*Inorg. Chem.* **2006**, *45*, 910–916

Inorganic Chemistry

Article

# Yttrium and Lanthanide Complexes Having a Chiral Phosphanylamide in the Coordination Sphere

**Tarun K. Panda, Michael T. Gamer, and Peter W. Roesky***

*Institut für Chemie und Biochemie, Freie Universität Berlin,*
*Fabeckstrasse 34-36, 14195 Berlin, Germany*

Received September 15, 2005

The chiral phosphanylamides $\{N(R\text{-}^*CHMePh)(PPh_2)\}^-$ and $\{N(S\text{-}^*CHMePh)(PPh_2)\}^-$ were introduced into rare earth chemistry. Transmetalation of the enantiomeric pure lithium compounds $Li\{N(R\text{-}^*CHMePh)(PPh_2)\}$ (**1a**) and $Li\{N(S\text{-}^*CHMePh)(PPh_2)\}$ (**1b**) with lanthanide bis(phosphinimino)methanide dichloride $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$ in a 2:1 molar ratio in THF afforded the enantiomeric pure complexes $[\{CH(PPh_2NSiMe_3)_2\}Ln(Cl)\{\eta^2\text{-}N(R\text{-}^*CHMePh)(PPh_2)\}]$ (Ln = Er (**2a**), Yb (**3a**), Lu (**4a**)) and $[\{CH(PPh_2NSiMe_3)_2\}Ln(Cl)\{\eta^2\text{-}N(S\text{-}^*CHMePh)(PPh_2)\}]$ (Ln = Er (**2b**), Yb (**3b**), Lu (**4b**)). The solid-state structures of **2a** and **3a**,**b** were established by single-crystal X-ray diffraction. Attempts to synthesize compounds **3** in a one-pot reaction starting from $K\{CH(PPh_2NSiMe_3)_2\}$, $YbCl_3$, and **1** resulted in the lithium chloride incorporated complex $[\{(Me_3SiNPPh_2)_2CH\}Yb(\mu\text{-}Cl)_2LiCl(THF)_2]$ (**5**). In an alternative approach to give chiral rare earth compounds in a one-pot reaction **1a** or **1b** was reacted with $LnCl_3$ and $K_2C_8H_8$ to give the enantiomeric pure cyclooctatetraene compounds $[\{\eta^2\text{-}N(R\text{-}^*CHMePh)(PPh_2)\}Ln(\eta^8\text{-}C_8H_8)]$ (Ln = Y (**6a**), Er (**7a**), Yb (**8**)) and $[\{\eta^2\text{-}N(S\text{-}^*CHMePh)(PPh_2)\}Ln(\eta^8\text{-}C_8H_8)]$ (Ln = Y (**6b**), Er (**7b**)). The structures of **6a**,**b**, **7a**, and **8** were confirmed by single-crystal X-ray diffraction in the solid state.

## Introduction

Numerous families of chiral phosphorus ligands have been synthesized over the years, and their coordination chemistry on various metals is widely studied.[1] In homogeneous catalysis usually bidentate phosphine ligands especially those having $C_2$ symmetry have been employed. In most cases the stereogenic centers are chiral phosphorus atoms or phosphines with chiral hydrocarbon substituents as derivative of the chiral pool. The third widely used method is the use of axial chirality in ligands such as BINAP.[2] The synthesis and limited use of heteroatom-substituted phosphines and their transition metal complexes have received some attention lately as a result of the search for new structural diversity.[3] However little has appeared on the use of chiral amines as backbone for chiral phosphorus ligands.[4] These chiral P,N ligands, which usually coordinate via the phosphorus atom to the center metal, were basically used in late transition metal chemistry.[5,6,7,8] We have been working for some time with P,N compounds such as amido (e.g. $(Ph_2P)_2N^-$)[9] or imido ($(Me_3SiNPPh_2)CH^-$) ligands[10,11] in early transition metal and lanthanide chemistry. These kinds of ligands always coordinate via the nitrogen atom and only sometimes via the phosphorus onto the metal center. Very recently we

---

* To whom correspondence should be addressed. E-mail: roesky@chemie.fu-berlin.de.

(1) For recent review on chiral phosphorous ligands, see: Tand, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029−3069.

(2) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; p 1235.

(3) (a) Balakrishna, M. S.; Reddy, V. S.; Krishnamurthy, S. S.; Burckett St. Laurent, J. C. T. R. *Coord. Chem. Rev.* **1994**, *129*, 1−90 and references therein. (b) M. Rodriguez i Zubiri, M.; Clarke, M. L.; Foster, D. F.; Cole-Hamilton, D. J.; Slawin A. M. Z.; Woollins, J. *J. Chem. Soc., Dalton Trans.* **2001**, 969−971. (c) Slawin, A. M. Z.; Wainwright M.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2002**, 513−519. (d) Magee, M. P.; Li, H.-Q.; Morgan O.; Hersh, W. H. *Dalton Trans.* **2003**, 387−394.

(4) Zijp, E. J.; van der Vlugt, J. I.; Tooke, D. M.; Spek, A. L.; Vogt, D. *Dalton Trans.* **2005**, 512−517.

(5) (a) Brunner, H.; Gastinger, R. G. *J. Organomet. Chem.* **1978**, *145*, 365−373. (b) Brunner, H.; G. O. Nelson *J. Organomet. Chem.* **1979**, *173*, 389−395. (c) Frauendorfer, E.; Brunner, H. *J. Organomet. Chem.* **1982**, *240*, 371−379.

(6) (a) Fiorini, M.; Giongo, G. M.; Marcati, F.; Marconi, W. *J. Mol. Catal.* **1976**, *1*, 451−453. (b) Fiorini, M.; Marcati, F.; Giongo, G. M. *J. Mol. Catal.* **1978**, *4*, 125−134. (c) Fiorini M.; Giongo, G. M. *J. Mol. Catal.* **1979**, *5*, 303−310.

(7) Guo, R.; Li, X.; Wu, J.; Kwok, W. H.; Chen, J.; Choi, M. C. K.; Chan, A. S. C. *Tetrahedron Lett.* **2002**, *43*, 6803−6806.

(8) Ansell, J.; Wills, M. *Chem. Soc. Rev.* **2002**, *31*, 259−268 and references therein.

(9) (a) Roesky, P. W.; Gamer, M. T.; Puchner, M.; Greiner, A. *Chem.—Eur. J.* **2002**, *8*, 5265−5271. (b) Roesky, P. W.; Gamer, M. T.; Marinos, N. *Chem. Eur. J.* **2004**, *10*, 3537−3542. (c) Gamer, M. T.; Roesky, P. W. *Inorg. Chem.* **2004**, *43*, 4903−4906.

(10) Gamer, M. T.; Dehnen S.; Roesky, P. W. *Organometallics* **2001**, *20*, 4230−4236.

10.1021/ic051584e CCC: $33.50

introduced both enantiomers of a chiral phosphanylamide, $\{N(R\text{-*}CHMePh)(PPh_2)\}^-$ and $\{N(S\text{-*}CHMePh)(PPh_2)\}^-$, into zirconium chemistry.[12] The amido ligands were obtained by deprotonation of the corresponding amines $HN(R\text{-*}CHMePh)(PPh_2)$ and $HN(S\text{-*}CHMePh)(PPh_2)$, respectively. The latter were originally introduced by Brunner into coordination chemistry of the late transition metals.[5]

Herein we report on the coordination chemistry of both enantiomers of the chiral phosphanylamide $\{N(\text{*}CHMePh)(PPh_2)\}^-$ in group 3 and lanthanide chemistry. As coligands, cyclooctatetraene and the bis(phosphinimino)methanide, $(Me_3SiNPPh_2)CH^-$,[13] were used.

## Experimental Section

**General Methods.** All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high-vacuum ($10^{-4}$ Torr) line, or in an argon-filled M. Braun glovebox. Ether solvents (tetrahydrofuran and ethyl ether) were predried over Na wire and distilled under nitrogen from K (THF) or Na wire (ethyl ether) benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid ($^{31}P$ NMR), respectively. Elemental analyses were carried out with an Elementar vario EL. $LnCl_3$,[14] $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$,[10] $K\{CH(PPh_2NSiMe_3)_2\}$,[13] $Li\{N(R\text{-*}CHMePh)(PPh_2)\}$ (**1a**),[12] and $Li\{N(S\text{-*}CHMePh)(PPh_2)\}$ (**1b**)[12] were prepared according to literature procedures.

**$[\{(Me_3SiNPPh_2)_2CH\}Ln(Cl)\{N(R\text{-*}CHMePh)(PPh_2)\}]$ (Ln = Er (2a), Yb (3a), Lu (4a)) and $[\{(Me_3SiNPPh_2)_2CH\}Ln(Cl)\{N(S\text{-*}CHMePh)(PPh_2)\}]$ (Ln = Er (2b), Yb (3b), Lu (4b)).** A 0.5 mmol amount of $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$ was mixed with 156 mg (0.5 mmol) of **1** under argon atmosphere. A 15 mL volume of THF was condensed onto it. The reaction solution was allowed to come at room temperature and kept under stirring for 24 h. THF was evaporated under vacuo, and the residue was dissolved in 15 mL of toluene and filtered. Toluene was removed, and the compound was washed with 10 mL of pentane. Finally title compounds were crystallized from THF/pentane (1:3).

**Ln = Er.** Yields: **2a**, 240 mg (45%), and **2b**, 235 mg (44%) (pink crystals). IR (KBr, $cm^{-1}$): 3053 (m), 2950 (m), 2893 (w), 1951 (w), 1888 (w), 1814 (w), 1589 (s), 1434 (s), 1305 (w), 1245 (m), 1170 (w), 1120 (br), 1095 (m), 952 (m), 835 (s), 740 (s), 694 (s). Anal. Calcd for $C_{51}H_{58}ErClN_3P_3Si_2$ ($M_r = 1064.84$): C, 57.53; H, 5.49; N, 3.95. Found: C, 57.21; H, 5.79; N, 3.55.

**Ln = Yb.** Yields: **3a**, 246 mg (45%), and **3b**, 255 mg (47%) (yellow crystals). IR (KBr, $cm^{-1}$): 3053 (m), 2948 (m), 2894 (w), 2850 (w), 1949 (w), 1888 (w), 1809 (w), 1660 (w), 1589 (s), 1479 (s), 1434 (s), 1352 (w), 1307 (w), 1245 (m), 1168 (w), 1122 (br), 1093 (m), 1026 (m), 999 (m), 954 (m), 835 (s), 740 (s), 694 (s). Anal. Calcd for $C_{51}H_{58}ClN_3P_3Si_2Yb$ ($M_r = 1070.62$): C, 57.22; H, 5.46; N, 3.92. Found: C, 57.39; H, 5.60; N, 3.85.

**Ln = Lu.** Yields: **4a**, 232 mg (43%), and **4b**, 236 mg (44%) (colorless crystals). $^1H$ NMR (THF-$d_8$, 400 MHz, 25 °C): $\delta$ 0.14 (s, 9H, $Me_3Si$), 0.18 (s, 9H, $Me_3Si$), 0.88 (t, 1H, CH, $^2J(H,P) = 7.2$ Hz), 1.30 (d, 3H, $CH_3$, $^3J(H,H) = 6.79$ Hz), 4.38 (q, 1H, CH, $^3J(H,H) = 6.79$ Hz), 6.73−7.09 (m, 15H, Ph), 7.20−7.35 (m, 13H, Ph), 7.50−7.81 (m, 7H, Ph). $^{31}P\{^1H\}$ NMR (THF-$d_8$, 161.7 MHz, 25 °C): $\delta$ 18.0, 18.8 (d, PCP, $^2J(P,P) = 8.89$ Hz), 19.1 (d, PCP, $^2J(P,P) = 10.35$). IR (KBr, $cm^{-1}$): 3055 (m), 3020 (m), 2950 (m), 2893 (w), 1965 (w), 1888 (w), 1814 (w), 1589 (w), 1481 (s), 1436 (s), 1259 (m), 1245 (m), 1166 (w), 1120 (br), 1026 (m), 999 (m), 948 (m), 833 (s), 781 (m), 740 (s), 692 (s). Anal. Calcd for $C_{51}H_{58}ClLuN_3P_3Si_2Cl$ ($M_r = 1072.55$): C, 57.11; H, 5.45; N, 3.92. Found: C, 56.67; H, 5.86; N, 3.66.

**$[\{(Me_3SiNPPh_2)_2CH\}Yb(\mu\text{-}Cl)_2LiCl(THF)_2]$ (5).** A 597 mg (1 mmol) amount of $K\{CH(PPh_2NSiMe_3)_2\}$ was mixed with 307 mg (1.1 mmol) of anhydrous $YbCl_3$ and 311 mg (1 mmol) of **1** under inert atmosphere. To this mixture 15 mL of THF was added and stirred for 24 h. Then THF was removed in vacuo, and the residue was extracted from 15 mL of toluene. The solution was filtered, and solvent was removed in vacuo. The compound was washed by pentane (10 mL) and crystallized from THF/pentane as colorless crystals.

Yield: 400 mg (37%). IR (KBr, $cm^{-1}$): 3056 (m), 3016 (m), 2950 (m), 2898 (w), 1963 (w), 1888 (w), 1811 (w), 1589 (w), 1481 (s), 1433 (s), 1307 (w), 1247 (m), 1166 (w), 1122 (br), 1091 (m), 1029 (m), 999 (m), 954 (m), 840 (s), 744 (s), 700 (s). Anal. Calcd for $C_{43}H_{55}Cl_3LiN_2O_3P_2Si_2Yb$ ($M_r = 1052.38$): C, 49.08; H, 5.27; N, 2.66. Found: C, 48.86; H, 5.36; N, 3.15.

**$[(\eta^8\text{-}C_8H_8)Ln\{N(R\text{-*}CHMePh)(PPh_2)\}]$ (Ln = Y (6a), Er (7a), Yb (8)) and $[\eta^8\text{-}(C_8H_8)Ln\{N(S\text{-*}CHMePh)(PPh_2)\}]$ (Ln = Y (6b), Er (7b)).** To a 50 mL reaction vessel, 1.1 mmol of anhydrous $LnCl_3$ was charged with 311 mg (1 mmol) of 1 in 15 mL of THF. After 20 h of stirring under room temperature, a THF solution of freshly prepared $K_2C_8H_8$ (1 mmol) was added slowly at room temperature to the reaction vessel and stirred for another 20 h. In each case a color change was noticed. The THF was removed in vacuo, and the residue was extracted with 15 mL of toluene. The solution was filtered, and solvent was evaporated. After washing of the compound by pentane, the title compounds were crystallized from either hot toluene or THF/pentane.

**Ln = Y.** Yields: **6a**, 180 mg (37%), and **6b**, 200 mg (35%) (yellow crystals). $^1H$ NMR ($C_6D_6$, 400 MHz, 25 °C): $\delta$ 0.93 (br, THF), 1.28 (d, 3H, $CH_3$, $^3J(H,H)$ 6.7 Hz), 2.90 (br, THF), 4.03 (q, 1H, CH, $^3J(H,H) = 6.67$ Hz), 6.76 (s, 8H, $C_8H_8$), 7.0−7.7 (m, 15H, Ph). $^{31}P\{H\}$ NMR ($C_6D_6$, 161.7 MHz 25 °C): $\delta$ 19.3 (d, $^2J(P,Y) = 17.8$ Hz). IR (KBr, $cm^{-1}$): 3060 (m), 2964 (m), 2860 (m), 1593 (w), 1473 (s), 1456 (m), 1433 (s), 1363 (w), 1269 (m), 1184 (w), 1110 (br), 1091 (m), 1066 (w), 1026 (m), 962 (m), 869 (s), 798 (m), 744 (s), 700 (w), 628 (s). Anal. Calcd for $C_{32}H_{35}NOPY$ ($M_r = 569.51$): C, 67.49; H, 6.19; N, 2.45. Found: C, 66.61; H, 6.91; N, 2.36.

**Ln = Er.** Yields: **7a**, 200 mg (31%), and **7b**, 195 mg (30%) (pink crystals). IR (KBr, $cm^{-1}$): 3055 (m), 3022 (m), 3001 (m), 2970 (m), 2923 (m), 2862 (m), 1591 (w), 1479 (s), 1450 (m), 1436 (s), 1396 (w), 1363 (w), 1340 (m), 1311 (w), 1272 (m), 1245 (m), 1176 (w), 1122 (br), 1110 (m), 1068 (w), 1026 (m), 999 (m), 966

---

(11) (a) Zulys, A.; Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Chem. Commun.* **2004**, 2584−2585. (b) Zulys, A.; Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2005**, *24*, 2197−2202. (c) Gamer, M. T.; Rastätter, M.; Roesky, P. W.; Steffens, A.; Glanz, M. *Chem. Eur. J.* **2005**, *11*, 3165−3172.

(12) Wiecko, M.; Girnt, D.; Rastätter, M.; Panda, T. K.; Roesky, P. W. *Dalton Trans.* **2005**, 2147−2150.

(13) Gamer, M. T.; Roesky, P. W. *Z. Anorg. Allg. Chem.* **2001**, *627*, 877−881.

(14) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387−391.

**Table 1.** Crystallographic Details of $[\{(Me_3SiNPPh_2)_2CH\}Er(Cl)\{N(R\text{-*}CHMePh)(PPh_2)\}]$ (Ln = Er (**2a**), Yb (**3a**))), $[\{(Me_3SiNPPh_2)_2CH\}Yb(Cl)\{N(S\text{-*}CHMePh)(PPh_2)\}]$ (**3b**), and $[\{(Me_3SiNPPh_2)_2CH\}Yb(Cl_2)LiCl(THF)_2]$ (**5**)[a]

| param | **2a** | **3a** | **3b** | **5**·THF |
|---|---|---|---|---|
| formula | $C_{51}H_{58}ClErN_3P_3Si_2$ | $C_{51}H_{58}ClN_3P_3Si_2Yb$ | $C_{51}H_{58}ClN_3P_3Si_2Yb$ | $C_{43}H_{55}Cl_3LiN_2O_3P_2Si_2Yb$ |
| fw | 1072.8 | 1078.6 | 1078.6 | 1060.4 |
| space group | $P1$ (No. 1) | $P1$ (No. 1) | $P1$ (No. 1) | $Pna2_1$ (No. 33) |
| $a$, Å | 9.960(2) | 9.9874(4) | 9.978(3) | 18.843(5) |
| $b$, Å | 11.612(2) | 11.6417(5) | 11.624(3) | 13.206(4) |
| $c$, Å | 12.478(3) | 12.5038(5) | 12.495(4) | 20.044(6) |
| $\alpha$,deg | 66.605(4) | 66.475(3) | 66.644(5) | |
| $\beta$, deg | 72.437(4) | 72.140(3) | 72.282(6) | |
| $\gamma$, deg | 78.481(4) | 78.311(3) | 78.429(6) | |
| $V$, $Å^3$ | 2011.1(6) | 1263.38(9) | 1262.0(6) | 4987(2) |
| $Z$ | 1 | 1 | 1 | 4 |
| $d$, $g/cm^3$ | 1.406 | 1.407 | 1.409 | 1.412 |
| radiatn ($\lambda$, Å) | Mo K$\alpha$ (0.71073) | Mo K$\alpha$ (0.71073) | Mo K$\alpha$ (0.71073) | Mo K$\alpha$ (0.71073) |
| $\mu$, $mm^{-1}$ | 1.901 | 2.082 | 2.085 | 2.185 |
| abs corr | empirical (SADABS) | integration (X-shape) | empirical (SADABS) | empirical (SADABS) |
| reflcns collcd | 15 394 | 36 476 | 15 709 | 59 949 |
| unique reflcns | 11 138 ($R_{int} = 0.0128$) | 16 088 ($R_{int} = 0.0420$) | 12 454 ($R_{int} = 0.0110$) | 15 158 ($R_{int} = 0.0800$) |
| obsd reflcns | 11 108 | 15 973 | 12 438 | 10 256 |
| data, params | 11 138, 557 | 16 088, 557 | 12 454, 557 | 15 158, 459 |
| $R1$,[b] $wR2$[c] | 0.0233, 0.0572 | 0.0259, 0.0593 | 0.0196, 0.0497 | 0.0456, 0.1078 |
| absolute struct param (Flack) | −0.013(3) | −0.014(3) | −0.016(3) | −0.005(7) |

[a] All data collected at 173 K except for **3a** (at 200 K) and **5**·THF (at 203 K). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

(m), 910 (m), 850 (s), 800 (m), 746 (s), 725 (m), 698 (s), 628 (s). Anal. Calcd for $C_{32}H_{35}ErNOP$ ($M_r = 647.87$): C, 59.33; H, 5.45; N, 2.16. Found: C, 59.38; H, 6.09; N, 2.02.

**Ln = Yb.** Yield of **8**: 175 mg (27%) (green crystals). IR (KBr, $cm^{-1}$): 3055 (m), 3022 (m), 2958 (m), 2921 (m), 2856 (m), 1959 (m), 1886 (w), 1812 (w), 1591 (w), 1490 (s), 1479 (s), 1450 (m), 1434 (s), 1363 (w), 1307 (w), 1272 (m), 1251 (m), 1203 (m), 1157 (w), 1122 (br), 1110 (m), 1091 (w), 1066 (w), 1022 (m), 999 (m), 960 (m), 852 (s), 802 (m), 740 (s), 725 (m), 696 (s), 628 (s).Anal. Calcd for $C_{32}H_{35}NOPYb$ ($M_r = 653.65$): C, 58.80; H, 5.40; N, 2.14. Found: C, 58.78; H, 5.55; N, 2.48.

**X-ray Crystallographic Studies of 2a, 3a,b, 5, 6a,b, 7a, and 8.** Single crystals of **2a**, **3a**,**b**, **5**, **6a**,**b**, **7a**, and **8** were grown from THF/pentane (1:3). Single crystals were obtained from THF/pentane (1:3) or hot toluene. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold $N_2$ stream of a Stoe IPDS 2T or a Bruker Smart 1000 CCD diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC.

All structures were solved by the Patterson method (SHELXS-97[15]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using the full-matrix least-squares techniques on $F$, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes using the program SHELXL-97.[16] In the final cycles of each refinement, all non-hydrogen atoms except the pentane molecules in C32−C43 and O3 in **5** and C30 and C31 in **6a**,**b** and **7a** were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded by assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated but not refined. The final values of refinement parameters are given in Tables 1 and 2. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-281366−281373. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+(44)1223-336-033; E-mail, deposit@ccdc.cam.ac.uk).

## Results and Discussion

To introduce the chiral phosphanylamides $\{N(R\text{-*}CHMePh)(PPh_2)\}^-$ and $\{N(S\text{-*}CHMePh)(PPh_2)\}^-$ into rare earth chemistry, we tried first to synthesize homoleptic complexes of composition $[Ln\{N(\text{*}CHMePh)(PPh_2)\}_3]$ via a salt metathesis of $Li\{N(R\text{-*}CHMePh)(PPh_2)\}$ (**1a**) and $Li\{N(S\text{-*}CHMePh)(PPh_2)\}$ (**1b**) with $LnCl_3$. A mixture of products was obtained. Up to now we were not able to isolate a definite product. Therefore, we implemented two different coligands into the coordination sphere of the metal to stabilize the corresponding chiral phosphanylamide complexes. The coligands are the well-established cyclooctatetraene[17] and the bis(phosphinimino)methanide, $(Me_3SiNPPh_2)CH^-$.[18]

**Bis(phosphinimino)methanide Complexes.** Transmetalation of the enantiomeric pure lithium compounds **1a**,**b** with lanthanide bis(phosphinimino)methanide dichloride, $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$,[10] in a 2:1 molar ratio in THF followed by extraction with toluene afforded the expected enantiomeric pure complexes $[\{CH(PPh_2NSiMe_3)_2\}Ln(Cl)\{\eta^2\text{-}N(R\text{-*}CHMePh)(PPh_2)\}]$ (Ln = Er (**2a**), Yb (**3a**), Lu (**4a**)) and $[\{CH(PPh_2NSiMe_3)_2\}Ln(Cl)\{\eta^2\text{-}N(S\text{-*}CHMePh)(PPh_2)\}]$ (Ln = Er (**2b**), Yb (**3b**), Lu (**4b**)) (Scheme 1). The

---

(15) Sheldrick, G. M. *SHELXS-97, Program of Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(16) Sheldrick, G. M. *SHELXL-97, Program of Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(17) Review: (a) Edelmann, F. T. *Angew. Chem.* **1995**, *107*, 2647−2669; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466−2488. (b) Edelmann, F. T.; Freckmann D. M. M.; Schumann H. *Chem. Rev.* **2002**, *102*, 1851−1896.

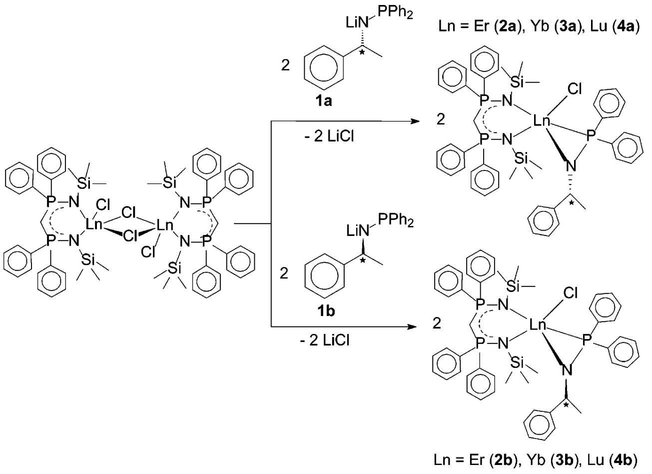
(18) Review: Roesky, P. W. *Heteroatom Chem.* **2002**, 13, 514−520.

**Table 2.** Crystallographic Details of [($\eta^8$-$C_8H_8$)Ln{N(*R*-*CHMePh)($PPh_2$)}] (Ln = Y (**6a**), Er (**7a**), Yb (**8**)) and [$\eta^8$-($C_8H_8$)Ln{N(*S*-*CHMePh)($PPh_2$)}] (Ln = Y (**6b**))[a]

| param | **6a** | **6b** | **7a** | **8** |
|---|---|---|---|---|
| formula | $C_{32}H_{35}NOPY$ | $C_{32}H_{35}NOPY$ | $C_{32}H_{35}ErNOP$ | $C_{32}H_{35}NOPYb$ |
| fw | 569.49 | 569.49 | 647.84 | 653.62 |
| space group | $P2_12_12_1$ (No. 19) | $P2_12_12_1$ (No. 19) | $P2_12_12_1$ (No. 19) | $P2_12_12_1$ (No. 19) |
| *a*, Å | 11.710(4) | 11.714(3) | 11.679(2) | 11.728(2) |
| *b*, Å | 13.453(4) | 13.445(3) | 13.395(2) | 13.378(2) |
| *c*, Å | 17.967(6) | 17.967(4) | 17.920(3) | 17.880(3) |
| *V*, Å$^3$ | 2830(2) | 2829.9(10) | 2803.3(7) | 2805.1(7) |
| *Z* | 4 | 4 | 4 | 4 |
| *d*, g/cm$^3$ | 1.336 | 1.337 | 1.535 | 1.548 |
| radiatn ($\lambda$, Å) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) |
| $\mu$, mm$^{-1}$ | 2.141 | 2.142 | 3.075 | 3.415 |
| abs corr | empirical (SADABS) | empirical (SADABS) | empirical (SADABS) | empirical (SADABS) |
| reflcns collcd | 25 497 | 35 445 | 30 078 | 35 038 |
| unique reflcns | 8633 ($R_{int}$ = 0.0372) | 8690 ($R_{int}$ = 0.0291) | 8169 ($R_{int}$ = 0.0534) | 8576 ($R_{int}$ = 0.0227) |
| obsd reflcns | 7086 | 7870 | 6977 | 8203 |
| data, params | 8633, 316 | 8690, 316 | 8169, 316 | 8576, 326 |
| *R*1,[b] *wR*2[c] | 0.0397, 0.0929 | 0.0344, 0.0845 | 0.0332, 0.0626 | 0.0177, 0.0410 |
| absolute struct param (Flack) | −0.026(4) | −0.027(4) | −0.034(8) | −0.024(5) |

[a] All data collected at 173 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

**Scheme 1**



compounds were crystallized from THF/pentane (1:3). All complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures of **2a** and **3a**,**b** were established by single-crystal X-ray diffraction.

The $^1H$ NMR spectra of the diamagnetic compounds **4a**,**b** show characteristic signals. Two sharp singlets ($\delta$ 0.14 and 0.18 ppm) are observed for two $Me_3Si$ groups of the bis(phosphinimino)methanide ligand as the $Me_3Si$ groups are chemically nonequivalent due to the asymmetric nature of the molecule. Because of the presence of a chiral phosphanyl group, there is no symmetry element through the molecule and thus gives three nonequivalent phosphorus atoms. As the chemical shift of methine protons is more sensitive toward the chemical surrounding, a triplet ($\delta$ 0.88 ppm) was observed which is upfield shifted compared to the chlorine precursor [{CH($PPh_2NSiMe_3$)$_2$}$LuCl_2$]$_2$ ($\delta$ 1.97 ppm).[10] A $^2J$(H,P) coupling constant of 7.2 Hz of the methine proton is observed. In the $^1H$ NMR spectra, the {N(*CHMePh)($PPh_2$)}$^-$ ligand shows a characteristic doublet for the $CH_3$ group ($\delta$ 1.30 ppm), which is downfield shifted compared to **1a**,**b** ($\delta$ 1.08 ppm), and a quartet for the proton of the chiral CH group ($\delta$ 4.38 ppm), which is in the range of the corresponding signal of **1a**,**b** ($\delta$ 4.30 ppm).[12] In the $^{31}P\{^1H\}$ NMR spectrum, the phosphorus atoms of the bis(phosphinimino)methanide ligand are not chemically equivalent in solution and show two doublets at 18.8 and 19.1 ppm. The phosphorus atom of the ligand {N(*CHMePh)($PPh_2$)}$^-$ shows a sharp singlet at 18.0 ppm. Thus, no coupling with the other two phosphorus atoms was noticed for the phosphorus atom of the {N(*CHMePh)($PPh_2$)}$^-$ ligand.

The structures of **2a** and **3a**,**b** were confirmed by single-crystal X-ray diffraction in the solid state. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 3. As a result of the similar ionic radii of the lanthanides, the single-crystal X-ray structures of **2a** and **3a** are isostructural, whereas **3b** forms the corresponding enantiomer (Figure 1). All the compounds crystallize in the triclinic space group *P*1 having one molecule in the unit cell. The coordination polyhedron is formed by the chlorine atom and the {N(*CHMePh)($PPh_2$)}$^-$ and {CH($PPh_2NSiMe_3$)$_2$}$^-$ ligands. As observed in zirconium chemistry, the {N(CHMePh)($PPh_2$)}$^-$ ligand is coordinated to the metal atom in a chelating ($\eta^2$) fashion.[12] Thus, the {N(*CHMePh)($PPh_2$)}$^-$ ligand coordinates to the center metal through nitrogen atom (N3) and the phosphorus atom (P3) forming a azaphosphametallacyclopropane structure featuring Ln−P3 distances of 2.7985(8) Å (**2a**), 2.7782(7) Å (**3a**), and 2.7849(8) Å (**3b**) and Ln−N3 distances of 2.254(2) Å (**2a**), 2.216(2) Å (**2b**), and 2.225(2) Å (**3b**), respectively. The observed long Ln−P3 distances are in the range of other lanthanide phosphanylamide (R−N−$PPh_2^-$) compounds, e.g., an average 2.762(8) Å in [Er{N($PPh_2$)$_2$}$_3$] and 2.885(2)−3.031(2) Å in [Li(THF)$_4$][($Ph_2PNPh$)$_4$Yb].[19] Values for the N−Ln−P bite angles (N3−Ln−P3 36.22(7)° (**2b**), 36.76(6)° (**3a**), and 36.70(5)° (**3b**)) show that the angle is rather small.

A six-membered metallacycle (N1−P1−C1−P2−N2−Ln) is formed by chelation of the two trimethlysilylimine groups to the lanthanide atom. The ring adopts a twist boat conformation, in which the central carbon atom and the lanthanide atom are displaced from the $N_2P_2$ least-squares

---

(19) Wetzel, T. G.; Dehnen, S.; Roesky, P. W. *Angew. Chem.* **1999**, *111*, 1155−1158; *Angew. Chem., Int. Ed.* **1999**, *38*, 1086−1088.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) of $[\{(Me_3SiNPPh_2)_2CH\}Er(Cl)\{N(R\text{-*}CHMePh)(PPh_2)\}]$ (Ln = Er (**2a**), Yb (**3a**)) and $[\{(Me_3SiNPPh_2)_2CH\}Yb(Cl)\{N(S\text{-*}CHMePh)(PPh_2)\}]$ (**3b**)

| param | **2a** | **3a** | **3b** |
|---|---|---|---|
| Bond Lengths (Å) | | | |
| Ln−N1 | 2.339(2) | 2.325(2) | 2.332(2) |
| Ln−N2 | 2.369(2) | 2.343(2) | 2.345(2) |
| Ln−N3 | 2.254(2) | 2.216(2) | 2.225(2) |
| Ln−P3 | 2.7985(8) | 2.7782(7) | 2.7849(8) |
| Ln−Cl | 2.5416(1) | 2.5208(7) | 2.5226(1) |
| Ln−C1 | 2.615(3) | 2.592(2) | 2.596(2) |
| N1−P1 | 1.607(3) | 1.602(2) | 1.603(2) |
| N2−P2 | 1.593(2) | 1.600(2) | 1.598(2) |
| P1−C1 | 173.9(3) | 1.740(3) | 1.741(2) |
| P2−C1 | 1.739(3) | 1.743(3) | 1.744(2) |
| P3−N3 | 1.653(3) | 1.663(2) | 1.664(2) |
| N3−C32 | 1.468(4) | 1.466(3) | 1.473(3) |
| Bond Angles (deg) | | | |
| N1−Ln−N2 | 96.06(8) | 96.46(8) | 96.24(7) |
| N1−Ln−N3 | 112.87(9) | 113.17(8) | 112.91(7) |
| N2−Ln−N3 | 135.54(8) | 136.45(8) | 136.79(7) |
| N1−Ln−Cl | 103.50(6) | 103.11(6) | 102.80(5) |
| N2−Ln−Cl | 100.67(6) | 99.68(6) | 100.01(6) |
| N3−Ln−Cl | 104.18(7) | 103.49(6) | 103.49(6) |
| N1−Ln−C1 | 65.95(8) | 66.34(8) | 66.36(7) |
| N2−Ln−C1 | 64.91(8) | 65.71(8) | 65.58(7) |
| N3−Ln−C1 | 96.08(8) | 96.92(8) | 96.85(8) |
| N1−Ln−P3 | 138.19(6) | 138.94(6) | 138.89(5) |
| N2−Ln−P3 | 100.27(6) | 100.40(5) | 100.89(5) |
| N3−Ln−P3 | 36.22(7) | 36.76(6) | 36.70(5) |
| Cl−Ln−C1 | 159.64(6) | 159.50(6) | 159.52(5) |
| Cl−Ln−P3 | 110.78(3) | 110.47(3) | 110.49(3) |
| C1−Ln−P3 | 86.79(6) | 87.11(6) | 87.32(5) |
| C32−N3−P3 | 122.13(2) | 121.5(2) | 121.56(2) |
| C32−N3−Ln | 147.24(2) | 147.5(2) | 147.58(2) |
| P3−N3−Ln | 90.12(1) | 90.34(10) | 90.28(9) |

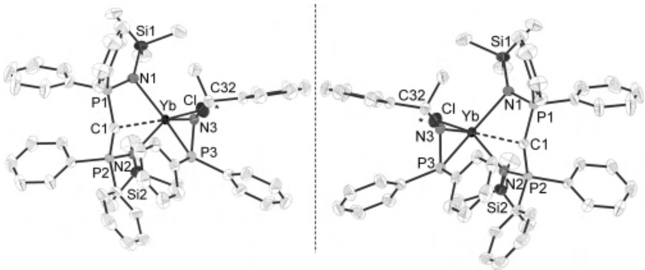


**Figure 1.** Perspective ORTEP view of the molecular structure of the enantiomers **3a** (left) and **3b** (right). Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

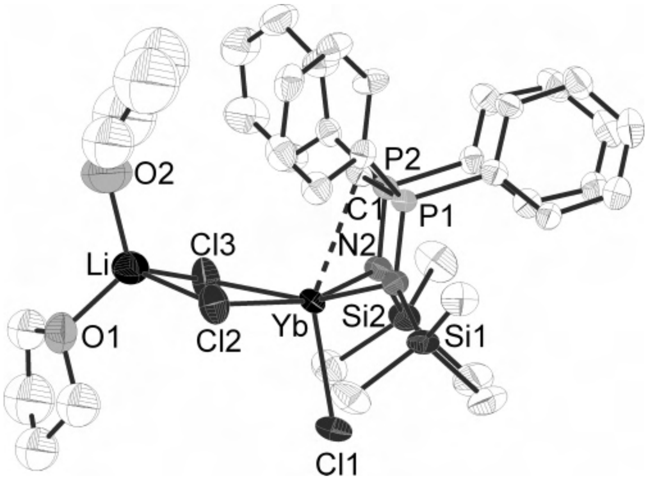


**Figure 2.** Perspective ORTEP view of the molecular structure of **5**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

plane. The distance between the central carbon atom (C1) and the lanthanide atom (2.615(3) Å (**2a**), 2.592(2) Å (**3a**), and 2.596(9) Å (**3b**)) is longer than usual Ln−C distances;[20] however, resultant tridentate coordination of the ligand was observed like before.[10,11,21] The $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand shows a slight asymmetrical attachment to the metal center (Ln−N1 2.339(2) Å (**2a**), 2.325(2) Å (**3a**), and 2.332(2) Å (**3b**); Ln−N2 2.369(2) Å (**2a**), 2.343(2) Å (**3a**), and 2.345(2) Å (**3b**)).

Recently, we discovered that many substituted bis(phosphinimino)methanide complexes such as $[\{CH(PPh_2NSiMe_3)_2\}Ln(\eta^8\text{-}C_8H_8)]$ (Ln = Y, Sm, Er, Yb, Lu) and $[\{CH(PPh_2NSiMe_3)_2\}Ln\{(Ph_2P)_2N\}Cl]$ (Ln = Y, La, Nd, Yb) can be obtained in a one-pot reaction starting from $K\{CH(PPh_2NSiMe_3)_2\}$, $LnCl_3$, and the potassium salt of the corresponding coligand, e.g. $K_2C_8H_8$ and $[K(THF)_nN(PPh_2)_2]$ ($n = 1.25$, 1.5), respectively.[11b,c] In this context we also tried to obtain compound **3** in a one-pot reaction starting from $K\{CH(PPh_2NSiMe_3)_2\}$, $YbCl_3$, and **1**. Performing the reaction in THF and subsequent extractions from toluene and crystallization from THF/pentane yielded not the desired product. Instead, the lithium chloride incorporated complex $[\{(Me_3SiNPPh_2)_2CH\}Yb(\mu\text{-}Cl)_2LiCl(THF)_2]$ (**5**) was obtained. The incorporation of lithium chloride into the coordination sphere of lanthanide complexes is common in the literature.[20] Thus, complexes such as $[(\eta^5\text{-}C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(THF)_2]$ have been known for many years.[22]

Complex **5** has been characterized by standard analytical techniques, and the solid-state structure was established by single-crystal X-ray diffraction (Figure 2). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 4. In the solid-state structure the lighter alkali metal lithium coordinates to the ytterbium through two $\mu$-chlorine atoms along with two solvent THF molecules to the lithium atom. Like before, the ligand, $\{CH(PPh_2NSiMe_3)_2\}^-$, forms a six-membered metallacycle (N1−P1−C1−P2−N2−Yb) by chelation of the two trimethylsilylimine groups to the lanthanide atom. The ring adopts a twist boat conformation in which the central carbon atom and the lanthanide atom are displaced from the $N_2P_2$ least-squares plane. A four-membered metallacyle (Yb−Cl(2)−Li−Cl(3)) was observed by $\mu$-bridging of two chlorine atoms toward

---

(20) Review: (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865−986. (b) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283−363. (c) Schumann, H. *Angew. Chem.* **1984**, *96*, 475−493; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474−493.

(21) (a) Imhoff, P.; Guelpen, J. H.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L.; Elsevier, C. J. *Inorg. Chim. Acta* **1995**, *235*, 77−88. (b) Ong, C. M.; McKarns, P.; Stephan, D. W. *Organometallics* **1999**, *18*, 4197−4208. (c) Kasani, A.; Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Organometallics* **1999**, *18*, 3775−3777. (d) Aparna, K.; McDonald, R.; Fuerguson, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4241−4243. (e) Wei, P.; Stephan, D. W. *Organometallics* **2002**, *21*, 1308−1310. (f) Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2002**, *647*, 123−127. (g) Sarsfield, M. J.; Steele, H.; Helliwell, M.; Teat, S. J. *Dalton Trans.* **2003**, 3443−3449. (h) Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2003**, 4570−4571. (i) Bibal, C.; Pink, M.; Smurnyy, Y. D.; Tomaszewski, J.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 2312−2313.

(22) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190−2191.

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) of $[\{(Me_3SiNPPh_2)_2CH\}Yb(Cl_2)LiCl(THF)_2]$ (**5**)

| | | | |
|---|---|---|---|
| | Bond Lengths (Å) | | |
| Yb−N1 | 2.350(4) | N2−P2 | 1.607(5) |
| Yb−N2 | 2.309(4) | C1−P1 | 1.739(5) |
| Yb−C1 | 2.617(5) | C1−P2 | 1.758(5) |
| Yb−Cl1 | 2.5185(2) | Li−O1 | 1.894(1) |
| Yb−Cl2 | 2.6253(2) | Li−Cl2 | 2.341(1) |
| Yb−Cl3 | 2.6187(2) | Li−Cl3 | 2.374(1) |
| N1−P1 | 1.608(5) | Li−Yb | 3.582(1) |
| | Bond Angles (deg) | | |
| N1−Yb−N2 | 98.21(2) | P2−N2−Yb | 99.8(2) |
| N1−Yb−Cl1 | 95.73(1) | Yb−Cl2−Li | 92.1(3) |
| N2−Yb−Cl1 | 95.41(1) | Yb−Cl3−Li | 91.5(3) |
| N1−Yb−C1 | 65.76(2) | Cl2−Li−Cl3 | 93.3(5) |
| N2−Yb−C1 | 66.13(2) | O1−Li−O2 | 119.7(8) |
| N1−Yb−Cl1 | 95.73(11) | O1−Li−Cl2 | 115.9(6) |
| N2−Yb−Cl1 | 95.41(12) | O2−Li−Cl2 | 111.3(6) |
| N1−Yb−Cl2 | 90.17(12) | O1−Li−Cl3 | 101.9(6) |
| N2−Yb−Cl2 | 162.19(1) | O2−Li−Cl3 | 110.8(6) |
| N1−Yb−Cl3 | 160.67(1) | Cl1−Yb−C1 | 150.01(1) |
| N2−Yb−Cl3 | 85.45(1) | Cl2−Yb−C1 | 103.83(12) |
| P1−C1−P2 | 125.2(3) | Cl3−Yb−C1 | 99.12(1) |
| P1−C(1)−Yb | 86.5(2) | Cl1−Yb−Cl2 | 99.38(6) |
| P2−C(1)−Yb | 85.26(2) | Cl1−Yb−Cl3 | 102.84(6) |
| P1−N1−Yb | 99.2(2) | Cl2−Yb−Cl3 | 81.64(5) |

**Scheme 2**

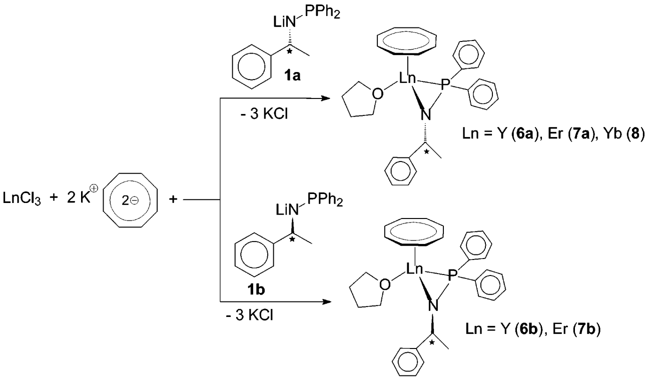


**Table 5.** Selected Bond Lengths (Å) and Angles (deg) of $[(\eta^8\text{-}C_8H_8)Ln\{N(R\text{-}^*CHMePh)(PPh_2)\}]$ (Ln = Y (**6a**), Er (**7a**), Yb (**8**)) and $[\eta^8\text{-}(C_8H_8)Ln\{N(S\text{-}^*CHMePh)(PPh_2)\}]$ (Ln = Y (**6b**), Er (**7b**))[a]

| param | 6a | 6b | 7a | 8 |
|---|---|---|---|---|
| | | Bond Lengths (Å) | | |
| Ln−C1 | 2.564(3) | 2.567(3) | 2.555(4) | 2.538(3) |
| Ln−C2 | 2.549(3) | 2.551(3) | 2.532(4) | 2.525(2) |
| Ln−C3 | 2.541(3) | 2.545(3) | 2.534(4) | 2.514(2) |
| Ln−C4 | 2.568(3) | 2.571(3) | 2.557(5) | 2.537(3) |
| Ln−C5 | 2.607(4) | 2.610(3) | 2.590(5) | 2.577(3) |
| Ln−C6 | 2.579(4) | 2.581(3) | 2.573(5) | 2.547(3) |
| Ln−C7 | 2.554(4) | 2.552(3) | 2.543(5) | 2.518(3) |
| Ln−C8 | 2.542(3) | 2.540(3) | 2.524(4) | 2.518(3) |
| Ln−N | 2.242(2) | 2.2452(2) | 2.233(3) | 2.2047(2) |
| Ln−P | 2.8471(1) | 2.8468(7) | 2.8279(10) | 2.8035(6) |
| Ln−O | 2.388(2) | 2.3885(2) | 2.370(3) | 2.3422(2) |
| Ln−$C_g$ | 1.81(1) | 1.88(10) | 1.78(10) | 1.757(10) |
| P−N | 1.659(2) | 1.6580(2) | 1.661(3) | 1.6626(2) |
| N−C9 | 1.474(3) | 1.472(3) | 1.467(5) | 1.469(3) |
| | | Bond Angles (deg) | | |
| N−Ln−O | 88.58(8) | 88.56(7) | 88.30(12) | 89.03(7) |
| N−Ln−P | 35.59(6) | 35.58(5) | 35.94(9) | 36.35(5) |
| O−Ln−P | 79.78(5) | 79.75(5) | 79.69(7) | 80.17(4) |
| N−P−Ln | 51.87(7) | 52.00(6) | 52.11(11) | 51.81(6) |
| N−Ln−$C_g$ | 147.08(1) | 147.26(1) | 146.34(1) | 145.52(1) |
| P−Ln−$C_g$ | 142.40(1) | 142.43(1) | 142.81(1) | 142.16(1) |
| O−Ln−$C_g$ | 124.21(1) | 124.07(1) | 125.06(1) | 125.22(1) |
| C9−N−P | 123.33(2) | 123.47(14) | 123.6(3) | 123.32(2) |
| C9−N−Ln | 144.13(2) | 144.11(14) | 144.5(3) | 144.83(1) |
| P−N−Ln | 92.54(9) | 92.42(7) | 91.95(14) | 91.84(7) |

[a] $C_g = C_8H_8$-ring centroid.

lithium and ytterbium atoms having a distance of 3.582(1) Å between ytterbium and lithium atoms.

**Cyclooctatetraene Complexes.** To learn more about the reactivity of complexes **1a**,**b**, we were interested in synthesizing some cyclooctatetraene derivatives. Cyclooctatetraene is besides cyclopentadienyl the most important $\pi$-perimeter ligand in f-element chemistry. Today it is well-accepted that the large flat cyclooctatetraene ligand represents an especially valuable alternative to the popular cyclopentadienyl ligands. Among non-cyclopentadienyl organolanthanide complexes, cyclooctatetraene derivatives form a large and well-investigated group of compounds.[17a]

The enantiomeric pure compounds $[\{\eta^2\text{-}N(R\text{-}^*CHMePh)(PPh_2)\}Ln(\eta^8\text{-}C_8H_8)]$ (Ln = Y (**6a**), Er (**7a**), Yb (**8**)) and $[\{\eta^2\text{-}N(S\text{-}^*CHMePh)(PPh_2)\}Ln(\eta^8\text{-}C_8H_8)]$ (Ln = Y (**6b**), Er (**7b**)) can be obtained by one-pot synthesis. The reaction between the lithium salt of the chiral phosphanylamine **1a** or **1b** with anhydrous lanthanide chloride in 1:1 ratio generates the phosphanylamide lanthanide dichloride in situ, which further reacts with dipotassium salt of cyclooctatetraene to produce the desired compounds (Scheme 2). Several attempts to isolate the phosphanylamide lanthanide dichloride were not successful. The new complexes have been characterized by standard spectroscopic techniques, and the solid-state structures of compounds **6a**,**b**, **7a**, and **8** were established in the single-crystal X-ray diffraction. In the $^1H$ NMR spectra, the diamagnetic compounds **6a**,**b** show a sharp signal at 6.76 ppm for the cyclooctatetraene ring. This is in the same range of previously observed $[\{CH(PPh_2NSiMe_3)_2\}Y(\eta^8\text{-}C_8H_8)]$ ($\delta$ 6.54 ppm).[11b] For the $\{N(^*CHMePh)(PPh_2)\}^-$ ligand, the $^1H$ NMR spectra show a characteristic doublet for the $CH_3$ group ($\delta$ 1.28 ppm), which is in the range of **4a**,**b**, and a quartet for the CH proton ($\delta$ 4.03 ppm), which is shifted high-field with respect to **4a**,**b** ($\delta$ 4.38 ppm). The $^{31}P\{^1H\}$ NMR spectrum is also typical. At room temperature **6a**,**b** each show one doublet in the $^{31}P\{^1H\}$ NMR spectrum ($\delta$ 19.3 ppm) for the phosphorus atom. The $^2J(P,Y)$ coupling constant of 17.8 Hz is in the expected range.[9b,19,23] Compared to complex **4a**,**b** there is slight high-field shifting in the $^{31}P\{^1H\}$ NMR spectrum for **6a**,**b**.

The structures of **6a**,**b**, **7a**, and **8** were confirmed by single-crystal X-ray diffraction in the solid state. Data collection parameters and selected bond lengths and angles are given in Tables 2 and 5. All the crystals were grown from THF/pentane (1:3). As a result of the similar ionic radii of the lanthanides, the single-crystal X-ray structures of **6a**, **7a**, and **8** are isostructural, whereas **6b** forms the corresponding enantiomer (Figure 3). All compounds crystallize in the chiral orthorhombic space group $P2_12_12_1$ having four molecules in the unit cell. The three leg piano stool of **6a**,**b**, **7a**, and **8** is formed by the $\eta^8$-coordinated cyclooctatetraene ring, which is located on top of the coordination polyhedron, one THF molecule, and the $\eta^2$-$\{N(^*CHMePh)(PPh_2)\}^-$ ligand. Thus,

---

(23) Coan, P. S.; Hubert-Pfalzgraf, L. G.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 1262−1267.

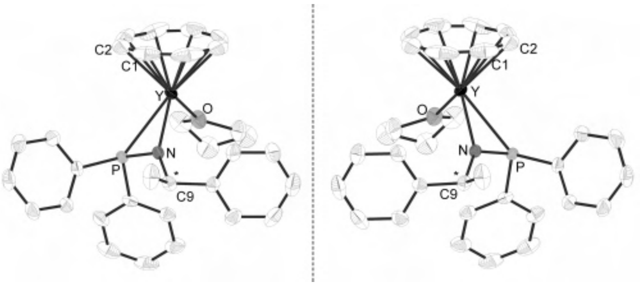


**Figure 3.** Perspective ORTEP view of the molecular structure of the enantiomers **6a** (left) and **6b** (right). Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

the lanthanide atom is 11-fold coordinated if $\eta^8$-cyclooctatetraene is considered as an octadentate ligand. The cyclooctatetraene ring is slightly asymmetrically bound to the lanthanide atom. The Ln−C bond lengths vary in the expected range of 2.541(3)−2.607(4) Å (**6a**), 2.540(3)−2.610(3) Å (**6b**), 2.524(4)−2.590(5) Å (**7a**), and 2.514(2)−2.577(3) Å (**8**). Beside the cyclooctatetraene ring, the $\{N(CHMePh)(PPh_2)\}^-$ ligand is coordinated to the central metal in a chelating $\eta^2$-fashion through nitrogen and phosphorus atom, thus forming a three-membered metallacycle. The Ln−N distances of 2.242(2) Å (**6a**), 2.2452(2) Å (**6b**), 2.233(3) Å (**7a**), and 2.2047(2) Å (**8**) are in the same range observed for **2a** (2.254(2) Å) and **3b** (2.225(2) Å). Also the Ln−P distances of 2.8471(1) Å (**6a**), 2.8468(7) Å (**6b**), 2.8279(10) Å (**7a**), and 2.8035(6) Å (**8**) are in a comparative range with **2a** (2.7985(8) Å) and **3b** (2.7848(8) Å).

## Summary

The chiral phosphanylamides $\{N(R\text{-}^*CHMePh)(PPh_2)\}^-$ and $\{N(S\text{-}^*CHMePh)(PPh_2)\}^-$ were introduced into rare earth chemistry. Since we were not able to isolate homoleptic complexes of composition $[Ln\{N(^*CHMePh)(PPh_2)\}_3]$, we implemented two different coligands into the coordination sphere of the metal to stabilize the corresponding chiral phosphanylamide complexes. The coligands are the well-established cyclooctatetraene and the bis(phosphinimino)-methanide, $\{CH(PPh_2NSiMe_3)_2\}^-$. By using these coligands, the enantiomeric pure complexes $[\{CH(PPh_2NSiMe_3)_2\}Ln(Cl)\{\eta^2\text{-}N(R\text{-}^*CHMePh)(PPh_2)\}]$ (Ln = Er, Yb, Lu), $[\{CH(PPh_2NSiMe_3)_2\}Ln(Cl)\{\eta^2\text{-}N(S\text{-}^*CHMePh)(PPh_2)\}]$ (Ln = Er, Yb, Lu), $[\{\eta^2\text{-}N(R\text{-}^*CHMePh)(PPh_2)\}Ln(\eta^8\text{-}C_8H_8)]$ (Ln = Y, Er, Yb), and $[\{\eta^2\text{-}N(S\text{-}^*CHMePh)(PPh_2)\}Ln(\eta^8\text{-}C_8H_8)]$ (Ln = Y, Er) were obtained. The structures of selected examples of all four different kinds of complexes were confirmed by single-crystal X-ray diffraction in the solid state.

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft (DFG Schwerpunktprogramm (SPP 1166): Lanthanoidspezifische Funktionalitäten in Molekül und Material). We thank Prof. Dr. G. Schröder (Karlsruhe, Germany) for the gift of cyclooctatetraene.

**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of **2a**, **3a**,**b**, **5**, **6a**,**b**, **7a**, and **8**. This material is available free of charge via the Internet at http:// pubs.acs.org.

IC051584E