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Synthesis and structure of monomeric and solvent-free $LPrX_2$ compounds supported by a new β-diketiminato ligand [$L = Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$, X = Cl, Br, BH_4]

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

Trivalent praseodymium complexes with a new β-diketiminato ligand, possessing two pendant arms, $LPrX_2$, (X = Cl (**3**), Br (**4**), BH_4 (**5**)), have been prepared by the reactions of the lithium salt of the ligand with the corresponding halides. X-ray structural and elemental analysis showed that **3**, **4**, and **5** are neutral, monomeric and solvent-free complexes. These complexes adopt a pseudo-octahedral geometry with the two X (X = Cl, Br, BH_4) arranged in the *trans* positions.

Keywords: β-Diketiminato ligand; Lanthanide; Halides; Borohydride

1. Introduction

Nitrogen-based ligands for preparing lanthanide complexes have been used increasingly over the past few years [1–7]. A broad range of chemistry of lanthanide complexes and important applications have also been described [8–10]. Nevertheless, there are only a few lanthanide complexes known with monoanionic β-diketiminato ligands [9–12]. Our interest in the chemistry of diorganolanthanide complexes of general formula $LLnR_2$ stems from the potential use of these systems as novel olefin polymerization catalysts [13], and as β-diketiminato-based ligands [14–16]. This led us to prepare some new starting materials. Consequently, given the importance of a solvent-free and bifunctional compound such as $LLnX_2$ as precursor for the synthesis of dialkyllanthanide complexes, we designed and synthesized a new β-diketiminato ligand with two pendant donor arms, which proved to be suitable for our purpose.

Herein, we report the synthesis of the ligand $L = Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$ (**2**–H) and the preparation of $LPrX_2$, (X = Cl (**3**), Br (**4**), BH_4 (**5**)), derivatives. To the best of our knowledge, we obtained and characterized the first nonmetallocene, neutral, monomeric and solvent-free lanthanide compounds ($LLnCl_2$, $LLnBr_2$ and $LLn(BH_4)_2$) by X-ray structural analysis. Moreover, we demonstrated that $LLnCl_2$ could be used in metathesis reaction with $NaBH_4$.

2. Results and discussion

2.1. Synthesis of LH (2)

LH was prepared in a two-step synthesis as shown in Scheme 1.

Acetylacetone reacted with *N*,*N*-diethyl(ethylenediamine) in 1:1 molar ratio giving **1** in a very high yield.

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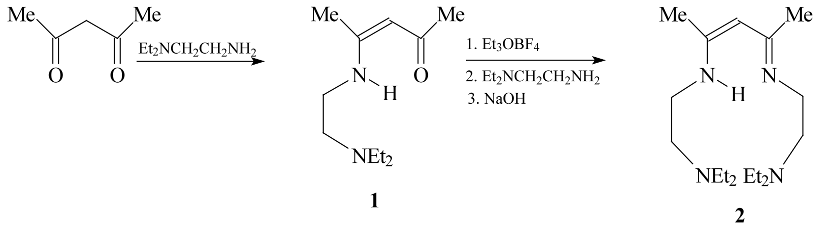

Scheme 1.

Compound **1** is the intermediary step for the preparation of **2**.

Treatment of **1** with Meerwein salt, $[Et_3O]BF_4$, in dichloromethane followed by *N*,*N*-diethyl(ethylenediamine) and NaOH afforded **2** in 52% yield. Compound **2** is a yellow oil at room temperature and soluble in any common organic solvent. It can be easily transformed into its lithium salt with LiMe (Eq. (1)), but attempts to solidify or to crystallize the LiL were unsuccessful. Therefore, every time when LiL was needed, it was prepared prior to use, and it was used without any further purification.

$$\underset{\mathbf{2}}{\mathrm{LH}} + \mathrm{LiMe} \xrightarrow[-\mathrm{CH_4}]{} \mathrm{LiL} \qquad (1)$$

2.2. Synthesis of $LPrX_2$, (X = Cl (3), Br (4), BH_4 (5))

Treatment of LiL with an equivalent amount of either anhydrous $PrCl_3$ or anhydrous $PrBr_3$ in toluene at refluxing temperature afforded $LPrX_2$ (X = Cl, Br), in good yields (Eq. (2)).

$$\mathrm{LiL} + \mathrm{PrX_3} \xrightarrow[-\mathrm{LiX}]{} \mathrm{LPrX_2} \quad \mathrm{X} = \mathrm{Cl}\,(\mathbf{3}), \mathrm{Br}\,(\mathbf{4}) \qquad (2)$$

Reaction of $LPrCl_2$ with an excess of $NaBH_4$ (1:3) in toluene under reflux afforded compound **5** (Eq. (3)) in moderate yield.

$$\mathrm{LPrCl_2} + 2\mathrm{NaBH_4} \xrightarrow[-2\mathrm{NaCl}]{} \underset{\mathbf{5}}{\mathrm{LPr(BH_4)_2}} \qquad (3)$$

It has to be noticed that compounds **3** and **4** were prepared using the anhydrous salts, not the THF adducts. Compounds **3**, **4**, and **5** are well soluble in toluene, acetonitrile and THF. These complexes are thermally very stable, their melting points are in the range of 142–188 °C. Mass spectroscopy and elemental analysis showed that compounds **3**, **4**, and **5** are monomeric, solvent-free compounds, and contain no lithium halides. The monomeric structures of **3**, **4**, and **5** were confirmed by the single-crystal X-ray structural analysis. A ^1H-NMR resonance was not observed in every case due to the paramagnetic nature of the praseodymium. Compound **5** exhibits a ^{11}B-NMR spectrum that showed one sharp resonance at room temperature. This suggests that there is either a rapid exchange of the BH_4 groups on the NMR timescale, or both BH_4 groups are equivalent. A temperature-dependent NMR spectrum indicated that both BH_4 groups are equivalent in solution. Moreover, any coupling between ^{11}B and ^1H nuclei was not observed in the ^{11}B-NMR spectrum.

2.3. X-ray structural analysis of $LPrX_2$ (X = Cl (3), Br (4) and BH_4 (5))

Single crystals of **3** and **4** suitable for X-ray structural analysis were obtained by recrystallization from toluene, while single crystals of **5** were formed when the solvent was slowly removed in vacuo. Compounds **3**, **4**, and **5** crystallize in the monoclinic $P2_1/c$ space group. X-ray structural analysis revealed that compounds **3**, **4**, and **5** are monomeric in the solid state. The X-ray crystal structure of **4** resembles that of **3**, therefore, only the X-ray crystal structure of **3** is given (Fig. 1). The crystal structure of **5** is given in Fig. 2.

Selected bond distances and angles for compounds **3**, **4**, and **5** are listed in Table 1. In all compounds, both pendant arms are coordinated to the metal center and all four nitrogen atoms and the praseodymium atom are in the same plane. Moreover, for compound **4**, the praseodymium atom is arranged in the plane of the

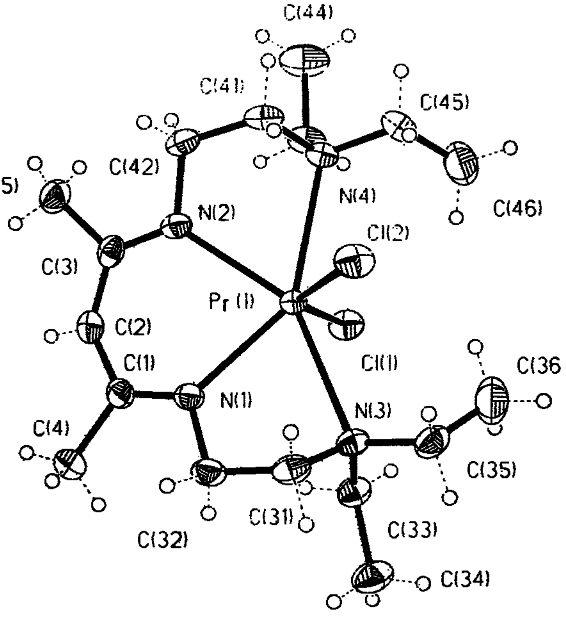

Fig. 1. Perspective view of molecule 3 in the crystal.

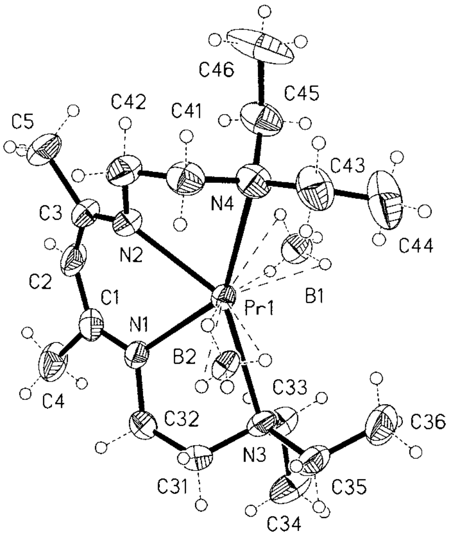

Fig. 2. Perspective view of molecule **5** in the crystal.

Table 1
Selected bond lengths (Å) and bond angles (°) for **3**, **4**, and **5**

X	3	4	5
Bond lengths			
Pr(1)–N(2)	2.442(2)	2.462(2)	2.421(4)
Pr(1)–N(1)	2.448(2)	2.455(2)	2.430(4)
Pr(1)–N(3)	2.692(2)	2.688(2)	2.739(4)
Pr(1)–N(4)	2.694(2)	2.682(2)	2.749(5)
Pr(1)–X(1)	2.6836(7)	2.852(1)	2.644(8)
Pr(1)–X(2)	2.6903(7)	2.868(1)	2.824(5)
Bond angles			
N(2)–Pr(1)–N(1)	75.79(8)	77.18(7)	76.66(14)
N(2)–Pr(1)–N(4)	67.81(7)	69.89(7)	67.17(15)
Pr(1)–N(1)–C(1)	126.3(2)	130.45(17)	124.7(4)
N(1)–C(1)–C(2)	123.9(2)	125.3(2)	124.2(5)
C(1)–C(2)–C(3)	130.6(3)	131.4(2)	130.8(5)
C(2)–C(3)–N(2)	124.5(3)	125.2(2)	124.2(5)
C(3)–N(2)–Pr(1)	125.6(2)	130.32(17)	122.9(4)
N(3)–Pr(1)–N(4)	145.95(7)	144.47(6)	146.08(14)
N(1)–Pr(1)–N(3)	69.26(8)	70.31(7)	68.57(14)
X(1)–Pr(1)–X(2)	136.42(3)	137.080(12)	144.1(2)

ligand framework, C_3N_2 (see Table 1). For compounds **3** and **5**, the praseodymium atom is positioned slightly out of this plane. The coordination number at the praseodymium atom in **3** and **4** is six and the geometry around the metal atom is pseudo-octahedral.

The Pr–N bond lengths of the pendant arm are longer than those of the backbone, due to the coordinative and covalent character involved in different bonding modes. The Pr–X (X = Cl, Br) bond length is similar to those found in the literature (X = Cl, 2.896, 2.872 Å) [6,17–20], (X = Br, 2.877, 2.897 Å) [19,20]. The coordination number of the praseodymium atom in **5** is 10. Each BH_4 group is coordinated via three hydrogen atoms to the praseodymium atom. The Pr–B bond lengths are different (Table 1). However, they are in the range of the previously reported Pr–B bond lengths of related compounds (2.757 Å) [21].

2.4. Conclusions

Herein, we have shown that compounds with the general formula $LLnX_2$ are easily available when β-diketiminato-based ligands, and metals in the +3 oxidation state are used. However, the metathesis to yield $LLnR_2$ compounds is one of the important challenges in this field. Compounds $LLnR_2$ resemble those of the well-known catalysts of the titanium congeners. Up to this date, only aryl [10,11], or alkyl [12,13] groups without donor functions were used as substituents at the nitrogen atoms of the β-diketiminato backbone in lanthanide chemistry. Thus, in order to increase their thermodynamic stability, we designed and obtained a ligand that contains two pendant arms on the nitrogen atoms, instead. This results in additional chelates, formed around the metal atom to yield monomeric and solvent-free complexes.

3. Experimental

All operations involving air- and moisture-sensitive compounds were performed using standard Schlenk line and dry box techniques under purified nitrogen atmosphere. Toluene, Et_2O, pentane, and CH_2Cl_2 were dried from appropriate drying agents (Na/K alloy (toluene, pentane), Na/benzophenone (Et_2O), CaH_2 (CH_2Cl_2)) and distilled under nitrogen prior to use. Benzene and hexane were used as received. *N*,*N*-diethyl(ethylenediamine) and water-free $PrCl_3$ were purchased from Aldrich and were used as received. Acetylacetone was distilled prior to use. $[Et_3O]BF_4$ was prepared as described in the literature and used as solution in CH_2Cl_2 [22]. C_6D_6 and C_7H_8 were dried over Na/K alloy and degassed. ^1H-, ^{13}C- and ^{11}B-NMR spectra were recorded using Bruker AM 200. Chemical shifts are reported in δ units downfield from Me_4Si with the solvent as the reference signal. Mass spectra were recorded using a Finnigan MAT 8230 instrument, and elemental analyses were carried out at the Analytical Laboratories of the Institute of Inorganic Chemistry of the University of Göttingen. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected.

*3.1. Preparation of LH (**2**)*

*3.1.1. Preparation of **1***

In a 500 ml round-bottomed flask equipped with a condenser, 29.3 g (0.29 mol) of acetylacetone and 34 g (0.29 mol) of *N*,*N*-diethylenediamine in 250 ml of benzene were refluxed for 2 days. Consequently, the solvent was removed and **1** distilled, as yellowish oil under dynamic vacuum (4.2 mbar). Yield 54.7 g (95%). ^{1}H-NMR (C_6D_6, 200 MHz): δ 11.1 (s, 1H), 4.86 (s, 1H), 2.8 (q, 2H, $J = 5$ Hz), 2.2 (m, 6H), 1.97 (s, 3H), 1.51 (s, 3H), 0.86 (t, 6H, $J = 7$ Hz). ^{13}C-NMR (C_6D_6, 125 MHz): δ 193.71, 161.54, 95.19, 53.19, 47.55, 41.80, 28.90, 18.70, 12.37. Anal. Found: C, 66.53; H, 11.21; N, 14.59. Calc. for $C_{11}H_{22}N_2O$: C, 66.62; H, 11.18; N, 14.13%. EIMS; *m/z* (relative intensity): 198 ([M$^+$], 4), 112 ([M$^+$ − $C_5H_{12}N$], 2), 86 ([$C_5H_{12}N$], 100).

3.1.2. Preparation of **2**

A 500 ml Schlenk flask topped with a 100 ml addition funnel was charged with 30 g (0.15 mol) of **1** in dry CH_2Cl_2 (150 ml). A solution of $[Et_3O]BF_4$ (54.1 g, 53.2%) in CH_2Cl_2 was transferred by a cannula to the addition funnel and was added dropwise to the stirring reaction mixture over a period of 1 h. Then, the reaction was allowed to proceed for one additional hour at room temperature (r.t.). Consequently, 17.58 g of *N*,*N*-diethylenediamine in 50 ml CH_2Cl_2 was syringed into the reaction mixture over a period of 30 min. Furthermore, stirring was continued overnight to ensure complete reaction. The solvent was removed and 6.05 g (0.15 mol) of NaOH in water (150 ml) and hexane (250 ml) was added. Using a separating funnel, the organic part was separated, washed with water (150 ml), dried over $MgSO_4$, concentrated and distilled under dynamic vacuum (4.2 mbar) to give **2** as yellow oil. Yield 23.3 g (52%). ^{1}H-NMR (C_6D_6, 200 MHz): δ 11.3 (s, 1H), 4.55 (s, 1H), 3.28 (t, 4H, $J = 6.7$ Hz), 2.63 (t, 4H, $J = 6.7$ Hz), 2.45 (q, 8H, $J = 7$ Hz), 1.73 (s, 6H), 0.97 (t, 12H, $J = 7.1$ Hz). ^{13}C-NMR (C_6D_6): δ 159.78, 95.04, 55.07, 47.84, 45.97, 19.44, 12.59. Anal. Found: C, 68.82; H, 12.23; N, 19.58. Calc. for $C_{17}H_{36}N_4$: C, 68.87; H, 12.24; N, 18.90%. EIMS; *m/z* (relative intensity): 296 ([M$^+$], 7), 210 ([M$^+$ − $C_5H_{12}N$], 36), 114 ([$C_6H_{14}N_2$], 100), 86 ([$C_5H_{12}N$], 78).

3.2. Preparation of **3**

Dry Et_2O (50 ml) was added to 3.0 g (10.1 mmol) of **2** in a 100 ml Schlenk flask. The mixture was cooled to − 78 °C and a solution of 6.32 ml (1.6 M, 10.1 mmol) LiMe in Et_2O was added dropwise. The reaction was stirred for 2 h at − 78 °C, and then stirred overnight at r.t. till the methane evolution had ceased. The solvent was removed and toluene (30 ml) was added. Finally, the solution was added dropwise to a suspension of 2.50 g (10.1 mmol) $PrCl_3$ in toluene (30 ml) in a 100 ml Schlenk flask. Then, the reaction mixture was refluxed overnight. The suspension was filtered, concentrated until crystals are formed. Finally, the resulting solution was warmed and it was left undisturbed for several hours at r.t. The large yellow crystals that formed were separated by filtration, washed with pentane (50 ml), and dried in vacuo. Yield 7.61 g (88.2%). M.p. 164 °C. Anal. Found: C, 40.53; H, 6.95; N, 11.04. Calc. for $C_{17}H_{35}Cl_2N_4Pr$: C, 40.25; H, 6.95; N, 11.04%. EIMS; *m/z* (relative intensity): 506 ([M$^+$], 12), 471 ([M$^+$ − Cl], 7), 420 ([M$^+$, − $C_5H_{12}N$], 100).

3.3. Preparation of **4**

Compound **4** was obtained by a method analogous to the preparation of **3**. Dry Et_2O (20 ml) was added to 0.58 g (1.98 mmol) of **2** in a 25 ml Schlenk flask. The mixture was cooled to − 78 °C and a solution of 1.3 ml (1.6 M, 2 mmol) LiMe in Et_2O was added dropwise. The reaction was stirred for 2 h at − 78 °C and then stirred overnight at r.t. Then, the volatiles were removed in vacuo and toluene (15 ml) was added. This solution was added dropwise to a suspension of 0.75 g (1.98 mmol) $PrBr_3$ in toluene (20 ml). Finally, the reaction mixture was refluxed overnight. The suspension was filtered, concentrated until crystals were formed. The resulting solution was warmed and it was left undisturbed for several hours at − 26 °C. The yellow crystals that formed were recovered by filtration, washed with pentane, and dried in vacuo. Yield 0.89 g (75.4%). M.p. 188 °C. Anal. Found: C, 34.25; H, 5.93; N, 8.86. Calc. for $C_{17}H_{35}Br_2N_4Pr$: C, 34.25; H, 5.92; N, 9.40%. EIMS; *m/z* (relative intensity): 596 ([M$^+$], 5), 515 ([M$^+$ − Br], 3), 510 ([M$^+$ − $C_5H_{12}N$], 30), 86 ([$C_5H_{12}N$], 100).

3.4. Preparation of **5**

A mixture of 0.5 g (0.98 mmol) **3** and 0.112 g (2.96 mmol) $NaBH_4$ in a 50 ml Schlenk flask equipped with a condenser was refluxed in toluene (35 ml) overnight. The suspension was filtered. The resulting clear solution was concentrated under reduced pressure to obtain yellow crystals of **5**, which were collected by filtration and washed with pentane (10 ml). Yield 0.31 g (68%). M.p. 142 °C. ^{11}B-NMR (C_7D_8/ext. $BF_3 \cdot OR_2$, 25 °C): δ 67.2 (s). Anal. Found: C, 43.56; H, 9.08; N, 11.47. Calc. for $C_{17}H_{43}B_2N_4Pr$: C, 43.81; H, 9.30; N, 12.02%. EIMS; *m/z* (relative intensity): 466 ([M$^+$], 4), 451 ([M$^+$ − BH_4], 76), 366 ([M$^+$ − ($C_5H_{12}N$ + BH_3)], 100).

4. X-ray crystallography

Data for crystal structures of **3** and **5** were collected on a Stoe–Siemens four-circle diffractometer, and data for the crystal structure of **4** were collected on a Stoe image plate IPDS II-system.

All structures were solved by direct methods (SHELXS-97) and refined against F^2 using SHELXS-97 [23]. The heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model

Table 2
Crystal data and structure refinement parameters for compounds **3**, **4**, and **5**

	3	**4**	**5**
Empirical formula	$C_{17}H_{35}Cl_2N_4Pr$	$C_{17}H_{35}Br_2N_4Pr$	$C_{17}H_{43}B_2N_4Pr$
Formula weight	507.30	596.22	466.08
Temperature (°C)	−70	−140	−73
Wavelength (Å)	0.71073	0.71073	0.71073
Color	Yellow	Yellow	Yellow
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	11.865(2)	10.8486(18)	11.9164(12)
b (Å)	11.5807(10)	7.9520(9)	12.4611(16)
c (Å)	16.085(3)	25.792(5)	15.949(3)
α (°)	90	90	90
β (°)	95.86(2)	90.898(15)	96.843(13)
γ (°)	90	90	90
V (Å^3)	2198.6(6)	2224.7(6)	2351.4(6)
Z	4	4	4
D_{calc} (g cm^{-3})	1.533	1.780	1.317
Absorption coefficient (mm^{-1})	2.466	5.789	2.078
Crystal size (mm)	0.90 × 0.50 × 0.50	0.50 × 0.60 × 0.50	0.60 × 0.50 × 0.30
Theta range for data collection (°)	3.52–25.04	1.88–24.80	3.51–22.51
Index ranges	$-14 \leq h \leq 14$, $-12 \leq k \leq 13$, $-17 \leq l \leq 19$	$-12 \leq h \leq 12$, $-8 \leq k \leq 9$, $-30 \leq l \leq 30$	$-12 \leq h \leq 12$, $-11 \leq k \leq 13$, $-15 \leq l \leq 17$
Reflections collected/unique	4804	43 720/3806	3680
Reflections observed [$I > 2\sigma(I)$]	3891 [$R_{int} = 0.0300$]	3560 [$R_{int} = 0.0794$]	3680 [$R_{int} = 0.0384$]
Data/restraints/parameters	3889/0/224	3806/0/223	3062/396/247
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0215$, $wR_2 = 0.0561$	$R_1 = 0.0182$, $wR_2 = 0.0451$	$R_1 = 0.0342$, $wR_2 = 0.0826$
R indices (all data)	$R_1 = 0.0222$, $wR_2 = 0.0579$	$R_1 = 0.0202$, $wR_2 = 0.0458$	$R_1 = 0.0421$, $wR_2 = 0.0880$
Goodness-of-fit on F^2	1.158	1.071	1.059
Largest difference peak and hole (e Å^{-3})	1.145 and −0.712	0.718 and −1.039	0.859 and −1.029

with U_{iso} tied to U_{iso} of the parent atoms. Crystal data collection details, and the solution and refinement procedures are summarized in Table 2.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 164078, 163836, and 164079 for compounds **3**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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