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Lanthanide(II) Complexes Bearing Linked Cyclopentadienyl−Anilido Ligands: Synthesis, Structures, and One-Electron-Transfer and Ethylene Polymerization Reactions

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Reactions of $Ln[N(SiMe_3)_2]_2(thf)_2$ (Ln = Sm, Yb) with 1 equiv of $(C_5Me_4H)SiMe_2NHPh$ afforded the first linked cyclopentadienyl−anilido (or amido) lanthanide(II) complexes $Me_2Si(C_5Me_4)(NPh)Ln(thf)_x$ (**1**, Ln = Yb, $x = 3$; **2**, Ln = Sm, $x = 0-1$) in 75−84% isolated yields. Recrystallization of **1** from toluene/hexane yielded the less solvated complex $[Me_2Si(C_5Me_4)(NPh)Yb(thf)]_2$ (**1′**). Complex **1** adopts a monomeric structure containing one chelating Cp−anilido ligand and three thf ligands, while **1′** forms a dimeric structure through an "intermolecular" Yb−Ph π-interaction. Reaction of **1** or **1′** with azobenzene gave the binuclear Yb(III) complex $Me_2Si(C_5Me_4)(NPh)Yb(thf)(\mu,\eta^2{:}\,\eta^3\text{-}N_2Ph_2)Yb(NPh)(C_5Me_4)SiMe_2$ (**3**), which contains a *cis*-oriented azobenzene dianion unit bonding in a η^3 fashion to one Yb atom and in a η^2 fashion to the other Yb atom. Reaction of **1** with 1 equiv of fluorenone gave the corresponding Yb(III) ketyl complex $Me_2Si(C_5Me_4)(NPh)Yb(thf)_2(OC_{13}H_8)$ (**4**) in 75% isolated yield. Treatment of **4** with hexane/ether led to formation of the pinacolate complex $[Me_2Si(C_5Me_4)(NPh)Yb(thf)]_2(\mu\text{-}O_2C_{26}H_{16})$ (**5**), in which the pinacolate unit is arranged in a gauche conformation. Dissolving of **5** in THF cleaved the central C−C bond of the pinacolate unit in **5** and regenerated **4** quantitatively. The Sm(II) complex **2** showed moderate activity (44.8 kg of polymer (mol of Sm)$^{-1}$ h^{-1}) for the polymerization of ethylene under 1 atm at room temperature, yielding linear polyethylene with $M_n = 7.26 \times 10^5$ and $M_w/M_n = 1.58$.

Introduction

Lanthanide complexes bearing silylene-linked cyclopentadienyl−amido ligands (e.g., $[Me_2Si(C_5Me_4)N^tBu]^{2-}$) have received much current interest, because of their electronically more unsaturated and sterically more accessible properties as compared to those of the metallocene analogues.[1,2] These types of lanthanide complexes reported so far in the literature have, however, been limited solely to those in the +3 oxidation state. Although analogous complexes in the +2 oxidation state are of great interest in view of the unique chemistry that has been developed with divalent lanthanide complexes bearing other ligand systems,[3] such a lanthanide(II) complex has not been reported to date.[4] During our recent studies on lanthanide(II) complexes bearing mixed (unlinked) C_5Me_5/ER ligands (ER = a monodentate anionic ligand such as an aryloxide, thiolate, amido, or phosphido group),[5] we found that the mixed-ligand-supported lanthanide(II) complexes, particularly those of samarium(II), could serve as a unique catalytic system for polymerization reactions.[5c] These

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[†] Special Postdoctoral Researcher under the Basic Science Program of RIKEN.

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(3) Reviews on the chemistry and application of low-valent lanthanides: (a) Evans, W. J. *Coord. Chem. Rev.* **2000**, *207−207*, 263. (b) Hou, Z.; Wakatsuki, Y. *Top. Organomet. Chem.* **1999**, *2*, 233. (c) Boffa, L. S.; Novak, B. M. *Tetrahedron* **1997**, *53*, 15367. (d) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307. (e) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Lappert, M. F., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 4, Chapter 2. (f) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (g) Evans, W. J. *Polyhedron* **1987**, *6*, 803.

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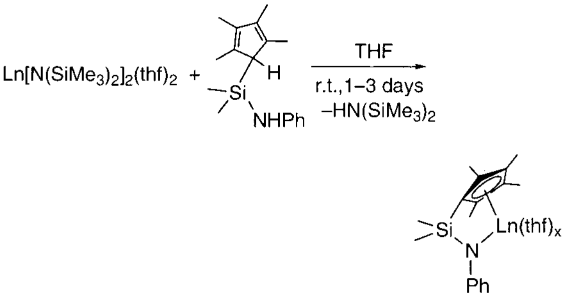
findings have now promoted us to examine the analogous lanthanide(II) complexes bearing linked cyclopentadienyl−monodentate anionic ligand systems, since such complexes could be anticipated to offer a ligand environment similar to that of the C_5Me_5/ER-ligated analogues but would not suffer from the ligand redistribution problems that usually occur with the unlinked, mixed-ligand systems.[5h] In this paper, we report the synthesis and structures of the first linked cyclopentadienyl−anilido lanthanide(II) complexes, $Me_2Si(C_5Me_4)(NPh)Ln(thf)_x$ (**1**, Ln = Yb, *x* = 3; **1′**, Ln = Yb, *x* = 1; **2**, Ln = Sm, *x* = 0−1), as well as some preliminary results that demonstrate the utility of these new complexes as one-electron-reducing agents and ethylene polymerization precatalysts.

Results and Discussion

Synthesis and Structures of Samarium(II) and Ytterbium(II) Complexes. The conventional metathetical approaches that have been successfully used for the synthesis of lanthanide(III) complexes bearing linked cyclopentadienyl−amido ligands[2f−l] could not be straightforwardly extended to the synthesis of the lanthanide(II) analogues.[6] However, the acid−base reactions between lanthanide(II) bis(silylamide) compounds and the aniline ligand $(C_5Me_4H)SiMe_2NHPh$ proved to be a useful route to the corresponding cyclopentadienyl−anilido lanthanide(II) complexes.[7,8] Thus, the reaction of $Yb[N(SiMe_3)_2]_2(thf)_2$ with 1 equiv of $(C_5Me_4H)SiMe_2NHPh$ in THF at room temperature occurred smoothly to give the Yb(II) complex $Me_2Si(C_5Me_4)(NPh)Yb(thf)_3$ (**1**) in 75% isolated yield, with quantitative release of $HN(SiMe_3)_2$ (eq 1). An analogous reaction of $Sm[N(SiMe_3)_2]_2(thf)_2$ with $(C_5Me_4H)SiMe_2NHPh$ afforded the corresponding Sm(II) complex $Me_2Si(C_5Me_4)(NPh)Sm(thf)_x$ in 84% yield (**2**, *x* = 0−1 on the basis of elemental analysis) (eq 1).[9] Two of the three thf ligands in **1** could be removed by recrystallization of **1** from toluene/hexane, which gave $[Me_2Si(C_5Me_4)(NPh)Yb(thf)]_2$ (**1′**) in almost quantitative yield (eq 2).



(1)

1: Ln = Yb, x = 3; 75%
2: Ln = Sm, x = 0–1; 84%

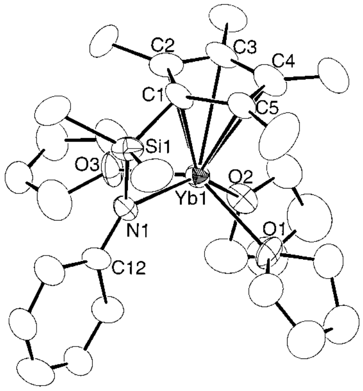
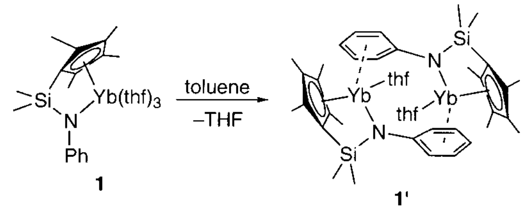


Figure 1. ORTEP drawing of **1** with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Yb(1)−O(1), 2.464(8); Yb(1)−O(2), 2.393(8); Yb(1)−O(3), 2.418(8); Yb(1)−N(1), 2.359(8); Yb(1)−C(1), 2.52(1); Yb(1)−C(2), 2.66(1); Yb(1)−C(3), 2.74(1); Yb(1)−C(4), 2.74(1); Yb(1)−C(5), 2.57(1); Yb(1)−Cp(centroid), 2.366(13); N(1)−Yb(1)−Cp(centroid), 94.7(11); N(1)−Si(1)−C(1), 102.1(5).



(2)

An X-ray analysis showed that **1** adopts a monomeric structure, in which the Yb(II) center is bonded to one chelating Cp−anilido ligand and three thf terminal ligands (Figure 1). The Yb−C(Cp) bond distances in **1** range from 2.52 to 2.74 Å, with an average value (2.65 Å) being almost the same as that found in the Yb(II) metallocene complex $(C_5Me_5)_2Yb(thf)$ (2.66 Å).[10] The Yb−Cp(centroid) (2.37(1) Å) and Yb−N (2.359(8) Å) bond distances in **1** are respectively longer than those found in the Cp−amido ytterbium(III) complexes $Me_2Si(C_5Me_4)(N^tBu)Yb(CH(SiMe_3)_2)$ (Yb−Cp(centroid) = 2.254 Å; Yb−N = 2.164(4) Å)[2e] and $[Me_2Si(C_5Me_4)(N^tBu)Yb(\mu\text{-}H)]_2$ (Yb−Cp(centroid) = 2.33(1), 2.32(1) Å; Yb−N = 2.231(7), 2.197(8) Å),[2a] which is in accordance with the difference in ion size between Yb(II) and Yb(III).[11] The ∠N−Yb−Cp(centroid) angle in **1** (95(1)°) is somewhat smaller than that found in the $C_5Me_5/N(SiMe_3)_2$-ligated Yb(II) complex $(C_5Me_5)Yb(N(SiMe_3)_2)(C_5Me_5)Na(thf)_3$ (115°)[5c] and those in the linked Cp−amido Yb(III) complexes $Me_2Si(C_5Me_4)(N^tBu)Yb(CH(SiMe_3)_2)$ (100.2(1)°)[2e] and $[Me_2Si(C_5Me_4)(N^tBu)Yb(\mu\text{-}H)]_2$ (99(1)°).[2a]

Complex **1′** adopts a dimeric structure via an "intermolecular" interaction between the Yb atom and the Ph group, and the whole molecule possesses a crystallographic 2-fold axis symmetry (eq 2 and Figure 2). The Yb−Ph distances range from 2.80(1) to 3.05(1) Å, which

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[6] The reactions between $LnI_2(thf)_2$ (Ln = Sm, Yb) and $Li_2[Me_2Si(C_5Me_4)N^tBu]$ did not give the expected salt-free, cyclopentadienyl−amido lanthanide(II) complexes. In the case of Sm, an unidentified yellow product, possibly a Sm(III) compound, was obtained, while in the case of Yb, incorporation of LiI seemed to take place.

[7] An acid−base approach for the synthesis of indenyl-derived ytterbocene(II) complexes has been recently reported. See: Klimpel, M. G.; Herrmann, W. A.; Anwander, R. *Organometallics* **2000**, *19*, 4666.

[8] Similar reactions of $Ln[N(SiMe_3)_2]_2(thf)_2$ with the less protonic alkylamine ligand $(C_5Me_4H)SiMe_2NH^tBu$ did not give the corresponding cyclopentadienyl−amido complexes but instead yielded the metallocene-type complexes $Ln(C_5Me_4SiMe_2NH^tBu)_2$ (Ln = Sm, Yb).

[9] Complex **2** might adopt a dimeric structure similar to that of **1′**, although a single-crystal suitable for X-ray analysis was not yet obtained. The lower THF content of the Sm(II) complex **2** as compared to that of the Yb(II) complex **1** might be due to the larger ion radius of Sm(II), which would thus more easily lead to formation of a further assembled structure through "intermolecular" metal−ligand interactions.

[10] Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999.

[11] Yb(II) is ca. 0.155 Å larger in radius than Yb(III) when both have the same coordination number. See: Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

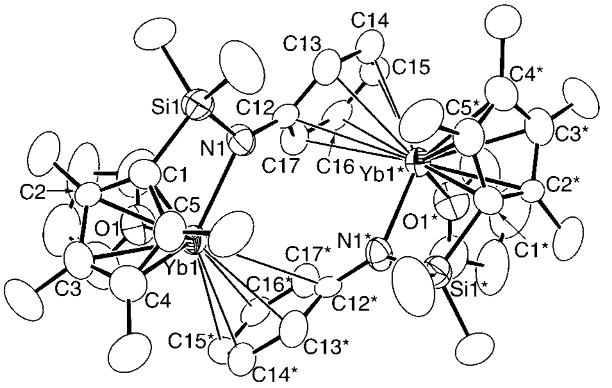
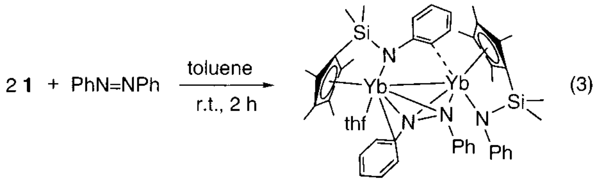


Figure 2. ORTEP drawing of **1′** with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Yb(1)−N(1), 2.393(9); Yb(1)−O(1), 2.405(8); Yb(1)−C(1), 2.577(11); Yb(1)−C(2), 2.682(10); Yb(1)−C(3), 2.803(11); Yb(1)−C(4), 2.768(11); Yb(1)−C(5), 2.610(12); Yb(1)−C(12)*, 3.099(9); Yb(1)−C(13)*, 2.941(12); Yb(1)−C(14)*, 2.798(14); Yb(1)−C(15)*, 2.796(13); Yb(1)−C(16)*, 2.916(11); Yb(1)−C(17)*, 3.046(10); Yb(1)−Cp_{1-5}(centroid), 2.406; Cp_{1-5}(centroid)−Yb(1)−N(1), 95.16; Cp_{1-5}(centroid)−Yb(1)−O(1), 109.67; N(1)−Si(1)−C(1), 100.6(5).

are in agreement with the interactions between a lanthanide ion and a neutral π donor ligand found in other complexes.[12] Other structural data for **1′** can be compared with those of **1** (Figures 1 and 2).

One-Electron-Transfer Reactions. The reaction of 1 or 2 mol of **1** or **1′** with 1 mol of azobenzene in toluene afforded the same 2:1 product **3** (eq 3), which is in contrast with the previously reported analogous reactions of lanthanide(II) complexes bearing other ligand systems such as $(C_5Me_5)_2Sm(thf)_2$,[13a] $(C_5H_5)_2Yb(thf)$,[13a] and $Sm[HB(3,5\text{-}Me_2pz)_3]_2$ (pz = pyrazolyl).[13b] Single crystals suitable for diffraction studies were obtained in the form of $\mathbf{3}\cdot 0.5N_2Ph_2$ from the reaction of **1** with 1 equiv of azobenzene. An X-ray analysis established that **3** is a dimeric Cp−anilido-chelated Yb(III) complex with a bridging azobenzene dianion ligand ($[PhNNPh]^{2-}$) (Figure 3). The azobenzene unit adopts a *cis* form, which is bonded in a η^3 fashion to one Yb atom (Yb1) and in a η^2 fashion to the other (Yb2). The Yb−N distances to the bridging azobenzene unit are highly asymmetric. The Yb1−N2 bond (2.271(5) Å) is much shorter than the Yb1−N1 bond (2.339(5) Å), while the Yb2−N2 bond (2.367(5) Å) is much longer than the Yb2−N1 bond (2.281(5) Å). An interaction between Yb2 and the Ph group (C25) of the Yb1-bonded anilido ligand was also observed (Yb2−C25 = 2.748(6) Å). Instead of such a Yb−Ph interaction, Yb1 is bonded to a thf ligand. All these structural features are in sharp contrast with those found in the samarocene(III)−azobenzene complex $[(C_5Me_5)_2Sm]_2(\mu,\eta^1{:}\eta^1\text{-}N_2Ph_2)$ and the half-metallocene Sm(III) and Yb(III) complexes $[(C_5Me_5)(thf)Sm]_2[\mu,\eta^2{:}\eta^2\text{-}N_2Ph_2]_2$ and $[(C_5H_5)(thf)Yb]_2[\mu,\eta^2{:}\eta^2\text{-}N_2Ph_2]_2$.[13a]



(3)

3, 75%

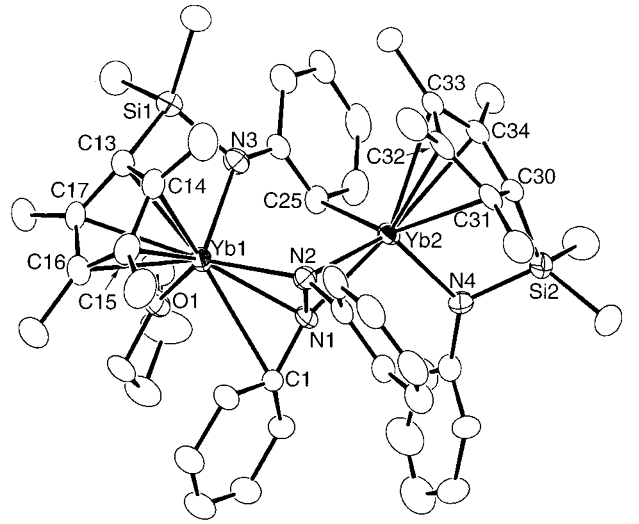


Figure 3. ORTEP drawing of **3** with 30% thermal ellipsoids. The lattice azobenzene is omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb(1)···Yb(2), 3.6919(4); Yb(1)−O(1), 2.355(5); Yb(1)−N(1), 2.339(5); Yb(1)−N(2), 2.271(5); Yb(1)−N(3), 2.283(5); Yb(2)−N(1), 2.281(5); Yb(2)−N(2), 2.367(5); Yb(2)−N(4), 2.189(6); Yb(1)−C(13), 2.500(7); Yb(1)−C(14), 2.546(7); Yb(1)−C(15), 2.635(8); Yb(1)−C(16), 2.658(7); Yb(1)−C(17), 2.600(6); Yb(2)−C(30), 2.529(6); Yb(2)−C(31), 2.588(6); Yb(2)−C(32), 2.678(7); Yb(2)−C(33), 2.718(6); Yb(2)−C(34), 2.641(6); Yb(1)−C(1), 2.747(6); Yb(2)−C(25), 2.748(6); N(1)−N(2), 1.468(7); Yb(1)−Cp_{13-17}(centroid), 2.287(6); Yb(2)−Cp_{30-34}(centroid), 2.335(9); Yb(1)−N(1)−Yb(2), 106.1(2); Yb(1)−N(2)−Yb(2), 105.5(2); N(3)−Yb(1)−Cp_{13-17}(centroid), 99.2(2); N(4)−Yb(2)−Cp_{30-34}(centroid), 96.8(2); N(3)−Si(1)−C(13), 98.4(3); N(4)−Si(2)−C(30), 95.6(3).

The reaction of **1** with 1 equiv of fluorenone gave the corresponding Yb(III) ketyl complex **4** in 75% isolated yield (Scheme 1 and Figure 4). Treatment of **4** with hexane/ether removed one of the two thf ligands in **4** and led to the dimerization of the radical unit to give the pinacolate complex **5** (Scheme 1 and Figure 5). Dissolution of **5** in THF cleaved the central C−C bond of the pinacolate unit in **5** and regenerated the ketyl species **4** quantitatively. These reactions are closely analogous to those reported for the bis(aryloxide)- or bis(silylamido)-supported lanthanide(III) ketyl/pinacolate complexes[14] but are different from those for the lanthanidocene(III) ketyl complexes $(C_5Me_5)_2Ln(OC_{13}H_8)(thf)$ (Ln = Sm, Yb). The latter remained unchanged under similar conditions.[14a] It is also noteworthy that the pinacolate unit in **5** is arranged in a *gauche* conformation (O1−C35−C48−O2 torsion angle −59(1)°) (Figure 3), in sharp contrast with the *trans* form found in the bis(aryloxide)- or bis(silylamido)-supported pinacolate complexes.[14] Complex **5** represents a rare example of a non-*trans*-oriented 1,2-diolate complex.

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[12] For a review on lanthanide complexes with neutral π donor ligands, see: Deacon, G. B.; Shen, Q. *J. Organomet. Chem.* **1996**, *506*, 1.

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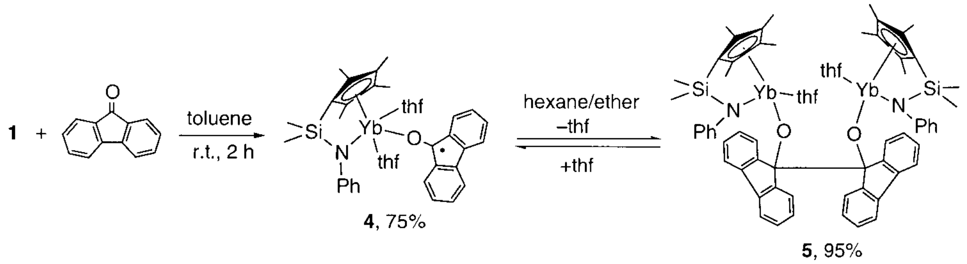
[14] (a) Hou, Z.; Fujita, A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754. (b) Hou, Z.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1995**, *117*, 4421.

Scheme 1



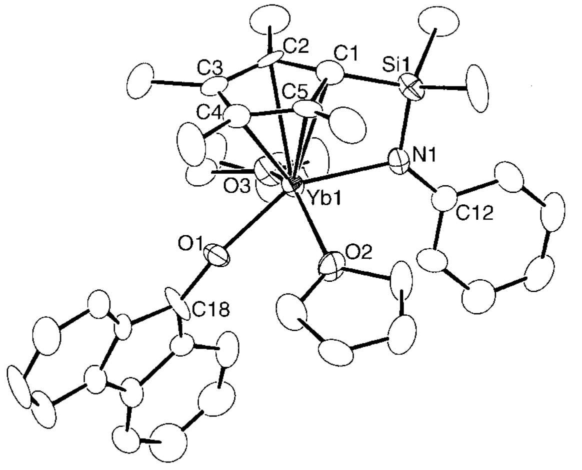


Figure 4. ORTEP drawing of **4** with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Yb(1)−N(1), 2.28(2); Yb(1)−C(1), 2.59(3); Yb(1)−C(2), 2.64(2); Yb(1)−C(3), 2.70(3); Yb(1)−C(4), 2.68(3); Yb(1)−C(5), 2.61(3); Yb(1)−O(1), 2.15(2); Yb(1)−O(2), 2.37(2); Yb(1)−O(3), 2.38(2); O(1)−C(18), 1.31(3); Yb(1)−Cp(centroid), 2.34(5); N(1)−Yb(1)−Cp(centroid), 96(1); Yb(1)−O(1)−C(18), 170(2); N(1)−Si(1)−C(1), 99(1).

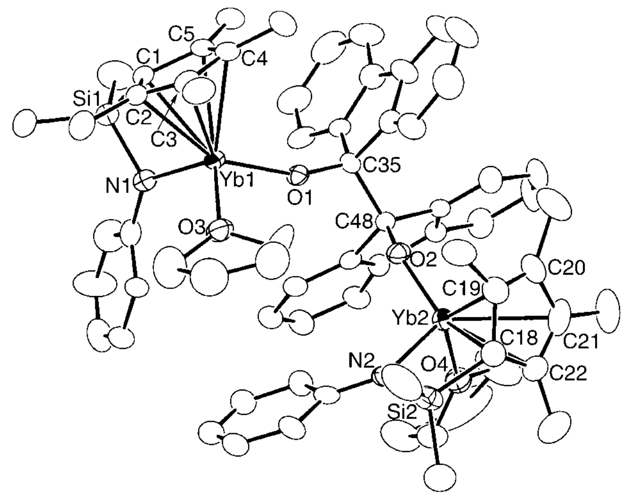


Figure 5. ORTEP drawing of **5** with 30% thermal ellipsoids. The lattice solvent is omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb(1)−O(1), 2.035(8); Yb(1)−O(3), 2.29(1); Yb(2)−O(2), 2.043(8); Yb(2)−O(4), 2.27(1); Yb(1)−N(1), 2.21(1); Yb(2)−N(2), 2.24(1); Yb(1)−C(1), 2.51(1); Yb(1)−C(2), 2.57(1); Yb(1)−C(3), 2.67(1); Yb(1)−C(4), 2.67(1); Yb(1)−C(5), 2.56(1); Yb(2)−C(18), 2.50(1); Yb(2)−C(19), 2.57(1); Yb(2)−C(20), 2.66(1); Yb(2)−C(21), 2.71(2); Yb(2)−C(22), 2.62(2); O(1)−C(35), 1.40(1); O(2)−C(48), 1.41(1); C(35)−C(48), 1.59(2); Yb(1)−Cp_{1-5}(centroid), 2.30(2); Yb(2)−Cp_{18-22}(centroid), 2.32(2); N(1)−Yb(1)−Cp_{1-5}(centroid), 98.6(6); N(2)−Yb(2)−Cp_{18-22}(centroid), 97.6(6); Yb(1)−O(1)−C(35), 156.3(8); Yb(2)−O(2)−C(48), 148.9(7); N(1)−Si(1)−C(1), 96.6(5); N(2)−Si(2)−C(18), 96.2(6); O(1)−C(35)−C(48)−O(2), −59(1).

The Sm(II) complex **2** also underwent electron-transfer reactions with azobenzene and fluorenone, but single crystals of the resulting products suitable for X-ray analysis were not yet obtained.

Ethylene Polymerization. The Yb(II) complex **1** or **1′** showed no activity for ethylene polymerization in toluene at room temperature under 1 atm, which is in agreement with the results previously reported for other Yb(II) complexes.[4,5c] In contrast, the more reducing Sm(II) complex **2** showed a moderate activity (44.8 kg of polymer (mol of Sm)$^{-1}$ h^{-1}) for the polymerization of ethylene under the same conditions, which yielded linear polyethylene with high molecular weight ($M_n = 7.26 \times 10^5$) and narrow polydispersity ($M_w/M_n = 1.58$). These polymerization data can be compared with those reported for the C_5Me_5/NHAr-ligated Sm(II) complex $[(C_5Me_5)Sm(NHAr)(C_5Me_5)K(thf)_2]_n$ (Ar = $C_6H_2{}^tBu_3$-2,4,6; 57.6 kg of polymer (mol of Sm)$^{-1}$ h^{-1}, $M_n = 5.0 \times 10^5$, $M_w/M_n = 2.9$)[5c] but are in contrast with those for the samarocene(II) complex $(C_5Me_5)_2Sm(THF)$ (5.06 kg of polymer (mol of Sm)$^{-1}$ h^{-1}, $M_n < 2.5 \times 10^4$, $M_w/M_n = 2.28$)[5c,15] and for the bis(silylamido) Sm(II) complex $Sm[N(SiMe_3)_2]_2(thf)_2$, which was inert toward ethylene under the same conditions.[5c]

In summary, we have shown that the silylene-linked cyclopentadienyl−anilido unit $[C_5Me_4SiMe_2NPh]^{2-}$ can serve as a useful ancillary ligand system for the divalent lanthanides. The results presented in this paper demonstrate that these types of lanthanide(II) complexes can constitute a new family of one-electron-reducing agents and polymerization precatalysts.

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. The argon was purified by being passed through a Dryclean column (4A 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 (4A) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (MBraun) to ensure both were always below 1 ppm. Samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve

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Table 1. Summary of Crystal Data

	1	**1′**	**3**·0.5N_2Ph_2	**4**	**5**·Et_2O
formula	$C_{29}H_{47}NO_3Yb$	$C_{42}H_{62}N_2O_2Si_2Yb_2$	$C_{56}H_{69}N_5OSi_2Yb_2$	$C_{38}H_{47}NO_3SiYb$	$C_{72}H_{88}N_2O_5Si_2Yb$
fw	658.82	1029.20	1230.44	766.92	1463.75
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	triclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)
a (Å)	12.401(3)	17.855(5)	12.1982(9)	18.599(6)	13.457(1)
b (Å)	13.045(3)	9.204(3)	12.8501(9)	41.820(8)	14.421(1)
c (Å)	19.345(4)	26.354(8)	19.509(1)	9.081(2)	19.964(1)
α (deg)			103.685(1)		111.647(1)
β (deg)	108.31(3)	99.629(6)	93.698(1)		98.953(2)
γ (deg)			114.185(1)		96.177(2)
V (Å^3)	2971(1)	4270(2)	2665.1(3)	7063(2)	3499.3(4)
Z	4	4	2	8	2
μ (cm^{-1})	32.16	44.44	35.75	27.17	27.38
F(000)	1344.00	2048.00	1232.00	3120.00	1484.00
D_{calcd} (g cm^{-3})	1.473	1.601	1.533	1.422	1.389
no. of unique rflns	8752	16 133	13 801	6862	18 588
no. of rflns with ($I > x\sigma(I)$)	2652 ($x = 2$)	6081 ($x = 2$)	8657 ($x = 2$)	4039 ($x = 3$)	10359 ($x = 2$)
no. of variables	316	232	595	397	703
R	0.043	0.069	0.040	0.069	0.074
R_w	0.042	0.129	0.045	0.131	0.094

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 Laboratory of RIKEN. Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze−thaw method (three times), and dried over fresh Na chips in the glovebox. (C_5Me_4H)SiMe_2Cl, BuLi, and PhNH_2 were obtained from Aldrich. LnI_2(thf)$_2$ [16] and Ln[N(SiMe_3)$_2$]$_2$(thf)$_2$ [17] (Ln = Sm, Yb) were prepared according to literature methods.

(C_5Me_4H)SiMe_2NHPh.[18] To a THF solution (20 mL) of (C_5Me_4H)SiMe_2Cl (500 mg, 2.33 mmol) was added a THF solution (10 mL) of PhNHLi (250 mg, 2.52 mmol), which was prepared by reaction of BuLi with 1 equiv of PhNH_2 in THF. The reaction mixture was stirred at room temperature for 24 h. After removal of the solvent under reduced pressure, the residue was extracted with hexane. Evaporation of hexane gave (C_5Me_4H)SiMe_2NHPh as a pale yellow oil (600 mg, 95%). ^{1}H NMR (22.5 °C, C_6D_6): δ 7.14 (t, 2 H, J = 7.2 Hz, C_6H_5-m), 6.82 (t, 1 H, J = 7.2 Hz, C_6H_5-p), 6.58 (d, 2 H, J = 7.2 Hz, C_6H_5-o), 3.07 (s, 1 H, NH), 3.04 (s, 1 H, $C_5Me_4\boldsymbol{H}$), 1.89 (s, 6 H, $C_5\boldsymbol{Me}_4H$), 1.79 (s, 6 H, $C_5\boldsymbol{Me}_4H$), 0.06 (s, 6 H, SiMe_2).

Me_2Si(C_5Me_4)(NPh)Yb(thf)$_3$ (1). To a THF solution (20 mL) of Yb[N(SiMe_3)$_2$]$_2$(thf)$_2$ (1.00 g, 1.57 mmol) was added a THF solution (2 mL) of C_5Me_4HSiMe_2NHPh (341 mg, 1.57 mmol) at room temperature. The mixture turned immediately from orange to reddish brown. After this mixture was stirred for 1 day, the solvent was removed under reduced pressure. The resulting orange powder was washed with hexane and then dissolved in THF. After reduction of the solution volume under reduced pressure, hexane was layered to give orange crystals of **1** (776 mg, 75%). A reaction in toluene was not as clean as that in THF. ^{1}H NMR (22.5 °C, C_6D_6): δ 6.76 (br s, 4 H, C_6H_5-o,m), 5.77 (s, 1 H, C_6H_5-p), 3.64 (br s, 12 H, THF), 2.47 (s, 6 H, C_5Me_4), 2.27 (s, 6 H, C_5Me_4), 1.44 (br s, 12 H, THF), 1.01 (s, 6 H, SiMe_2). ^{1}H NMR (22.5 °C, THF-d_8): δ 6.68 (t, J = 7.15 Hz, 2 H, C_6H_5-m), 6.17 (d, J = 7.15 Hz, 2 H, C_6H_5-o), 5.95 (t, J = 7.15 Hz, 1 H, C_6H_5-p), 2.01 (s, 6 H, C_5Me_4), 1.99 (s, 6 H, C_5Me_4), 0.46 (s, 6 H, SiMe_2). Anal. Calcd for $C_{29}H_{47}NO_3SiYb$: C, 52.86; H, 7.19; N, 2.12. Found: 52.37; H, 7.18; N, 2.08.

[Me_2Si(C_5Me_4)(NPh)Yb(thf)]$_2$ (1′). Dissolution of **1** (100 mg) in toluene gave a dark blue solution (the color change could be caused by the change in THF coordination), which was concentrated under reduced pressure. Layering of hexane yielded brown crystals of **1′** (71 mg, 91%). ^{1}H NMR (22.5 °C, C_6D_6): δ 6.81 (br s, 4 H, C_6H_5-o,m), 5.82 (s, 1 H, C_6H_5-p), 3.56 (br s, 12 H, THF), 2.56 (s, 6 H, C_5Me_4), 2.34 (s, 6 H, C_5Me_4), 1.40 (br s, 12 H, THF), 1.08 (s, 6 H, SiMe_2). In THF-d_8, the ^{1}H NMR spectrum of **1′** was identical with that of **1**. Anal. Calcd for $C_{42}H_{62}N_2O_2Si_2Yb_2$: C, 49.01; H, 6.07; N, 2.72. Found: 48.89; H, 6.02; N, 2.74.

Me_2Si(C_5Me_4)(NPh)Sm(thf)$_x$ (2; x = 0−1). To a THF solution (20 mL) of Sm[N(SiMe_3)$_2$]$_2$(THF)$_2$ (500 mg, 0.815 mmol) was added a THF solution (2 mL) of C_5Me_4HSiMe_2NHPh (221 mg, 0.815 mmol) at room temperature. The mixture turned immediately from purple to dark brown. After this mixture was stirred for 3 days, the solvent was removed under reduced pressure. The resulting brown powder was washed with hexane and dried in vacuo to give **2** (312 mg, 84% based on x = 0.5). ^{1}H NMR (22.5 °C, THF-d_8): δ 6.01 (br s, 3 H, C_6H_5-m,p), 4.36 (d, J = 7.15 Hz, 2 H, C_6H_5-o), 2.96 (s, 3 H, C_5Me_4), 2.70 (s, 3 H, C_5Me_4), 1.42 (s, 3 H, C_5Me_4), −0.11 (s, 3 H, C_5Me_4), −0.67 (s, 3 H, SiMe_2), −1.47 (s, 3 H, SiMe_2). Anal. Calcd for $C_{17}H_{23}$NSiSm (x = 0): C, 48.64; H, 5.52; N, 3.34. Calcd for $C_{19}H_{27}NO_{0.5}$SiSm (x = 0.5): C, 50.06; H, 5.97; N, 3.07. Calcd for $C_{21}H_{31}$NOSiSm (x = 1): C, 51.27; H, 6.35; N, 2.85.; Found: 49.49; H, 6.40; N, 3.02.

Me_2Si(C_5Me_4)(NPh)Yb(thf)($\mu,\eta^2{:}\eta^3$-PhNNPh)Yb(NPh)(C_5Me_4)SiMe_2 (3). To a toluene solution (2 mL) of **1** (150 mg, 0.228 mmol) was added azobenzene (42 mg, 0.228 mmol) at room temperature. The solution color turned from dark blue to dark brown in 30 min. After this mixture was stirred for 2 h, the solvent was removed under reduced pressure. The resulting dark brown solid was washed with hexane and then dissolved in toluene. Concentration of the solution under reduced pressure deposited reddish green crystals of **3**·0.5N_2Ph_2 (88 mg, 63% based on **1**).[19] Anal. Calcd for $C_{56}H_{69}N_5OSi_2Yb_2$ (**3**·0.5N_2Ph_2): C, 54.66; H, 5.65; N, 5.69. Found: 54.74; H, 5.79; N, 5.46. A similar reaction of azobenzene with 2 equiv of **1** afforded azobenzene-free **3** in 75% yield.

Me_2Si(C_5Me_4)(NPh)Yb($OC_{13}H_8$)(thf)$_2$ (4). To a toluene solution (5 mL) of **1** (360 mg, 0.568 mmol) was added a toluene solution (1 mL) of 9-fluorenone (170 mg, 0.568 mmol) at room temperature. The reaction mixture changed immediately from dark blue to deep purple. After this mixture was stirred for 2 h, the solvent was removed under reduced pressure. The resulting dark brown solid was washed with hexane and then dissolved in THF. After reduction of the solution volume under reduced pressure, hexane was layered to give dark purple

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[19] The ^{1}H NMR spectra of **3**−**5** did not offer any structural information, owing to the strong paramagnetic influence of the Yb(III) ion and/or the ketyl radical species.

crystals of **4**, which after being dried under vacuum for 30 min afforded "**4**-THF" (301 mg, 75%).[19] Anal. Calcd for $C_{34}H_{39}NO_2SiYb$ (**4**-THF): C, 58.77; H, 5.66; N, 2.02. Found: C, 58.70; H, 5.95; N, 1.84.

[Me$_2$Si(C$_5$Me$_4$)(NPh)Yb(thf)]$_2$(μ-O$_2$C$_{26}$H$_{16}$) (5). Into a diethyl ether solution (1 mL) of "**4**-THF" (100 mg, 0.144 mmol) was slowly layered 5 mL of hexane. After 24 h, orange crystals of **5**·OEt$_2$ (95 mg, 95%) were deposited. Similar treatment of **4** with Et$_2$O/hexane also gave **5**·OEt$_2$.[19] Anal. Calcd for $C_{72}H_{88}N_2O_5Si_2Yb_2$ (**5**·OEt$_2$): C, 59.07; H, 6.06; N, 1.91. Found: 59.15; H, 6.22; N, 1.83.

Polymerization of Ethylene. In the glovebox, **2** (23 mg, 0.05 mmol), a magnetic stir bar, and toluene (15 mL) were placed in a 100 mL three-neck flask. The flask was taken outside, set in a water bath (25 °C), and then connected to a Schlenk line, a well-purged ethylene line, and a mercury-sealed stopper. Introduction of ethylene resulted in immediate formation (precipitation) of polyethylene. The mixture was stirred for 10 min, during which a slightly positive ethylene pressure was maintained by the stopper. MeOH (20 mL) was added. The resultant mixture was poured into 300 mL of MeOH in a 1 L beaker and then stirred to further precipitate the polymer product. After filtration, the polymer product was dried under vacuum in an oven (80 °C) overnight, yielding 370 mg of polyethylene. The molecular weight (against polystyrene standard) and polydispersity of the polymer were measured by gel permeation chromatography (GPC) at 135 °C using *o*-dichlorobenzene as an eluent.

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. Data collections for **1**, **1′**, **3**, and **5** were performed at 20 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[20] The raw frame data were processed using SAINT[21] and SADABS[22] to yield the reflection data file. Data collection for **4** was performed at 20 °C on a Rigaku RAXIS CS imaging plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å). All structures were solved by using the teXsan software package. Refinements were performed 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 1.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for **1**, **1′**, and **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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