Reduction of Ketimines by Samarium(II) Complexes. Isolation and Structural Characterization of Samarium(III) η^1-Amine/η^1-Ketimido and η^2-Ketimine Complexes

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The reaction of $(C_5Me_5)_2Sm(THF)_2$ with 2 equiv of benzophenone imine ($Ph_2C=NH$) in THF at room temperature gave the samarocene(III) amine/ketimido complex $(C_5Me_5)_2Sm$-$(N=CPh_2)(NH_2CHPh_2)$ (**1**) in 58% isolated yield. The use of 1 equiv of $Ph_2C=NH$ also afforded **1** as the only isolable product, albeit in a lower yield (ca. 20%). Deuterium-labeling experiments suggest that **1** is formed via hydrogen abstraction by the in-situ-generated imine radical anion species, followed by acid−base reaction between the resulting amido species and another molecule of $Ph_2C=NH$. The reactions of 2 equiv of $Sm(OAr)_2(THF)_3$ (Ar = C_6H_2-$^tBu_2$-2,6-Me-4) with *N*-phenyl benzophenone imine ($Ph_2C=NPh$) and *N*-phenyl fluorenone imine ($C_{12}H_8C=NPh$) yielded the Sm(III) η^2-imine-dianion/aryloxide complexes $Sm(\eta^2$-Ph_2-$CNPh)(OAr)(THF)_3$ (**3**, 65%) and $Sm(\eta^2$-$C_{12}H_8CNPh)(OAr)(THF)_3$ (**4**, 77%), respectively, together with the byproduct $Sm(OAr)_3$. The reaction of 1 equiv of $Sm(OAr)_2(THF)_3$ with $Ph_2C=NPh$ also gave the imine-dianion complex **3**, whereas an imine radical anion species was not observed. Similarly, the reactions of 2 equiv of $Sm\{N(SiMe_3)_2\}_2(THF)_2$ with Ph_2-$C=NPh$ and $C_{12}H_8C=NPh$ yielded the η^2-imine-dianion/silylamido complexes $Sm(\eta^2$-Ph_2-$CNPh)\{N(SiMe_3)_2\}(THF)_3$ (**5**, 87%) and $Sm(\eta^2$-$C_{12}H_8CNPh)\{N(SiMe_3)_2\}(THF)_3$ (**6**, 71%), respectively. Complexes **3**−**6** represent the first examples of structurally characterized trivalent lanthanide η^2-imine complexes.

Introduction

The reduction of imines by low-valent lanthanides (e.g., SmI_2[1] and Yb[2]) and other reducing metals[3] has attracted considerable current interest. The reductive homocoupling of imines offers a convenient route to vicinal diamines, while the cross-coupling of imines with ketones or aldehydes affords α-amino alcohols,[1−3] both of which are valuable subunits found in medicinally important compounds or biologically active natural products. Although imine radical anion or imine-dianion species are thought to be important intermediates in

these reactions, the isolation and structural characterization of such an intermediate species from the reduction of imines remains very rare.[2b,3a,b,e] For the lanthanides only one example of a structurally characterized Yb(II) imine-dianion complex, $Yb(\eta^2$-$Ph_2CNPh)(HMPA)_3$, has been reported previously, which was isolated from the reaction of metallic Yb with $Ph_2C=NPh$ in the presence of hexamethylphosphoric triamide (HMPA).[2b] The isolation and structural characterization of an imine radical anion species, which is isoelectronic with ketyls,[4,5] remains a challenge for any metal.

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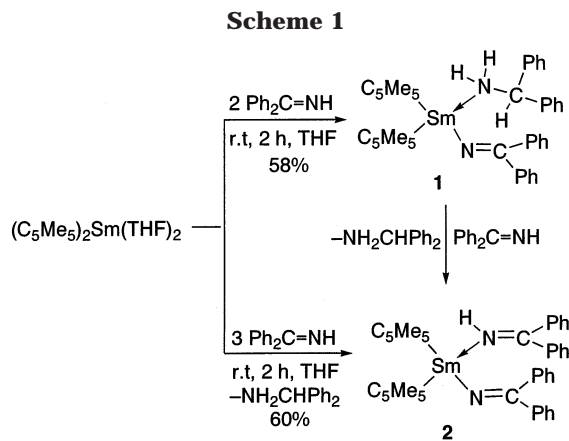† RIKEN.
‡ Chuo University.
§ University of Alberta.
(1) (a) Tanaka, Y.; Taniguchi, N.; Uemura, M. *Org. Lett.* **2002**, *4*, 835. (b) Taniguchi, N.; Uemura, M. *J. Am. Chem. Soc.* **2000**, *122*, 8301. (c) Machrouhi, F.; Namy, J.-L. *Tetrahedron Lett.* **1999**, *40*, 1315. (d) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Raimondi, L. *Tetrahedron Lett.* **1998**, *39*, 3333. (e) Taniguchi, N.; Uemura, M. *Synlett.* **1997**, 51. (f) Lebrun, A.; Rantze, E.; Namy, J.-L.; Kagan, H. B. *New J. Chem.* **1995**, *19*, 699. (g) Imamoto, T.; Nishimura, S. *Chem. Lett.* **1990**, 1141. (h) Enholm, E. J.; Forbes, D. C.; Holub, D. P. *Synth. Commun.* **1990**, *20*, 981.
(2) (a) Jin, W.-S.; Makioka, Y.; Taniguchi, Y.; Kitamura, T.; Fujiwara, Y. *Chem. Commun.* **1998**, 1101. (b) Makioka, Y.; Taniguchi, Y.; Fujiwara, Y.; Takaki, K.; Hou, Z.; Wakatsuki, Y. *Organometallics* **1996**, *15*, 5476. (c) Takaki, K.; Tanaka, S.; Fujiwara, Y. *Chem. Lett.* **1991**, 493. (d) Takaki, K.; Tsubaki, Y.; Tanaka, S.; Beppu, F.; Fujiwara, Y. *Chem. Lett.* **1990**, 203.

(3) For examples, see: (a) Cameron, T. M.; Ortiz, C. G.; Abboud, K. A.; Boncella, J. M.; Baker, R. T.; Scott, B. L. *Chem. Commun.* **2000**, 573. (b) Takai, K.; Ishiyama, T.; Yasue, H.; Nobunaga, T.; Itoh, M.; Oshiki, T.; Mashima, K.; Tani, K. *Organometallics* **1998**, *17*, 5128. (c) Rieke, R. D.; Kim, S.-H. *J. Org. Chem.* **1998**, *63*, 5235, and references therein. (d) Talukdar, S.; Banerji, A. *J. Org. Chem.* **1998**, *63*, 3468. (e) Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. Rosenthal, U. *Organometallics* **1995**, *14*, 3090. (f) Tanaka, H.; Dhimane, H.; Fujita, H.; Ikemoto, Y. *Tetrahedron Lett.* **1992**, *33*, 4469. (g) Ito, H.; Taguchi, T.; Hanazawa, Y. *Tetrahedron Lett.* **1988**, *29*, 3811. (h) Mangeney, P.; Tejero, A.; Alexakis, A.; Grosjean, F.; Normant, J. *Synthesis* **1988**, 255. (i) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551.
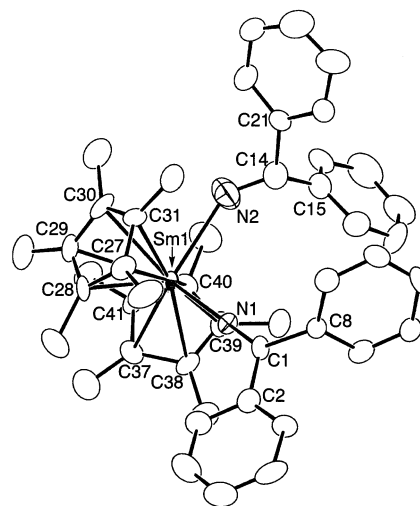(4) For examples of structurally characterized ketyl complexes formed by one-electron reduction of ketones, see: (a) Hou, Z.; Koizumi, T.; Nishiura, M.; Wakatsuki, Y. *Organometallics* **2001**, *20*, 3323. (b) Hou, Z.; Jia, X.; Fujita, A.; Tezuka, H.; Yamazaki, H.; Wakatsuki, Y. *Chem. Eur. J.* **2000**, *6*, 2994. (c) Hou, Z.; Fujita. A.; Koizumi, T.; Yamazaki, H.; Wakatsuki, Y. *Organometallics* **1999**, *18*, 1979. (d) Hou,

Scheme 1

Figure 1. ORTEP drawing of **1** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 1

Sm1−N1	2.24(1)	Sm1−N2	2.62(1)
Sm1−C27	2.76(1)	Sm1−C28	2.71(1)
Sm1−C29	2.74(1)	Sm1−C30	2.73(1)
Sm1−C31	2.75(1)	Sm1−C37	2.79(1)
Sm1−C38	2.72(1)	Sm1−C39	2.73(1)
Sm1−C40	2.779(9)	Sm1−C41	2.78(1)
N1−C1	1.23(1)	N2−C14	1.37(1)
Sm1−N1−C1	177.0(7)	Sm1−N2−C14	137.6(8)
N1−C1−C2	123.9(10)	N1−C1−C8	121.2(9)
C2−C1−C8	114.8(9)	N2−C14−C15	117(1)
N2−C13−C21	117(1)	C15−C14−C21	110(1)

In attempts to isolate a lanthanide imine radical anion species, we examined the reactions of several sterically demanding Sm(II) complexes with aromatic ketimines, as we did in the isolation of ketyl complexes.[4,5] In this paper, we report on the reactions of benzophenone imine, *N*-phenyl benzophenone imine, and *N*-phenyl fluorenone imine with the Sm(II) complexes $(C_5Me_5)_2Sm(THF)_2$, $Sm(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2$-$(THF)_3$, and $Sm\{N(SiMe_3)_2\}_2(THF)_2$, which afforded structurally characterizable Sm(III) η^1-amine/η^1-ketimido and η^2-ketimine complexes, depending on the structures of the imines and the reducing agents.[6] Some mechanistic aspects of these reactions are also described.

Results and Discussion

Reduction of Benzophenone Imine with $(C_5Me_5)_2$-$Sm(THF)_2$. Because of its similarity with a ketone, an N-H ketimine was first chosen as an imine substrate. The reaction of benzophenone imine ($Ph_2C=NH$) with 1 equiv of $(C_5Me_5)_2Sm(THF)_2$ in THF at room temperature gave an orange-red complex, **1**, as the only isolable product (ca. 20% yield based on Sm). When 2 equiv of $Ph_2C=NH$ was used, **1** was obtained in 58% isolated yield as orange-red blocks (Scheme 1). The well-resolved ^{1}H NMR spectrum in THF-d_8 showed that **1** is a samarocene(III) diphenylketimido/diphenylmethylamine complex, $(C_5Me_5)_2Sm(N=CPh_2)(NH_2CHPh_2)$, rather than a radical species. A 30:20 integration of the C_5Me_5 signal at δ 1.44 (s) and the Ph peaks at 7.12−7.70 (m)

suggested the presence of two benzophenone imine-derived units per two C_5Me_5 groups. A triplet at δ 5.15 ($J = 7$ Hz, 1 H) and a broad singlet at δ 1.74 (2 H, NH_2) with an integration of 1:2 were evident for the presence of a diphenylmethylamine unit (NH_2CHPh_2). The IR spectrum of **1** in Nujol showed a strong absorption at 1600 cm^{-1} for the C=N double bond of the ketimido unit, which is slightly low-frequency shifted from that of free benzophenone imine (1605 cm^{-1}).

In agreement with the spectral data, an X-ray crystallographic study showed that **1** bears two C_5Me_5 ligands and two significantly different benzophenone imine-derived ligands (Figure 1 and Table 1). The Sm−C(Cp*) bond distances, ranging from 2.71(1) to 2.79(1) Å, are typical for a trivalent decamethylsamarocene complex. The Sm1−N1 bond distance (2.239(9) Å) is comparable with that of the Sm−N(ketimido) bond found in $(C_5Me_5)_2Sm[N=CPh(C_5Me_5)](NCPh)$ (2.225(8) Å),[7] but much shorter than that of the Sm1−N2 bond (2.62(1) Å). The C1−N1 bond distance (1.23(1) Å) in **1** is also comparable with that of the C=N double bond in $(C_5Me_5)_2Sm[N=CPh(C_5Me_5)](NCPh)$ (1.26(1) Å),[7] but significantly shorter than that of the C14−N2 bond (1.37(1) Å). The sum of the angles around C1 is 360(1)° (sp^2-hybrid), which is in contrast with that around C14 (344(1)°). These data strongly suggest that the N1 moiety in **1** is a ketimido ligand, while N2 belongs to a neutral amine ligand.

Addition of 1 equiv of $Ph_2C=NH$ to a THF solution of **1** yielded quantitatively the imine-coordinated complex

Z.; Fujita. A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754. (e) Hou, Z.; Jia, X.; Wakatsuki, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1292. (f) Takats, J. *J. Alloys Compd.* **1997**, *249*, 51. (g) Clegg, W.; Eaborn, C.; Izod, K.; O'Shaughnessy, P.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2815. (h) Hou, Z.; Fujita. A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7843. (i) Hou, Z.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 2503. (j) Hou, Z.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1995**, *117*, 4421. (k) Bock, H.; Herrmann, H.-F.; Fenske, D.; Goesmann, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1067.

(5) For examples of structurally characterized ketone-dianion complexes formed by two-electron reduction of ketones, see: (a) Tardif, O.; Hou, Z.; Nishiura, M.; Koizumi, T.; Wakatsuki, Y. *Organometallics* **2001**, *20*, 4565. (b) Hou, Z.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *Chem. Commun.* **1998**, 669. (c) Yoshimura, T.; Hou, Z.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5382. (d) Hou, Z.; Yamazaki, H.; Kobayashi, K.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1992**, 722. (e) Hou, Z.; Yamazaki, H.; Fujiwara, Y.; Taniguchi, H. *Organometallics* **1992**, *11*, 2711. (f) Bogdanovic, B.; Kruger, C.; Wermeckes, B. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 817.

(6) No reaction occurred between the insoluble $Sm(Tp^{Me2})_2$ (Tp^{Me2} = $HB(3,5\text{-}Me_2\text{-}pyrazolyl)_3$) and the imines under similar conditions.

(7) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. J. *J. Am. Chem. Soc.* **1998**, *120*, 9273.
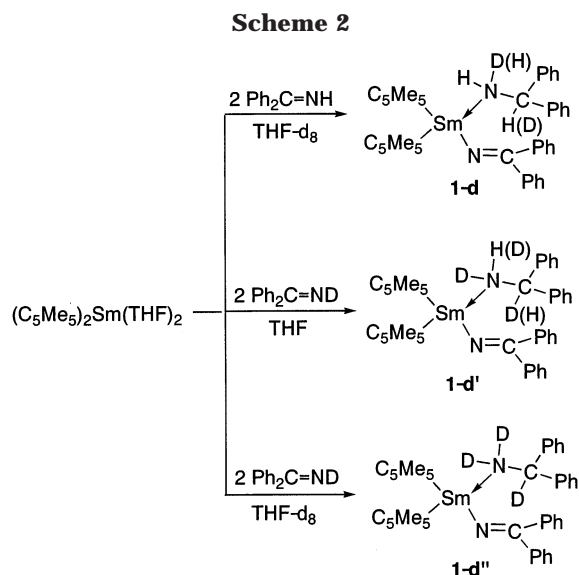
Scheme 2

Scheme 3

$(C_5Me_5)_2Sm(N=CPh_2)(NH=CPh_2)$ (**2**) with release of NH_2CHPh_2 (Scheme 1), indicating that $Ph_2C=NH$ is a stronger ligand for Sm(III) than Ph_2CHNH_2. Alternatively, the reaction of 3 equiv of $Ph_2C=NH$ with $(C_5Me_5)_2Sm(THF)_2$ also afforded **2** in 60% isolated yield (Scheme 1). The IR absorption of the C=N double bond of the ketimido unit shifted to 1625 cm^{-1} in **2** from 1600 cm^{-1} in **1**, suggesting that the C=N double bond of the ketimido unit in **2** is stronger than that in **1**. This is probably due to the influence of the stronger coordination of the imine ligand to the metal center in **2**, which weakens the Sm−ketimido bond and thus strengthens the ketimido C=N bond. The absorption of the C=N bond of the coordinated imine ligand $Ph_2C=NH$ in **2** appeared at 1595 cm^{-1}, 10 cm^{-1} lower than that of free $Ph_2C=NH$ (1605 cm^{-1}).

The formation of **1** apparently requires the reduction (hydrogenation) of the C=N bond of one $Ph_2C=NH$ molecule and the cleavage of the N−H bond of another $Ph_2C=NH$ molecule. To gain more information about the hydrogen transfer processes, deuterium-labeling experiments were carried out as shown in Scheme 2. The reaction of $Ph_2C=ND$ with $(C_5Me_5)_2Sm(THF)_2$ in THF-d_8 led to complete deuteration at both the methine carbon and the amino group of the diphenylmethylamine unit to give **1-d''**. However, the reaction of $Ph_2C=NH$ with $(C_5Me_5)_2Sm(THF)_2$ in THF-d_8 or that of $Ph_2C=ND$ with $(C_5Me_5)_2Sm(THF)_2$ in normal THF resulted in only partial deuteration at the methine carbon and the amino group of the diphenylmethylamine unit.[8] These results suggest that an intramolecular hydrogen atom transfer from the N atom to the methine C atom, as well as hydrogen (or deuterium) abstraction from the solvent by both the N atom and the methine C atom, took place. On the basis of these results, a possible mechanism for the formation of **1**, as shown in Scheme 3, can be proposed. One-electron
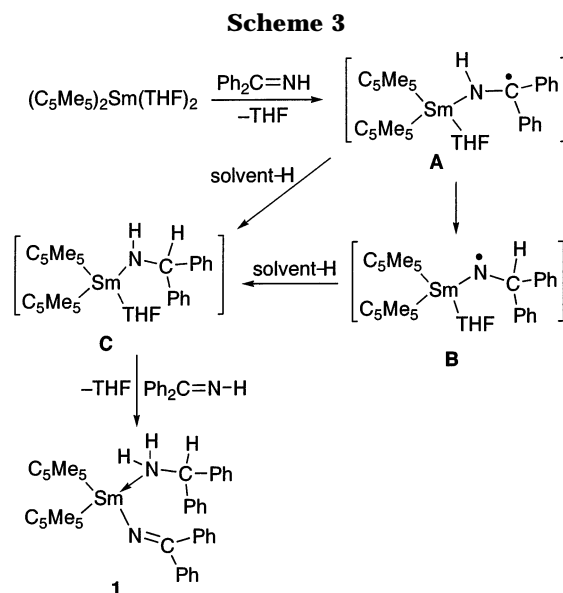
transfer from $(C_5Me_5)_2Sm(THF)_2$ to $Ph_2C=NH$ would generate the radical species **A**. Intramolecular hydrogen radical (H•) transfer from the N atom to the radical carbon atom in **A** could generate the nitrogen radical species **B**, which upon abstraction of H• from THF solvent gives **C**. The H• abstraction from the solvent by **A** could also occur to yield **C**. Hydrogen abstraction from another molecule of $Ph_2C=NH$ by the amido species **C** ultimately affords **1**.

The isolation of the amine/ketimido complex **1** instead of a amido complex such as **C** as the final product even when only 1 equiv of $Ph_2C=NH$ was used shows that benzophenone imine ($Ph_2C=NH$) is much more acidic than diphenylmethylamine (Ph_2CHNH_2) and the acid−base reaction between **C** and $Ph_2C=NH$ is much faster than the electron transfer from $(C_5Me_5)_2Sm(THF)_2$ to $Ph_2C=NH$. These results are in contrast with what was observed previously in the reactions of titanocene and zirconocene reducing agents with $Ph_2C=NH$, in which the corresponding amido/ketimido complexes $Cp_2M(NHCHPh_2)(N=CPh_2)$ (M = Ti, Zr) were obtained.[3e] The easy formation of the amine/ketimido complex **1** in the present reactions also suggests that the acid−base reaction between a lanthanide amido species and an N-H ketimine compound could constitute a convenient method for the synthesis of the corresponding lanthanide ketimido complexes.[9,10]
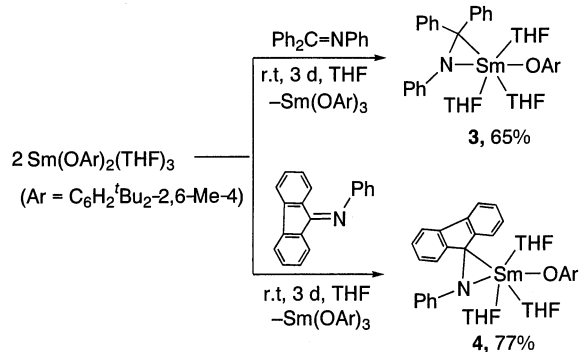
Reduction of *N*-Phenyl Benzophenone Imine and *N*-Phenyl Fluorenone Imine by Sm(OAr)$_2$-(THF)$_3$ and Sm{N(SiMe$_3$)$_2$}$_2$(THF)$_2$. To prevent the intramolecular H transfer reaction observed above and generate a more stable radical species, *N*-phenyl benzophenone imine ($Ph_2C=NPh$) and *N*-phenyl fluorenone imine ($C_{12}H_8C=NPh$) were then examined. The reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of $Ph_2C=NPh$, how-

(8) The D/H contents in **1-*d*** and **1-*d*** seemed different. An accurate determination of the D/H-incorporation percentages was, however, difficult, because the corresponding NMR signals (^{1}H and ^{2}H) were too weak to give an accurate integration ratio. It was roughly estimated that **1-*d*** bears ca. 0.3−0.4 H (0.6−0.7 D) at the methine carbon and ca. 1.6−1.7 H (0.3−0.4 D) at the amino group of the diphenylmethylamine unit, while **1-*d*** possesses ca. 0.1−0.2 H (0.8−0.9 D) at the methine carbon and ca. 0.8−0.9 H (1.1−1.2 D) at the amino group.
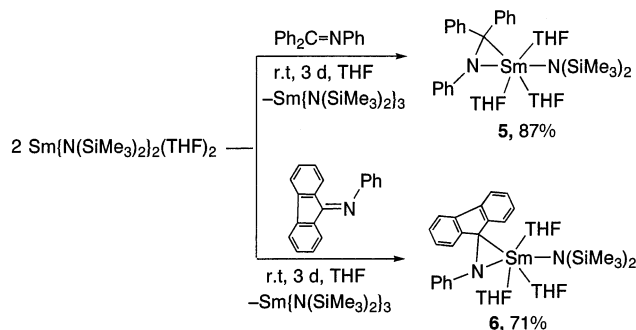
(9) For examples of the formation of group 3 (Sc, Y) metal ketimido or aldimido complexes, see: (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (b) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (c) den Haan, K. H.; Luinstra, G. A.; Meetsma, A. Teuben, J. H. *Organometallics* **1987**, *6*, 1509. (d) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291. See also ref 7.

(10) For the synthesis and structural characterization of an actinide ketimido complex, see: Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 3073.
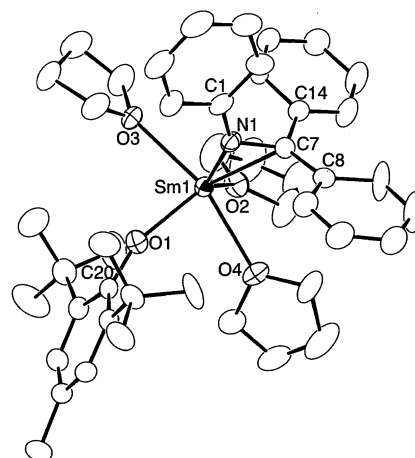
Scheme 4

Scheme 5

Figure 2. ORTEP drawing of **3** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Figure 3. ORTEP drawing of **4** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Figure 4. ORTEP drawing of **5** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

ever, did not afford a structurally characterizable product. Under similar conditions, the reaction of $Sm(OAr)_2(THF)_3$ (Ar = C_6H_2-$^tBu_2$-2,6-Me-4) with 1 equiv of $Ph_2C=NPh$ in THF at room temperature gave the Sm(III) monoaryloxide/imine-dianion complex $Sm(\eta^2$-$Ph_2CNPh)(OAr)(THF)_3$ (**3**, ca. 20%) together with the tris(aryloxide) complex $Sm(OAr)_3$ and unreacted Ph_2-C=NPh. A radical species was not observed. When 2 equiv of $Sm(OAr)_2(THF)_3$ was used in this reaction, the η^2-imine-dianion complex **3** was isolated in 65% yield (based on imine) as green crystals (Scheme 4). The similar reaction of *N*-phenyl fluorenone imine ($C_{12}H_8$-C=NPh) with $Sm(OAr)_2(THF)_3$ afforded $Sm(\eta^2$-$C_{12}H_8$-CNPh)(OAr)(THF)_3$ (**4**). Analogously, the reactions of $Sm\{N(SiMe_3)_2\}_2(THF)_2$ with $Ph_2C=NPh$ and *N*-phenyl fluorenone imine yielded the corresponding η^2-imine-dianion/silylamido complexes **5** and **6**, respectively, as shown in Scheme 5.
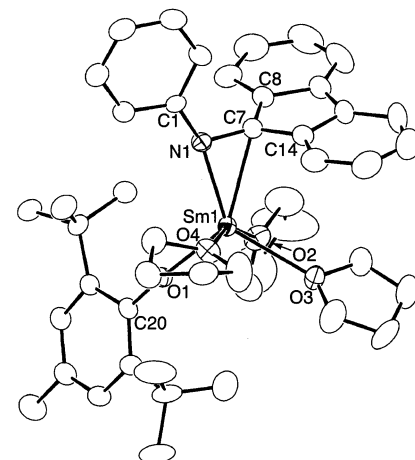
Complexes **3**–**6** adopt a similar overall structure (see Figures 2–5 and Tables 2 and 3). The Sm–N1(imine) bond distances in **3**–**6** (2.203(6)–2.270(4) Å) are somewhat shorter than those of the Sm–N2(silylamido) bonds in **5** (2.351(5) Å) and **6** (2.34(2) Å), but comparable with that of the Sm–N1(ketimido) bond in **1** (2.24(1) Å). The Sm–C7(imine) bond distances in **3**–**6** (2.564(4)–2.64(2) Å) are longer than the Sm–C(benzyl) distance in $(C_5Me_5)_2SmCH_2Ph(THF)$ (2.498(5) Å)[11] and the Sm–C(phenyl) distance in $(C_5Me_5)_2SmPh(THF)$ (2.511(5) Å),[12] but shorter than a typical Sm(III)–C(Cp*) distance (2.7–2.8 Å). The N1–C7 bond distances in **3**–**6** (1.43(3)–1.45(3) Å) are comparable with those in Yb-(η^2-Ph_2CNPh)(HMPA)$_3$ (1.43(3) Å),[2b] (PhN)Mo{1,2-(Me$_3$SiN)$_2C_6H_3$}(η^2-Ph(Me)CNPh) (1.414(3) Å),[3a] and TaCl$_3$-

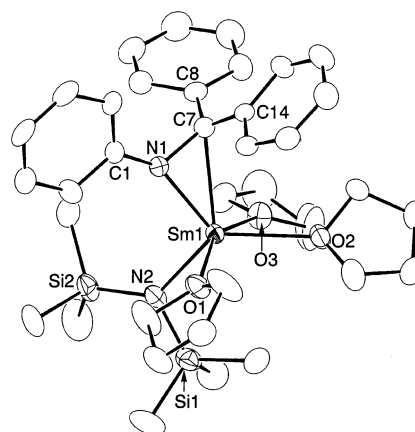(11) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423.
(12) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112.

(η^2-Ph(H)CNCH$_2$Ph)(MeOCH$_2$CH$_2$OMe) (1.401(6) Å)[3b] and can be considered as C–N single bonds. The sums of the angles formed by N1, C8, and C14 around C7 in **3**–**6** (357.3(7)°, 359.1(4)°, 356.9(5)°, and 360(2)°, respectively) are comparable with that in Yb(η^2-Ph_2CNPh)-(HMPA)$_3$ (359(1)°)[2b] and those reported for ketone-dianion complexes (358–360°),[5] suggesting that the C7 carbon atoms in **3**–**6** are still sp²-hybridized. As far as we are aware, complexes **3**–**6** represent the first ex-
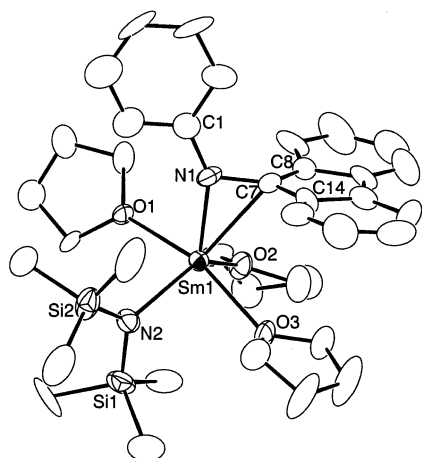
Figure 5. ORTEP drawing of **6** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

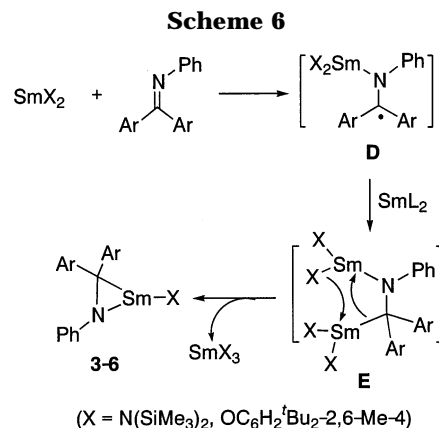**Table 2. Selected Bond Distances (Å) and Angles (deg) of 3 and 4**

	3	4
Sm1−N1	2.255(6)	2.270(4)
Sm1−C7	2.557(7)	2.564(4)
Sm1−O1	2.187(6)	2.168(3)
Sm1−O2	2.571(6)	2.504(4)
Sm1−O3	2.523(5)	2.543(3)
Sm1−O4	2.513(5)	2.486(6)
N1−C1	1.372(9)	1.386(5)
N1−C7	1.450(10)	1.441(6)
Sm1−N1−C1	150.4(5)	153.4(3)
Sm1−N1−C7	84.3(4)	84.2(2)
Sm1−C7−N1	61.3(4)	61.8(2)
Sm1−C7−C8	127.6(5)	127.1(4)
Sm1−C7−C14	91.9(5)	94.9(3)
N1−Sm1−O1	111.4(2)	133.3(1)
O1−Sm1−C7	136.4(2)	138.4(1)
Sm1−O1−C20	158.7(5)	164.5(3)
N1−C7−C8	116.0(7)	127.1(4)
N1−C7−C14	115.8(7)	124.8(4)
C8−C7−C14	125.5(7)	107.2(4)

Table 3. Selected Bond Distances (Å) and Angles (deg) of 5 and 6

	5	6
Sm1−N1	2.203(6)	2.22(2)
Sm1−C7	2.588(7)	2.64(2)
Sm1−N2	2.351(5)	2.34(2)
Sm1−O1	2.525(4)	2.46(1)
Sm1−O2	2.562(4)	2.46(1)
Sm1−O3	2.522(4)	2.53(2)
N1−C1	1.390(8)	1.39(3)
N1−C7	1.450(7)	1.43(3)
Sm1−N1−C1	146.4(4)	151(1)
Sm1−N1−C7	87.7(4)	89(1)
Sm1−C7−N1	58.3(3)	57(1)
Sm1−C7−C8	116.4(4)	106(1)
Sm1−C7−C14	107.5(4)	115(1)
N1−Sm1−N2	105.6(4)	118.4(7)
N2−Sm1−C7	130.4(2)	139.0(8)
N1−C7−C8	115.2(5)	125(2)
N1−C7−C14	119.9(5)	128(2)
C8−C7−C14	121.8(5)	107(2)

amples of structurally characterized trivalent lanthanide η^2-imine complexes.[13]

The formation of **3−6** could be explained by the mechanism shown in Scheme 6. One-electron transfer

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(13) For an example of a divalent lanthanide η^2-imine complex, see ref 2b.

Scheme 6

$(X = N(SiMe_3)_2, OC_6H_2\text{-}^tBu_2\text{-}2,6\text{-}Me\text{-}4)$

from SmX_2 ($X = N(SiMe_3)_2$, OC_6H_2-$^tBu_2$-2,6-Me-4) to a ketimine should give the radical species **D**, which upon reduction by another equivalent of SmX_2 would afford the disamarium imine-dianion species **E**. Ligand redistribution in **E** could give SmX_3 and **3−6**. The isolation of the imine-dianion complexes **3−6** rather than an imine radical anion species such as **D**, even when only 1 equiv of SmX_2 was used, suggests that an N-Ph ketimine radical species is more easily reduced than its neutral imine precursor. The easier formation of an imine-dianion species than that of an imine radical anion was also observed previously in the reduction of *N*-phenyl ketimines by SmI_2.[1g] These results are in contrast with what was observed in ketone reductions, in which both ketyl radical and ketone-dianion species could be isolated by control of the reducing agent/substrate ratio.[4,5]

Conclusion

We have demonstrated that the reaction of a Sm(II) complex such as $(C_5Me_5)_2Sm(THF)_2$ with an N-H ketimine compound easily gives an η^1-amine/η^1-ketimido complex such as **1** through hydrogen abstraction of the in-situ-generated imine radical anion species and the subsequent acid−base reaction between the resulting amido species and another molecule of the N-H ketimine. In the case of N-Ph ketimines, two-electron reduction is preferred to yield the corresponding η^2-imine-dianion complexes. The isolation of a structurally characterizable imine radical anion species remains a challenge.

Experimental Section

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. Argon was purified by being passed through a Dryclean column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4 Å) catalyst unit. The oxygen and moisture level in the glovebox was monitored by an O_2/H_2O Combi-Analyzer (MBraun) to ensure that both were always below 1 ppm. Samples of the lanthanide complexes for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H NMR spectra were recorded on a JNM-EX 270 (FT, 270 MHz) spectrometer. Elemental analyses were carried out by the Chemical Analysis Team, Advanced D&S Center, RIKEN. Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze−

Table 4. Summary of Crystallographic Data

	1	3	4	5	6
formula	$C_{46}H_{53}N_2Sm$	$C_{46}H_{62}NO_4Sm$	$C_{46}H_{60}NO_4Sm$	$C_{37}H_{57}N_2O_3Si_2Sm$	$C_{37}H_{55}N_2O_3Si_2Sm$
mol wt	784.34	843.40	841.38	784.44	782.42
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (Å)	16.653(5)	11.773(1)	14.033(6)	19.345(2)	40.520(10)
b (Å)	12.028(2)	18.527(3)	14.487(8)	9.905(2)	10.915(6)
c (Å)	20.108(5)	10.551(4)	10.565(1)	20.905(3)	17.896(3)
α (deg)		105.978(6)	98.01(2)		
β (deg)	94.260(8)	100.84(2)	94.08(1)	103.772(9)	96.796(10)
γ (deg)		72.68(1)	97.82(4)		
V (Å^3)	4017(1)	2098.0(9)	2098(1)	3890.8(10)	7858(5)
Z	4	2	2	4	8
μ (cm^{-1})	14.97	14.44	14.44	16.09	15.93
$F(000)$	1620.00	878.00	874.00	1628.00	3244.00
D_{calcd} (g cm^{-1})	1.297	1.335	1.332	1.339	1.322
no. of unique reflns	9536	8748	9291	7869	7007
no. of reflns with $I > 3\sigma(I)$	6903	8389	8327	6201	3408
no. of variables	442	469	469	406	406
R	0.078	0.068	0.043	0.044	0.092
R_w	0.078	0.079	0.063	0.067	0.115

pump–thaw method (three times), and dried over fresh Na chips in the glovebox. $Ph_2C=NH$ was purchased from Aldrich. $Ph_2C=ND$ was prepared by reaction of CD_3OD with $Ph_2-C=NLi$, which was generated by reaction of BuLi with 1 equiv of $Ph_2C=NH$ in THF at −78 °C. $Ph_2C=NPh$,[14] $C_{12}H_8C=NPh$ (*N*-phenyl fluorenone imine),[14] $(C_5Me_5)_2Sm(THF)_2$,[15] $Sm(OC_6H_2-{}^tBu_2-2,6-Me-4)_2(THF)_3$,[16] $Sm\{N(SiMe_3)_2\}_2(THF)_2$,[17] and $Sm-(Tp^{Me2})_2$ ($Tp^{Me2} = HB(3,5-Me_2-pyrazolyl)_3$)[6,18] were prepared according to literature methods.

$(C_5Me_5)_2Sm(N=CPh_2)(NH_2CHPh_2)$ (1). To $(C_5Me_5)_2Sm-(THF)_2$ (200 mg, 0.35 mmol) in THF (20 mL) was added $Ph_2-C=NH$ (130 mg, 0.72 mmol) at room temperature. The mixture soon turned from purple to dark brown and then to reddish orange. After the reaction mixture was stirred for 2 h, THF was removed under reduced pressure. The orange-red solid residue was washed with hexane and recrystallized from THF/hexane to give orange-red blocks of **1** (160 mg, 58%). The reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of $Ph_2C=NH$ also afforded **1** in ca. 20% yield (based on Sm). ^1H NMR (THF-d_8, 25 °C): δ 7.12–7.70 (m, 20 H, Ph), 5.15 (t, 1 H, $J = 7$ Hz, C*H*Ph$_2$), 1.74 (br s, 2 H, NH$_2$), 1.44 (s, 30 H, C$_5$Me$_5$). IR (Nujol): 3265 (ν_{N-H}), 3220 (ν_{N-H}), 1600 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{46}H_{53}N_2Sm$: C, 70.44; H, 6.81; N, 3.57. Found: C, 70.01; H, 6.76; N, 3.55.

$(C_5Me_5)_2Sm(N=CPh_2)\{N(H/D)_2C(H/D)Ph_2\}$ (1-*d*). This complex was prepared by reaction of $Sm(C_5Me_5)_2(THF)_2$ with $Ph_2C=NH$ in THF-d_8 analogously to the synthesis of **1**. ^1H NMR (THF-d_8, 25 °C):[8] δ 7.12–7.70 (m, 20 H, Ph), 5.15 (br s, ca. 0.3–0.4 H, C(*H/D*)Ph$_2$), 1.73 (br s, ca. 1.6–1.7 H, N(H/D)$_2$), 1.44 (s, 30 H, C$_5$Me$_5$).

$(C_5Me_5)_2Sm(N=CPh_2)\{N(D/H)_2C(D/H)Ph_2\}$ (1-*d′*). This complex was prepared by reaction of $Sm(C_5Me_5)_2(THF)_2$ with $Ph_2C=ND$ in THF analogously to the synthesis of **1**. ^1H NMR (THF-d_8, 25 °C):[8] δ 7.12–7.70 (m, 20 H, Ph), 5.15 (br s, ca. 0.1–0.2 H, C(*D/H*)Ph$_2$), 1.73 (br s, 0.8–0.9 H, N(D/H)$_2$), 1.44 (s, 30 H, C$_5$Me$_5$).

$(C_5Me_5)_2Sm(N=CPh_2)(ND_2CDPh_2)$ (1-*d″*). This complex was prepared by reaction of $Sm(C_5Me_5)_2(THF)_2$ with $Ph_2C=ND$ in THF-d_8 analogously to the synthesis of **1**. ^1H NMR (THF-d_8, 25 °C): δ 7.12–7.70 (m, 20 H, Ph), 1.44 (s, 30 H, C$_5$Me$_5$).

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$(C_5Me_5)_2Sm(N=CPh_2)(NH=CPh_2)$ (2). To $Sm(C_5Me_5)_2-(THF)_2$ (180 mg, 0.32 mmol) in THF (20 mL) was added $Ph_2-C=NH$ (190 mg, 1.1 mmol) at room temperature. The reaction mixture soon turned from deep purple to dark brown and then to reddish orange. After the mixture was stirred for 2 h at room temperature, the solvent was removed under reduced pressure. The red solid was recrystallized from THF/hexane to give **2** as fine red crystals (150 mg, 60%). Reaction of **1** with 1 equiv of $Ph_2C=NH$ also afforded **2** almost quantitatively. ^1H NMR (THF-d_8, 25 °C): δ 10.10 (br s, 1 H, NH), 7.10–7.29 (m, 20 H, Ph), 1.43 (s, 30 H, C$_5$Me$_5$). IR (Nujol): 3265 (ν_{N-H}), 3220 (ν_{N-H}), 1625 ($\nu_{C=N}$), 1595 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{46}H_{51}N_2Sm$: C, 70.63; H, 6.57; N, 3.58. Found: C, 70.55; H, 6.50; N, 3.53.

$Sm(\eta^2-Ph_2CNPh)(OC_6H_2{}^tBu_2-2,6-Me-4)(THF)_3$ (3). To $Sm-(OC_6H_2-{}^tBu_2-2,6-Me-4)_2(THF)_3$ (700 mg, 0.80 mmol) in THF (20 mL) was added $Ph_2C=NPh$ (102 mg, 0.40 mmol) at room temperature. The reaction mixture soon turned from reddish brown to greenish brown. After the reaction mixture was stirred for 3 days, THF was removed under reduced pressure. The residue was washed with hexane, and the resulting green solid was collected by filtration to give **3** (220 mg, 65%) after drying in vacuo. The hexane filtrate was concentrated under reduced pressure to give yellow crystals of $Sm(OC_6H_2{}^tBu_2-2,6-Me-4)_3$ (270 mg, 83%). Single crystals of **3** could be obtained by recrystallization of the green solid from THF/hexane. ^1H NMR for **3** (THF-d_8, 25 °C): δ 11.85 (d, 2 H, $J = 7$ Hz, N-Ph-*o*), 9.51 (br s, 4 H, Ph-*o*), 7.79 (t, 1 H, $J = 7$ Hz, N-Ph-*p*), 7.62 (br s, 2 H, N-Ph-*m*), 7.25–7.45 (m, 4 H, Ph-*o*, C$_6$H$_2$), 5.51 (br s, 4 H, Ph-*m*), 2.28 (s, 3 H, Me), 1.75 (br s, 18 H, ^{t}Bu). Anal. Calcd for $C_{46}H_{62}NO_4Sm$: C, 64.50; H, 7.62; N, 1.70. Found: C, 64.70; H, 7.42; N, 1.49.

$Sm(\eta^2-C_{12}H_8CNPh)(OC_6H_2{}^tBu_2-2,6-Me-4)(THF)_3$ (4). Complex **4** was prepared in 77% yield analogously to the synthesis of **3** by reaction of 2 equiv of $Sm(OC_6H_2{}^tBu_2-2,6-Me-4)_3$ with *N*-phenyl fluorenone imine. ^1H NMR (THF-d_8, 25 °C): δ 11.17 (d, 2 H, $J = 7$ Hz, Ph-*o*), 8.69 (d, 2 H, $J = 7$ Hz, C$_{13}$H$_8$), 7.61 (br s, 3 H, C$_{13}$H$_8$, N-Ph-*p*), 7.49 (t, 2 H, $J = 7$ Hz, C$_{13}$H$_8$), 7.22 (s, 2 H, C$_6$H$_2$), 5.66 (t, 2 H, $J = 7$ Hz, C$_{13}$H$_8$), 4.94 (d, 2 H, $J = 7$ Hz, C$_{13}$H$_8$), 2.21 (s, 3 H, Me), 1.26 (br s, 18 H, ^{t}Bu). Anal. Calcd for $C_{46}H_{60}NO_4Sm$: C, 64.66; H, 7.39; N, 1.71. Found: C, 64.80; H, 7.01; N, 1.76.

$Sm(\eta^2-Ph_2CNPh)\{N(SiMe_3)_2\}(THF)_3$ (5). To $Sm\{N(Si-Me_3)_2\}_2(THF)_2$ (1.50 g, 2.44 mmol) in THF (20 mL) was added $Ph_2C=NPh$ (311 mg, 1.22 mmol) at room temperature. The reaction mixture soon turned from purple to greenish brown. After the solution was stirred for 3 days, THF was removed under reduced pressure. The residue was washed with hexane, and the resulting green solid was collected by filtration to give **5** (835 mg, 87%) after drying in vacuo. The hexane filtrate was

concentrated under reduced pressure to give pale yellow needles of $Sm\{N(SiMe_3)_2\}_3$ (690 mg, 90%). Single crystals of **5** could be obtained by recrystallization of the green solid from THF/hexane. ^1H NMR for **5** (THF-d_8, 25 °C): δ 11.50 (br s, 2 H, N-Ph-*o*), 9.27 (d, 4 H, $J = 8$ Hz, Ph-*o*), 7.58 (t, 2 H, $J = 8$ Hz, Ph-*p*), 7.30−7.50 (m, 3 H, N-Ph-*m,p*), 5.78 (t, 4 H, $J = 7$ Hz, Ph-*m*), 0.15 (s, 18 H, SiMe$_3$). Anal. Calcd for $C_{37}H_{57}N_2O_3$-Si_2Sm: C, 56.65; H, 7.32; N, 3.57. Found: C, 56.33; H, 6.90; N, 3.40.

$Sm(\eta^2\text{-}C_{12}H_8CNPh)\{N(SiMe_3)_2\}(THF)_3$ (6). Complex **6** was prepared in 71% yield analogously to the synthesis of **5** by reaction of 2 equiv of $Sm\{N(SiMe_3)_2\}_2(THF)_2$ with *N*-phenyl fluorenone imine. ^1H NMR (THF-d_8, 25 °C): δ 10.76 (d, 2 H, $J = 7$ Hz, Ph-*o*), 8.58 (d, 2 H, $J = 7$ Hz, $C_{13}H_8$), 7.30−7.60 (m, 5 H, $C_{13}H_8$, Ph), 5.88 (t, 2 H, $J = 7$ Hz, $C_{13}H_8$), 5.20 (d, 2 H, $J = 7$ Hz, $C_{13}H_8$), −0.42 (s, 18 H, SiMe$_3$). Anal. Calcd for $C_{37}H_{55}N_2O_3Si_2Sm$: C, 56.80; H, 7.08; N, 3.58. Found: C, 56.33; H, 6.90; N, 3.40.

X-ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glovebox under a microscope mounted on the glovebox window and were sealed in thin-walled glass capillaries under N$_2$ atmosphere. Data collections were performed at 20 °C on a Rigaku RAXIS CS imaging plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The structures were solved by using the teXsan software package. Refinements were performed on F anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystal data and processing parameters are summarized in Table 4.

Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for complexes **1** and **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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