Inorg. Chem. **2004**, *43*, 5771–5779

Inorganic Chemistry
Article

Preparation, Characterization, and Magnetic Behavior of the Ln Derivatives (Ln = Nd, La) of a 2,6-Diiminepyridine Ligand and Corresponding Dianion

Hiroyasu Sugiyama, Ilia Korobkov, and Sandro Gambarotta*

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Angela Möller*

Department of Inorganic Chemistry, Köln University, Köln, Germany

Peter H. M. Budzelaar*

Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld 1,
6525 ED Nijmegen, The Netherlands

Received February 12, 2004

An unprecedented $Nd[2,6\text{-}\{[2,6\text{-}(i\text{-}Pr)_2C_6H_5]N{=}C(CH_3)\}_2(C_5H_3N)]NdI_2(THF)$ (**1**) complex was prepared by oxidizing metallic Nd with I_2 in THF and in the presence of $2,6\text{-}\{[2,6\text{-}(i\text{-}Pr)_2C_6H_5]N{=}C(CH_3)\}_2(C_5H_3N)$. The magnetic behavior at variable T clearly indicated that the complex should be regarded as a trivalent Nd atom antiferromagnetically coupled to a radical anion. By using the doubly deprotonated form of the diimino pyridine ligand $\{[2,6\text{-}\{[2,6\text{-}(i\text{-}Pr)_2C_6H_5]N{-}C{=}CH_2\}_2(C_5H_3N)]^{2-}$ (**2**) the corresponding trivalent complexes $\{[2,6\text{-}\{[2,6\text{-}(i\text{-}Pr)_2C_6H_5]N{-}C{=}CH_2\}_2\text{-}(C_5H_3N)]Ln\,(THF)\}(\mu\text{-}Cl)_2[Li(THF)_2]\cdot 0.5$ (hexane) [Ln = Nd (**3**), La (**4**)] were obtained and characterized. Reduction of these species afforded electron transfer to the ligand system which gave ligand dimerization via C–C bond formation through one of the two ene-amido functions of each molecule. The resulting dinuclear $\{[\{[2,6\text{-}(i\text{-}Pr)_2C_6H_5]N{-}C{=}(CH_2)\}(C_5H_3N)\{[2,6\text{-}(i\text{-}Pr)_2C_6H_5]N{=}CCH_2\}]Ln(THF)_2(\mu\text{-}Cl)[Li(THF)_3]\}_2\cdot 2(THF)$ [Ln = Nd (**5**), La (**6**)] were isolated and characterized.

Introduction

The interest in the chemistry of low-valent lanthanides has traditionally been driven by the remarkable chemical behavior of divalent Sm,[1] which makes these species particularly promising for molecular activation purposes. In this context, the recent synthesis of solvated forms[2a,b] of divalent Tm, Dy, and Nd salts,[2c] which gave access to new potent divalent reductants,[3] can be considered as a major breakthrough in lanthanide chemistry.

The major difficulty in dealing with such reactive species is finding the appropriate ligand systems capable of (a) preventing disproportionation, (b) having a lower possibility of being attacked or fragmented by the metal, and (c) efficiently delocalizing the metal valence electrons. An alternate and effective strategy for investigating the chemistry of these species, which otherwise are not readily available, might consist of preparing low-valent synthetic equivalents (synthons). These complexes may have the formal appearance of low-valent derivatives where spin density, however,

---

* Author to whom correspondence should be addressed. E-mail: sgambaro@science.uottawa.ca.

(1) See for example: (a) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285. (b) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270. (c) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L. *Organometallics* **1986**, *5*, 2389. (d) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877. (e) Evans, W. J.; Keyer, R. K.; Zhang, H.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1987**, 837. (f) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L *J. Am. Chem. Soc.* **1987**, *109*, 3928. (g) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1989**, *111*, 3329. (h) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671. (i) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292. (j) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728. (k) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2772. (l) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983. (m) Evans, W. J. Drummond, D. K. *J. Am. Chem. Soc.* **1986**, *108*, 7440. (n) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283 and references therein. (n) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry;* Pergamon: Oxford, 1982; Chapter 21. (o) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (p) Ephritikhine, M. *Chem. Rev.* **1997**, 21933. (q) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1995**, *19*, 727.

10.1021/ic049820t CCC: $27.50

has been transferred to the ligand system. This methodology was successfully used in the chemistry of *f*-block elements to simulate the reactivity of unknown divalent actinide complexes[4a−c] as well as to expand the reactivity of divalent Sm derivatives.[4d] Central to obtaining these species is the use of appropriate ligand systems capable of embarking in substantial charge-transfer interactions with the metal. Bispyridine and neutral diimines appear to be particularly versatile for this type of interaction with lanthanides. The first gave a spectacular case of a paramagnetic decamethyl ytterbocene derivative,[5] while by using a diazabutadiene type of ligand it was possible to obtain complexes of di- or trivalent lanthanides[6] with the formal aspect of zerovalent species.[7]

Our recent work in the field of olefin polymerization catalysts supported by the popular 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N) ligand[8] has highlighted the unprecedented ability of this unique molecule to accept up to three electrons in the π-system without modification of the ligand backbone.[9] Thus, we became interested in its Nd complexes since this ligand might well be a suitable candidate for stabilizing highly reactive divalent synthons, including Nd, whose divalent state is expected to provide a very strong reducing power.[1,2]

In this paper, we wish to describe the preparation and characterization of a NdI$_2$ adduct of the 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N) ligand, together with a modification of the ligand system, and the results of further reduction reactions of the corresponding Nd and La complexes.

Experimental Section

All operations were performed under inert atmosphere using standard Schlenk type techniques. LnCl$_3$(THF)$_3$,[10] 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N),[11] were prepared according to published procedures. Magnetic measurements were carried out using a Quantum Design MPMS5S SQUID magnetometer at 5 kG and 10 kG, in the temperature range 2−300 K. Samples of **1** were measured in "gelcaps". The sample was weighed into a standard "gelcap" inside a drybox and sealed in a glass tube under inert atmosphere for shipment. The gelcap was sealed with "Kapton" tape on breaking the glass tube and quickly loaded into the SQUID magnetometer. Background corrections for the gelcap were included in the magnetic calculations. Standard corrections for underlying diamagnetism were applied to the data.[12] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination were obtained with a Bruker diffractometer equipped with a Smart CCD area detector. NMR spectra were recorded on a Bruker AMX-500 spectrometer. Optical spectra were recorded with a Varian-Cary IE UV−vis spectrophotometer.

Preparation of [2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N)]-NdI$_2$(THF) (1). A suspension of 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N=C(CH$_3$)}$_2$-(C$_5$H$_3$N) (0.48 g, 1.0 mmol) in THF (40 mL) was stirred at room temperature in the presence of Nd powder (0.22 g, 1.5 mmol) and iodine (0.25 g, 1.0 mmol). The initially brown color gradually disappeared to form a gray precipitate of NdI$_3$. Stirring was continued at 50 °C overnight until the color of the mixture turned dark-purple. The mixture was centrifuged to remove unreacted Nd metal. After solvent evaporation, the residue was extracted with toluene and centrifuged to remove insoluble materials. The combined extracts were concentrated to ca. 1/3 of the initial volume. Layering with hexane resulted in the separation of brown-pinkish crystals of **1** (0.31 g, 0.33 mmol, 33%). Anal. Calcd. (found) for: C$_{37}$H$_{51}$I$_2$N$_3$NdO: C 46.69 (46.37) H 5.40 (5.37) N 4.41 (4.28).

Preparation of {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N−C=(CH$_2$)}$_2$(C$_5$H$_3$N)]-Li(THF)}[Li(THF)$_4$] (2). A solution of 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N) (2.0 g, 4.15 mmol) in THF (30 mL) was treated with LiCH$_2$Si(CH$_3$)$_3$ (0.85 g, 9.03 mmol) in THF (40 mL) and allowed to stand at room temperature overnight. After evaporation of the solvent, the resulting residue was washed with two portions of hexane (20 mL) and dried under vacuum to yield **2** which was isolated as a very air-sensitive yellow powder (2.73 g, 3.20 mmol, 77%). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 25 °C) δ: 1.27 (m, 20H, OCH$_2$C$\boldsymbol{H}_2$), 1.32 (d, J = 7.0 Hz, 12H, (C$\boldsymbol{H}_3$)$_2$CH), 1.57 (d, J = 6.9 Hz, 12H, (C$\boldsymbol{H}_3$)$_2$CH), 3.18 (m, 20H, OC$\boldsymbol{H}_2$CH$_2$), 3.41 (br. s, 2H, NC=C$\boldsymbol{H}_2$), 3.74 (quint, J = 6.9 Hz, 4H, (CH$_3$)$_2$C$\boldsymbol{H}$), 4.05 (br. s, 2H, NC=C$\boldsymbol{H}_2$), 7.17 (t, J = 7.7 Hz, 1H, p-C$_5$$\boldsymbol{H}_3$N), 7.24 (t, J = 7.6 Hz, 2H, p-C$_6$$\boldsymbol{H}_3^{i}Pr_2$), 7.39 (d, J = 7.6 Hz, 4H, m-C$_6$$\boldsymbol{H}_3^{i}Pr_2$), 7.76 (d, J = 7.7 Hz, 2H, m-C$_5$$\boldsymbol{H}_3$N). ^{13}C{^{1}H} NMR (C$_6D_6$, 123.72 MHz, 25 °C), δ: 25.52 (($\boldsymbol{C}$H$_3$)$_2$CH)), 25.54 (($\boldsymbol{C}$H$_3$)$_2$CH)), 25.78 (OCH$_2$$\boldsymbol{C}H_2$), 28.56 ((CH$_3$)$_2$$\boldsymbol{C}$H), 68.54 (O$\boldsymbol{C}H_2CH_2$), 71.74 (NC=$\boldsymbol{C}H_2$), 118.06 ($m$-$\boldsymbol{C}_5H_3$N), 121.93 ($p$-$\boldsymbol{C}_6H_3^{i}Pr_2$), 123.69 ($m$-$\boldsymbol{C}_6H_3$-^{i}Pr$_2$), 136.72 ($p$-$\boldsymbol{C}_5H_3$N), 144.18 ($o$-$\boldsymbol{C}_6H_3^{i}Pr_2$), 153.61 ($ipso$-$\boldsymbol{C}_6H_3$-^{i}Pr$_2$), 160.31 ($o$-$\boldsymbol{C}_5H_3$N), 163.36 (N$\boldsymbol{C}$=CH$_2$). Spontaneous loss of variable amounts of THF from the solid prevented obtaining meaningful elemental analysis data.

Synthesis of {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N−C=(CH$_2$)}$_2$(C$_5$H$_3$N)]-Ln(THF)}(μ-Cl)$_2$[Li (THF)$_2$]·0.5(hexane) [Ln = Nd (3), La (4)].

---

(2) (a) Bochkarev, M. N.; Fedushkin, I. L.; Dechert, S.; Fagin, A. A.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3176. (b) Evans, W. J.; Allen, N. T.; Workman, P. S.; Meyer, J. C. *Inorg. Chem.* **2003**, *42*, 3097. (c) For a general review about reduced lanthanide halides (extended solids) see: Meyer, G. *Chem. Rev.* **1988**, *88*, 93.

(3) (a) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7927. (b) Evans, W. J.; Allen, N. T.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 359. (c) Evans, W. J.; Workman, P. S.; Allen, N. T. *Org. Lett.* **2003**, *42*, 3097. Evans, W. J.; Zucchi, G.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 10.

(4) (a) Diaconescu, P. L. Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2000**, *122*, 6108. (b) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 814. (c) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 959 and references cited therein. (d) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119 and references cited therein.

(5) Schultz, M.; Boncella, J. M.; Berg, D. J.; Tilley, T. D.; Andersen, R. A. *Organometallics* **2002**, *21*, 460.

(6) Bochkarev, M. N.; Trifonov, A. A.; Cloke, F. G. N.; Dalby, C. I.; Matsunaga, P. T.; Andersen, R. A.; Schumann, H.; Loebel, J.; Hemling, H. *J. Organomet. Chem.* **1995**, *486*, 177.

(7) Cloke, F. G. N.; de Lemos, H. C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1344.

(8) (a) Gibson, V. C.; Kimberley, B. S.; White, A. P. J.; Williams, D. J.; Howard, P. *J. Chem. Soc., Chem. Commun.* **1998**, 313. (b) Small, B. L.; Brookhart, M. S.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (c) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 849.

(9) Enright, D.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 3873.

(10) (a) Anhydrous NdCl$_3$ was prepared following a standard procedure: (a) Freeman, J. H.; Smith, M. L. *J. Inorg. Nucl. Chem.* **1958**, *7*, 224 and was transformed into the corresponding tetrahydrofuranate. (b) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135. (c) Angelici, R. J. *Inorg. Synth.* **1990**, *27*, 136.

(11) Johnson, L. K.; Killian, C. M.; Brookhart, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(12) (a) Mabbs, M. B.; Machin, D. *Magnetism and Transition Metal Complexes;* Chapman and Hall: London, 1973. (b) Foese, G.; Gorter, C. J.; Smits, L. J. *Constantes Selectionnes, Diamagnetisme, Paramagnetism, Relaxation Paramagnetique;* Masson: Paris, 1957.

Table 1. Crystal Data and Structure Analysis Results

	1	**3**	**4**	**5**	**6**
formula	$C_{37}H_{51}I_2N_3NdO$	$C_{48}H_{72}Cl_2LiN_3NdO_3$	$C_{48}H_{72}Cl_2LaLiN_3O_3$	$C_{114}H_{178}Cl_2Li_2N_6Nd_2O_{12}$	$C_{114}H_{178}Cl_2La_2Li_2N_6O_{12}$
Mw	951.85	961.17	955.84	2197.88	2187.22
crystal system	rhombohedral	monoclinic	monoclinic	triclinic	triclinic
space group	*R*-3	$P2_1/c$	$P2_1/c$	*P*-1	*P*-1
a(Å)	29.079(2)	18.938(3)	19.044(2)	13.6306(16)	13.7858(14)
b(Å)	29.079(2)	12.8774(18)	12.8775(14)	15.4084(18)	15.4990(16)
c(Å)	25.623(4)	20.907(3)	20.944(2)	15.4759(18)	15.5071(16)
α(deg)	90	90	90	90.594(2)	90.532(2)
β(deg)	90	100.155(2)	100.309(2)	114.9279(19)	115.013(2)
γ(deg)	120	90	90	92.662(2)	92.711(2)
V(Å^3)	18764(3)	5018.9(12)	5053.3(10)	2942.7(6)	2997.7(5)
radiation (Kα Mo)	0.71073Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
T(K)	203(2)	203(2)	203(2)	203(2)	203(2)
D_{calcd} (g cm^{-3})	1.516	1.272	1.256	1.240	1.212
μ_{calcd} (cm^{-1})	2.754	1.180	0.990	0.975	0.804
F_{000}	8424	2008	1996	1160	1154
R, $R_w{}^2$,[a]	0.057, 0.138	0.055, 0.124	0.031, 0.067	0.069, 0.091	0.058, 0,095
GoF	1.021	1.047	1.022	1.013	1.004

[a] $R = \Sigma_o - F_c/\Sigma F_o R_w = [(\Sigma(F_o - F_c)^2/\Sigma_w F_o{}^2)]^{1/2}$.

A solution of $NdCl_3(THF)_3$ (0.81 g, 1.75 mmol) in THF (60 mL) was treated with **2** (1.50 g, 1.76 mmol) and stirred at room-temperature overnight. After THF was evaporated, the residue was extracted with Et_2O (80 mL) and centrifuged to remove LiCl. Et_2O was again evaporated, and the residue was recrystallized from THF (10 mL)/hexane (80 mL) to give brown-orange crystals of the crude product, which were again recrystallized to give analytically pure brown crystals of **3** (0.93 g, 0.97 mmol, 55%). Anal. Calcd. (found) for $C_{48}H_{72}Cl_2NdLiN_3O_3$: C 59.98 (59.67), H 7.55 (7.44), N 4.37 (4.35). The NMR spectra only showed very broad and overlapping features in the range 16−6.55 ppm. $\mu_{eff} = 3.65\ \mu_B$ at room temperature.

Identical reaction of $LaCl_3(THF)_3$ (0.82 g, 1.76 mmol) with **2** (1.50 g, 1.76 mmol) afforded the isostructural diamagnetic **4** that was isolated as green crystals (1.28 g, 1.33 mmol, 76%). ^1H NMR (C_6D_6, 500 MHz, 25 °C) δ: 0.88 (double t, 3H, hexane), 1.23 (m, 4H, hexane) 1.31 (m, 12H, $OCH_2C\boldsymbol{H}_2$), 1.41 (d, $J = 6.6$ Hz, 12H, $(C\boldsymbol{H}_3)_2CH$), 1.63 (d, $J = 6.7$ Hz, 12H, $(C\boldsymbol{H}_3)_2CH$), 3.38 (m, 12H, $OC\boldsymbol{H}_2CH_2$), 3.52 (quint, $J = 6.7$ Hz, 4H, $(CH_3)_2C\boldsymbol{H}$), 3.54 (br. s, 2H, $NC{=}C\boldsymbol{H}_2$), 4.59 (br. s, 2H, $NC{=}C\boldsymbol{H}_2$), 7.05 (t, $J = 7.9$ Hz, 1H, p-$C_5\boldsymbol{H}_3N$), 7.14 (t, $J = 7.6$ Hz, 2H, p-$C_6\boldsymbol{H}_3{}^iPr_2$), 7.28 (d, $J = 7.6$ Hz, 4H, m-$C_6\boldsymbol{H}_3{}^iPr_2$), 7.49 (d, $J = 7.9$ Hz, 2H, m-$C_5\boldsymbol{H}_3N$). ^{13}C-{^1H} NMR (C_6D_6, 123.72 MHz, 25 °C), δ: 14.64 (hexane), 23.36 (hexane), 32.27 (hexane), 24.98 ($(\boldsymbol{C}H_3)_2CH$)), 25.85 ($OCH_2\boldsymbol{C}H_2$), 27.82 ($(\boldsymbol{C}H_3)_2CH$)), 29.32 ($(CH_3)_2\boldsymbol{C}H$), 69.33 ($O\boldsymbol{C}H_2CH_2$), 82.77 ($NC{=}\boldsymbol{C}H_2$), 118.98 (m-$\boldsymbol{C}_5H_3N$), 124.78 (p-$\boldsymbol{C}_6H_3{}^iPr_2$), 124.34 ($m$-$\boldsymbol{C}_6H_3{}^iPr_2$), 137.21 ($p$-$\boldsymbol{C}_5H_3N$), 145.45 ($o$-$\boldsymbol{C}_6H_3{}^iPr_2$), 146.65 (*ipso*-$\boldsymbol{C}_6H_3{}^iPr_2$), 158.47 ($o$-$\boldsymbol{C}_5H_3N$), 160.03 ($N\boldsymbol{C}{=}CH_2$). Anal. Calcd. (found) for $C_{48}H_{72}Cl_2LaLiN_3O_3$: C 60.31 (59.68), H 7.59 (7.38), N 4.40 (4.45).

Isolation of {[{[2,6-(i-Pr)$_2$C$_6$H$_5$]N−C=(CH$_2$)}(C$_5$H$_3$N){[2,6-(i-Pr)$_2$C$_6$H$_5$]N=CCH$_2$}]Ln (THF)$_2$(μ-Cl)[Li(THF)$_3$]}$_2$·2(THF) [Ln = Nd (5), La (6)]. A solution of **3** (0.48 g, 0.50 mmol) in THF (5 mL) was treated with a THF solution (10 mL) of K/naphthalene prepared from K metal (20 mg, 0.50 mmol) and naphthalene (64 mg, 0.50 mmol). The mixture was allowed to stand overnight at room temperature and subsequently centrifuged to remove dark-brown insoluble material. The mother liquor was concentrated to ca. 80% of the original volume and layered with hexane to give **5** as dark-brown crystals in low yield (9%). Identical procedure and amounts were used for the preparation of **6**. Yield 5%. Regrettably, a combination of air-sensitivity and spontaneous loss of interstitial solvent prevented the obtaining of meaningful elemental analysis data. The NMR spectra of both compounds only showed very broad and overlapping features.

X-ray Crystallography. Compounds **1**, **3**, **4**, **5**, and **6** consistently yielded crystals that diffract weakly, and the results presented are the best of several trials. The crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[13]

Systematic absences in the diffraction data-sets and unit-cell parameters were consistent with rhombohedral, *R*-3 for **1**, monoclinic, $P2_1/c$ for **3** and **4**, triclinic, *P*-1 for **5** and **6**. Solution in the centrosymmetric space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2.

The compound molecule was not located on symmetry operators in **1**, **3**, and **4**. Vice versa, molecules **5** and **6** were located at an inversion center. Cocrystallized hexane solvent molecules were located each on a 2-fold axis in **3** and **4**. One symmetry-unique molecule and one symmetry generated molecule of THF solvent were found in the lattice of **5** and **6**. All non-hydrogen atoms, except those of the solvent molecules and which were refined isotropically with idealized geometry, were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library with the latest used version being v.6.12 (Sheldrick, G. M., Bruker AXS, Madison, WI, 2001). Crystallographic data and relevant bond distances and angles are reported in Tables 1 and 2.

DFT Calculations. The calculations were performed at the nonlocal DFT level of theory using the exchange functional of Becke[14a] and the correlation functional of Perdew.[14b] Scalar relativistic effects have been considered using the ZORA formalism.[14c] Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations.[14d] Double-ξ basis set have been used for all elements. The $(1s)^2$ core electrons of carbon, nitrogen,

---

(13) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

Table 2. Selected Bond Distances (Å) and Angles (deg)

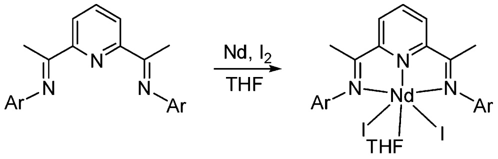
1	**3**	**4**	**5**	**6**
Nd−I(1) = 3.0636(9)	Nd−Cl(1) = 2.7804(14)	La−Cl(1) = 2.8409(8)	Nd−Cl = 2.8962(14)	La−Cl = 2.9690(11)
Nd−I(2) = 3.1074(9)	Nd−Cl(2) = 2.7069(15)	La−Cl(2) = 2.7763(9)		
Nd−N(1) = 2.479(7)	Nd−N(1) = 2.351(4)	La−N(1) = 2.403(2)	Nd−N(1) = 2.377(4)	La−N(1) = 2.425(3)
Nd−N(2) = 2.376(7)	Nd−N(2) = 2.520(4)	La−N(2) = 2.583(2)	Nd−N(2) = 2.384(4)	La−N(2) = 2.454(3)
Nd−N(3) = 2.555(7)	Nd−N(3) = 2.372(4)	La−N(3) = 2.415(2)	Nd−N(3) = 2.392(4)	La−N(3) = 2.450(3)
Nd−O(1) = 2.546(6)	Nd−O(1) = 2.569(4)	La−O(1) = 2.623(2)	Nd−O(1) = 2.539(3)	La−O(1) = 2.607(3)
			Nd−O(2) = 2.555(4)	La−O(2) = 2.625(3)
			C(1)−C(1)′ = 1.548(9)	C(1)−C(1)′ = 1.543(8)
C(13)−C(14) = 1.500(13)	C(1)−C(2) = 1.350(9)	C(1)−C(2) = 1.349(4)	C(1)−C(2) = 1.527(6)	C(1)−C(2) = 1.525(5)
C(13)−C(15) = 1.434(13)	C(2)−C(3) = 1.484(7)	C(2)−C(3) = 1.489(4)	C(2)−C(3) = 1.367(6)	C(2)−C(3) = 1.365(5)
C(13)−N(1) = 1.352(11)	C(2)−N(1) = 1.384(6)	C(2)−N(1) = 1.387(4)	C(2)−N(1) = 1.433(6)	C(2)−N(1) = 1.448(5)
C(20)−C(21) = 1.519(13)	C(8)−C(9) = 1.350(8)	C(8)−C(9) = 1.347(4)	C(8)−C(9) = 1.359(6)	C(8)−C(9) = 1.353(6)
C(19)−C(20) = 1.460(13)	C(7)−C(8) = 1.489(8)	C(7)−C(8) = 1.496(4)	C(7)−C(8) = 1.523(7)	C(7)−C(8) = 1.516(5)
C(20)−N(3) = 1.307(11)	C(8)−N(3) = 1.385(6)	C(8)−N(3) = 1.386(4)	C(8)−N(3) = 1.395(6)	C(8)−N(3) = 1.394(5)
	Cl(1)−Li = 2.362(12)	Cl(1)−Li = 2.370(7)	Cl−Li = 2.355(10)	Cl−Li = 2.360(9)
	Cl(2)−Li = 2.393(11)	Cl(2)−Li = 2.391(6)		
I(1)−Nd-I(2) = 146.45(3)	Cl(1)−Nd-Cl(2) = 80.32(5)	Cl(1)−La-Cl(2) = 79.32(3)	O(1)−Nd-O(2) = 150.42(12)	O(1)−La-O(2) = 150.76(10)
N(1)−Nd-N(3) = 127.5(2)	N(1)−Nd-N(3) = 128.11(14)	N(1)−La-N(3) = 125.58(8)	N(1)−Nd-N(3) = 131.45(14)	N(1)−La-N(3) = 129.40(10)
N(2)−Nd-O(1) = 150.2(2)	N(2)−Nd-Cl(1) = 158.24(10)	N(2)−La-Cl(1) = 157.78(5)	N(2)−Nd-Cl = 150.17(10)	N(2)−La-Cl = 149.44(8)
N(2)−Nd-I(1) = 121.93(18)	N(2)−Nd-Cl(2) = 121.32(10)	N(2)−La-Cl(2) = 122.78(5)	O(1)−Nd-Cl = 74.55(9)	O(1)−La-Cl = 74.56(7)
N(2)−Nd-I(2) = 85.58(17)	O(1)−Nd-Cl(1) = 79.07(9)	O(1)−La-Cl(1) = 79.29(5)	O(2)−Nd-Cl = 78.94(9)	O(2)−La-Cl = 79.43(7)
O(1)−Nd-I(1) = 79.94(16)	O(1)−Nd-Cl(2) = 159.16(10)	O(1)−La-Cl(2) = 158.30(5)		
O(1)−Nd-I(2) = 83.25(15)	Nd−Cl(1)−Li = 91.1(3)	La−Cl(1)−Li = 90.87(15)	Nd−Cl−Li = 146.0(3)	La−Cl−Li = 146.1(2)
	Nd−Cl(2)−Li = 92.3(3)	La−Cl(2)−Li = 92.02(16)		
C(14)−C(13)-C(15) = 119.2(8)	C(1)−C(2)-C(3) = 120.1(5)	C(1)−C(2)-C(3) = 120.5(3)	C(1)−C(2)-C(3) = 122.0(5)	C(1)−C(2)-C(3) = 123.2(3)
C(14)−C(13)-N(1) = 124.2(9)	C(1)−C(2)-N(1) = 126.8(5)	C(1)−C(2)-N(1) = 126.1(3)	C(1)−C(2)-N(1) = 121.2(4)	C(1)−C(2)-N(1) = 120.1(3)
C(21)−C(20)-C(19) = 118.5(8)	C(9)−C(8)-C(7) = 120.1(5)	C(9)−C(8)-C(7) = 120.5(3)	C(9)−C(8)-C(7) = 120.2(5)	C(9)−C(8)-C(7) = 121.1(4)
C(21)−C(20)-N(3) = 124.1(8)	C(9)−C(8)-N(3) = 126.5(5)	C(9)−C(8)-N(3) = 126.4(3)	C(9)−C(8)-N(3) = 127.0(5)	C(9)−C(8)-N(3) = 125.1(4)
			C(2)−C(1)-C(1)′ = 115.4(5)	C(2)−C(1)-C(1)′ = 115.0(4)

oxygen, (1s2s2p3s3p3d4s4p)^{36} core electrons of iodine, and (1s2s2p3s3p3d4s4p4d)^{46} core electrons of neodymium were treated by using the frozen-core approximation.[14e] An auxiliary set of s, p, d, f, and g STOs was used to present coulomb and exchange potentials accurately in each SCF cycle.[14f] The calculations were carried out using the program package ADF-2002.03.[14g] A standard Mulliken population analysis was carried out to obtain total atomic populations and charges. Atomic contributions were also determined for selected individual molecular orbitals (Tables 3 and 4).

Results and Discussion

The reaction of metallic Nd with iodine in THF and in the presence of 2,6-[2,6-(i-Pr)$_2$C$_6$H$_5$N═C(Me)]$_2$(C$_5$H$_3$N) afforded a dark brown solution from which brown-pinkish crystals of [2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N═C(CH$_3$)}$_2$(C$_5$H$_3$N)]NdI$_2$(THF) (**1**) which were isolated in moderate yield (Scheme 1).

Scheme 1



Ar = 2,6-(i-Pr)$_2$C$_6$H$_3$

The structure of **1** (Figure 1) shows a Nd atom in a severely distorted octahedral environment [N(1)−Nd−N(2) = 65.9(2)°, N(1)−Nd−N(3) = 127.5(2)°, N(1)−Nd−I(1) = 106.19(18)°, N(1)−Nd−I(2) = 102.54(18)°, N(1)−Nd−O(1) = 89.7(2)°, I(1)−Nd−I(2) =146.45(3)°, O(1)−Nd−I(1) = 79.94(16)°, N(2)−Nd−I(2) = 85.58(17)°] defined by the three ligand nitrogen atoms [Nd−N(1) = 2.479(7) Å, Nd−N(2) = 2.376(7) Å, Nd−N(3) = 2.555(7) Å], two iodine [Nd−I(1) = 3.0636(9) Å, Nd−I(2) = 3.1074(9) Å], and one molecule of THF [Nd−O(1) = 2.546(6) Å]. The C−C distances formed by the methyl groups attached to the imine functions [C(13)−C(14) = 1.500(13) Å, C(20)−C(21) = 1.519(13) Å] are normal as well as the bond distances and angles within the pyridine ring. The imine C−N distances [N(3)−C(20) = 1.307(11) Å, N(1)−C(13) = 1.352(11) Å] as well as the C$_{py}$−C$_{im}$ distances [1.434(11) and 1.460(11) Å] suggest considerable transfer of metal electron density to the ligand (expected ca. 1.28/1.50 Å for no transfer, 1.32/1.44 Å for transfer of a full electron).[15] However, the errors in the bond lengths are too large to draw a firm conclusions.

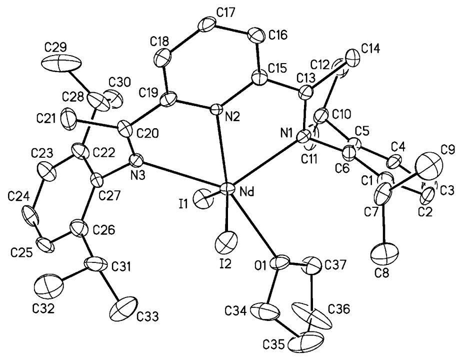
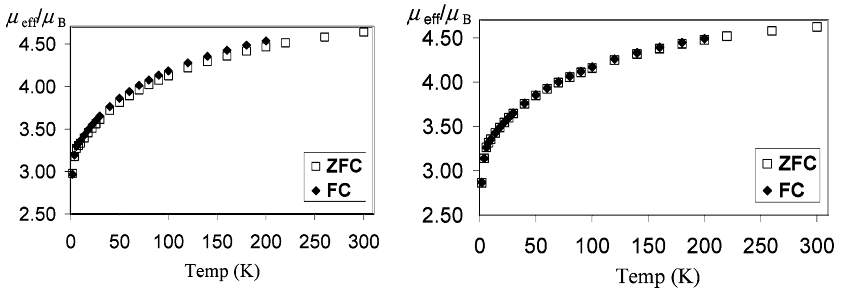


Figure 1. Thermal ellipsoid plot of **1**.

---

(14) (a) ADF2002.03, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, *http://www.scm.com* Baerends, E. J.; Ros, P. *Chem Phys.* **1975**, *8*, 412. (b) Fonseca Guerra, C.; Snijders, J. G.; Velde, G. T.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391. (c) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931. (d) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (e) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. (f) Snijdler, J. G.; Baerends, E. J.; Vernooijs, P. *At. Data Nucl. Data Tables* **1982**, *26*, 483. (g) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.



5kG field

10kG field

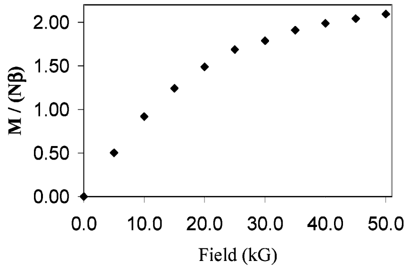
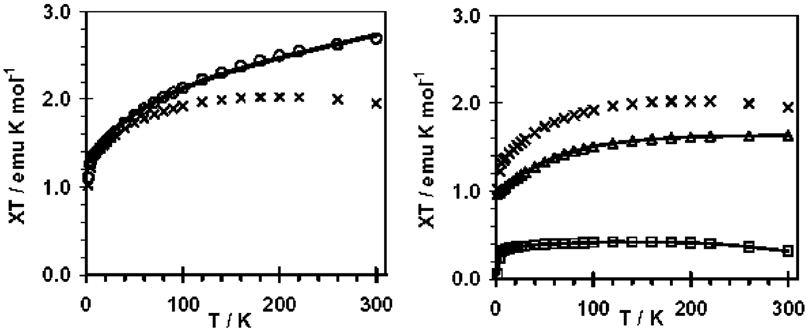


Figure 2. Diagrams of the magnetic moment versus temperature (above) and of the field dependence of the magnetization of **1** at 2 K (below).



A

B

Figure 3. Diagram **A** shows the behavior of χT versus T at 5 kG (○, *zfc*). Illustrated are the overall fit (−) including the temperature independent, calculated Nd^{3+}, and derived monoradical contribution. The data corrected only for the temperature independent contribution are shown as well (×). Diagram **B** shows the calculated Nd^{3+} (△) and monoradical (□) contribution to the data corrected for temperature independent paramagnetism (×).

The two aryl substituents adopt the typical conformation perpendicular to the ligand main core, thus forming two sorts of protective “wings” that define a cavity hosting the two iodine atoms.

At first glance, complex **1** might mistakenly be regarded as the adduct of NdI_2[2c] with a neutral diiminepyridine ligand. The other molecular compounds of NdI_2, i.e., mononuclear $NdI_2(THF)_5$ and $NdI_2(dme)_3$,[2a] have room-temperature magnetic moments respectively of 2.4 and 2.5 μ_B which are slightly lower than expected for the $^5I_4$ ground state of divalent neodymium ($g_J = 3/5$, calcd. $\mu_{eff} = 2.68\ \mu_B$). The magnetic moment of **1** rises as a function of the temperature (Figure 2) from the initial value of 2.87 μ_B at 2.0 K to reach the room-temperature value of 4.63 (±0.3) μ_B. This is even substantially higher than expected for Nd(III) species [trivalent iodide derivatives display magnetic moments in the range of 3.6 and 3.7 μ_B as expected for the $^4I_{9/2}$ ground state ($g_J = 8/11$, $\mu_{eff} = 3.62\ \mu_B$)]. Furthermore, no field dependence was observed (Figure 2) in the static susceptibility at 5 and 10 kG [field cooled (*fc*) and zero field cooling (*zfc*)] as well as in the field dependent magnetization measurements at 2 K, thus ruling out the presence of ferromagnetism. From the inspection of the magnetization at 50 kG, which is close to the saturation, a value of 2.05 Kemu/mol can be derived, which is of the order of what is to be expected for a Nd^{3+} ion and a radical with $S = 1/2$.

From these observations we conclude that a trivalent Nd is present in complex **1**. This implies that internal reduction of the ligand occurred with consequent formation of a radical anion. Figure 3 reports the fitting of χT versus T according to this proposal. For the lanthanoid complexes of the aminoxyl radical ligand, a qualitative interpretation of the magnetic data has been reported by Kahn.[16] A similar concept was used for interpreting the magnetic data of $Cp^*{}_2Yb$(bispyridine)[5] and of $(diazabutadiene)_3Ln$.[6] Assuming that at high temperatures there are no cooperative interactions effects, the data can be treated as a noncorrelated spin system of

---

(15) Budzelaar, P. H. M.; De Bruin, B.; Gal, A. W.; Wieghardt, K.; Van Lenthe, J. H. *Inorg. Chem.* **2001**, *40*, 4649.

(16) (a) Kahn, M. L.; Sutter, J. P.; Golhen, S.; Guionneau, P.; Ouahab, L.; Khan, O.; Chasseau, D. *J. Am. Chem. Soc.* **2000**, *122*, 3413. (b) Sato, O. *Acc. Chem. Res.* **2003**, *36*, 692. (c) Gutlich, P.; Garcia, Y.; Goodwin, H. A. *Chem. Soc. Rev.* **2000**, *29*, 419. (d) Chun, H.; Bill, E.; Weyhermuller, T.; Wieghardt, K. *Inorg. Chem.* **2003**, *42*, 5612. (e) Jenkins, D. M.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 11162.

Table 3. Percent Mulliken Contribution of Various Atomic Orbitals in the Relevant MOs of Compound **1**[a]

orbitals energy (eV) (spin α/spin β)	spin A		spin B	
	Nd %, AO	other atoms, %	Nd %, AO	other atoms, %
85 $-5.30/-5.32$	3 f 3 d 1 p	89 (I atoms)	2 p 2 d	92 (I atoms)
86 $-4.21/-4.07$	95 f	N/S	2 f 1 d	80 (C and N atoms of the ligand) 3 (I atoms)
87 $-4.14/-3.67$	89 f	1 (I atoms)	1 d	77 (C and N atoms of the ligand) 1 (I atoms)
88 $-4.12/-2.50$	98 f	N/S	95 f	N/S
89 $-4.03/-2.48$	67 f	23 (C and N atoms of the ligand) 3 (I atoms)	92 f	N/S
90 $-4.02/-2.44$	94 f	N/S	92 f	N/S
LUMO + 2 $-3.99/-2.15$	90 f	N/S	9 f 3 s 1 d	83 (C and N atoms of the ligand)
LUMO + 3 $-3.86/-2.07$	89 f	1 (C and N atoms of the ligand) 1 (I atoms)	70 f 1 p 1 d	17 (C and N atoms of the ligand)

[a] Two unpaired electrons calculations: spin A $-$ spin B $= 2$.

Nd^{3+} ($\chi T = 1.64$ Kemu/mol, free ion value) and a radical ($S = 1/2$, $\chi T = 0.375$ Kemu/mol). Since the experimental values of χT are larger than the expected value of 2.02 Kemu/mol (e.g. 2.7 Kemu/mol at 300 K) and there is a significant slope in the high temperature region, we have introduced a temperature independent paramagnetic contribution (0.0024 emu/mol) which might result from delocalization of the radical not only on the ligand but also on the neodymium (see below) or perhaps from undetected impurities such as metallic Nd.

At lower temperatures (<150 K) the susceptibility of Nd^{3+} becomes anisotropic. By analogy with the Kahn's model[16] the function $f(T) = -a \cdot \exp(-T/b) + c = \chi T(\mathrm{Nd}^{3+})$ has been used for **1** ($a = 0.7$ Kemu/mol, $b = 60$ K, and $c = 1.64$ Kemu/mol). Subtraction of the calculated $\chi T(\mathrm{Nd}^{3+})$ values and the temperature independent contribution gave the result as expected for a radical anion with $S = 1/2$. At temperatures below 10 K, the χT values show a more rapid decrease, which might be indicative of antiferromagnetic ordering. This cooperative effect can be attributed to either intramolecular (involving Nd^{3+} and the radical) or intermolecular ordering (radical−radical interaction) or to a combination of both. A small θ value of less than -1.5K for the Weiss constant is extrapolated for the data of complex **1**.

To substantiate this model, ADF-DFT calculations were carried out on the model compound as obtained from the X-ray crystal structure without further geometry optimization (other than replacing the coordinated molecule of THF with water and the aryl isopropyl groups with methyls). Given the behavior of the magnetic moment, both the $S = 1$ and $S = 2$ configurations were calculated. The results were very similar in both cases, showing comparable values of the total binding energy ($\Delta E = 7.5$ kcal/mol). Given the fact that only the X-ray (unoptimized) structures were used for these calculations, this small difference nicely accounts for thermal population of the high-spin state at the expense of the low-spin state. This is somewhat reminiscent of a spin crossover as reported by Khan for a Nd compound.[12a] Such spin crossovers are relatively common for Fe but much rarer for other metals.[12] Calculation for $S = 3$ gave instead a substantially higher value of the total binding energy, making involvement of higher spin states unlikely. The calculation of the $S = 1$ configuration (Table 3), which is the most consistent with the value of the magnetic moment obtained from extrapolation to 0 K, clearly indicated that complex **1** is a Nd(III) antiferromagnetically coupled to a ligand radical anion. The Mulliken analysis shows a total Nd 4*f* occupation of 3.22 (α) and 0.15 (β). The three highest occupied α-orbitals (86−88) are Nd 4*f* orbitals, the lowest empty α-orbital (89) being a Nd 4*f* mixed with ligand π^*. The highest occupied β-orbital (86) is mainly ligand π^* and the Nd 4*f*-orbitals are just above this. These results clearly indicate that the most likely increase in magnetic moment comes from flipping the spin of the highest β-electron. The results of a calculation on the $S = 2$ configuration (Table 4) confirm this. The population of the Nd 4*f* orbitals remains nearly unchanged: 3.29 (α) and 0.11 (β), but extensive mixing between Nd 4*f* and ligand π^*-orbitals is observed in occupied α orbitals 86 and 89.

As expected, complex **1** is air-sensitive. Diluted solutions of **1**, carefully prepared to avoid any exposure to trace of air and moisture, display a brown-pinkish color which instantly turns very intense pink upon exposure to traces of air. Unfortunately, attempts to isolate crystalline compounds out of the reaction of **1** with dry oxygen failed. Nevertheless, the comparison of the optical spectra of a solution of **1** before and after exposure to O_2 (Figure 4) strongly suggests that the ligand system was retained upon oxidation of the metal center. This is in striking contrast with the result of several attempts to replace the two iodine atoms with a variety of alkyl, aryloxides, and amides. In all cases, trivalent species were obtained aside the invariable presence of $\mathrm{NdI_3(THF)_3}$ (probably arising from disproportionation and ligand scrambling). In addition, NMR spectra of the reaction mixtures always showed that *the ligand was completely dissociated from the metal.* Moreover, attempts to prepare a simple $\mathrm{NdCl_3}$

Table 4. Percent Mulliken Contribution of Various Atomic Orbitals in the Relevant MOs of Compound **1**[a]

orbitals energy (eV) (spin α/spin *β*)	spin A		spin B	
	Nd %, AO	other atoms, %	Nd %, AO	other atoms, %
85 −5.31/−5.30	2 d 2 p 2 f	90 (I atoms)	2 d 2 p	93 (I atoms)
86 −4.26/−3.76	40 f	49 (C and N atoms of the ligand) 1 (I atoms)	3 f 1 d	80 (C and N atoms of the ligand)
87 −4.04/−3.46	94 f	N/S	2 d	87 (C and N atoms of the ligand) 1 (I atoms)
88 −4.00/−2.30	88 f	5 (C and N atoms of the ligand)	92 f	1 (I atoms)
89 −3.86/−2.21	74 f	16 (C and N atoms of the ligand) 2 (I atoms)	96 f	N/S

[a] Four unpaired electrons calculations: spin A − spin B = 4.

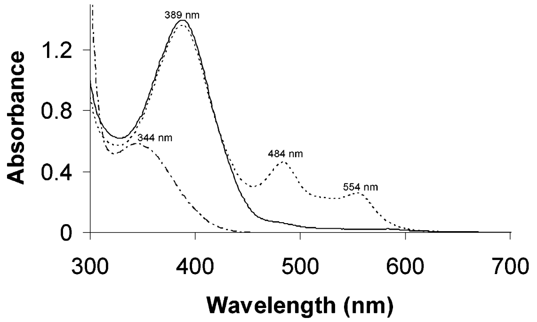
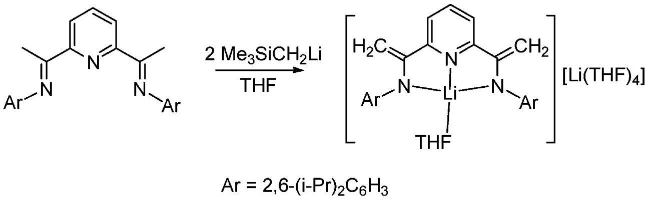


Figure 4. Optical spectrum of **1** (solid line) in THF, after exposure to O_2 (dotted line) and of free ligand (broken line).

complex of the diimino pyridinate ligand (thus containing more electronegative and smaller halides and possibly more versatile for reduction reactions) did not afford complexation but gave instead unreacted starting materials. The poor ability of trivalent Nd complexes to retain this ligand was not anticipated and is in striking contrast with the behavior of transition metals, with which robust diimine olefin polymerization catalysts can be prepared.[4] Furthermore, this behavior is obviously a serious obstacle for developing the reactivity of its low-valent Nd derivatives. To circumvent this problem, we have attempted the transformation of the ligand into the corresponding anion by deprotonating the two imine methyl groups. Our previous work in transition metal chemistry using 2,6-[2,6-$(i\text{-Pr})_2C_6H_5N{=}C(Me)]_2(C_5H_3N)$ has highlighted not only its ability to accept electrons but also the possibility of being attacked by M-alkyl functions thus triggering a surprising variety of unpredictable transformations.[17] Among these, there was the deprotonation of one of the two methyl groups attached to the imine function and consequent transformation of the neutral ligand into the corresponding ene-amido anion $[\{2\text{-}[2,6\text{-}(i\text{-Pr})_2C_6H_5N{=}C(Me)]\}\{6\text{-}[2,6\text{-}(i\text{-Pr})_2C_6H_5N{-}C(CH_2)]\}(C_5H_3N)]^-$.[18] Since the deprotonation of the ligand improves its binding to the metal, we have now explored the possibility of rationally preparing and using this organic anion for the preparation and stabilization of Nd complexes with the aim of investigating their behavior in strongly reducing environments.

Scheme 2



The deprotonation of 2,6-[2,6-$(i\text{-Pr})_2PhN{=}C(Me)]_2(C_5H_3N)$ by MeLi[18] is a complex reaction that cannot be used for the large scale preparation of the corresponding monoanion. The same reaction carried out in THF with 1 equivalent of a different organolithium such as $LiCH_2Si(CH_3)_3$ afforded instead a reasonable yield of the corresponding *dilithium* salt $[\{2,6\text{-}[(2,6\text{-}(i\text{-Pr})_2Ph)N{-}C{=}(CH_2)]_2(C_5H_3N)\}Li(THF)][Li(THF)_4]$ (**2**) where both methyl groups attached to the imine functions were deprotonated and transformed into the corresponding ene-diamido functions (Scheme 2). As expected, the yield was substantially increased (up to 72%) by using two equivalents of the alkyllithium reagent. The formulation of **2** was based on NMR data which were in excellent agreement with the proposed formulation. The most salient characteristic consists of the two ene-amido hydrogen atoms showing two slightly broad singlets at 3.41 and 4.05 ppm coupled to the same ^{13}C resonance at 71.74 ppm of the ^1H-$\{^{13}C\}$ HMQC spectrum. The four isopropyl groups gave rise to two sets of methyl groups and only one set of methyne, indicating that there is a substantial magnetic anisotropy between the methyl groups pointing to the side of the $={CH_2}$ groups and those pointing to the opposite direction. This furthermore suggests that rotation of the phenyl groups is slow in the NMR time scale (rapid rotation of the i-Pr groups will not remove their diastereoisotopism). The ^7Li NMR spectrum displayed only one single resonance at δ 1.63 which confirms that the two nonequivalent lithium atoms of the solid-state structure (one coordinated to the ligand and the other solvated by four molecules of THF) rapidly exchange in solution.

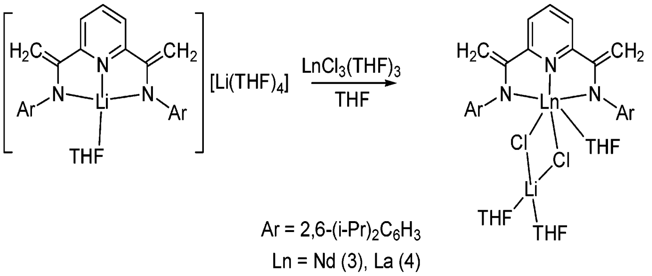
Given the lability of the complexation of the intact diimine to lanthanides, its transformation into the corresponding dianion **2** certainly offers better opportunities for more robust binding to the metal. The dianion **2** reacted readily at room

---

(17) (a) Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2002**, *124*, 12268. (b) Reardon, D.; Conan, F.; Gambarotta, S.; Yap, G. P. A.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318.

(18) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 3088.

Scheme 3



temperature with $LnCl_3(THF)_3$ {Ln = Nd, La] in THF (Scheme 3) to afford the corresponding isostructural complexes $\{2,6\text{-}[(2,6\text{-}(i\text{-}Pr)_2Ph)N{-}C{=}(CH_2)]_2(C_5H_3N)\}Ln(THF)(\mu\text{-}Cl)_2[Li\ (THF)_2]\cdot 0.5$ (hexane) [Ln = Nd (**3**), La (**4**)] that were isolated as brown and green crystals, respectively.

In the two isostructural compounds (Figure 5), the coordination sphere around the metal is defined by two chlorine atoms [Nd−Cl(1) = 2.7804(14) Å, Nd−Cl(2) = 2.7069(15) Å, La−Cl(1) = 2.8409(8) Å, La−Cl(2) = 2.7763(9) Å] located cis to each other [Cl(1)−Nd−Cl(2) = 80.32(5)°, Cl(1)−La−Cl(2) = 79.32(3)°], the three N atoms of the ligand [N(1)−Nd = 2.351(4) Å, N(2)−Nd = 2.520(4) Å, N(3)−Nd = 2.472(4) Å, N(1)−La = 2.403(2) Å, N(2)−La = 2.583(2) Å, N(3)−La = 2.415(2) Å], and one molecule of THF [Nd−O(1) = 2.569(4) Å, La−O(1) = 2.623(2) Å]. The two cis chlorine atoms are also bridged to the same Li cation [Li−Cl(1) = 2.362(12) Å, Li−Cl(2) = 2.393(11) Å for **3**, Li−Cl(1) = 2.370(7) Å, Li−Cl(2) = 2.391(6) Å for **4**] which in turn is solvated by two molecules of THF. The overall geometry around the metal is distorted octahedral [N(1)−Nd−N(3) = 128.11(14)°, N(2)−Nd−Cl(1) = 158.24(10)°, O(1)−Nd−Cl(2) = 159.16(10)°; N(1)−La−N(3) = 125.58(8)°, N(2)−La−Cl(1) = 157.78(5)°, O(1)−La−Cl(2) = 158.30(5)°]. The ligand system shows the usual arrangement with the pyridine ring coplanar with the two ene-amide functions, while the planes of the two bulky phenyl rings are oriented perpendicularly. The deprotonation of the two former methyl groups is apparent from the values of the C−C distances (ranging from 1.347(4) Å to 1.350(9) Å) as expected for a conjugated double bond. The C−N bond distances [1.384(6) Å, 1.385(6) Å for **3** and 1.387(4) Å, 1.386(4) Å for **4**], although considerably longer than a C═N double bond, are still shorter than the expected value for a C−N single bond, thus indicating the presence of a delocalized π-system along the $CH_2{-}C{-}N$ framework.

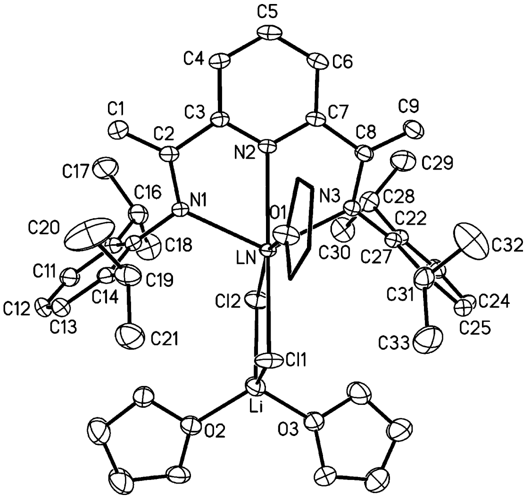


Figure 5. Thermal ellipsoid plot of **3** and **4**.

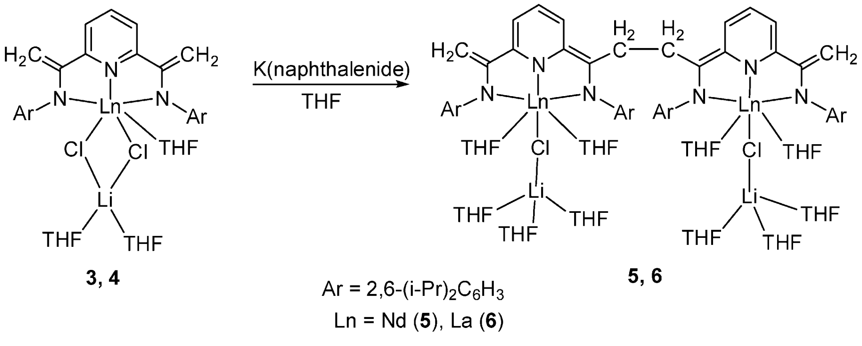
Conversely the conjugation with the pyridine ring seems to be interrupted given that the C−C bond is fairly long [C(2)−C(3) = 1.484(7) Å (**3**) and 1.489(4) Å (**4**); C(7)−C(8) = 1.489(8) Å (**3**) and 1.496(4) Å (**4**)] and close to a single bond. The pyridine rings also displayed bond distances and angles as expected for a coordinated pyridine.

Complex **3** is paramagnetic with a value of the room-temperature magnetic moment normal for a Nd(III) complex [$\mu_{eff} = 3.65\ \mu_B$], whereas complex **4** is diamagnetic. Its NMR spectra are consistent with the solid-state structure displaying close similarities to those of the doubly lithiated ligand **2**. Even in this case, the two methylene groups of the ene-amido functions showed the two broad singlets at 3.54 and 4.59 coupled to the same C resonance at 82.77 ppm, two sets of methyl groups, and only one set of methyne signals for the four i-Pr groups.

Reduction of **3** and **4** were carried out with the aim of elucidating the ability of the dianion ligand to engage in internal redox with the metal. Treatment of the corresponding THF solutions with equivalent amounts of K(naphthalenide) (Scheme 4) afforded an instantaneous color change to dark-brown. Homogeneous and well-formed crystalline **5** and **6** were isolated in low yield as the only tractable products of the reaction mixtures.

The two compounds are isostructural (Figure 6) with very comparable crystallographic cell parameters. The structure is a symmetry-generated dimer showing the metal surrounded by the ligand system [Nd−N(1) = 2.377(4) Å, Nd−N(2) =

Scheme 4



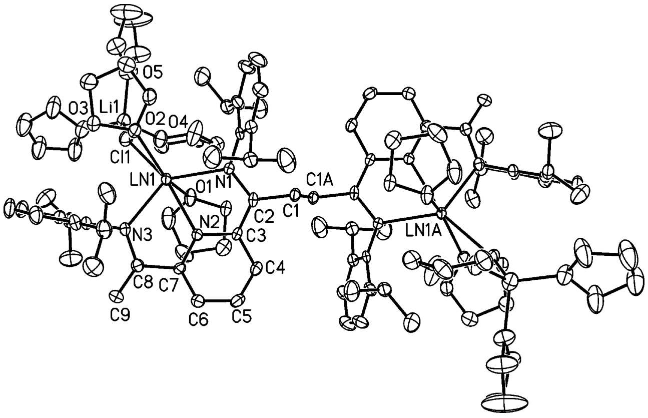
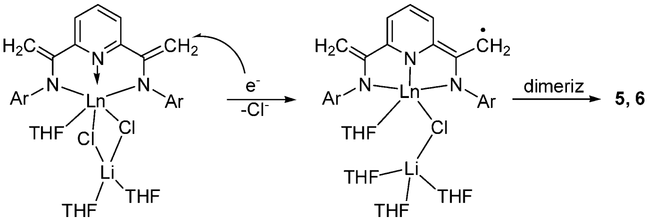


Figure 6. Thermal ellipsoid plot of **5** and **6**.

2.384(4) Å, Nd−N(3) = 2.392(4) Å; N(1)−La = 2.423(5) Å, N(2)−La = 2.454(3) Å, N(3)−La = 2.450(3) Å], two molecules of THF [Nd−O(1) = 2.539(3) Å, Nd−O(2) = 2.555(4) Å; La−O(1) = 2.607(3) Å, La−O(2) = 2.625(3) Å], and one chlorine atom [Nd−Cl = 2.8962(14) Å; La−Cl = 2.9690(11) Å] which in turn bridges one Li(THF)$_3$ unit [Li−Cl = 2.355(10) Å for **5**, Li−Cl = 2.360(9) Å for **6**]. Thus, the coordination geometry around the metal center is severely distorted octahedral with the two molecule of THF on the axial positions [O(1)−Nd−O(2) = 150.42(12)°, O(1)−La−O(2) = 150.76(10)°] and the three N donor atoms and the chlorine identifying the equatorial plane [N(2)−Nd−Cl = 150.17(10)°, N(1)−Nd−N(3) = 131.45(14)°, N(2)−La−Cl = 149.44(8)°, N(1)−La−N(3) = 129.40(10)°]. Of the two ene-amido functions present in the starting **3** and **4**, only one remained intact showing the characteristically short C−C distance indicative of a double bond [C(8)−C(9) = 1.359(6) Å (**5**) and 1.353(6) Å (**6**)]. The second was instead reduced and used for assembling the dinuclear structure via formation of a C−C single bond [C(1)−C(2) = 1.527(6) Å (**5**) 1.525(5) Å (**6**)] with an identical unit.

Although the very low yield of the reaction detracts from its usefulness for further reactivity studies and regrettably prevented a complete characterization, nevertheless, the isolation and characterization of **5** and **6** has some important implications. The overall result of the reduction (i.e. ligand coupling) doubtlessly shows that the ligand system is again the recipient of the electron. Furthermore, the one electron reduction of one of the two ene-amide functions, with consequent dimerization and formation of the C−C single bond, implies that the ligand system has become trianionic (Scheme 5).

Scheme 5



In conclusion, we have prepared a Nd complex supported by the 2,6-[2,6-(i-Pr)$_2$C$_6$H$_5$N=C(Me)]$_2$(C$_5$H$_3$N) ligand system. The magnetic behavior clearly indicated that the ligand acts as a spin carrier magnetically coupled to a Nd(III) cation. The unexpected lability of the diimine while the metal is in its trivalent state prompted efforts to transform the ligand into the corresponding anion via double deprotonation of the two methyl groups attached to the imine functions. The corresponding dianion readily bonds trivalent Nd to afford stable trivalent precursors. Subsequent reduction gave even in this case electron transfer to the ligand which was followed by dimerization and formation of a dinuclear structure.

Acknowledgment. This work was supported by the Natural Science and Engineering Council of Canada (NSERC). Prof. L. Thompson (Memorial University) is gratefully acknowledged for his assistance with magnetic measurements.

Supporting Information Available: Complete crystallographic data (CIF) for all the complexes, magnetic data for **1**, and simplified output file for DFT calculation of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049820T