide complexes, [(η-C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Ln], which were long thought to be nonexistent; their discovery has certainly revitalized the interest in the chemistry of homoleptic Cp lanthanide complexes, see for instance: (a) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119. (b) Evans, W. J. *J. Organomet. Chem.* **2002**, *647*, 2. (c) Evans, W. J. *Inorg. Chem.* **2007**, *46*, 3435.

(6) Anwander, R. in *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 2000; p 866.

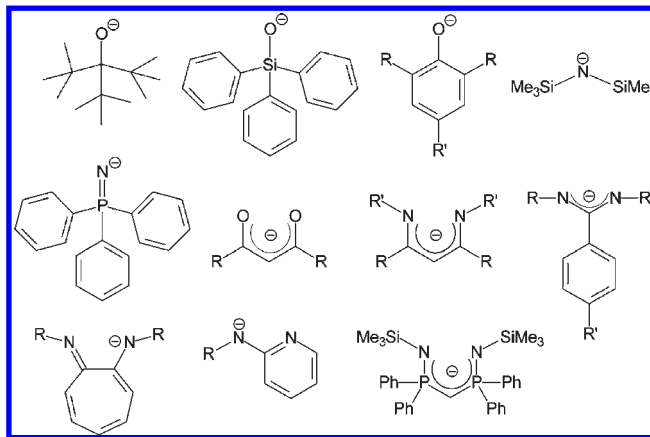
(7) (a) Wilson, D. J. *Polym. Int.* **1996**, *39*, 235–242. (b) Taube, R.; Sylvester, G. *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Wiley: New York, 2002; Vol. 1, p 285. (c) Thiele, S. K.-H.; Wilson, D. R. *Polym. Rev.* **2003**, *43*, 581.

(8) (a) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *103*, 1401. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.

(9) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673.

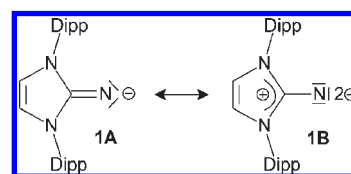
[(Cp)M(X)<sub>2</sub>(L)<sub>n</sub>] in homogeneous catalysis, since the selective synthesis of these half-sandwich complexes is generally made difficult by the greater thermodynamic stability of the corresponding metallocene derivatives.<sup>13</sup>

In addition to cyclopentadienyl ligands, a growing number of monoanionic heteroatom ligands that can be regarded as Cp-analogous ligands because of their charge and steric requirements play a key role in organolanthanide and organo rare earth metal chemistry. The most important ancillary ligands are monodentate alkoxides (OR), siloxides (OSiR<sub>3</sub>), aryloxides (OR),<sup>14</sup> amides (NR<sub>2</sub>),<sup>15</sup> and phosphoraneiminates (NPR<sub>3</sub>)<sup>16</sup> together with polydentate ligands such as β-diketonates,<sup>17</sup> β-diketiminates,<sup>18</sup> benzamidinates,<sup>19</sup> aminotroponiminates,<sup>20</sup> aminopyridinato,<sup>21</sup> bis(phosphinimino)methanides<sup>22</sup> and



**Figure 1.** Selection of monoanionic ancillary ligands in rare-earth metal chemistry.

**Scheme 1.** Mesomeric Structures for the Imidazolin-2-imide **1** (Dipp = 2,6-diisopropylphenyl)



other phosphanoamides;<sup>23,24</sup> Figure 1 shows a selection of important ligands for the application of rare earth metal complexes in homogeneous catalysis and material science.

Recently, we and others<sup>25</sup> have introduced monoanionic imidazolin-2-iminato ligands such as Im<sup>Dipp</sup>N (**1**)<sup>26</sup> to this growing family of ancillary ligands and were able to demonstrate that these ligands are viable systems for the preparation of catalytically active transition metal and rare earth metal complexes.<sup>27,28</sup> The structural characterization of scandium, yttrium, gadolinium and lutetium complexes of the type [(1)MCl<sub>2</sub>(THF)<sub>3</sub>] (**2**) and [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)M(1)(THF)<sub>n</sub>] revealed in all cases the presence of terminal imidazolin-2-iminato ligands with exceptionally short metal–nitrogen bonds.<sup>29,30</sup> The potential of imidazolin-2-iminato ligands such as **1** to form particularly strong metal–nitrogen bonds is illustrated by the two limiting resonance structures **1A** and **1B** (Scheme 1),<sup>26,31</sup> indicating that the ability of the imidazole ring to stabilize a positive charge affords highly basic ligands with a strong

(25) Kuhn, N.; Göhner, M.; Grathwohl, M.; Wiethoff, J.; Frenking, G.; Chen, Y. *Z. Anorg. Allg. Chem.* **2003**, *629*, 793.

(26) Tamm, M.; Petrovic, D.; Beer, S.; Bannenberg, T.; Jones, P. G.; Grunenberg, J. *Org. Biomol. Chem.* **2007**, *5*, 523.

(27) (a) Tamm, M.; Randall, S.; Bannenberg, T.; Herdtweck, E. *Chem. Commun.* **2004**, 876. (b) Tamm, M.; Beer, S.; Herdtweck, E. *Z. Naturforsch.* **2004**, *59b*, 1497. (c) Tamm, M.; Randall, S.; Herdtweck, E.; Kleigrew, N.; Kehr, G.; Erker, G.; Rieger, B. *Dalton Trans.* **2006**, 459. (d) Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8890. (e) Beer, S.; Brandhorst, K.; Grunenberg, J.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Org. Lett.* **2008**, *10*, 981. (f) Stelzig, S. H.; Tamm, M.; Waymouth, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6064. (g) Beer, S.; Brandhorst, K.; Hrib, C. G.; Wu, X.; Haberlag, B.; Grunenberg, J.; Jones, P. G.; Tamm, M. *Organometallics* **2009**, *28*, 1534.

(28) Panda, T. K.; Hrib, C. G.; Jones, P. G.; Jenter, J.; Roesky, P. W.; Tamm, M. *Eur. J. Inorg. Chem.* **2008**, 4270.

(29) Panda, T. K.; Randall, S.; Hrib, C. G.; Jones, P. G.; Bannenberg, T.; Tamm, M. *Chem. Commun.* **2007**, 5007.

(30) Panda, T. K.; Trambitas, A. G.; Bannenberg, T.; Hrib, C. H.; Randall, S.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2009**, *48*, 5462.

(31) Frison, G.; Sevin, A. *J. Chem. Soc., Perkin Trans.* **2002**, 1692.

(10) (a) Molander, G. A.; Romero, J. A. *C. Chem. Rev.* **2002**, *102*, 2161. (b) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *117*, 7157. (c) Castillo, I.; Tilley, T. D. *Organometallics* **2000**, *19*, 4733. (d) Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1996**, *524*, 275. (e) Schumann, H.; Keitsch, M. R.; Winterfeld, J.; Muhle, S.; Molander, G. A. *J. Organomet. Chem.* **1998**, *559*, 181.

(11) (a) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220. (b) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal.* **1995**, *95*, 121.

(12) (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **2002**, *18*, 51. (b) Edlmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 247.

(13) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953.

(14) (a) Anwander, R. *Top. Curr. Chem.* **1996**, *179*, 149. (b) Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem. Rev.* **1991**, *91*, 1287. (c) Boyle, T.; Ottly, L. A. *Chem. Rev.* **2008**, *108*, 1896.

(15) Anwander, R. *Top. Curr. Chem.* **1996**, *179*, 33.

(16) Dehnicke, K.; Greiner, A. *Angew. Chem.* **2003**, *115*, 1378. *Angew. Chem., Int. Ed.* **2003**, *42*, 1340.

(17) (a) Tsukube, H.; Shinoda, S.; Tamiaki, H. *Coord. Chem. Rev.* **2002**, *226*, 227. (b) Kaizaki, S. *Coord. Chem. Rev.* **2006**, *250*, 1804. (c) Condorelli, G. G.; Malandrino, G.; Fagala, I. L. *Coord. Chem. Rev.* **2007**, *251*, 1931.

(18) (a) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031. (b) Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V. *Dalton Trans.* **2009**, 2383. (c) Lappert, M. F. *J. Organomet. Chem.* **2000**, *600*, 144. (d) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404. (e) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233–234*, 131. (f) Vitanova, D. V.; Hampel, F.; Hultsch, K. C. *J. Organomet. Chem.* **2005**, *690*, 5182. (g) Lazarov, B. B.; Hampel, F.; Hultsch, K. C. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2367. (h) Yao, Y.; Zhang, Z.; Peng, H.; Zhang, Y.; Shen, Q.; Lin, J. *Inorg. Chem.* **2006**, *45*, 2175. (i) Sanchez-Barba, L. F.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. *Organometallics* **2005**, *24*, 3792. (j) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947. (k) Hayes, P. G.; Piers, W. E.; Parvez, M. *Organometallics* **2005**, *24*, 1173. (l) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622.

(19) (a) Edlmann, F. T. *Adv. Organomet. Chem.* **2008**, *57*, 183. (b) Edlmann, F. T. *Chem. Soc. Rev.* **2009**, *38*, 2253.

(20) (a) Bürgstein, M. R.; Berberich, H.; Roesky, P. W. *Organometallics* **1998**, *17*, 1452. (b) Meyer, N.; Zulys, A.; Roesky, P. W. *Organometallics* **2006**, *25*, 4179. (c) Meyer, N.; Roesky, P. W. *Dalton Trans.* **2007**, 2652. (d) Meyer, N.; Roesky, P. W. *Organometallics* **2009**, *28*, 306.

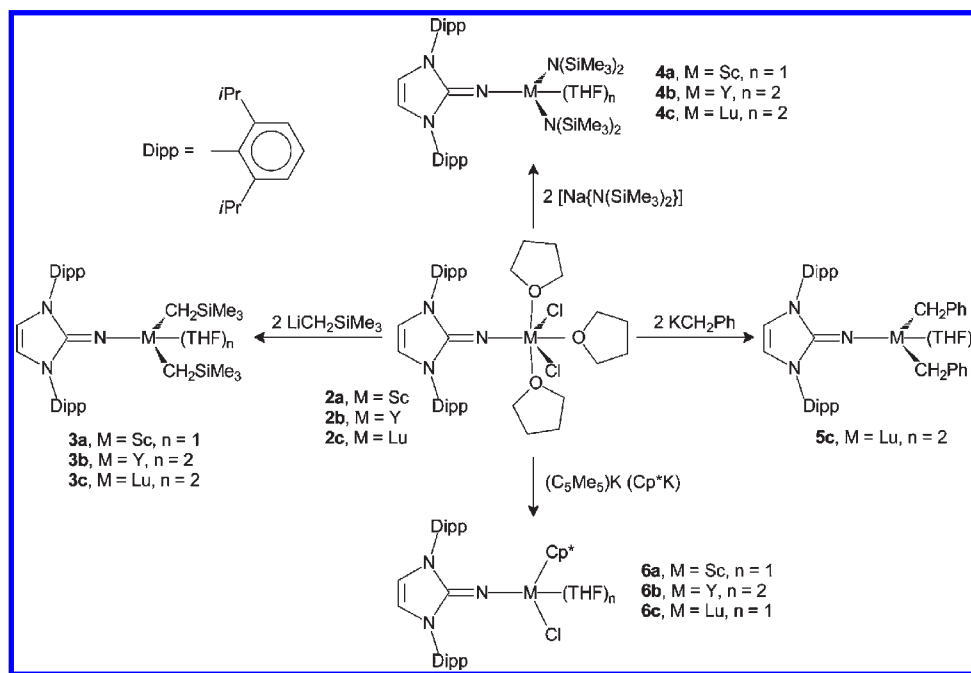
(21) (a) Kempe, R. *Eur. J. Inorg. Chem.* **2003**, *2003*, 791. (b) Kempe, R.; Noss, H.; Irrgang, T. *J. Organomet. Chem.* **2002**, *647*, 12. (c) Glatz, G.; Demeshko, S.; Motz, G.; Kempe, R. *Eur. J. Inorg. Chem.* **2009**, 1385. (d) Scott, N. M.; Schareina, T.; Tok, O.; Kempe, R. *Eur. J. Inorg. Chem.* **2004**, 3297–3304. (e) Scott, N. M.; Kempe, R. *Eur. J. Inorg. Chem.* **2005**, 1319.

(22) (a) Gamer, M. T.; Rastätter, M.; Roesky, P. W.; Steffens, A.; Glanz, M. *Chem.—Eur. J.* **2005**, *11*, 3165. (b) Gamer, M. T.; Roesky, P. W.; Palard, I.; Le Hellaye, M.; Guillaume, S. M. *Organometallics* **2007**, *26*, 651. (c) Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Inorg. Chem.* **2006**, *45*, 910. (d) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2005**, *24*, 2197. (e) Zulys, A.; Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Chem. Commun.* **2004**, 2584.

(23) (a) Wedler, M.; Kösel, F.; Pieper, U.; Stalke, D.; Edlmann, F.; Amberger, H.-D. *Chem. Ber.* **1992**, *125*, 2171. (b) Edlmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 113. (c) Skinner, M. R. G.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2002**, 1694. (d) Yao, S.; Chan, H.-S.; Lam, C.-K.; Lee, H. K. *Inorg. Chem.* **2009**, *48*, 9936.

(24) (a) Roesky, P. W. *Heteroatom Chem.* **2002**, *13*, 514. (b) Power, P. P. *J. Organomet. Chem.* **2004**, *689*, 3904. (c) Fei, Z.; Dyson, P. J. *Coord. Chem. Rev.* **2005**, *249*, 2056.

Scheme 2. Preparation of Imidazolin-2-iminato Rare-Earth Metal Complexes



electron-donating capacity toward early transition metals or metals in a higher oxidation state. In these cases, the imidazolin-2-iminato ligands are able to display their full potential as  $2\sigma,4\pi$ -electron donors and can thus be regarded as monodentate analogues of cyclopentadienyls,  $\text{C}_5\text{R}_5$ , and as monoanionic imido ligands in a similar fashion to that described for related phosphoraneiminato ligands.<sup>16,32</sup> Accordingly, we aimed at the preparation of complexes with one, two or three imidazolin-2-iminato ligands for comparison with the corresponding mono-, bis- and tris(cyclopentadienyl) complexes. With this contribution, we begin by reporting the synthesis and structural characterization of various mono(imidazolin-2-iminato) complexes of the type  $[(1)\text{M}(\text{X})_2(\text{THF})_n]$  (M = Sc, Y, Gd, Lu) with X = trimethylsilylmethyl ( $\text{CH}_2\text{SiMe}_3$ ), benzyl ( $\text{CH}_2\text{Ph}$ ), bis(trimethylsilyl)amido  $[(\text{Me}_3\text{Si})_2\text{N}]$ , and pentamethylcyclopentadienyl ( $\text{Cp}^*$ ). In addition, the application of several neosilyl ( $\text{CH}_2\text{SiMe}_3$ ) complexes as catalysts for hydrosilylation and hydroamination reactions is presented.

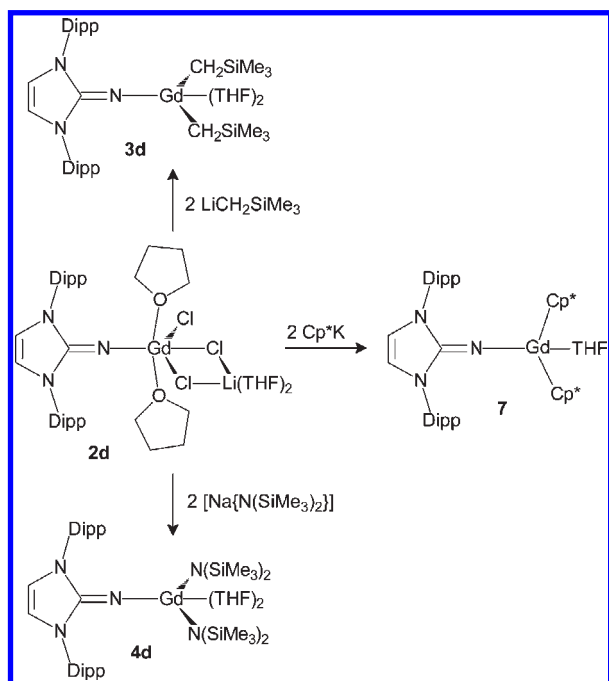
## Results and Discussion

**Preparation and Structural Characterization of Imidazolin-2-iminato Neosilyl Complexes.** In most cases, bis(neosilyl) rare earth metal complexes have been prepared by the reaction of  $[\text{M}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$  with the protonated form of a desired ancillary ligand, which is accompanied by release of tetramethylsilane (TMS).<sup>33</sup> In our hands, however, the dichloro complexes  $[(1)\text{MCl}_2(\text{THF})_3]$  (**2a**, M = Sc; **2b**, M = Y; **2c**, M = Lu) proved to be superior starting materials,<sup>30</sup> and their reaction with two equivalents of  $\text{LiCH}_2\text{SiMe}_3$  afforded the bis(neosilyl) complexes  $[(1)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$  (**3a**),  $[(1)\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2]$  (**3b**), and  $[(1)\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2]$  (**3c**) as pale yellow solids in high yield (Scheme 2). In contrast, the corresponding gadolinium complex  $[(1)\text{Gd}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2]$  (**3d**) was obtained from the ate complex  $[(1)\text{GdCl}_2(\text{THF})_2] \cdot [\text{LiCl}(\text{THF})_2]$  (**2d**) by treatment with the neosilyl lithium reagent (Scheme 3). All complexes showed good solubility in common organic solvents, such as THF, pentane, and toluene. Well-resolved NMR spectra are obtained for the diamagnetic scandium, yttrium, and lutetium complexes **3a–3c**, and each complex shows one set of  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances for the  $\text{CH}_2\text{SiMe}_3$  and THF moieties. Additionally, each  $^1\text{H}$  NMR spectrum exhibits two doublet resonances for the diastereotopic isopropyl  $\text{CH}_3$  groups, indicating that rotation around the C–N–metal axis is fast on the NMR time scale. The methylene protons of the neosilyl groups in complexes **3a** and **3c** are observed as singlet peaks at  $-0.37$  and  $-1.03$  ppm, respectively, whereas the yttrium complex **3b** shows a doublet at  $-0.97$  ppm because of  $^{89}\text{Y}-^1\text{H}$  coupling ( $^2J_{\text{Y-H}} = 2.8$  Hz). Accordingly, this methylene group in **3b** gives rise to a doublet at 26.2 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR with a  $^{89}\text{Y}-^{13}\text{C}$  coupling of  $^1J_{\text{Y-C}} = 36.4$  Hz; these values fall in the range that was previously reported for yttrium-neosilyl complexes.<sup>28,34</sup>

(32) (a) Dehnicke, K.; Krieger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19. (b) Dehnicke, K.; Weller, F. *Coord. Chem. Rev.* **1997**, *158*, 103. (c) Dehnicke, K.; Strähle, J. *Polyhedron* **1989**, *6*, 707.

(33) (a) Fryzuk, M. D.; Griesbrecht, G.; Rettig, S. *Organometallics* **1996**, *15*, 3329. (b) Evans, W. J.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *J. Organomet. Chem.* **1998**, *569*, 89. (c) Lara-Sanchez, A.; Rodriguez, A.; Hughes, D. L.; Schormann, M.; Bochmann, M. *J. Organomet. Chem.* **2002**, *663*, 63. (d) Cameron, T. M.; Gordon, J. C.; Michalczyk, R.; Scott, B. L. *Chem. Commun.* **2003**, 2282. (e) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2003**, 522. (f) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182. (g) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem. Int. Ed.* **2005**, *44*, 962. (h) Li, S.; Miao, W.; Tang, T.; Cui, D.; Chen, X.; Jing, X. *J. Organomet. Chem.* **2007**, *692*, 4943. (i) Yang, Y.; Liu, B.; Lv, K.; Gao, W.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 4575. (j) Luo, Y.; Nishiura, M.; Hou, Z. *J. Organomet. Chem.* **2007**, *692*, 536. (k) Chen, J.; Saliu, K.; Kiel, G. Y.; Ferguson, M. J.; McDonald, R.; Takats, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 4910. (l) Zimmermann, M.; Törnroos, K. W.; Waymonth, R. M.; Anwender, R. *Organometallics* **2008**, *26*, 4310. (m) Zhang, Z.; Cui, D.; Liu, X. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6810. (n) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 3131. (o) Li, S.; Cui, D.; Li, D.; Hou, Z. *Organometallics* **2009**, *28*, 4814.

(34) (a) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227. (b) Zhang, W.-X.; Nishiura, M.; Hou, Z. *Chem.—Eur. J.* **2007**, *13*, 4037.

**Scheme 3.** Preparation of Imidazolin-2-iminato Gadolinium Complexes

**3b** was additionally characterized by  $^{89}\text{Y}$  NMR spectroscopy, affording a resonance at 813.8 ppm, which is upfield from the resonance at 882.7 ppm reported for  $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ .<sup>35</sup> This high-field shift is in agreement with the trend derived for other yttrium complexes upon substitution of alkyl groups by  $\pi$ -donor ligands.<sup>36</sup>

The solid-state structures of complexes **3a–3d** were determined by X-ray diffraction analyses, and selected bond lengths and angles are summarized in Table 1. The molecular structure of the scandium complex **3a** is shown in Figure 2, revealing the formation of a mono(tetrahydrofuran) complex  $[(1)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ . Accordingly, the scandium atom in **3a** is only four-coordinate and displays a strongly distorted tetrahedral coordination sphere with scandium–carbon and scandium–oxygen distances of 2.223(3) Å (Sc–C28), 2.225(3) Å (Sc–C32), and 2.1593(18) Å (Sc–O) that are similar to those found in related four-coordinate complexes of the type  $[\text{Sc}(\text{X})(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$  (X = anionic ligand).<sup>33g,j</sup> The imidazolin-2-iminato ligand coordinates in an essentially linear fashion [ $\text{Sc}-\text{N}1-\text{C}1 = 178.90(18)^\circ$ ], and the Sc–N bond length of 1.9520(18) Å is shorter than observed for the six-coordinate dichloride **2a**.<sup>30</sup> In fact, there is only one complex featuring a shorter Sc–N distance of 1.9366(14) Å, and that is the  $\text{AlMe}_3$  adduct of the transient scandium-imido complex  $[(\text{PNP})\text{Sc}(\text{N}-\text{Dipp})]$  containing the PNP pincer ligand bis(2-diisopropylphosphino-4-methylphenyl)amide.<sup>37</sup> The only other Sc–N bond lengths that also lie below 2 Å have been observed in **2a** and in the  $\beta$ -diketiminato complexes  $[(\text{nacnac})\text{ScCl}(\text{NH}t\text{Bu})]$  [1.986(2) Å] and  $[(\text{nacnac})\text{Sc}$

$(\text{CH}_3)(\text{NH}t\text{Bu})\cdot\text{B}(\text{C}_6\text{F}_5)_3$  [1.969(3) Å] with  $\text{nacnac} = [\text{Dipp}-\text{NC}(t\text{Bu})\text{CHC}(t\text{Bu})\text{N}-\text{Dipp}]$ .<sup>38</sup>

The larger ionic radii<sup>39</sup> allow the yttrium, lutetium, and gadolinium atoms in **3a–3d** to accommodate an additional THF ligand, and in agreement with the NMR data, complexes of the type  $[(1)\text{M}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2]$  are formed. **3b** and **3c** are isostructural and crystallize in the orthorhombic space group  $P2_12_12_1$ , whereas **3d** crystallizes in the space group  $Pna2_1$ . As representatives, the molecular structures of **3b** and **3d** are shown in Figures 3 and 4; all three complexes exhibit a five-coordinate metal atom with a trigonal-bipyramidal coordination sphere, in which the THF ligands adopt the axial positions, albeit with a pronounced deviation of the  $\text{O}1-\text{M}-\text{O}2$  angles from  $180^\circ$  [ $160.50(4)^\circ$  (**3b**),  $161.15(8)^\circ$  (**3c**),  $165.73(4)^\circ$  (**3d**)]. Because the  $\text{C}28-\text{M}-\text{C}32$  angles in **3b–3d** are larger than the  $\text{N}1-\text{M}-\text{C}28/\text{C}32$  angles, the orientation of the equatorial ligands deviates significantly from an ideal trigonal-planar geometry; however, the sum of these angles is in all cases almost exactly  $360^\circ$ , thus indicating a nearly perfect coplanarity with the metal atom.

The isostructural complexes **3b** and **3c** exhibit almost linear  $\text{M}-\text{N}1-\text{C}1$  angles with metal–nitrogen bond lengths of 2.1255(13) and 2.089(3) Å that are shorter than those observed for the dichlorides **2b** and **2c**.<sup>30</sup> For yttrium, we are only aware of one complex featuring an even shorter Y–N distance (2.116(6) Å), and this is a tetranuclear Cp–yttrium complex containing  $\mu_3$ -ethylimido ligands.<sup>40</sup> In contrast, the Lu–N bond length in **3c** is shorter than any other previously published Lu–N bonds, and the previous shortest Lu–N distances of 2.145(2) and 2.149(4) Å were found in benzamidate and amido complexes, respectively.<sup>40,41</sup> Nevertheless, it should be noted that the value in **3c** is reduced even further in **5c** and **6c** (vide infra). **3d** features a gadolinium–nitrogen distance of 2.1643(13) Å, which is slightly longer than that found for the ate complex **2d** [2.153(3) Å].<sup>30</sup> Therefore, the latter value still represents the shortest Gd–N bond ever reported; the previous shortest Gd–N distances ranging from 2.190(3) to 2.240(3) Å were observed for five-membered amidolanthanide heterocycles.<sup>42</sup>

**Preparation and Structural Characterization of Imidazolin-2-iminato Bis(trimethylsilyl)amido Complexes.** In a similar fashion to that described for bis(neosilyl) rare earth metal complexes, related diamido complexes are usually prepared from the triamides  $[\text{M}\{\text{N}(\text{SiRMe}_2)_2\}_3(\text{THF})_2]$  (R = Me, H), which release one amine  $\text{HN}(\text{SiRMe}_2)_2$  upon treatment with the protonated form of an appropriate ancillary ligand.<sup>43</sup> Again, the reaction of the dichlorides  $[(1)\text{MCl}_2(\text{THF})_3]$  (**2a**, M = Sc; **2b**, M = Y; **2c**, M = Lu) with two equivalents of  $[\text{Na}\{\text{N}(\text{SiMe}_3)_2\}]$  in THF proved to be a superior method, and the complexes **4a–4c** of the composition  $[(1)\text{M}(\text{HMDS})_2(\text{THF})]$  [HMDS = hexamethyldisilazide,  $\text{N}(\text{SiMe}_3)_2$ ] were isolated

(38) (a) Knight, L. K.; Piers, W. E.; Fleurat-Lessard, P.; Parvez, M.; McDonald, R. *Organometallics* **2004**, *23*, 2087. (b) Knight, L. K.; Piers, W. E.; McDonald, R. *Organometallics* **2006**, *25*, 3289.

(39) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *B25*, 925.

(40) Cui, D.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 959.

(41) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184.

(42) Shah, S. A. A.; Dorn, H.; Roesky, H. W.; Lubini, P.; Schmidt, H.-G. *Inorg. Chem.* **1997**, *36*, 1102.

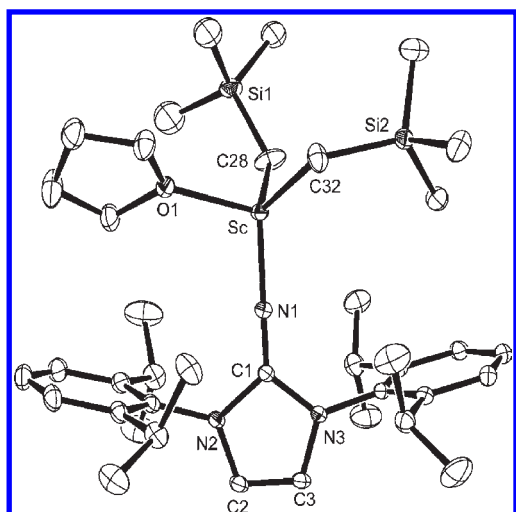
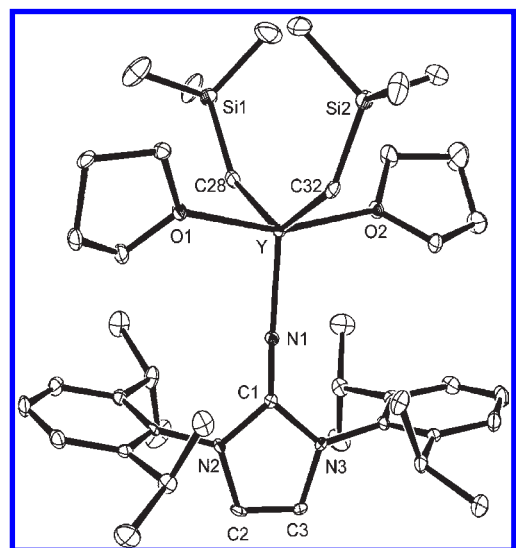
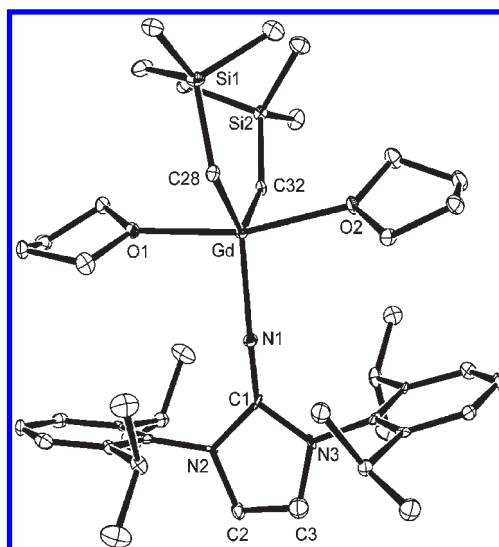
(35) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339.

(36) (a) Schaverien, C. J. *Organometallics* **1994**, *13*, 69. (b) White, R. E.; Hanusa, T. P. *Organometallics* **2006**, *25*, 5621.

(37) Scott, J.; Basuli, F.; Fout, A. R.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 8502.

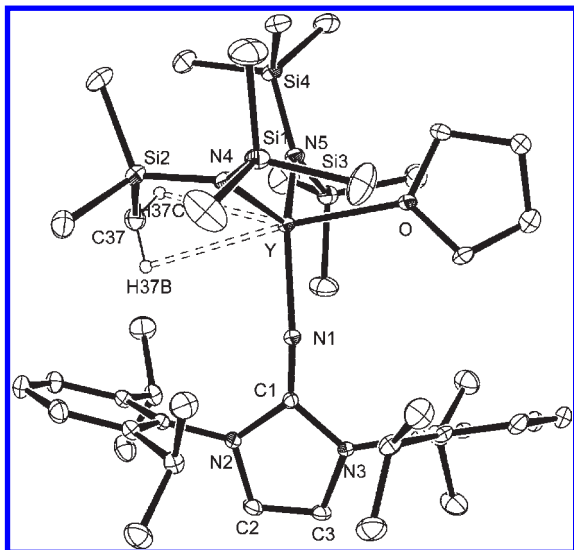
**Table 1.** Selected Bond Lengths (Å) and Angles (deg) in Complexes 3–5

	3a (M = Sc)	3b (M = Y)	3c (M = Lu)	3d (M = Gd)	4b·THF (M = Y)	4d (M = Gd)	5c (M = Lu)
M–N1	1.9520(18)	2.1255(13)	2.089(3)	2.1643(13)	2.135(2)	2.172(5)/2.180(5)	2.0752(18)
M–O1	2.1593(18)	2.3629(10)	2.3138(17)	2.444(3)	2.3314(16)	2.366(4)/2.392(4)	2.3102(15)
M–O2		2.3697(10)	2.327(2)	2.428(3)			2.3117(16)
M–C28	2.223(3)	2.4469(15)	2.399(3)	2.4795(17)			
M–N4					2.264(2)	2.316(5)/2.180(5)	
M–C36							2.428(2)
M–C32	2.225(3)	2.4334(17)	2.391(3)	2.4983(17)			
M–N5					2.294(2)	2.311(5)/2.275(5)	
M–C43							2.427(2)
N1–C1	1.271(3)	1.2653(19)	1.268(3)	1.2678(19)	1.261(3)	1.242(7)/1.259(8)	1.267(3)
M–N1–C1	178.90(18)	176.85(12)	176.4(2)	170.85(12)	166.08(17)	164.9(4)/166.1(5)	178.27(16)
N1–M–O1	106.61(7)	97.85(5)	97.64(9)	96.60(14)	97.50(7)	97.75(17)/95.71(17)	101.04(6)
N1–M–O2		101.61(5)	101.19(9)	97.42(14)			103.11(6)
O1–M–O2		160.50(4)	161.15(8)	165.73(4)			155.82(6)
C28–M–C32	109.82(15)	135.84(6)	136.22(10)	130.79(6)			
N4–M–N5					117.70(8)	124.40(18)/115.68(18)	
C36–M–C43							130.96(8)
N1–M–C28	115.00(11)	114.37(5)	114.21(9)	113.86(6)			
N1–M–N4					111.81(7)	114.51(18)/113.321(18)	
N1–M–C36							111.60(8)
N1–M–C32	118.81(12)	109.77(5)	109.56(9)	115.35(5)			
N1–M–N5					126.30(8)	118.42(18)/113.32(18)	
N1–M–C43							117.31(8)
N2–C1–N3	102.61(16)	101.64(13)	101.4(2)	101.72(13)	101.93(18)	102.4(5)/102.2(5)	102.22(16)

**Figure 2.** ORTEP diagram of 3a with thermal displacement parameters drawn at the 15% probability level.**Figure 3.** ORTEP diagram of 3b with thermal displacement parameters drawn at the 30% probability level.**Figure 4.** ORTEP diagram of 3d with thermal displacement parameters drawn at the 30% probability level.

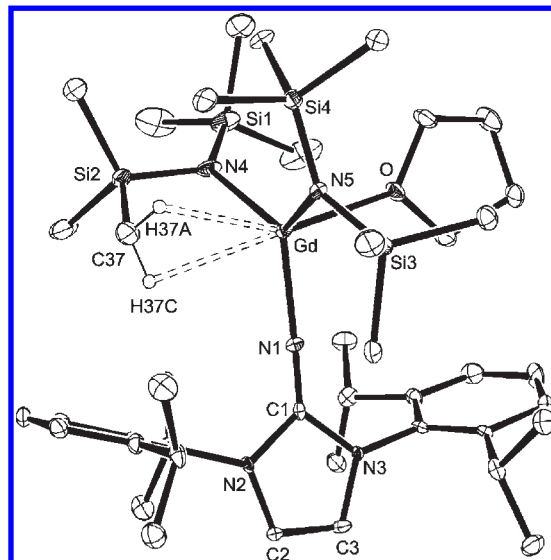
as off-white crystalline solids in good yield after extraction with pentane. The  $^1\text{H}$  NMR spectra (in  $\text{C}_6\text{D}_6$ ) of the diamagnetic complexes 4a–4c exhibit in all cases one singlet resonance for the  $\text{SiCH}_3$  groups and, similarly to complexes 3a–3c, two doublet resonances for the diastereotopic isopropyl  $\text{CH}_3$  groups. In contrast, the paramagnetic nature of the gadolinium complex 4d prevents its characterization by NMR spectroscopy.

(43) (a) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *Dalton Trans.* **1989**, 623. (b) Hermann, W. A.; Anwender, R.; Munch, F. C.; Scherer, W.; Dufaud, V.; Huber, N. W.; Artus, G. R. J. *Z. Naturforsch.* **1994**, 49b, 1789. (c) Karl, M.; Harms, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, 625, 1774. (d) Klimpel, M. G.; Görlitzer, H. W.; Tafipolsky, M.; Spiegler, M.; Scherer, W.; Anwender, R. *J. Organomet. Chem.* **2002**, 647, 236. (e) Niemeyer, M. *Inorg. Chem.* **2006**, 45, 9085. (f) Rastätter, M.; Zylus, A.; Roesky, P. W. *Chem. Commun.* **2006**, 874. (g) Rastätter, M.; Zylus, A.; Roesky, P. W. *Chem.—Eur. J.* **2007**, 13, 3606. (h) Döring, C.; Kempe, R. *Eur. J. Inorg. Chem.* **2009**, 412.



**Figure 5.** ORTEP diagram of **4b** in **4b**·THF with thermal displacement parameters drawn at the 30% probability level; selected bond lengths (Å): Y–H37B, 2.73(4); Y–H37C, 2.82(3).

The high solubility of complexes **4a**–**4d** in aromatic and aliphatic solvents suggested the formation of mononuclear metal complexes, which was confirmed for the yttrium and gadolinium complexes **4b** and **4d** via X-ray diffraction analysis. Suitable single crystals were obtained from THF/pentane solution at  $-30\text{ }^{\circ}\text{C}$ ; the yttrium complex **4b** crystallizes as a THF solvate in the space group  $P\bar{1}$ , whereas the gadolinium complex **4d** crystallizes without an additional THF solvate molecule in the space group  $P2_12_12_1$  with two independent molecules in the asymmetric unit. In both cases, the metal atoms attain a coordination number of four, being coordinated by one imidazolin-2-iminato ligand, two bis(trimethylsilyl)amido groups and one THF unit, and thus, the coordination spheres around the metal atoms could be described as distorted tetrahedral geometries. However, in both cases, short intramolecular C–H $\cdots$ M contacts are observed with the methyl groups of one HMDS ligand as is commonly found for related silylamido rare earth metal complexes (Figures 5 and 6).<sup>44,45</sup> Because the methyl groups involved in these weak agostic interactions are located trans to the THF ligand, the metal coordination spheres in **4b** and **4d** should preferably be described as distorted trigonal-bipyramidal with the nitrogen ligands adopting the equatorial positions. As expected,



**Figure 6.** ORTEP diagram of **4d** (one of two independent molecules) with thermal displacement parameters drawn at the 30% probability level; selected bond lengths (Å): Gd1–H37A, 2.64; Gd1–H37C, 2.65; Gd2–H87A, 2.59; Gd2–H87C, 2.84.

the imidazolin-2-iminato ligands exhibit significantly shorter metal–nitrogen distances in comparison with the HMDS ligands; however, they are slightly longer than those found for the neosilyl complexes **3b** and **3d** (Table 1).

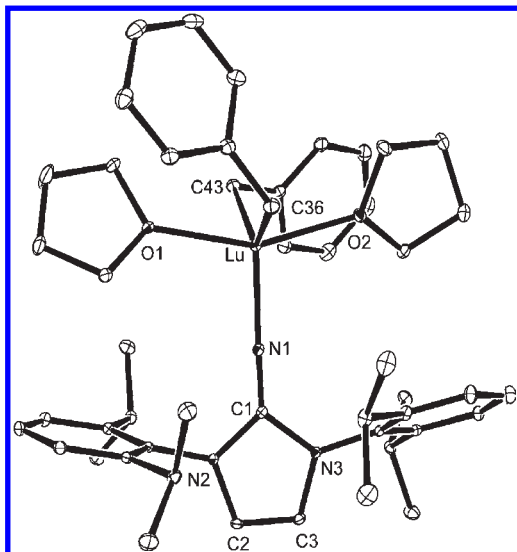
**Preparation and Structural Characterization of an Imidazolin-2-iminato Benzyl Complex.** Benzyl ( $\text{CH}_2\text{Ph}$ ) complexes are also very common in organolanthanide chemistry and are often encountered as precatalysts in various rare earth metal catalyzed organic transformations;<sup>46</sup> therefore, the possibility of introducing benzyl ligands was tested for the lutetium dichloride **2c** as an alternative to the established preparation from tribenzyl complexes of the type  $[\text{M}(\text{CH}_2\text{Ph})_3(\text{THF})_n]$ .<sup>47</sup> Accordingly, the dibenzyl complex **5c** was synthesized by treatment of **2c** with two equivalents of benzylpotassium ( $\text{KCH}_2\text{Ph}$ ) in THF solution and was isolated as a white crystalline solid by crystallization from THF/pentane solution at  $-30\text{ }^{\circ}\text{C}$  in 66% yield. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra show one set of signals for the  $\text{CH}_2\text{Ph}$  ligands with the methylene resonances appearing as singlets at 1.52 and 59.5 ppm, respectively. The NMR spectroscopic data and the elemental analysis suggested the composition  $[(1)\text{M}(\text{CH}_2\text{Ph})_2(\text{THF})_2]$ , which was also confirmed by X-ray diffraction analysis (Figure 7). The two benzyl ligands are coordinated in a monohapto fashion, and, in a similar fashion to that described for complexes **3b**–**3d** (vide supra), the lutetium metal in **5c** is five-coordinate with the ligands forming a distorted trigonal-bipyramidal coordination sphere. Again, the

(44) For yttrium complexes, see: (a) Haan, K. H.; de Boer, J. L.; Teuben, J. H. *Organometallics* **1986**, *5*, 1726. (b) Klooster, W. T.; Brammer, L.; Schaverien, C. J.; Budzelaar, H. M. *J. Am. Chem. Soc.* **1999**, *121*, 1381. (c) Fryzuk, M. D.; Jafarpour, L.; Kerton, F. M.; Love, J. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1387. (d) Matsuo, Y.; Mashima, K.; Tani, K. *Organometallics* **2001**, *20*, 3510. (e) Douglas, M. R.; Ogasawara, M.; Hong, S.; Metz, M.; Marks, T. J. *Organometallics* **2002**, *21*, 283. (f) Kim, Y. K.; Livinghouse, T.; Horino, Y. *J. Am. Chem. Soc.* **2003**, *125*, 9560. (g) Arnold, P. L.; Mungur, S. A.; Blake, A. J.; Wilson, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 5981. (h) Hultzsck, K. C.; Gribkov, D. V.; Hampel, F. *J. Organomet. Chem.* **2005**, *690*, 4441. (i) Arnold, P. L.; Liddle, S. T. *Organometallics* **2006**, *25*, 1485. (j) Edworthy, I. S.; Blake, A. J.; Wilson, C.; Arnold, P. L. *Organometallics* **2007**, *26*, 3684. (k) Zhou, S.; Wang, S.; Yang, G.; Li, Q.; Zhang, L.; Yao, Z.; Zhou, Z.; Song, H. *Organometallics* **2007**, *26*, 3755. (l) Xiang, L.; Wang, Q.; Song, H.; Zi, G. *Organometallics* **2007**, *26*, 5323.

(45) For gadolinium, see: (a) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. *J. Chem. Soc.* **1985**, 1585. (b) Tardif, O.; Kaita, S. *Dalton Trans.* **2008**, 2531.

(46) (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134. (b) Mandel, A.; Magull, J. Z. *Anorg. Allg. Chem.* **1996**, *622*, 1913. (c) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197. (d) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533. (e) Avent, A. G.; Cloke, G. N.; Elvidge, B. R.; Hitchcock, P. B. *Dalton Trans.* **2004**, 1083. (f) Bambirra, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3454. (g) Hitzbleck, J.; Beckerle, K.; Okuda, J. *J. Organomet. Chem.* **2007**, *692*, 4702. (h) Carver, C. T.; Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, *27*, 363.

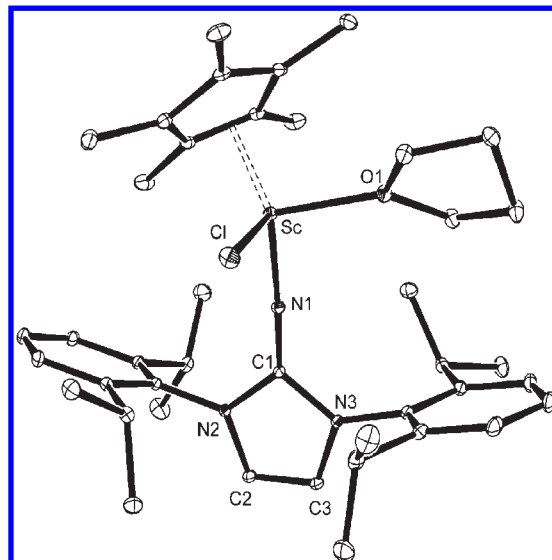
(47) Meyer, N.; Roesky, P. W.; Bambirra, S.; Meetsma, A.; Hessen, B.; Salin, K.; Takas, J. *Organometallics* **2008**, *27*, 1501.



**Figure 7.** ORTEP diagram of **5c** with thermal displacement parameters drawn at the 30% probability level.

O1–Lu–O2 angle of  $155.82(6)^\circ$  deviates significantly from a linear orientation, which can be mainly attributed to the steric demand of the diisopropylphenyl substituents of the imidazolin-2-iminato ligand. This ligand coordinates to the lutetium atom in an almost linear fashion [Lu–N1–C1 =  $178.27(16)^\circ$ ] with a very short Lu–N1 bond of  $2.0752(18)$  Å, which falls below the values found for **2c** and **3c**. The two benzyl ligands point away from each other, and the Lu–C distances of  $2.428(2)$  and  $2.427(2)$  Å fall in the range observed for other benzyl lutetium complexes.<sup>48</sup>

**Preparation and Structural Characterization of Imidazolin-2-iminato Cyclopentadienyl Complexes.** In view of the isolobal relationship between imidazolin-2-iminato and cyclopentadienyl (Cp) ligands, we also pursued the reaction of the dichlorides **2a–2d** with pentamethylcyclopentadienyl potassium (KCp\*). To introduce two Cp\* ligands, we treated the complexes [(1)MCl<sub>2</sub>(THF)<sub>3</sub>] (**2**) with 2 equiv of KCp\* in THF for 12 h at ambient temperature. White solids were isolated from the reactions of **2a**, **2b**, and **2c** after extraction with toluene followed by evaporation, and their spectroscopic characterization indicated the formation of mono(pentamethylcyclopentadienyl) complexes [(1)Sc(Cp\*)Cl(THF)] (**6a**), [(1)Y(Cp\*)Cl(THF)<sub>2</sub>] (**6b**), and [(1)Lu(Cp\*)Cl(THF)] (**6c**). In contrast, the product obtained from the reaction of **2d** with KCp\* could be extracted with pentane, and an elemental analysis indicated that [(1)Gd(Cp\*)<sub>2</sub>(THF)] (**7**) has formed and that the larger gadolinium ion is able to accommodate two Cp\* ligands. The <sup>1</sup>H NMR spectra (in C<sub>6</sub>D<sub>6</sub>) of the Sc and Lu complexes **6a** and **6c** are very similar, indicating the coordination of just one sterically demanding Cp\* ligand ( $\delta = 1.91$  ppm for **6a**,  $\delta = 1.93$  ppm for **6c**) and one THF ligand. In both complexes, the THF ligand gives rise to four resonances, indicating non-fluxional behavior and strong coordination to the metal atom, which results in the formation of configurationally



**Figure 8.** ORTEP diagram of **6a** with thermal displacement parameters drawn at the 30% probability level.

stable, chiral-at-metal complexes.<sup>49</sup> Consequently, two septets are observed for the CHCH<sub>3</sub> protons for **6a** and **6c**, in agreement with the presence of diastereotopic isopropyl groups; **6a** also shows the required four doublets for the CHCH<sub>3</sub> protons, whereas **6c** exhibits only three doublets in a 6:6:12 ratio with two isochronous methyl resonances as confirmed by two-dimensional <sup>1</sup>H–<sup>1</sup>H COSY experiments (see the Supporting Information). In contrast, the <sup>1</sup>H NMR spectrum of **6b** indicates the coordination of a second THF ligand, and only two doublets are observed for the diastereotopic isopropyl methyl groups. It should be noted, however, that the resonances are rather broad at room temperature, suggesting a higher fluxionality of the yttrium system **6b** on the NMR time scale.

The molecular structures of **6a** and **6c** were additionally established by single-crystal X-ray diffraction; both complexes are isostructural and crystallize in the space group *P2*<sub>1</sub>/*c*. As a representative, the molecular structure of **6a** is shown in Figure 8, confirming the spectroscopically derived pseudotetrahedral geometry. Yet again, the Sc–N and Lu–N bond lengths of  $1.9575(10)$  and  $2.0697(18)$  Å are very short, with the latter being the shortest ever reported for lutetium–nitrogen systems (Table 2). The metal–carbon distances range from  $2.4752(13)$ – $2.5305(12)$  Å in **6a** and from  $2.565(2)$ – $2.618(2)$  Å in **6c**, which is comparable to the values found for related Cp\* complexes.<sup>33g,50</sup>

The highly paramagnetic nature of the gadolinium complexes prohibited the use of NMR spectroscopy for the characterization of **7**; however, its solid-state structure could be established by X-ray diffraction, confirming that a complex with two Cp\* ligands had formed. The coordination sphere around the Gd atom is completed by the imidazolin-2-iminato and one THF ligand to afford a

(48) (a) Meyer, N.; Roesky, P. W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2171. (b) Lin, D.; Chen, J.; Luo, C.; Zhang, Y.; Yao, Y.; Luo, Y. *J. Organomet. Chem.* **2009**, *694*, 2976.

(49) These structures are closely related to chiral three-legged half-sandwich transition metal complexes of the type [(Cp)ML<sup>1</sup>L<sup>2</sup>L<sup>3</sup>], see: (a) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194. (b) Brunner, H. *Eur. J. Inorg. Chem.* **2001**, 905. (c) Brunner, H.; Tsuno, T. *Acc. Chem. Res.* **2009**, *42*, 1501.

(50) Van der Heijden, H.; Pasman, P.; de Boer, R. J. M.; Schaverien, C. J. *Organometallics* **1989**, *8*, 1459.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) in Complexes **6** and **7**

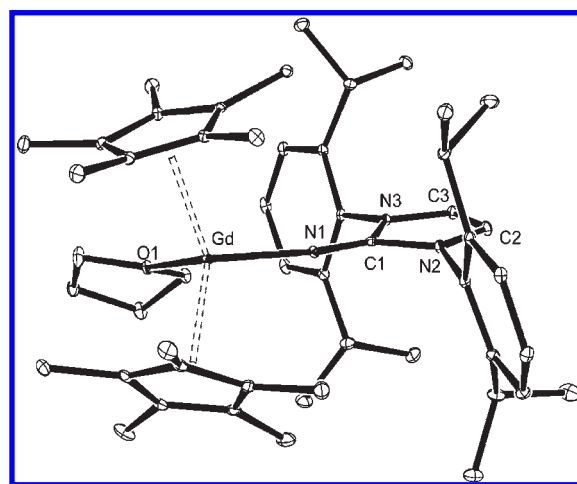
	<b>6a</b> (M = Sc)	<b>6c</b> (M = Lu)	<b>7·THF</b> (M = Gd)
M–N1	1.9575(10)	2.0697(18)	2.2388(13)
M–O	2.173(09)	2.2529(15)	2.4227(11)
M–Cl	2.4100(4)	2.4951(6)	
M–Ct1 <sup>a</sup>	2.4752(13)–2.5302(12)	2.565(2)–2.618(2)	2.6877(13)–2.7228(14)
M–Ct2 <sup>a</sup>			2.7327(14)–2.8604(14)
N1–C1	1.2707(15)	1.262(3)	1.2640(18)
M–N1–C1	169.72(9)	171.24(17)	174.57(11)
N1–M–O	104.01(4)	104.25(6)	97.62(4)
N1–M–Cl	106.28(3)	108.33(5)	
N1–M–Ct1 <sup>a</sup>	123.64	124.33	108.68
N1–M–Ct2 <sup>a</sup>			112.40
Cl–M–O	90.30(3)	91.05(4)	
N2–C1–N3	102.42(9)	102.09(17)	100.22(10)
Ct1–M–Ct2 <sup>a</sup>			130.94
Ct1–M–Cl <sup>a</sup>	114.71	113.85	

<sup>a</sup> Ct1, Ct2 = centroids of the five-membered rings.

distorted pseudotetrahedral geometry (Figure 9). The presence of two bulky Cp\* rings leads to an elongation of the Gd–N bond [2.2388(13) Å] in comparison with the previously described imidazolin-2-iminato gadolinium complexes such as **2d**, **3d**, **4d** (vide supra), and [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Gd(1)(THF)<sub>2</sub>].<sup>30</sup> The lanthanocene moiety is bent with a centroid–Gd–centroid angle of 130.94°, and the Gd–C distances range from 2.6877(13) to 2.8604(14) Å (Table 2), which is in good agreement with the data reported for other complexes containing a (Cp)<sub>2</sub>Gd fragment.<sup>51</sup>

#### Catalytic Hydroamination and Hydrosilylation Studies.

Rare earth metal complexes have proven to be favorable catalysts for a number of catalytic applications ranging from polymerization to small molecule activation.<sup>9,12,52</sup> In particular, organo-rare earth metal complexes were found to be suitable catalysts for the hydroamination of alkenes or alkynes.<sup>9,53</sup> Typical catalytic systems for hydroamination contain a trivalent (+3 oxidation state) metal atom and at least one kinetically labile, σ-bonded ligand (e.g., H, CH(SiMe<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>SiMe<sub>3</sub>, CH<sub>2</sub>Ph, N(SiMe<sub>3</sub>)<sub>2</sub>), which can be replaced by the amine substrate to generate a metal-amido species. The mechanism of



**Figure 9.** ORTEP diagram of **7** with thermal displacement parameters drawn at the 30% probability level.

the lanthanocene-catalyzed hydroamination/cyclization reaction was established some years ago by Marks et al.<sup>9,54</sup> Thereby, cyclopentadienyl-based lanthanide complexes played a pioneering role; however, in recent years,<sup>20,43g,43h,55</sup> a number of active noncyclopentadienyl lanthanide catalysts with amido<sup>44f,56</sup> and alkoxide<sup>44h,57</sup> ligands have been developed. Herein, we report a study of the intramolecular hydroamination/cyclization reaction of terminal aminoalkenes and of one aminoalkyne using catalytic amounts of the yttrium and lutetium bis(neosilyl) complexes **3b** and **3c**, with the intention of evaluating their catalytic activity in comparison with other rare earth metal complexes.

The rigorously anaerobic reaction between the complexes **3b** and **3c** and dry, degassed aminoalkene or aminoalkyne proceeded regiospecifically, leading in almost all cases to full conversion into the cyclic products (Table 3). Kinetic studies were undertaken by in situ <sup>1</sup>H NMR spectroscopy. The reaction behavior of a 20-fold molar excess of the substrate with constant catalyst concentration was monitored until complete substrate consumption was

(56) (a) Riegert, D.; Collin, J.; Meddour, A.; Schulz, E.; Trifonov, A. *J. Org. Chem.* **2006**, *71*, 2514. (b) Ailland, I.; Lynbov, D.; Collin, J.; Guillet, R.; Handdouche, J.; Schulz, E.; Trifonov, A. *Organometallics* **2008**, *27*, 5929. (c) Kim, Y. K.; Livinghouse, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 3645.

(57) (a) Hultzsich, K. C.; Gribkov, D. V.; Hampel, F. *Chem.—Eur. J.* **2003**, *9*, 4796. (b) Hultzsich, K. C.; Gribkov, D. V. *Chem. Commun.* **2004**, 730. (c) Hultzsich, K. C.; Hampel, F.; Wagner, T. *Organometallics* **2004**, *23*, 2601.

(51) (a) Ibers, J. A.; Pernin, C. G. *Inorg. Chem.* **2000**, *39*, 1216. (b) Zhang, J.; Zhou, X.; Cai, R.; Weng, L. *Inorg. Chem.* **2005**, *44*, 716. (c) Daniel, S. D.; Lehn, J.-S. M.; Van der Heide, P.; Wang, Y.; Hoffmann, D. M. *Inorg. Chim. Acta* **2006**, *359*, 257. (d) Layfield, R. A.; Bashall, A.; McPartlin, M.; Rawson, J. M.; Wright, D. S. *Dalton Trans.* **2006**, 1660.

(52) (a) Molander, G. A.; Dowdy, E. D. *Top. Organomet. Chem* **1999**, 119. (b) Molander, G. A. *Pure Appl. Chem.* **2000**, *72*, 1757. (c) Shibaski, M.; Yoshikawa, N. *Chem. Rev.* **2002**, *102*, 2187. (d) Mikami, K.; Terada, M.; Matzuzawa, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3554. (e) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1. (f) Nakayama, Y.; Yasuda, H. *J. Organomet. Chem.* **2004**, *689*, 4489. (g) Hou, Z.; Luo, Y.; Li, Y. *J. Organomet. Chem.* **2006**, *691*, 3114.

(53) (a) Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108. (b) Gagne, M. R.; Stern, C.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275. (c) Roesky, P. W.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4705. (d) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1757. (e) Arrendondo, V. M.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4871. (f) Arrendondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633. (g) Douglass, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824. (h) Douglass, M. R.; Stern, C.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221. (i) Hong, S.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 7886. (j) Ryu, J.-S.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 12584.

(54) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295.

(55) (a) Bürgstein, M. R.; Berberich, H.; Roesky, P. W. *Chem.—Eur. J.* **2001**, *7*, 3078. (b) Roesky, P. W.; Müller, T. E. *Angew. Chem. Int. Ed.* **2003**, *42*, 2708. (c) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2005**, *690*, 5078. (d) Datta, S.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2008**, *27*, 1207.



achieved. The decrease in the substrate peak was integrated vs the product signals. Additionally, ferrocene was used as internal standard. The hydroamination/cyclization reaction could be achieved in high yields at room temperature (entries 1, 4, 5), at 60 °C (entry 3) or at 120 °C (entry 2), respectively. The substrates bearing bulky geminal substituents in the  $\beta$ -position to the amino group could be cyclized with 5 mol % catalyst loading in good reaction time (5 min) at room temperature. In contrast, when the substrate bears small substituents in the  $\beta$ -position, the reaction time increases, and also a higher reaction temperature is required. This could be explained by the Thorpe–Ingold effect,<sup>58</sup> an effect observed in organic synthesis where increasing the size of two substituents at a tetrahedral center leads to enhanced reaction rates between parts of the other two substituents.

The dependency of the rate on the ionic radius of the metal center ( $\text{Ln}^{3+}$ ) was demonstrated first for the metallocene catalysts of the lanthanides,<sup>53</sup> and the rates increase with increasing ionic radii.<sup>39</sup> In the present contribution, however, the difference in activity between the yttrium and lutetium catalysts is not significant. A comparison of complexes **3b** and **3c** using substrates from entry 1, 4, and 5 (see Table 3) with noncyclopentadienyl complexes, for example  $[\text{La}\{\text{N}(\text{SiHMe}_2)_2\}_2\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)\}]$ ,<sup>55d</sup> shows a significantly higher turnover for the first catalysts<sup>54</sup>, albeit at different reaction conditions. In comparison with the corresponding metallocene catalysts, for example  $[(\text{Cp}^*)_2\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}]$ <sup>54</sup> ( $\text{Ln} = \text{La}, \text{Sm}, \text{Nd}$ ), the rates for the hydroamination/cyclization reaction, using as catalysts complexes **3b** and **3c**, are rather slower.

In addition, compounds **3b** and **3c** were also screened for the catalytic hydrosilylation of alkenes, because this reaction represents an important and efficient method for the synthesis of alkylsilanes and for the production of organosilanes on an industrial scale.<sup>23b,59</sup> It could be demonstrated that rare-earth metal complexes with  $\text{Cp}^{10,60}$  and non- $\text{Cp}^{55,61}$  ligands are efficient catalysts or precatalysts for the hydrosilylation of olefins, and the mechanism is generally believed to involve the insertion of the olefin into the  $\text{M}-\text{Si}$  or  $\text{M}-\text{H}$  bond of a metal–silyl or metal–

Table 3. Catalytic Hydroamination Reactions<sup>a</sup>

Entry	Substrate	Product	Cat.	[Cat.]	T [°C]	t [min]	Yield <sup>b</sup> [%]
1			<b>3b</b>	5 mol%	RT	5	quant <sup>c</sup>
			<b>3c</b>	5 mol%	RT	5	quant.
2			<b>3b</b>	5 mol%	120	180	quant. (cis:trans = 1:3)
			<b>3c</b>	5 mol%	120	60	quant. (cis:trans = 1:3)
3			<b>3b</b>	5 mol%	60	60	92 <sup>c</sup>
			<b>3c</b>	5 mol%	60	60	90
4			<b>3b</b>	5 mol%	RT	5	98
			<b>3c</b>	5 mol%	RT	5	98 <sup>c</sup>
5			<b>3b</b>	5 mol%	RT	5	quant.
			<b>3c</b>	5 mol%	RT	5	quant.

<sup>a</sup> Conditions: Cat. 15–20 mg,  $\text{C}_6\text{D}_6$ . <sup>b</sup> Calculated by  $^1\text{H}$  NMR. <sup>c</sup> Ferrocene as internal standard

hydride species, followed by  $\sigma$ -bond metathesis.<sup>10e,60b,62</sup> In our hands, the bis(neosilyl) complexes **3b** and **3c** proved to be highly efficient precatalysts for the intermolecular hydrosilylation of hexene and octene using a small excess (4%) of phenylsilane ( $\text{PhSiH}_3$ ) and 2 mol% catalyst loadings. In all cases, the reaction went essentially to completion in < 5 min at ambient temperature as judged by  $^1\text{H}$  NMR spectroscopy. Full selectivity for the anti-Markovnikov products and no side reactions were observed (for example hydrogenation, alkene dimerization, and/or dehydrogenative coupling of organosilanes).

With regard to reaction temperature, catalyst loadings, and yields, the activity of compounds **3b** and **3c** is higher than that reported for metallocene complexes, and for instance, a TOF of  $120 \text{ h}^{-1}$  was reported for the hydrosilylation of 1-hexene in the presence of  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_5)_2\text{-SmCH}(\text{SiMe}_3)_2]$  at room temperature.<sup>60b</sup> It is not surprising that the activities of **3b** and **3c** fall in the range that was recently observed for closely related organoyttrium catalysts of the type  $[\{\text{PhC}(\text{NAr})_2\}\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$  and  $[\{\text{Me}_2\text{NC}(\text{NAr})_2\}\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$  with sterically demanding amidinate and guanidinate ligands, which were shown to be excellent catalysts for the hydrosilylation of various terminal alkenes (see Table 4) with phenylsilane and which displayed higher turnover frequencies than any other rare-earth or early transition metal catalysts.<sup>61d</sup>

## Conclusions

The present study showed that the rare earth metal dichlorides **2** are convenient starting materials for the preparation of alkyl, amido, and cyclopentadienyl complexes containing ancillary imidazolin-2-iminato ligands, which are capable of forming particularly short and strong metal–nitrogen bonds.

(62) Horino, Y.; Livinghouse, T. *Organometallics* **2004**, *23*, 12.

(58) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, 107, 1080. (b) Ingold, C. K. *J. Chem. Soc.* **1921**, 119, 305. (c) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183. (d) Jung, M. E.; Gervay, J. J. *Am. Chem. Soc.* **1991**, *113*, 224.

(59) (a) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 8, Chapter 3, p 12. (b) Marciniak, B. In *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, U.K., 1992. (c) Ojima, I.; Li, Z.; Zhu, J. In *Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds; Wiley: Chichester, U.K., 1998; Vol. 2, p 1687. (d) Marciniak, B. In *Applied Homogenous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley: Weinheim, Germany, 2002; Vol. 1, p 491. (e) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Pergamon Press: Oxford, U.K., 1995; Vol. 4, pp 11–210.

(60) (a) Sakakura, Y.; Lautenschlager, H. J.; Tanaka, M. *J. Chem. Commun.* **1991**, 40. (b) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (c) Hou, Z.; Zhang, Y.; Tardif, O.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9216. (d) Voskoboinikov, A. Z.; Shestakova, A. K.; Beletskaya, I. P. *Organometallics* **2001**, *20*, 2794. (e) Tardif, O.; Nishiura, M.; Hou, Z. *Tetrahedron* **2003**, *59*, 10525. (f) Robert, D.; Trifonov, A. A.; Voth, P.; Okuda, J. *J. Organomet. Chem.* **2006**, *691*, 4393.

(61) (a) Takaki, K.; Sonoda, K.; Kousaka, T.; Koshiji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 9211. (b) Gribkov, D. V.; Hampel, F.; Hultsch, K. C. *Eur. J. Inorg. Chem.* **2004**, 4091. (c) Konkol, M.; Kondracka, M.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2008**, *27*, 3774. (d) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 3131.

In all cases, the steric bulk of the Im<sup>Dipp</sup>N ligand (**1**) supports the formation of mononuclear rare earth metal complexes, which, in an inert atmosphere, are easy to handle and stable in solution and in the solid state. In addition, it was shown that efficient catalysts for hydroamination and hydrosilylation reactions can be developed based on the imidazolin-2-iminato rare earth metal scaffold, thus demonstrating that this ligand class represents a useful addition to the growing number of noncyclopentadienyl ligands in organolanthanide chemistry.

## Experimental Section

**General Information.** All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum ( $1 \times 10^{-4}$  Torr) line, or in an argon-filled glovebox (MBraun 200B). All solvents were purified by a solvent purification system from MBraun and stored over molecular sieve (4 Å) prior to use. Deuterated solvents were obtained from Sigma Aldrich (all  $\geq 99$  atom % D) and were degassed, dried, and stored in the argon-filled glovebox. NMR spectra were recorded on Bruker DPX 200 and Bruker DRX 400 devices. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard ( $^1\text{H}$ ,  $^{13}\text{C}$ ).  $^{89}\text{Y}$  NMR spectra were obtained on a Bruker-400 spectrometer and were externally referenced to  $\text{Y}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  in  $\text{D}_2\text{O}$ . Elemental analysis (C, H, N) succeeded by combustion and gas chromatographically analysis with an Elementar vario MICRO. Some results gave low values for carbon content, despite acceptable H and N measurements. As observed by other groups,<sup>63</sup> this might be ascribed to the extreme sensitivity of the complexes and to the possibility of metal carbide formation during combustion. 1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-iminato rare earth metal dichlorides [(1)MCl<sub>2</sub>(THF)<sub>3</sub>] (**2a–c**, M = Sc, Y, Lu) and [(1)GdCl<sub>2</sub>(THF)<sub>2</sub>]·[LiCl(THF)<sub>2</sub>] (**2d**),<sup>30</sup> [KCH<sub>2</sub>Ph],<sup>64</sup> [KC<sub>5</sub>Me<sub>5</sub>],<sup>65</sup> and [LiCH<sub>2</sub>SiMe<sub>3</sub>]<sup>66</sup> were prepared according to published procedures. [Na{N(SiMe<sub>3</sub>)<sub>2</sub>}] was purchased from Sigma-Aldrich and used as received.

**General Procedure for the Preparation of Imidazolin-2-iminato Rare-Earth Metal Neosilyl Complexes [(1)M(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>n</sub>] (**3a**, M = Sc, n = 1; **3b**, M = Y, n = 2; **3c**, M = Lu, n = 2, **3d**, M = Gd, n = 2).** To a THF solution of 0.5 mmol of [(1)MCl<sub>2</sub>(THF)<sub>3</sub>] (M = Sc, Y, Lu) or [(1)GdCl<sub>2</sub>(THF)<sub>2</sub>]·[LiCl(THF)<sub>2</sub>], 94 mg (1.0 mmol) of LiCH<sub>2</sub>SiMe<sub>3</sub> in THF (5 mL) was added dropwise at ambient temperature and then the reaction mixture was stirred for 12 h. The solvent was evaporated and subsequently the compound was extracted with pentane. After filtration and evaporation, the complexes were crystallized from THF/pentane at  $-30$  °C.

**Analytical Data for [(1)Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)] (**3a**).** Yield: 326 mg (94%). Anal. Calcd for [C<sub>39</sub>H<sub>66</sub>N<sub>3</sub>O<sub>5</sub>Si<sub>2</sub>Sc]: C, 67.49; H, 9.58; N, 6.05. Found: C, 66.56; H, 9.41; N, 6.12.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C):  $\delta$  7.18–7.08 (m, 6H, *m*-H, *p*-H), 5.86 (s, 2H, NCH), 3.34 (br, 4H, THF), 3.24 (sept., 4H, CHMe<sub>2</sub>), 1.41 (d, 12H, CHCH<sub>3</sub>), 1.18 (d, 12H, CHCH<sub>3</sub>), 1.32–1.11 (br, 4H, THF), 0.18 (s, 18H, SiMe<sub>3</sub>),  $-0.37$  (s, 4H, Sc-CH<sub>2</sub>) ppm.  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C):  $\delta$  148.1 (*o*-C), 135.7 (*ipso*-C), 128.6 (*p*-C), 123.5 (*m*-C), 113.5 (NCH), 70.8 (THF), 34.5 (Sc-CH<sub>2</sub>), 28.6 (CHMe<sub>2</sub>), 24.8 (THF), 23.9 (CHCH<sub>3</sub>), 23.8 (CHCH<sub>3</sub>), 3.8 (SiMe<sub>3</sub>) ppm; the NCN resonance was not observed.


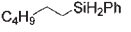

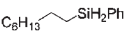
(63) Elvidge, B. R.; Arndt, S.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2006**, 890, and references cited therein.

(64) Schlosser, M.; Hartmann, J. *Angew. Chem.* **1973**, 85, 544. (b) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed.* **1973**, 12, 508.

(65) Schumann, H.; Albrecht, I.; Loebel, J.; Hahn, E.; Hossain, M. B.; van der Helm, D. *Organometallics* **1986**, 5, 1296.

(66) Vaughn, G. D.; Krein, K. A.; Gladysz, J. A. *Organometallics* **1986**, 5, 936.

**Table 4.** Catalytic Hydrosilylation Reactions

Entry	Substrate	Product	Cat.	[Cat.]	T [°C]	t [min]	Yield <sup>a</sup> [%]
1			<b>3b</b>	2 mol%	RT	< 5	99:1 (AM:M) <sup>b</sup>
			<b>3c</b>	2 mol%	RT	< 5	99:1 (AM:M) <sup>b</sup>
2			<b>3b</b>	2 mol%	RT	< 5	99:1 (AM:M) <sup>b</sup>
			<b>3c</b>	2 mol%	RT	< 5	99:1 (AM:M) <sup>b</sup>

<sup>a</sup> Calculated by  $^1\text{H}$  NMR. <sup>b</sup> AM = *anti*-Markovnikov; M = Markovnikov.

**Analytical Data for [(1)Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>] (**3b**).** Yield: 390 mg (97%). Anal. Calcd for [C<sub>43</sub>H<sub>74</sub>N<sub>3</sub>O<sub>2</sub>Si<sub>2</sub>Y]: C, 63.75; H, 9.21; N, 5.19. Found: C, 62.19; H, 9.00; N, 5.20.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C):  $\delta$  7.06–7.04 (m, 6H, *m*-H, *p*-H), 5.81 (s, 2H, NCH), 3.43–3.39 (m, 4H, THF), 3.35 (sept., 4H, CHMe<sub>2</sub>), 1.40 (d, 12H, CHCH<sub>3</sub>), 1.32–1.29 (m, 4H, THF), 1.21 (d, 12H, CHCH<sub>3</sub>), 0.27 (s, 18H, SiMe<sub>3</sub>),  $-0.97$  (d, 4H, Y-CH<sub>2</sub>),  $^2J_{89\text{Y},\text{H}} = 2.8$  Hz) ppm.  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz, 25 °C):  $\delta$  149.1 (*o*-C), 137.6 (*ipso*-C), 136.128.4 (*p*-C), 123.7 (*m*-C), 112.9 (NCH), 70.1 (THF), 28.8 (CHMe<sub>2</sub>), 26.2 (Y-CH<sub>2</sub>),  $J_{89\text{Y},\text{C}} = 36.4$  Hz), 25.5 (THF), 24.3 (CHCH<sub>3</sub>), 23.3 (CHCH<sub>3</sub>), 5.04 (SiMe<sub>3</sub>) ppm; the NCN resonance was not observed.  $^{89}\text{Y}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz; 25 °C):  $\delta$  813.8 ppm.

**Analytical Data for [(1)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>] (**3c**).** Yield: 435 mg (97%). Anal. Calcd for [C<sub>43</sub>H<sub>74</sub>LuN<sub>3</sub>O<sub>2</sub>Si<sub>2</sub>]: C, 57.63; H, 8.32; N, 4.69. Found: C, 57.52; H, 8.13; N, 5.02.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 25 °C):  $\delta$  7.09–7.06 (m, 6H, *m*-H, *p*-H), 5.87 (s, 2H, NCH), 3.44–3.38 (m, 4H, THF), 3.34 (sept., 4H, CHMe<sub>2</sub>), 1.41 (d, 12H, CHCH<sub>3</sub>), 1.31–1.26 (m, 4H, THF), 1.22 (d, 12H, CHCH<sub>3</sub>), 0.25 (s, 18H, SiMe<sub>3</sub>),  $-1.03$  (s, 4H, Lu-CH<sub>2</sub>) ppm.  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz, 25 °C):  $\delta$  148.4 (*o*-C), 137.0 (*ipso*-C), 127.9 (*p*-C), 123.3 (*m*-C), 112.94 (NCH), 69.4 (THF), 36.3 (Lu-CH<sub>2</sub>), 28.3 (CHMe<sub>2</sub>), 25.0 (THF), 24.7 (CHCH<sub>3</sub>), 23.6 (CHCH<sub>3</sub>), 4.48 (SiMe<sub>3</sub>) ppm; the NCN resonance was not observed.

**Analytical Data for [(1)Gd(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>] (**3d**).** Yield: 427 mg (97%). Anal. Calcd for [C<sub>43</sub>H<sub>74</sub>GdN<sub>3</sub>O<sub>2</sub>Si<sub>2</sub>]: C, 58.79; H, 8.49; N, 4.78. Found: C, 56.74; H, 8.02; N, 4.96. Because of the highly paramagnetic nature of the compound, no NMR spectra were recorded. We were unable to obtain a satisfactory elemental analysis, presumably because incomplete combustion.

**General Procedure for the Preparation of Imidazolin-2-iminato Rare-Earth Metal Amides [(1)M(HMDS)<sub>2</sub>(THF)] (**4a**, M = Sc; **4b**, M = Y; **3c**, M = Lu; **3d**, M = Gd).** To a THF solution of 0.5 mmol of [(1)MCl<sub>2</sub>(THF)<sub>3</sub>] (M = Sc, Y, Lu) or [(1)GdCl<sub>2</sub>(THF)<sub>2</sub>]·[LiCl(THF)<sub>2</sub>] was added 183 mg (1.0 mmol) of [Na{N(SiMe<sub>3</sub>)<sub>2</sub>}] in THF (5 mL) dropwise at ambient temperature and then the reaction mixture was stirred for 12 h. The solvent was evaporated and subsequently the compound was extracted with pentane. After filtration and evaporation, the complexes were crystallized from THF/pentane at  $-30$  °C.

**Analytical Data for [(1)Sc(HMDS)<sub>2</sub>(THF)] (**4a**).** Microcrystalline product was obtained. Yield: 345 mg (82%). Anal. Calcd for [C<sub>43</sub>H<sub>80</sub>N<sub>5</sub>O<sub>5</sub>Si<sub>4</sub>Sc]: C, 61.45; H, 9.59; N, 8.33. Found: C, 61.11; H, 9.36; N, 8.07.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 25 °C):  $\delta$  7.24–7.17 (m, 4H, *m*-H), 7.12–7.10 (m, 2H, *p*-H), 5.86 (s, 2H, NCH), 3.58 (br, 4H, THF), 3.23 (sept., 4H, CHMe<sub>2</sub>), 1.45 (d, 12H, CHCH<sub>3</sub>), 1.32–1.20 (m, 4H, THF), 1.16 (d, 12H, CHCH<sub>3</sub>), 0.23 (s, 36H, SiMe<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz, 25 °C):  $\delta$  148.2 (*o*-C), 137.5 (*ipso*-C), 128.3 (*p*-C), 123.6 (*m*-C), 113.1 (NCH), 69.2 (THF), 28.3 (CHMe<sub>2</sub>), 25.2 (THF),

24.1 (CHCH<sub>3</sub>), 23.3 (CHCH<sub>3</sub>), 5.7 (SiMe<sub>3</sub>) ppm; the NCN resonance was not observed.

**Analytical Data for [(1)Y(HMDS)<sub>2</sub>(THF)] (4b).** Yellow crystals were obtained. Yield: 360 mg (81%). Anal. Calcd for [C<sub>43</sub>H<sub>80</sub>N<sub>5</sub>OSi<sub>4</sub>Y]: C, 58.39; H, 9.11; N, 7.91. Found: C, 57.96; H, 8.87; N, 7.59. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 25 °C): δ 7.21–7.16 (m, 4H, *m*-H), 7.13–7.10 (m, 2H, *p*-H), 5.98 (s, 2H, NCH), 3.46 (sept., 4H, CHMe<sub>2</sub>), 1.47 (d, 12H, CHCH<sub>3</sub>), 1.21 (d, 12H, CHCH<sub>3</sub>), 0.27 (s, 36H, SiMe<sub>3</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz, 25 °C): δ 148.8 (*o*-C), 138.1 (*ipso*-C), 127.9 (*p*-C), 123.2 (*m*-C), 113.7 (NCH), 69.1 (THF), 28.4 (CHMe<sub>2</sub>), 24.9 (THF), 24.1 (CHCH<sub>3</sub>), 23.1 (CHCH<sub>3</sub>), 5.9 (SiMe<sub>3</sub>) ppm; the NCN resonance was not observed.

**Analytical Data for [(1)Lu(HMDS)<sub>2</sub>(THF)] (4c).** Microcrystalline compounds were obtained. Yield: 364 mg (75%). Anal. Calcd for [C<sub>43</sub>H<sub>80</sub>LuN<sub>5</sub>OSi<sub>4</sub>]: C, 53.22; H, 8.30; N, 7.21. Found: C, 52.86; H, 7.91; N, 7.01. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 25 °C): δ 7.22–7.16 (m, 4H, *m*-H), 7.13–7.11 (m, 2H, *p*-H), 6.01 (s, 2H, NCH), 3.52 (sept., 4H, CHMe<sub>2</sub>), 1.47 (d, 12H, CHCH<sub>3</sub>), 1.21 (d, 12H, CHCH<sub>3</sub>), 0.36 (s, 36H, SiMe<sub>3</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz, 25 °C): δ 149.1 (*o*-C), 137.1 (*ipso*-C), 128.4 (*p*-C), 123.2 (*m*-C), 113.5 (NCH), 69.5 (THF), 28.7 (CHMe<sub>2</sub>), 25.1 (THF), 24.3 (CHCH<sub>3</sub>), 23.4 (CHCH<sub>3</sub>), 5.6 (SiMe<sub>3</sub>) ppm; the NCN resonance was not observed.

**Analytical Data for [(1)Gd(HMDS)<sub>2</sub>(THF)] (4d).** Colorless crystals were obtained. Yield: 371 mg (78%). Anal. Calcd for [C<sub>43</sub>H<sub>80</sub>GdN<sub>5</sub>OSi<sub>4</sub>]: C, 54.20; H, 8.46; N, 7.35. Found: C, 53.86; H, 8.11; N, 7.13. Because of the highly paramagnetic nature of the compound, no NMR spectra were recorded.

**Preparation of the Imidazolin-2-iminato Lutetium Benzyl Complex [(1)Lu(CH<sub>2</sub>Ph)<sub>2</sub>(THF)<sub>2</sub>] (5c).** To a 10 mL THF solution of 432 mg (0.5 mmol) of [(1)LuCl<sub>2</sub>(THF)<sub>3</sub>] was added 145 mg (1.0 mmol) of KCH<sub>2</sub>Ph in 10 mL THF dropwise at ambient temperature, and the product was extracted with pentane. After filtration and evaporation, the complex was crystallized from THF/pentane at –30 °C. Yield: 300 mg (66%). Anal. Calcd for [C<sub>49</sub>H<sub>66</sub>LuN<sub>3</sub>O<sub>2</sub>]: C, 65.10; H, 7.36; N, 4.64. Found: C, 64.86; H, 7.11; N, 4.41. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 25 °C): δ 7.24–7.18 (m, 8H, *o*-Bz, *m*-Dipp), 7.14–7.6.99 (m, 2H, *p*-Dipp), 6.84 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 4H, *o*-Bz), 6.56 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2H, *p*-Bz), 5.90 (s, 2H, NCH), 3.34 (br, 4H, CHMe<sub>2</sub>), 1.52 (s, 4H, Lu–CH<sub>2</sub>), 1.33 (d, 12H, CHCH<sub>3</sub>), 1.21 (d, 12H, CHCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz, 25 °C): δ 149.6 (*o*-C), 148.5 (Bz, *ipso*-C), 137.3 (*ipso*-C), 129.1 (Bz, *o*/*m*-C), 127.5 (*p*-C), 124.5 (Bz, *o*/*m*-C), 123.2 (*m*-C), 119.0 (Bz, *p*-C), 113.3 (NCH), 59.5 (Lu–CH<sub>2</sub>), 28.7 (CHMe<sub>2</sub>), 25.7 (CHCH<sub>3</sub>), 24.4 (CHCH<sub>3</sub>) ppm; the NCN resonance was not observed.

**General Procedure for the Preparation of Imidazolin-2-iminato mono(pentamethylcyclopentadienyl) Complexes [(1)M(C<sub>5</sub>Me<sub>5</sub>)Cl(THF)<sub>n</sub>] (6a, M = Sc, n = 1; 6b, M = Y, n = 2; 6c, M = Lu, n = 1).** To a 10 mL THF solution of 481 mg (0.5 mmol) of [(1)MCl<sub>2</sub>(THF)<sub>3</sub>] (M = Sc, Lu, Y) 87.5 mg (0.5 mmol) of KCp\* in 10 mL THF was added dropwise at ambient temperature, and the reaction mixture was stirred for 12 h. The solvent was evaporated and subsequently the compound was extracted with pentane/toluene solution. After filtration and evaporation, the complexes were crystallized from THF/pentane at –30 °C.

**Analytical Data for [(1)Sc(C<sub>5</sub>Me<sub>5</sub>)Cl(THF)] (6a).** Yield: 321 mg (93%). Anal. Calcd for [C<sub>41</sub>H<sub>59</sub>ClN<sub>3</sub>OSc]: C, 71.33; H, 8.61; N 6.09. Found: C, 70.35; H, 8.51; N, 6.10. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ 7.10–7.08 (m, 6H, *m*-H, *p*-H), 5.86 (s, 2H, NCH), 3.58 (sept, 2H, CHMe<sub>2</sub>), 3.53–3.45 (m, 2H, THF), 3.26 (sept, 2H, CHMe<sub>2</sub>), 2.66–2.60 (m, 2H, THF), 1.91 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.53 (d, 6H, CHCH<sub>3</sub>), 1.47 (d, 6H, CHCH<sub>3</sub>), 1.22 (d, 6H, CHCH<sub>3</sub>), 1.20 (d, 6H, CHCH<sub>3</sub>), 1.14–1.05 (m, 4H, THF) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ 149.0 (*o*-C), 148.5 (*o*-C), 137.0 (*ipso*-C), 128.6 (*p*-C), 124.2 (*m*-C), 123.7 (*m*-C), 118.9 (C<sub>5</sub>Me<sub>5</sub>) 113.7 (NCH), 72.2 (THF), 28.9 (CHMe<sub>2</sub>), 28.7

Table 5. Crystallographic Data

	3a	3b	3c	3d	4b-THF	4d	5c	6a	6c	7-THF
empirical formula	C <sub>39</sub> H <sub>66</sub> N <sub>3</sub> O <sub>2</sub> Si <sub>2</sub> Sc	C <sub>43</sub> H <sub>74</sub> N <sub>3</sub> O <sub>2</sub> Si <sub>2</sub> Y	C <sub>43</sub> H <sub>74</sub> N <sub>3</sub> O <sub>2</sub> Si <sub>2</sub> Gd	C <sub>43</sub> H <sub>74</sub> N <sub>3</sub> O <sub>2</sub> Si <sub>2</sub> Lu	C <sub>47</sub> H <sub>88</sub> N <sub>5</sub> O <sub>2</sub> Si <sub>4</sub> Y	C <sub>43</sub> H <sub>80</sub> N <sub>5</sub> O <sub>2</sub> Si <sub>4</sub> Gd	C <sub>49</sub> H <sub>66</sub> N <sub>3</sub> O <sub>2</sub> Lu	C <sub>41</sub> H <sub>59</sub> N <sub>3</sub> OClSc	C <sub>41</sub> H <sub>59</sub> N <sub>3</sub> OClLu	C <sub>53</sub> H <sub>82</sub> N <sub>3</sub> O <sub>2</sub> Gd
<i>a</i> (Å)	18.4747(10)	12.6293(10)	19.5496(2)	12.5828(16)	12.2968(16)	17.6583(16)	12.1831(14)	17.7138(16)	17.8284(2)	11.1505(6)
<i>b</i> (Å)	13.2232(8)	14.5373(18)	13.3110(2)	14.5515(10)	13.1799(18)	17.7745(16)	12.1890(14)	13.5905(12)	13.4866(2)	12.2155(6)
<i>c</i> (Å)	18.1488(10)	25.4917(14)	18.0652(2)	25.4170(6)	17.6690(2)	32.430(3)	18.0660(2)	16.3325(14)	16.4114(2)	19.0791(10)
$\alpha$ (deg)	90	90	90	90	85.783(5)	90	105.715(3)	90	90	90
$\beta$ (deg)	99.605(6)	90	90	90	84.522(5)	90	91.8444(3)	98.181(3)	97.6243(16)	105.752(2)
$\gamma$ (deg)	90	90	90	90	77.737(5)	90	118.797(3)	90	90	90
<i>V</i> (Å <sup>3</sup> )	4371.5(4)	4680.2(7)	4701.01(10)	4653.80(13)	2781.3(6)	10178.7(16)	2220.6(4)	3891.9(6)	3911.14(9)	2501.1(2)
<i>Z</i>	4	4	4	4	2	8	2	4	4	2
<i>fw</i>	694.09	810.14	878.48	896.20	956.49	952.73	904.02	690.32	820.33	974.49
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i> 2 <sub>1</sub>	<i>P</i> na2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i> 2 <sub>1</sub>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i> 2 <sub>1</sub>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub>
<i>T</i> (°C)	–100	–173	–173	–173	–140	–173	–173	–140	–173	–173
$\lambda$ (Å)	1.54184	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>D</i> <sub>calcd</sub> (g cm <sup>–3</sup> )	1.055	1.150	1.241	1.279	1.142	1.243	1.352	1.178	1.393	1.294
$\mu$ (mm <sup>–1</sup> )	2.179	1.332	1.496	2.208	1.172	1.432	2.263	0.292	2.626	1.368
flack parameter		–0.028(2)	0.483(5)	–0.007(5)		–0.024(8)				–0.001(3)
<i>R</i> ( <i>F</i> <sub>o</sub> )	0.0542	0.0316	0.0212	0.0274	0.0437	0.0467	0.0231	0.0391	0.0206	0.0198
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> )	0.1665	0.0513	0.0308	0.0517	0.1222	0.0995	0.0524	0.1121	0.0399	0.0448

(CHMe<sub>2</sub>), 25.8 (THF), 24.9 (CHCH<sub>3</sub>), 24.5 (CHCH<sub>3</sub>), 24.1 (CHCH<sub>3</sub>), 23.7 (CHCH<sub>3</sub>), 11.6 (C<sub>5</sub>Me<sub>5</sub>) ppm; the NCN resonance was not observed

**Analytical Data for [(1)Y(C<sub>5</sub>Me<sub>5</sub>)Cl(THF)<sub>2</sub>] (6b).** Yield: 242 mg (86%). Anal. Calcd for [C<sub>45</sub>H<sub>67</sub>ClN<sub>3</sub>O<sub>2</sub>Y]: C, 67.02; H, 8.37; N, 5.21. Found: C, 67.23; H, 8.20; N, 5.82. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ 7.14–7.06 (m, 6H, *m*-H, *p*-H), 5.89 (s, 2H, NCH), 3.56–3.34 (m, br, 8H, THF), 3.11 (sept, br, 4H, CHMe<sub>2</sub>), 1.94 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.48 (d, 12H, CHCH<sub>3</sub>), 1.22 (d, 12H, CHCH<sub>3</sub>), 1.19–1.15 (br, 8H, THF) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ 148.7 (*o*-C), 138.9 (NCN), 136.9 (*ipso*-C), 128.6 (*p*-C), 123.3 (*m*-C), 117.5 (C<sub>5</sub>Me<sub>5</sub>), 113.2 (NCH), 70.9 (THF), 28.7 (CHMe<sub>2</sub>), 25.7 (THF), 24.4 (CHCH<sub>3</sub>), 24.3 (CHCH<sub>3</sub>), 11.0 (C<sub>5</sub>Me<sub>5</sub>) ppm.

**Analytical Data for [(1)Lu(C<sub>5</sub>Me<sub>5</sub>)Cl(THF)] (6c).** Yield: 397 mg (97%). Anal. Calcd for [C<sub>41</sub>H<sub>59</sub>LuN<sub>3</sub>ClO]: C 60.03, H 7.25, N 5.12. Found C 60.02, H 7.29, N 5.16. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ 7.15–7.09 (m, 6H, *m*-H, *p*-H), 5.91 (s, 2H, NCH), 3.51 (sept., 2H, CHMe<sub>2</sub>), 3.40–3.31 (m, 2H, THF), 3.26 (sept., 2H, CHMe<sub>2</sub>), 2.68–2.62 (m, 2H, THF), 1.93 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.50 (d, 16H, CHCH<sub>3</sub>), 1.47 (d, 6H, CHCH<sub>3</sub>), 1.22 (d, 12H, CHCH<sub>3</sub>), 1.14–1.05 (m, 4H, THF) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ 149.0 (*o*-C), 148.6 (*o*-C), 142.3 (NCN), 137.1 (*ipso*-C), 128.6 (*p*-C), 124.1 (*m*-C), 123.6 (*m*-C), 116.8 (C<sub>5</sub>Me<sub>5</sub>), 113.3 (NCH), 72.0 (THF), 28.9 (CHMe<sub>2</sub>), 28.7 (CHMe<sub>2</sub>), 25.7 (THF), 24.6 (CHCH<sub>3</sub>), 24.5 (CHCH<sub>3</sub>), 24.4 (CHCH<sub>3</sub>), 23.9 (CHCH<sub>3</sub>), 11.1 (C<sub>5</sub>Me<sub>5</sub>) ppm.

**Preparation of the Imidazolin-2-iminato Bis(pentamethylcyclopentadienyl) Complex [(1)Gd(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(THF)] (7).** To a 10 mL THF solution of 481 mg (0.5 mmol) of [(1)GdCl<sub>2</sub>(THF)<sub>2</sub>]·[LiCl(THF)<sub>2</sub>] was added 175 mg (1.0 mmol) of KC<sub>5</sub>Me<sub>5</sub> in 10 mL THF dropwise at ambient temperature and the reaction mixture was stirred for 12 h. The solvent was evaporated and subsequently the compound was extracted from pentane. After filtration and evaporation, the complex was crystallized from THF/pentane at –30 °C. Yield: 350 mg (71%). Anal. Calcd for [C<sub>55</sub>H<sub>82</sub>GdN<sub>3</sub>O<sub>2</sub>]: C, 67.78; H, 8.48; N, 4.31. Found: C, 67.16; H, 8.18; N, 4.11. Because of the highly paramagnetic nature of the compound, no NMR spectra were recorded.

**General Procedure for Catalytic Hydroamination of Alkenes.** The catalyst was weighed in a glovebox under argon gas into an NMR tube. C<sub>6</sub>D<sub>6</sub> (~ 0.5 mL) was condensed into the NMR tube, and the mixture was frozen to –196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (*t*<sub>0</sub>). The ratio between the reactant and the product was calculated by comparison of the integrations of the corresponding signals. Ferrocene was used as internal standard for the kinetic measurements. The substrates *C*-(1-allyl-cyclohexyl)-methylamine,<sup>67</sup> 2-amino-5-hexene<sup>68</sup> 2,2-dimethylpent-4-

en-1-amine,<sup>53b</sup> 2,2-diphenyl-pent-4-enylamine,<sup>66</sup> [1-(pent-2-ynyl)-cyclohexyl]methanamine<sup>43h</sup> were synthesized according to the literature procedures. <sup>1</sup>H NMR spectra of 3-methyl-2-aza-spiro[4.5]decane,<sup>66</sup> 2,5-dimethylpyrrolidine,<sup>67</sup> 2,4,4-trimethylpyrrolidine,<sup>53b</sup> 2-methyl-4,4-diphenylpyrrolidine,<sup>66</sup> and 3-propyl-2-azaspiro[4.5]dec-2-ene<sup>43h</sup> conform with the literature.

#### General Procedure for Catalytic Hydrosilylation of Alkenes.

An NMR tube was charged in the glovebox with **3b** or **3c** (7 μmol), PhSiH<sub>3</sub> (0.36 mmol), olefin (1-hexene or 1-octene, 0.35 mmol), and C<sub>6</sub>D<sub>6</sub> (3 mL). The tube was closed and taken out of the glovebox. The disappearance of the substrates and formation of new organosilanes can be conveniently monitored by <sup>1</sup>H NMR spectroscopy.

**X-ray Crystal Structure Determinations.** Data were recorded on various area detectors (Oxford Diffraction or Bruker) at low temperature using Mo Kα radiation. Absorption corrections were performed on the basis of multiscans. Structures were refined anisotropically using the program SHELXL-97.<sup>69</sup> Hydrogen atoms were included using rigid methyl groups or a riding model. Numerical details are summarized in Table 5. Special details and exceptions: Compound **3a** diffracted weakly and was also mechanically unstable at very low temperature (presumably because of a phase change). Data were accordingly measured with Cu Kα radiation at –100 °C. However, the *U* values are large and one SiMe<sub>3</sub> group is disordered, so molecular dimensions should be interpreted with caution. Compounds **3b**, **3d**, **4d**, and **7** crystallize by chance in chiral space groups; in each case, the chirality was determined unambiguously, but applies only to the measured crystal and not to the bulk material. Compound **3c** crystallizes as a racemic twin in the noncentrosymmetric space group *Pna*2<sub>1</sub>, but all atom positions except for the trimethylsilyl and isopropyl groups correspond to the centrosymmetric space group *Pnam*; the refinement is therefore less stable because of near-singularity effects, and *U* values of light atoms were restrained to be approximately isotropic. Two carbons of one THF ligand in **5c** are disordered over two sites. The agostic Y···H contacts in **4b** were established by free refinement of the relevant methyl H atoms. However, the data for **4d** did not allow free hydrogen refinement (probably because of the noncentrosymmetric space group) so the usual idealized methyl geometry was assumed; metal–hydrogen distances are therefore less reliable.

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**Supporting Information Available:** Presentation of selected NMR spectra (PDF) and crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(67) Horrillo Martínez, P.; Hultsch, K. C.; Hampel, F. *Chem. Commun.* **2006**, 2221.

(68) Kim, J. Y.; Livinghouse, T. *Org. Lett.* **2005**, 7(20), 4391.

(69) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, 64, 112.