# Preparation of an Active Neodymium Catalyst for Regioselective Butadiene *cis*-Polymerization Supported by a Dianionic Modification of the 2,6-Diiminopyridine Ligand

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Treatment of the 2,6-diiminopyridine ligand 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N) with 2 equiv of Me$_3$SiCH$_2$Li afforded the corresponding {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$-(C$_5$H$_3$N)]}$^{2-}$ (**1**) dianion via deprotonation of the two methyl groups attached to the two imine functions. Reaction of **1** with NdCl$_3$(THF)$_3$ yielded {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$-(C$_5$H$_3$N)]Nd(THF)}($\mu$-Cl)$_2$[Li(THF)$_2$]·0.5(hexane) (**2a**), whose recrystallization from DME gave the corresponding ionic {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$(C$_5$H$_3$N)]NdCl$_2$(DME)}{Li(DME)$_3$}-(**2b**). With the exception of the reaction with (allyl)MgBr, which proceeded readily with **2b** to form the allyl derivative {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$(C$_5$H$_3$N)]Nd($\eta^3$-C$_3$H$_5$)Br}{Li-(DME)$_3$} (**3**), compounds **2a,b** are not suitable starting substrates for further alkylation reactions. A viable synthetic strategy for the preparation of alkyl derivatives of **2** consisted instead of the pretreatment of NdCl$_3$(THF)$_3$ with RLi [R = Me$_3$SiCH$_2$, CH$_3$] at low *T* followed by treatment with either the diimine ligand or **1**. According to this procedure, the terminally bound alkyl derivative [2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$(C$_5$H$_3$N)]Nd[CH$_2$Si (CH$_3$)$_3$](THF) (**4**) was prepared and subsequently crystallographically characterized. The same synthetic procedure with MeLi afforded {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$(C$_5$H$_3$N)]Nd}($\mu$-CH$_3$)$_2$[Li-(THF)$_2$] (**5**) and {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$(C$_5$H$_3$N)]Nd}($\mu$-Cl)($\mu$-X)[Li (THF)$_2$] (**6**) [X = Cl 53%, Me 47%] depending on the MeLi/Nd ratio. Both **5** and **6** as well as **2a** are potent catalysts for the *cis*-polymerization of butadiene.

## Introduction

The discovery of the ability of the tridentate diiminopyridine ligand 2,6-{[2,6-(i-Pr)$_2$ C$_6$H$_3$]N=C(CH$_3$)}$_2$-(C$_5$H$_3$N) to support exceptionally high levels of catalytic activity with several transition metals of very different natures[1] has marked a milestone in Ziegler–Natta catalysis and also prompted efforts aimed at understanding the reasons for the unique performance of this ligand.[2] The results of these studies have shown an unanticipated ability of the diimine to be involved in the reactivity of the metal center[3,4] and to undergo a number of diverse transformations.[4] Of particular interest to us is the possibility shown by the conjugated $\pi$-system of efficiently accepting considerable amounts of electronic charge to form radical anions.[5] The recent isolation and characterization of a NdI$_2$ adduct[6] indi-

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cates that this characteristic can effectively be used for the stabilization of highly reactive species.

During these studies, the ability to perform mono- and double-deprotonations of the methyl groups attached directly to the imine carbon atoms was serendipitously discovered.[3b,4b] This has in turn provided a novel class of dianionic ligands which, although very similar in structure to the versatile diketimine ligand, are electronically very different. Given the remarkable performance of the intact ligand in supporting exceptionally high catalytic activity,[1,3] the next most obvious step was to probe the rational preparation and use of the mono- and double-deprotonated forms of $2,6-\{[2,6-(i-Pr)_2C_6H_3]N=C(CH_3)\}_2(C_5H_3N)$ as supporting ligands for polymerization catalysts. The dianion in particular is of interest given its close relationship to a large family of dianionic chelating ligands based on nitrogen donor atoms, which have been employed for the preparation of nonmetallocene catalysts[7] capable of performing a wide range of polymerization reactions including stereospecific polymerization of dienes.[8]

In this first paper we describe the preparation and characterization of the $[2,6-\{[2,6-(i-Pr)_2C_6H_3]N-C=(CH_2)\}_2(C_5H_3N)]^{2-}$ dianion and its use in the preparation of potent Nd catalysts for stereoselective butadiene polymerization.

## Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenk type techniques. $NdCl_3(THF)_3$[9] and $2,6-\{[2,6-(i-Pr)_2C_6H_3]N=C(CH_3)\}_2(C_5H_3N)$[1a] were prepared according to published procedures. Samples for magnetic susceptibility measurements at room temperature were preweighed inside a drybox equipped with an analytical balance and flame sealed into calibrated 5 mm o.d. quartz tubes. Magnetic measurements were carried out using a Johnson Matthey magnetic balance. Background corrections for the sample holder were included in the magnetic calculations. Standard corrections for the underlying diamagnetism were applied to the data.[10] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for the X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector. NMR spectra were recorded on a Bruker AMX-500 spectrometer.

**Preparation of $\{[2,6-\{[2,6-(i-Pr)_2C_6H_3]N-C=(CH_2)\}_2(C_5H_3N)]Li(THF)\}\{Li(THF)_4\}$ (1).** Treatment of a solution of $2,6-\{[2,6-(i-Pr)_2C_6H_3]N=C(CH_3)\}_2(C_5H_3N)$ (2.0 g, 4.15 mmol) in THF (30 mL) with $LiCH_2Si(CH_3)_3$ (0.85 g, 9.03 mmol) in THF (40 mL), followed by evaporation of the solvent, afforded a solid residue. The mass was washed with two portions of hexane (20 mL) and dried under vacuum. Compound **1** was thus obtained as a very air-sensitive yellow powder (2.73 g,

3.20 mmol, 77%). Crystals suitable for X-ray analysis were grown from a THF−hexane mixture. $^1H$ NMR ($C_6D_6$, 500 MHz, 25 °C) δ: 1.27 (m, 20H, $OCH_2CH_2$), 1.32 (d, $J$ = 7.0 Hz, 12H, $(CH_3)_2CH$), 1.57 (d, $J$ = 6.9 Hz, 12H, $(CH_3)_2CH$), 3.18 (m, 20H, $OCH_2CH_2$), 3.41 (br s, 2H, NC=$CH_2$), 3.74 (quint, $J$ = 6.9 Hz, 4H, $(CH_3)_2CH$), 4.05 (br s, 2H, NC=$CH_2$), 7.17 (t, $J$ = 7.7 Hz, 1H, $p$-$C_5H_3N$), 7.24 (t, $J$ = 7.6 Hz, 2H, $p$-$C_6H_3^iPr_2$), 7.39 (d, $J$ = 7.6 Hz, 4H, $m$-$C_6H_3^iPr_2$), 7.76 (d, $J$ = 7.7 Hz, 2H, $m$-$C_5H_3N$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 123.72 MHz, 25 °C) δ: 25.52 (($CH_3)_2CH$)), 25.54 (($CH_3)_2CH$)), 25.78 ($OCH_2CH_2$), 28.56 (($CH_3)_2CH$), 68.54 ($OCH_2CH_2$), 71.74 (NC=$CH_2$), 118.06 ($m$-$C_5H_3N$), 121.93 ($p$-$C_6H_3^iPr_2$), 123.69 ($m$-$C_6H_3^iPr_2$), 136.72 ($p$-$C_5H_3N$), 144.18 ($o$-$C_6H_3^iPr_2$), 153.61 ($ipso$-$C_6H_3^iPr_2$), 160.31 ($o$-$C_5H_3N$), 163.36 (N$C$=$CH_2$). Meaningful analytical data could not obtained probably due to spontaneous loss of the crystallization solvent.

**Preparation of $\{[2,6-\{[2,6-(i-Pr)_2C_6H_3]N-C=(CH_2)\}_2(C_5H_3N)]Nd(THF)\}[(\mu-Cl)_2Li(THF)_2]\cdot0.5$ (hexane) (2a).** Compound **1** (1.50 g, 1.76 mmol) was added to a solution of $NdCl_3(THF)_3$ (0.81 g, 1.75 mmol) in THF (60 mL), and the resulting mixture was stirred overnight at room temperature. After removal of the volatiles, the residue was extracted with $Et_2O$ (80 mL) and centrifuged to remove LiCl. After further evaporation to dryness, 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 **2a** (0.93 g, 0.97 mmol, 55%). Anal. Calcd (found) for $C_{48}H_{72}Cl_2NdLiN_3O_3$: C 59.98 (58.58), H 7.55 (7.36), N 4.37 (4.50), Cl 7.38 (7.27), Nd 15.01 (15.10). The NMR spectra showed only very broad and overlapping features. $\mu_{eff}$ = 3.65 $\mu_B$.

**Preparation of $\{[2,6-\{[2,6-(i-Pr)_2C_6H_3]N-C=(CH_2)\}_2(C_5H_3N)]NdCl_2(DME)\}\{Li(DME)_3\}$ (2b).** Complex **2a** (0.93 g, 0.97 mmol) was dissolved into a minimum amount of DME (20 mL) with heating. The solution was allowed to stand at room temperature overnight, upon which crystals of **2b** separated (0.78 g, 0.74 mmol, 76% yield). Anal. Calcd (found) for $C_{49}H_{81}Cl_2NdLiN_3O_8$: C 55.40 (55.28), H 7.69 (7.66), N 3.96 (3.89). $\mu_{eff}$ = 3.59 $\mu_B$.

**Preparation of $\{[2,6-\{[2,6-(i-Pr)_2C_6H_3]N-C=(CH_2)\}_2(C_5H_3N)]Nd(\eta^3-C_3H_5)Br\}\{Li(DME)_3\}$ (3).** Complex **2a** (0.19 g, 0.20 mmol) was gradually dissolved into DME (8 mL), from which it precipitated as **2b**. The addition of $C_3H_5MgBr$ (0.2 M, 2 mL, 0.40 mmol) at 0 °C to the suspension gave a homogeneous orange solution. An insoluble material was gradually formed while stirring overnight at ambient temperature. The mixture was concentrated to about 6 mL and centrifuged. Cyclohexane (2 mL) was added to the solution, and the resulting suspension was allowed to stand for 1 day at room temperature. The precipitated solid was eliminated by centrifugation, and the clear solution was layered with cyclohexane to afford crystals of **3** (0.14 g, 0.11 mmol, 56% yield). Anal. Calcd (found) for $C_{48}H_{76}N_3BrNdLiO_6$: C 56.40 (56.38), H 7.49 (7.36), N 4.11 (4.02). $\mu_{eff}$ = 3.61 $\mu_B$.

**Preparation of $[2,6-\{[2,6-(i-Pr)_2C_6H_3]N-C=(CH_2)\}_2(C_5H_3N)]Nd(CH_2Si(CH_3)_3)(THF)$ (4). Method A.** A THF (20 mL) solution of $NdCl_3(THF)_3$ (0.23 g, 0.5 mmol) was treated at −60 °C with a THF (24 mL) solution of $LiCH_2Si(CH_3)_3$ (0.09 g, 1.0 mmol.). Stirring was continued at 0 °C for 1 h. A THF (30 mL) solution of **1** (0.43 g, 0.5 mmol) was added, and the resulting mixture was stirred overnight. Solvent was evaporated to dryness. The residue was extracted with warm hexane (50 °C, 200 mL), and the extract was transferred to a Schlenk tube and concentrated to 40 mL. The mixture was warmed again with a hot water bath and centrifuged to remove the colorless precipitate. The resulting green solution was cooled to −36 °C, upon which yellowish-green crystals of **4** separated (0.21 g, 0.26 mmol, 52%). Anal. Calcd (found) for $C_{47}H_{74}N_3NdOSi$: C 64.93 (64.56) H 8.58 (8.39) N 4.83 (4.71). $\mu_{eff}$ = 3.65 $\mu_B$.

**Method B.** A 250 mL Schlenk flask was loaded with solid $NdCl_3(THF)_3$ (0.47 g, 1.0 mmol) and $LiCH_2Si(CH_3)_3$ (0.38 g,

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## Table 1.  Crystal Data and Structure Analysis Results

|                                      | 1                         | 2b                            | 3                            | 4                         | 6                                      |
|--------------------------------------|---------------------------|-------------------------------|------------------------------|---------------------------|----------------------------------------|
| formula                              | $C_{53}H_{81}Li_2N_3O_5$  | $C_{49}H_{81}Cl_2LiN_3NdO_8$  | $C_{48}H_{76}BrLiN_3NdO_6$   | $C_{47}H_{74}N_3NdOSi$    | $C_{44.47}H_{66.41}Cl_{1.53}NdLiN_3O_3$ |
| MW                                   | 854.09                    | 1062.25                       | 1022.21                      | 869.42                    | 908.48                                 |
| cryst syst                           | monoclinic                | monoclinic                    | monoclinic                   | monoclinic                | triclinic                              |
| space group, $Z$                     | $P2/c$, 2                 | $P2_1/c$, 4                   | $P2_1/n$, 4                  | $P2_1/c$, 4               | $P\bar{1}$                             |
| $a$ (Å)                              | 11.8557(11)               | 9.2962(11)                    | 15.045(2                     | 15.267(3)                 | 10.896(2)                              |
| $b$ (Å)                              | 13.2992(13)               | 23.836(3)                     | 18.592(3)                    | 16.123(3)                 | 13.002(3)                              |
| $c$ (Å)                              | 18.4462(17)               | 25.096(3)                     | 20.340(3)                    | 20.375(4)                 | 18.807(4)                              |
| $\alpha$ (deg)                       |                           |                               |                              |                           | 70.579(7)                              |
| $\beta$ (deg)                        | 108.480(2)                | 96.225(2)                     | 111.432(2)                   | 109.613(4)                | 80.152(4)                              |
| $\gamma$ (deg)                       |                           |                               |                              |                           | 68.397(4)                              |
| $V$ (Å$^3$)                          | 2758.5(5)                 | 5528.0(12)                    | 5295.9(13)                   | 4724.4(15)                | 2332.7(9)                              |
| $\lambda$(Mo K$\alpha$)              | 0.71073                   | 0.71073                       | 0.71073                      | 0.71073                   | 0.71073                                |
| $T$ (K)                              | 298(2)                    | 203(2)                        | 223(2)                       | 203(2)                    | 203(2)                                 |
| $D_{calcd}$ (g cm$^{-3}$)            | 1.028                     | 1.276                         | 1.286                        | 1.222                     | 1.293                                  |
| $\mu_{calcd}$ (cm$^{-1}$)            | 0.064                     | 1.085                         | 1.282                        | 1.159                     | 1.240                                  |
| $F_{000}$                            | 932                       | 2228                          | 2124                         | 1836                      | 946                                    |
| $R$, $R_w^{2\ a}$                    | 0.0963, 0.3235            | 0.0731, 0.1789                | 0.0623, 0.572                | 0.0617, 0.0742            | 0.0408, 0.1009                         |
| GoF                                  | 1.024                     | 1.025                         | 1.056                        | 1.074                     | 1.030                                  |

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

4.0 mmol). A mixture of hexane (30 mL) and Et$_2$O (10 mL) was subsequently added after cooling at −60 °C, and the resulting suspension was stirred for 30 min. The mixture became emerald green, indicating the formation of partially alkylated Nd(III) species. To this mixture, a THF solution (40 mL) of the neutral 2,6-diiminopyridine (0.48 g, 1.0 mmol) was added. The color immediately turned brown. The mixture was allowed to warm to room temperature, and stirring was continued overnight. The resulting dark orange-brown mixture was evaporated to dryness under reduced pressure. The dried residue was extracted with hexane (60 mL) and centrifuged to remove some insoluble residue. The resulting green solution was concentrated to ca. 30 mL and cooled to −36 °C to afford yellowish-green crystals of **4** (0.19 g, 0.22 mmol, 22%).

**Preparation of** {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N−C=(CH$_2$)}$_2$-(C$_5$H$_3$N)]Nd(THF)}($\mu$-CH$_3$)$_2$[Li(THF)$_2$]·0.5(hexane) (5). A suspension of NdCl$_3$(THF)$_3$ (1.45 g, 3.11 mmol) in THF (60 mL) was treated at 0 °C with a solution of CH$_3$Li in ether (1.4 M, 8.9 mL, 12.5 mmol). The mixture was allowed to warm to room temperature, upon which the neutral 2,6-diiminopyridine ligand (1.50 g, 3.11 mol) was added to the mixture. Stirring was continued overnight. The solvent was evaporated at reduced pressure, and the residue was extracted with Et$_2$O (50 mL) and centrifuged to remove a small amount of insoluble precipitate. After evaporation of Et$_2$O at reduced pressure, the residue was redissolved in hexane (80 mL) and cooled to −35 °C, upon which crystalline **5** separated (1.46 g, 1.58 mmol, 51%). Anal. Calcd (found) for C$_{50}$H$_{78}$NdLiN$_3$O$_3$: C 65.25 (64.58), H 8.54 (8.36), N 4.57 (4.50). $\mu_{eff}$ = 3.63 $\mu_B$.

**Preparation of the Cocrystallite** {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]-N−C=(CH$_2$)}$_2$(C$_5$H$_3$N)]Nd}($\mu$-Cl)($\mu$-X)[Li(THF)$_2$] (6) [X = Cl 53%, Me 47%]. A suspension of NdCl$_3$(THF)$_3$ (1.45 g, 3.11 mmol) in THF (60 mL) containing the neutral 2,6-diiminopyridine ligand (1.50 g, 3.11 mol) was treated with a solution of CH$_3$Li in ether (1.4 M, 6.7 mL, 9.4 mmol) at 0 °C. The mixture was allowed to warm to room temperature, and stirring was continued overnight. The solvent was evaporated at reduced pressure, and the residue was extracted with Et$_2$O (50 mL) and centrifuged to remove a small amount of insoluble solid. After evaporation of Et$_2$O at reduced pressure, the residue was redissolved in THF (6 mL) and layered with hexane (80 mL) to afford crystalline **6** (1.25 g, 1.37 mmol, 44%). $\mu_{eff}$ = 3.57 $\mu_B$.

**X-ray Crystallography.** Compounds **1**, **2b**, **3**, **4**, and **6** consistently yielded crystals that diffracted weakly, and the results presented are the best of several trials. The crystals were 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° $\omega$-scans at 0°, 120°, and 240° in $\varphi$. Initial unit cell parameters were determined from 45 data frames collected at the different

sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[11] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic, $P2/c$ for **1**, **2b**, and **4**; monoclinic, $P2_1/n$ for **3**; triclinic, $P\bar{1}$ for **6**. Solutions 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 **2b**, **3**, **4**, and **6**. Vice versa, the molecule of **1** was located on a 2-fold axis. One symmetry-unique molecule of hexane was found in the lattice of **4**. All non-hydrogen atoms, except those of the hexane solvent molecule in **4**, were refined with anisotropic displacement coefficients. Hexane solvent molecule carbon atoms in **4** were refined isotropically. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library with the latest version used 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.

**Butadiene Polymerization.** The polymerizations were performed under exclusion of moisture and oxygen under a nitrogen atmosphere. The products were characterized by means of SEC (size exclusion chromatography), elemental analysis, NMR, and IR. The IR samples were prepared by using CS$_2$ as a swelling agent and using a 2- or 4-fold dissolution. $M_n$ and $M_w$ were determined by a universal calibration of SEC against a polystyrene standard. The ratio between the 1,4-*cis*, 1,4-*trans*, and 1,2-polydiene contents of the butadiene was determined by IR and $^{13}$C NMR spectroscopy. Polymerization experiments were carried out in a double-wall 2 L steel reactor, which was purged with nitrogen before the addition of organic solvent, metal complex, and cocatalyst at 50 °C. In a typical experiment, a solution of MAO cocatalyst (30.3 mmol) in either cyclohexane or toluene (500 mL) was treated with butadiene (54 g) and stirred for 1 h. The addition of a solution of the appropriate amount of catalyst (0.1 mmol) started the polymerization. The reaction mixture was quenched with methanol and stripped of the volatile components in vacuo, and the resulting polymer was dried in an air-circulating oven at 70 °C for at least 24 h until constant weight.

## Results and Discussion

The possibility of deprotonating the methyl groups attached to the two imino functions of 2,6-{[2,6-(i-

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

| 1 | 2b | 3 | 4 | 6 |
|---|---|---|---|---|
| Li(1)−N(1) = 2.104(4) | Nd(1)−Cl(1) = 2.7372(19) | Nd(1)−Br(1) = 2.8358(12) | Nd−N(1) = 2.316(5) | Nd−N(1) = 2.385(3) |
| Li(1)−O(1) = 2.114(12 | Nd(1)−Cl(2) = 2.720(2) | Nd(1)−N(1) = 2.332(6) | Nd−N(2) = 2.475(5) | Nd−N(2) = 2.515(3) |
| Li(1)−N(2) = 2.020(12) | Nd(1)−N(1) = 2.435(5) | Nd(1)−N(2) = 2.521(5) | Nd−N(3) = 2.321(5) | Nd−N(3) = 2.379(3) |
| C(1)−C(2) = 1.358(7) | Nd(1)−N(2) = 2.556(5) | Nd(1)−N(3) = 2.375(6) | Nd−O = 2.463(5) | Nd−Cl(1) = 2.8024(10) |
| C(2)−C(3) = 1.495(7) | Nd(1)−N(3) = 2.439(5) | Nd(1)−C(34) = 2.782(10) | Nd−C(34) = 2.432(7) | Nd−C(46) = 2.74(3) |
| C(3)−N(2) = 1.334(5) | Nd(1)−O(1) = 2.691(6) | Nd(1)−C(35) = 2.718(11) | C(1)−C(2) = 1.347(9) | Nd−O(1) = 2.584(2) |
| O(1)−LI(1)−N(2) = 180.000(1) | C(1)−C(2) = 1.362(10) | Nd(1)−C(36) = 2.671(10) | C(8)−C(9) = 1.337(8) | C(13)−C(14) = 1.364(5) |
| O(1)−Li(1)−N(1) = 102.1(3) | C(8)−C(9) = 1.351(11) | C(1)−C(2) = 1.365(11) | C(2)−C(3) = 1.492(9) | C(13)−C(15) = 1.492(5) |
| N(1)−Li(1)−N(2) = 77.9(3) | C(2)−C(3) = 1.481(10 | C(8)−C(9) = 1.332(12) | C(7)−C(8) = 1.486(9) | C(20)−C(21) = 1.353(5) |
| N(1)−Li(1)−N(1a) =155.9(6) | C(7)−C(8) = 1.470(9) | C(34)−C(35) = 1.32(2) | O−Nd−N(1) = 107.76(19) | C(19)−C(20) = 1.498(5) |
| | Cl(1)−Nd(1)−Cl(2) = 158.69(7) | C(35)−C(36) = 1.24(2) | O−Nd−N(2) = 156.09(19) | O(1)−Nd−N(1) = 90.11(9) |
| | Cl(1)−Nd(1)−N(1) = 92.92(14 | Br(1)−Nd(1)−N(1) = 101.75(15) | O−Nd−N(3) = 10.08(19) | O(1)−Nd−N(2) = 77.59(8) |
| | Cl(1)−Nd(1)−N(2) = 85.49(12) | Br(1)−Nd(1)−N(2) = 90.86(13) | O−Nd−C(34) = 102.7(2) | O(1)−Nd−N(3) = 93.68(9) |
| | Cl(1)−Nd(1)−N(3) = 94.27(14) | Br(1)−Nd(1)−N(3) = 98.32(16) | N(1)−Nd−N(2) = 64.96(19) | O(1)−Nd−Cl(1) = 79.21(6) |
| | Cl(1)−Nd(1)−O(1) = 82.72(15) | Br(1)−Nd(1)−C(36) = 132.6(3) | N(1)−Nd−N(3) = 126.6(2) | O(1)−Nd−C(46) = 159.0(5) |
| | Cl(1)−Nd(1)−O(2) = 78.12(15) | N(2)−Nd(1)−C(34) = 169.4(3) | N(1)−Nd−C(34) = 102.1(2) | O(1)−Nd−C(46) = 159.0(5) |
| | Cl(2)−Nd(1)−N(1) = 95.14(14) | N(1)−Nd(1)−N(3) = 124.1(2) | N(2)−Nd−N(3) = 65.06(19) | N(1)−Nd−N(2) = 65.01(9) |
| | Cl(2)−Nd(1)−N(2) = 115.77(13) | C(36)−Nd(1)−N(1) = 107.6(3) | N(2)−Nd−C(34) = 101.2(2) | N(1)−Nd−N(3) = 127.54(9) |
| | Cl(2)−Nd(1)−N(3) = 96.46(14) | C(36)−Nd(1)−N(2) = 135.4(3) | N(3)−Nd−C(34) = 104.7(2) | N(1)−Nd−C(46) = 91.2(7) |
| | Cl(2)−Nd(1)−O(1) = 78.12(15) | C(36)−Nd(1)−C(34) = 52.9(4) | C(1)−C(2)−C(3) = 120.4(7) | N(2)−Nd−N(3) = 64.90(9) |
| | Cl(2)−Nd(1)−O(2) = 78.76(16) | C(36)−Nd(1)−N(2) = 135.4(3) | | N(2)−Nd−C(46) = 121.6(5) |
| | N(1)−Nd(1)−N(2) = 64.48(18) | N(1)−Nd(1)−C(34) = 109.0(4) | | N(3)−Nd−C(46) = 102.0(6) |
| | N(1)−Nd(1)−N(3) = 127.25(19) | N(3)−Nd(1)−C(34) = 125.1(4) | | N(1)−Nd−Cl(1) = 119.57(7) |
| | N(1)−Nd(1)−O(1) = 86.5(2) | C(1)−C(2)−N(1) = 127.5(7) | | N(2)−Nd−Cl(1) = 156.39(7) |
| | N(1)−Nd(1)−O(2) = 146.7(2) | C(1)−C(2)−C(3) = 120.9(7) | | N(3)−Nd−Cl(1) = 112.51(7) |
| | N(2)−Nd(1)−N(3) = 64.14(17) | | | Cl(1)−Nd−C(46) = 82.0(5) |
| | N(2)−Nd(1)−O(1) = 148.03(18) | | | Nd−Cl−Li = 85.74(19) |
| | N(2−Nd(1)−O(2) = 147.35(19) | | | |
| | C(1)−C(2)−C(3) = 118.3(7) | | | |
| | C(2)−C(3)−N(2) = 116.0(6) | | | |
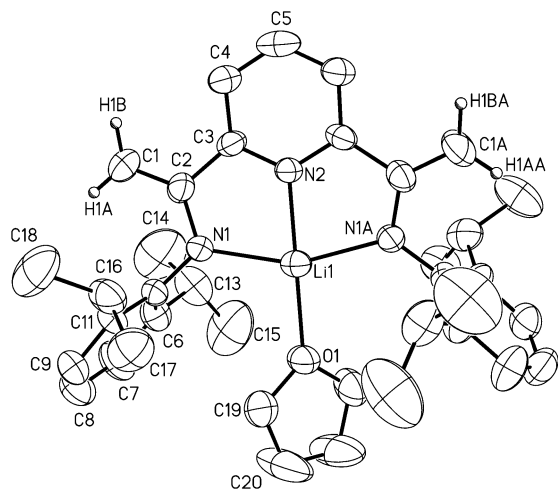
**Figure 1.** ORTEP plot of the anionic unit of **1** showing the thermal ellipsoids drawn at the 30% probability level.

**Scheme 1**



Ar = 2,6-(i-Pr)$_2$C$_6$H$_3$
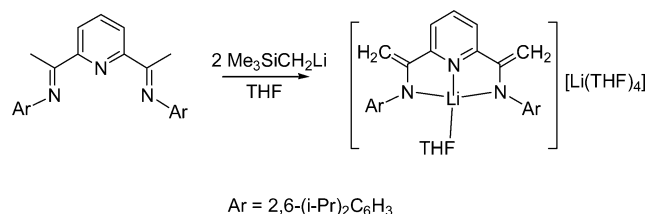
Pr)$_2$C$_6$H$_3$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N) was serendipitously discovered while attempting the alkylation of the diimine complex with MeLi.[3b] The reaction is rather complex since it proceeds via initial alkylation of the pyridine N atom followed by elimination of methane.[3a,b] In addition, the reaction is not suitable for the large-scale preparation of the corresponding monoanion given the modest yield and the formation of more than one product in the reaction mixture. However, a similar reaction carried out with 1 equiv of LiCH$_2$Si(CH$_3$)$_3$ in THF cleanly afforded the corresponding *dilithium* salt [{2,6-[(2,6-(i-Pr)$_2$Ph]N=C=(CH$_2$)}$_2$(C$_5$H$_3$N)]Li(THF)][Li(THF)$_4$] (**1**) where *both* methyl groups attached to the imine functions have been deprotonated (Scheme 1). The use of 2 equiv of the alkyllithium reagent gave the expected yield improvement (up to 72%). The formula and connectivity of **1** were provided by single-crystal diffraction data (Figure 1). Unfortunately, attempts to obtain a satisfactory data file for the crystal structure were always plagued by low-quality data, which resulted in high convergence values of the anisotropic refinement indices. Nonetheless, the data were sufficient to provide the connectivity. The structure shows an ionic arrangement comprising one tetrahedrally solvated lithium cation and one symmetry-generated anionic unit. The anionic unit is formed by one double-deprotonated ligand [C(1)−C(2) = 1.358(7) Å] surrounding a second Li cation [Li(1)−N(1) = 2.104(4) Å, Li(1)−N(2) = 2.020(12) Å]. The C−N bond distances [C(2)−N(1) = 1.366(7) Å] are substantially longer for a C−N double bond but shorter for a regular single bond. One molecule of THF completes the saddle-shaped coordination geometry of the Li cation [N(1)−Li(1)−N(1A) = 155.9(6)°, N(2)−Li(1)−O(1) = 180.00(1)°, N(1)−Li(1)−O(1) = 102.1(3)°, N(1)−Li(1)−N(2) = 77.9(3)°].
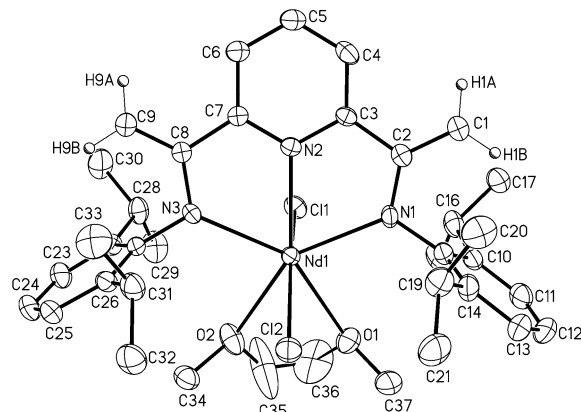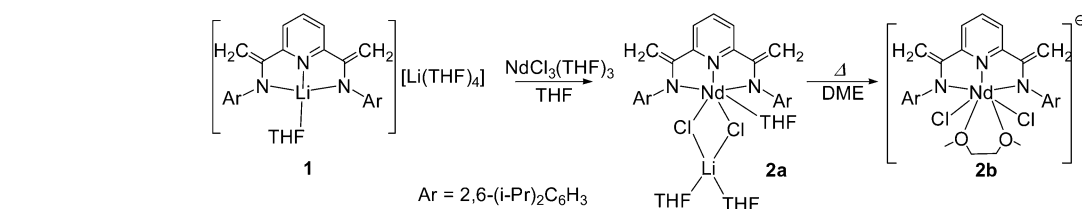
The NMR spectra feature the four isopropyl groups as two sets of methyl groups and only one set of methyne. This indicates the presence of a substantial magnetic anisotropy between the methyl groups pointing on the side of the =CH$_2$ groups and those pointing in the opposite direction. There was only one resonance present in the $^7$Li NMR spectrum ($\delta$ = 1.63 ppm), indicating a rapid exchange in solution between the two nonequivalent lithium atoms of the solid state structure (one coordinated to the ligand and the other solvated by four molecules of THF). The two ene-amido hydrogen atoms gave two slightly broad singlets at 3.41 and 4.05 ppm coupled to the same $^{13}$C resonance at 71.74 ppm of the $^1$H{$^{13}$C} HMQC spectrum.

The dianion **1** is closely reminiscent of the diketene-iminato benzene dianion reported by Burger.[12] It reacts readily at room temperature with NdCl$_3$(THF)$_3$ in THF to afford {2,6-[(2,6-(i-Pr)$_2$Ph)N-C=(CH$_2$)$_2$(C$_5$H$_3$N)}Nd-(THF)($\mu$-Cl)$_2$[Li(THF)$_2$]·0.5(hexane) (**2a**), which was isolated as a brown crystalline solid (Scheme 2). While the NMR spectra were uninformative due to the paramagnetism, simple recrystallization from DME afforded the DME-solvated analogue {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$(C$_5$H$_3$N)]NdCl$_2$(DME)}{Li(DME)$_3$} (**2b**), which produced crystals suitable for X-ray diffraction analysis.

The structure of **2b** is formed by one anionic unit containing the Nd atom and a cationic moiety consisting of a Li atom surrounded by three molecules of DME. The heptacoordination around the Nd metal in the anionic moiety (Figure 2) is defined by two chlorine atoms [Nd−Cl(1) = 2.720(2) Å, Nd−Cl(2) = 2.7372(19) Å] located *trans* to each other [Cl(1)−Nd−Cl(2) = 158.69(7)°], the three N atoms of the ligand [N(1)−Nd = 2.435(5) Å, N(2)−Nd = 2.556(5) Å, N(3)−Nd = 2.439-(5) Å], and the two oxygen atoms of one molecule of DME [Nd−O(2) = 2.715(6) Å, Nd−O(1) = 2.691(6) Å]. The overall geometry around the metal is distorted pentagonal bipyramidal with the equatorial plane defined by the three N atoms of the ligand and the two oxygen atoms of DME [N(1)−Nd(1)−N(2) = 64.48(18)°, N(3)−Nd(1)−N(2) = 64.14(17)°, N(1)−Nd(1)−O(1) = 86.5(2)°, N(3)−Nd(1)−O(2) = 86.05(19)°, O(1)−Nd(1)−O(2) = 60.2(2)°]. The two chlorine atoms are located above and below the molecular plane [N(1)−Nd(1)−Cl-(2) = 95.14(14)°, N(3)−Nd(1)−Cl(2) = 96.46(14)°, O(1)−Nd(1)−Cl(2) = 78.12(15)°, N(1)−Nd(1)−Cl(1) = 92.92-(14)°, N(3)−Nd(1)−Cl(1) = 94.27(14)°, O(1)−Nd(1)−Cl(1) = 82.72(15)°, O(2)−Nd(1)−Cl(1) = 83.68(15)°]. The two ene-amido groups display values for the C−C distances [C(1)−C(2) = 1.362(10) Å, C(8)−C(9) = 1.351(11) Å] as expected for conjugated double bonds and compare well with those of the other complexes reported in this work. Accordingly, the C−N bond distances [N(1)−C(2) = 1.380(9) Å, N(3)−C(8) = 1.395(9) Å] are also shorter than C−N single bonds, thus indicating the presence of a delocalized $\pi$-system along the CH$_2$−C−N framework. The Nd−N distances are slightly longer than those of other lanthanide complexes of chelating amide ligands,[13] possibly indicating that the bonding character is somewhat intermediate between Nd−N(amido) and Nd−N(imine).

Attempts to replace the two chlorine atoms on **2a** were unsuccessful. Its treatment with a variety of

(12) Nuckel, S.; Burger, P. *Organometallics* **2000**, *19*, 3305.

**Scheme 2**

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

**Figure 2.** ORTEP plot of the anionic unit of **2b** showing the thermal ellipsoids drawn at the 30% probability level.
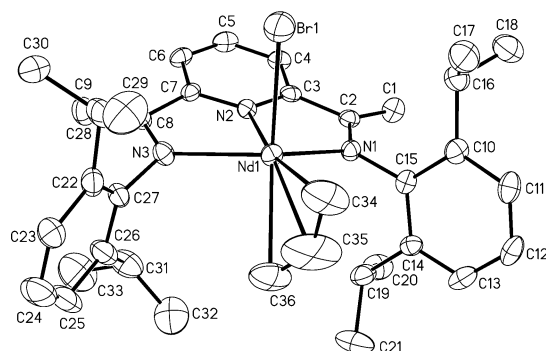
**Figure 3.** ORTEP plot of the anionic unit of **3** showing the thermal ellipsoids drawn at the 30% probability level.

alkylating agents, including several Grignard and organolithiums, unfortunately gave only intractable materials. Similarly disappointing behavior was observed for **2b**, with the only exception being the reaction with (allyl)MgBr. The resulting crystalline species was formulated as {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$(C$_5$H$_3$N)]-Nd($\eta^3$-C$_3$H$_5$)Br}{Li(DME)$_3$} (**3**). The crystal structure shows that the ionic arrangement was preserved during the allylation reaction, although a Li rather than the Mg counterion was retained in the structure. In addition, one of the two chlorine atoms of **2b** was replaced by the allyl group, while the second was surprisingly replaced by one bromine atom. The crystal structure (Figure 3) shows a severely distorted pseudo-octahedral arrangement around the Nd atom in the anionic moiety [N(1)−Nd−N(3) = 124.1(2)°, N(2)−Nd−C(34) = 169.4-(3)°, Br−Nd−C(36) = 132.6(3)°, Br−Nd−N(1) = 101.75-(15)°, Br−Nd−N(2) = 90.86(13)°, Br−Nd−N(3) = 98.32-(16)°]. The ligand displays the usual arrangement with the three N donor atom attachments [Nd−N(1) = 2.332-(6) Å, Nd−N(2) = 2.521(5) Å, Nd−N(3) = 2.375(6) Å] nearly coplanar with Nd. The fourth coordination site is occupied by one of the terminal carbon atoms of the allyl group. Orthogonally placed are the bromine atom

[Nd−Br = 2.8358(12) Å] and the second terminal carbon atom of the allyl group. Similar to the case of some other Nd-allyl derivatives,[14] the allyl group [C(34)−C(35)−C(36) = 144(2)°] displays an arrangement with respect to the Nd, which deviates from the classical $\eta^3$-bonding mode in the sense that the metal is nearly coplanar with the three carbon atoms rather than being placed on the axis perpendicular to the allyl plane. However, the central carbon atom shows rather large thermal parameters possibly indicative of some disorder, which could not be modeled. Thus, it is possible that the observed coplanar arrangement may in reality be an artifact of the disorder of the allyl groups over two skewed positions. However, even in the most favorable case, the deviation of the Nd atom from perpendicularity to the allyl plane remains substantial. The three allyl carbon atoms form bonding distances with the metal [Nd−C(34) = 2.782(10) Å, Nd−C(35) = 2.718(11) Å, Nd−C(36) = 2.671(10) Å] comparable to those of other Nd-allyl derivatives[14] and which, when combined with the C−C distances [C(34)−C(35) = 1.32(2) Å, C(35)−C(36) = 1.24-(2) Å], indicate a substantial contribution of a $\sigma,\pi$-$\eta^1$: $\eta^2$-bonding mode for the allyl group.[15] Similar to **2b**, the two ene-amido groups form C−C bond distances [C(1)−C(2) = 1.365(11) Å, C(8)−C(9) = 1.332(12) Å] in good agreement with the presence of a substantial C−C double-bond character. Overall, the ligand displays bond distances and angles comparable to those of complex **2b**, although the Nd−N distances are a little shorter. Similarly, an octahedrally solvated Li cation surrounded by three molecules of DME completes the structure of **3**.
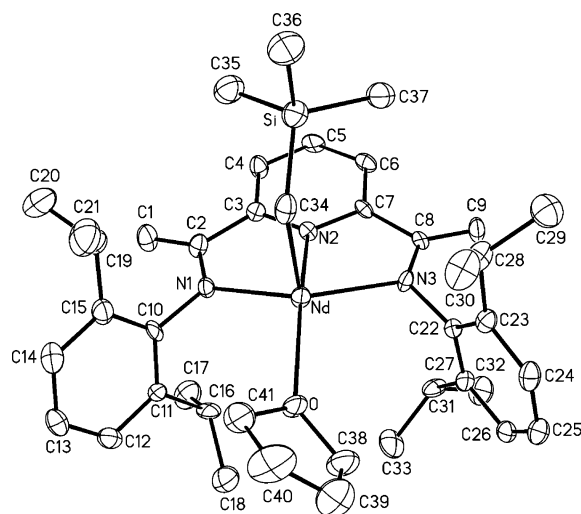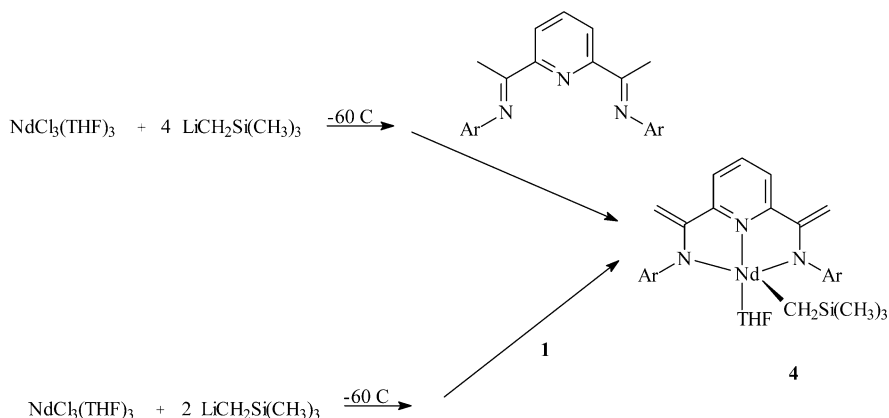
With the exception of the formation of **3**, complexes **2a,b** are generally not suitable starting materials for further alkylation reactions. Nevertheless, alkyl derivatives can still be prepared by modifying the synthetic pathway (Scheme 3). Namely, partial alkylation of NdCl$_3$(THF)$_3$ with RLi [R = Me$_3$SiCH$_2$, CH$_3$] followed by reaction with either the diimime or **1** (depending on the Nd/R ratio) enabled the synthesis of the neutral, halogen- and alkali cation-free compound [2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N-C=(CH$_2$)}$_2$(C$_5$H$_3$N)]Nd[CH$_2$Si(CH$_3$)$_3$]-(THF) (**4**). The coordination geometry around the Nd atom can be described as a severely distorted trigonal bipyramid. The equatorial plane is defined by two N donor atoms from the ligand [N(1)−Nd−N(3) = 126.6-

(13) See for example: (a) Graf, D. D.; Davis, W. M.; Schrock, R. R.; *Organometallics* **1998**, *17*, 5820. (b) Fryzuk, M. D.; Yu, P.; Patrick, B. O.; *Can. J. Chem.* **2001**, *79*, 1194. (c) Lee, L.; Berg, D. J.; Bushnell, G. W.; *Inorg. Chem.* **1994**, *33*, 5302.

(14) See for example: (a) Taube, R.; Maiwald, S.; Sieler, J. *J. Organomet. Chem.* **2001**, *621*, 327. (b) Wu, W.; Chen, M.; Zhou, P. *Organometallics* **1991**, *10*, 98,

(15) There are a few example of this type of bonding for allylic groups; see for example: (a) Perez, J.; Riera, V.; Rodriguez, A.; Garcia-Granda, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 1427. (b) Barbaro, P.; Currao, A.; Hermann, J.; Nesper, R.; Pregosin, P. S.; Salzmann, R. *Organometallics* **1996**, *15*, 1879. (c) Abbenhuis, H. C. L.; Burckhardt, U.; Gramlich, V.; Martelletti, A.; Spencer, J.; Steiner, I.; Togni, A. *Organometallics* **1996**, *15*, 1614.

**Scheme 3**

$$\text{NdCl}_3(\text{THF})_3 \quad + \quad 4 \text{ LiCH}_2\text{Si}(\text{CH}_3)_3 \quad \xrightarrow{-60 \text{ C}}$$

**1**

$$\text{NdCl}_3(\text{THF})_3 \quad + \quad 2 \text{ LiCH}_2\text{Si}(\text{CH}_3)_3 \quad \xrightarrow{-60 \text{ C}}$$

**4**



**Figure 4.** ORTEP plot of **4** showing the thermal ellipsoids drawn at the 30% probability level.

(2)°] and the C atom of the Me$_3$SiCH$_2$ group [N(1)−Nd−C(34) = 102.1(2)°, N(3)−Nd−C(34) = 104.7(2)°] (Figure 4), whereas the O atom of THF [Nd−O = 2.463(5) Å] and the N atom from the pyridine moiety of the ligand system [Nd−N(2) = 2.475(5) Å] are located in the two axial positions [O−Nd−N(2) = 156.09(19)°]. The plane of the ligand system is defined by the three N donor atoms [Nd−N(1) = 2.316(5) Å, Nd−N(3) = 2.321(5) Å] and is folded along the Nd−N(2) vector. The bond distances and angles of the ligand system compare well with those of the other compounds reported in this work [C(1)−C(2) = 1.347(9) Å, C(8)−C(9) = 1.337(8) Å, C(2)−C(3) = 1.492(9) Å, C(7)−C(8) = 1.486(9) Å]. The Nd−C distance [Nd−C(34) = 2.432(7) Å] also is in the expected range.

Neodymium alkyl derivatives are well-known to promote a range of catalytic processes. Allyl derivatives, in particular, are widely used as stereoselective butadiene polymerization catalysts.[16] However, complex **3** displayed only marginal activity as a butadiene polymerization initiator and similarly disappointing behavior was also observed for **4**. By contrast, complex **2a**

displays very good activity as a stereospecific butadiene polymerization catalyst. Addition of a solution of **2a** in cylohexane to a cyclohexane solution of butadiene containing excess MMAO at 50 °C started a polymerization affording *cis*-polybutadiene with 95−97% *cis* configuration in good yield (about 70%). Such high stereoselectivity of the polymerization reaction, in addition to the high catalyst activity, the high molecular weight, the relatively narrow polydispersity, and other desirable rheological properties, places this catalyst above other transition metal-based catalysts[17] but below the remarkably performing Cp*$_2$Sm.[18] The activity also is substantially higher with respect to that of NdCl$_3$-(THF)$_2$,[19] thus indicating that the ligand system is indeed beneficial to the catalytic behavior of the metal. While it is reasonable to expect that an in situ-generated Nd-C function is the polymerization initiator, attempts to form such a group via reaction of **2a** or **2b** with Me$_3$-Al (including in large excess) gave only intractable material. Furthermore, the use of more aggressive alkylating agents such as MeLi resulted only in complicated mixture. It is possible that, similar to the cases of V, Cr, and even Al, the ligand pyridine ring engages in complex ring alkylation and cycloaddition reactions.[4] By using the same synthetic protocol described for **4** (i.e., treatment of NdCl$_3$(THF)$_3$ with 4 equiv of MeLi followed by addition of the intact diimine ligand 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N) in lieu of treating **2a,b** with MeLi) it was possible to isolate a new species, formulated as {2,6-[(2,6-(i-Pr)$_2$Ph)N-C=(CH$_2$)]$_2$(C$_5$H$_3$N)}-Nd (THF)($\mu$-Me)$_2$[Li (THF)$_2$] (**5**). Complex **5** is also a potent polymerization catalyst while activated by alkyl aluminum derivatives. Although the activity was somewhat lower than **2a**, the molecular weight of the polymer produced by this organometallic complex was higher. The stereoselectivity decreased only slightly, while the overall yield of the polymer was disappointingly low. To date, attempts to isolate suitable crystals of complex **5** have failed. Nevertheless, support for

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(17) (a) Gehrke, K.; Harwart, M. *Plast. Kautsch.* **1993**, *40*, 356. (b) Anzai, S.; Irako, K.; Onishi, A.; Furukawa, J. *Kogyo Kagaku Zasshi* **1969**, *72*, 2081. (c) Kaita, S.; Kobayashi, E.; Sakikibara, S.; Aoshima, S.; Furukawa, J. *J. Polym Sci. Polym. Chem. Ed.* **1996**, *34*, 3431. (d) Oehme, A.; Gebauer, U.; Gehrke, K. *Macromol. Rapid Commun.* **1995**, *16*, 563. (e) Zambelli, A.; Proto, A.; Longo, P.; Oliva, P. *Macromol. Chem. Phys.* **1994**, *195*, 2623.

(18) (a) Kaita, S.; Hou, Z.; Wakatsuki, Y. M*acromolecules* **1999**, *32*, 9078. (b) Kaita, S.; Hou, Z.; Wakatsuki, Y. M*acromolecules* **2001**, *34*, 1539.

(19) Yang, J. H.; Tsutsui, M.; Chen, Z.; Bergbreiter, D. E. *Macromolecules* **1982**, *15*, 230.

**Table 3. Polymerization Results**[a]

| run | complex | activity | yield (%) | *cis*-1,4 | *trans*-1,4 | 1,2-PB | $M_w$ | $M_n$ | $M_z$ | $M_w/M_n$ |
|-----|---------|----------|-----------|-----------|-------------|--------|-------|-------|-------|-----------|
| 1 | **6** | 0.74 | 77.3 | 97.0 | 2.5 | 0.5 | 659 000 | 263 000 | 1 220 000 | 2.5 |
| 2 | **6** | 0.12(5) | 67.5 | 95.0 | 4.5 | 0.5 | 380 000 | 164 000 | 715 000 | 2.31 |
| 3 | **6** | 0.034(5) | 84.8 | 96.1 | 4.5 | 3.4 | 385 000 | 164 000 | 727 000 | 2.34 |
| 4 | **2a** | 0.71 | 78.6 | 97.0 | 2.3 | 0.7 | 725 000 | 262 000 | 1 440 000 | 2.8 |
| 5 | **5** | 0.40 | 17.2 | 95.9 | 3.3 | 0.8 | 910 000 | 155 000 | 2 200 000 | 4.9 |
| 6 | **4** | 0.08 | 75.0 | 61.8 | 36.4 | 1.8 | 96 000 | 44 000 | 235 000 | 2.18 |

[a] The activity is calculated from polymer samples taken from the reactor after 15 min run time for runs 1–3 and 5, after 10 min for run 4, and after 30 min for run 6. Activity is given as kg of polymer per mmol of catalyst/h. Runs 2 and 3 were performed in toluene rather than cyclohexane. In run 3 the order of addition of MMAO and Nd catalysts was inverted.
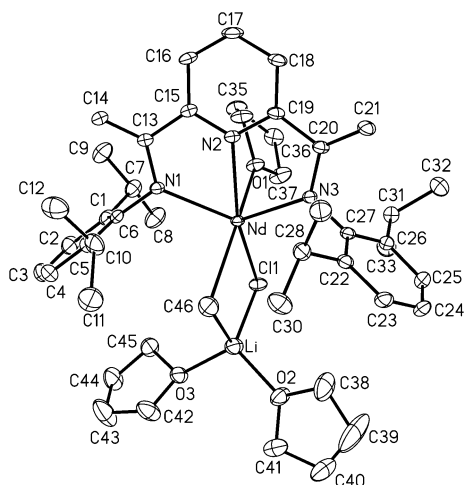


**Figure 5.** ORTEP plot of **6** showing the thermal ellipsoids drawn at the 30% probability level.

the formulation of **5**, as suggested by analytical data, was indirectly provided by the isolation and structural crystallographic determination of {[2,6-{[2,6-(i-Pr)₂-C₆H₃]N-C=(CH₂)}₂(C₅H₃N)]Nd}(μ-Cl)(μ-X)[Li(THF)₂] [X = Cl 53%, Me 47%] (**6**). This new species was prepared by following the same protocol adopted for **5** except for the use of a different stoichiometric ratio of Nd/MeLi. The rationale for attempting its preparation was simply to obtain a species in which one chlorine atom would be retained without substantial structural modification. It was hoped that the presence of the electron-withdrawing halogen could lead to improved catalytic activity, hopefully without the need of initiators, while still preserving the characteristics of **2** in terms of polymer quality.

The structure of **6** shows the species being a cocrystallite of **2a** and {[2,6-{[2,6-(i-Pr)₂C₆H₃]N-C=(CH₂)}₂-(C₅H₃N)]Nd}(μ-Cl)(μ-CH₃)[Li(THF)₂]. The anisotropic refinement of the thermal parameters clearly shows that one of the two bridging atoms between Nd and the Li(THF)₂ unit is a chlorine with 100% occupancy. Conversely, the second bridging atom could only be refined by arbitrarily attributing the 47% Me and 53% Cl occupancy. Figure 5 shows the structure of **6**. The coordination sphere around the metal is defined by the chlorine atom [Nd−Cl(1) = 2.8024(10) Å] and the partly occupied Me group [Nd−C(46) = 2.74(3) Å] located *cis* to each other [Cl(1)−Nd-C(46) = 82.0(5)°], the three N atoms of the ligand [N(1)−Nd = 2.385(3) Å, N(2)−Nd = 2.515(3) Å, N(3)−Nd = 2.379(3) Å], and the O atom of one molecule of THF [Nd−O(1) = 2.584(2) Å]. The chlorine and the methyl carbon atoms are also bridged to the same Li cation [Li−Cl(1) = 2.371(7) Å, Li−C(46) = 2.27(3) Å], which in turn is solvated by two molecules

of THF. The overall geometry around Nd is distorted octahedral [N(1)−Nd−N(3) = 127.54(9)°, N(2)−Nd−Cl-(1) = 156.39(7)°, O(1)−Nd−C(46) = 159.0(5)°]. The ligand system shows the usual arrangement where the pyridine ring is nearly coplanar with the two ene-amide functions, while the planes of the two bulky phenyl rings are oriented perpendicularly. The Nd−N and Nd−C bond distances do not show any particularly significant feature.

Complex **6** is an excellent polymerization catalyst for the preparation of *cis*-polybutadiene (Table 3) and has characteristics very similar to those of **2a**. This clearly indicates that partial alkylation is occurring during the treatment of **2a** with MMAO. Furthermore, the choice of solvent plays an important role in the polymerization reaction. Polymerizations carried out in toluene rather than in cyclohexane afforded substantially lower activity and produced polymers with significantly lower molecular weights. Such a marked effect of the solvent on the polymerization reaction, as well as the lack of catalytic activity of **5** and **6** in the absence of cocatalyst, can be taken as an indication (among other hypotheses) that one of the primary functions of the Lewis acidic cocatalyst is to dissociate the residual THF from the coordinatively saturated Nd atom. In other words, labile coordination of toluene might be a competitive process for the coordination of butadiene at the metal's empty coordination site, which is the preliminary step to trigger the polymerization. Finally, the high stereospecificity of the polymerization process and the linearity of the polymer strongly indicate that the coordination of butadiene occurs in a $\eta^4$ mode with a substantial participation of the Nd atom in a back-bonding interaction.

In conclusion, we have described the preparation of the dianion modification of the versatile diiminopyridine ligand and its use in the preparation of novel chloro and alkyl neodymium complexes, which were identified and characterized by standard techniques. The dilithium salt **1** and the neodymium complex **2b** and organometallic derivatives **3**, **4**, and **6** were characterized by single-crystal X-ray crystallography. Complexes **2a**, **5**, and **6** were found to be active precatalysts for stereoselective *cis*-butadiene polymerization.

**Supporting Information Available:** Complete crystallographic data (CIF) for all the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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