# Synthesis, structure, and reactivity of diamidophosphine complexes of yttrium and the lanthanides

#### Michael D. Fryzuk, Peihua Yu, and Brian O. Patrick

**Abstract**: The reaction of the dilithiodiamidophosphine ligand precursor PhP(CH<sub>2</sub>SiMe<sub>2</sub>NPh)<sub>2</sub>Li<sub>2</sub>(THF)<sub>2</sub>([NPN]Li<sub>2</sub>(THF)<sub>2</sub>) with LnCl<sub>3</sub>(THF)<sub>3</sub> (Ln = Y, Sm, Ho, Yb, Lu; THF = tetrahydrofuran) in refluxing toluene generates the mononuclear complexes [NPN]LnCl(THF) in good yield. The molecular structures have been shown to be five-coordinate in the solid state and in solution. Attempts to prepare alkyl derivatives have only met with partial success; the reaction of MeMgCl with [NPN]YCl(THF) generates the partially characterized mixed-metal derivative [NPN]YMe<sub>2</sub>MgCl. The reaction with LiAlH<sub>4</sub> results in complete ligand exchange and the formation of the tetranuclear lithium aluminum hydride derivative {[NPN]AlH<sub>2</sub>Li(THF)}<sub>2</sub>. Reduction of the lutetium derivative with KC<sub>8</sub> and naphthalene generated the dinuclear naphthalene-bridged species {[NPN]Lu}<sub>2</sub>( $\mu$ - $\eta^4$ : $\eta^4$ -C<sub>10</sub>H<sub>8</sub>) wherein each Lu centre engages in  $\eta^4$ -coordination to opposite sides of the arene moiety. X-ray crystallography was used to characterize the four complexes.

Key words: lanthanides, yttrium, mixed-donor ligands, aluminum, lithium, naphthalene.

**Résumé** : La réaction du précurseur de ligand dilithiodiamidophosphine PhP(CH<sub>2</sub>SiMe<sub>2</sub>NPh)<sub>2</sub>Li<sub>2</sub>(THF)<sub>2</sub>([NPN]Li<sub>2</sub>(THF)<sub>2</sub>) avec du LnCl<sub>3</sub>(THF)<sub>3</sub> (Ln = Y, Sm, Ho, Yb, Lu; THF = tétrahydrofurane), dans du toluène au reflux, génère des complexes mononucléaires [NPN]LnCl(THF) avec de bons rendements. Il a été démontré que, à l'état solide ainsi qu'en solution, les structures moléculaires sont pentacoordinées. Les essais effectués en vue de préparer des dérivés alkylés n'ont donné que des succès partiels; la réaction du MeMgCl avec le [NPN]YCl(THF) conduit à la formation du dérivé métallique mixte [NPN]YMe<sub>2</sub>MgCl, qui a été partiellement caractérisé. La réaction avec le LiAlH<sub>4</sub> donne lieu à un échange complet de ligands et à la formation de l'hydrure de lithium et d'aluminium tétranucléaire {[NPN]AlH<sub>2</sub>Li(THF)}<sub>2</sub>. La réduction du dérivé du lutécium avec du KC<sub>8</sub> et du naphtalène génère l'espèce dinucléaire ponté par du naphtalène, {[NPN]Lu<sub>2</sub>( $\mu$ -η<sup>4</sup>:η<sup>4</sup>-C<sub>10</sub>H<sub>8</sub>) dans lequel chaque centre Lu est engagé dans une coordination η<sup>4</sup> avec les côtés opposés de la portion arène. On a fait appel à la diffraction des rayons X pour caractériser quatre des complexes.

Mots clés : lanthanides, yttrium, ligands à donneurs mixtes, aluminium, lithium, naphtalène.

[Traduit par la Rédaction]

#### Introduction

Early transition metal complexes with formally  $d^0$  electronic configurations have been prominent as catalyst precursors for the polymerization of  $\alpha$ -olefins (1). While the cyclopentadienyl ancillary ligand provided the initial surge of activity, recent reports have focused on nonmetallocene systems, and in particular, multidentate amido ligands (2–4). Our strategy for ligand design has centred on the combination of two vastly different donor types in a chelate array in an effort to allow access to a variety of different oxidation states at the metal centre. Several new multidentate ligands

Received January 30, 2001. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on August 10, 2001.

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<sup>1</sup>Corresponding author (telephone: (604) 822-2897; fax: (604) 822-2847; e-mail: fryzuk@chem.ubc.ca). <sup>2</sup>UBC X-ray crystallographic service. based on varying the number of amide and phosphine moieties have been developed in our lab (5–7). Herein we report on the preparation of a series of lanthanide complexes [NPN]LnCl(THF) that incorporate a tridentate ligand containing one phosphine and two amido donors ([NPN] = [PhP(CH<sub>2</sub>SiMe<sub>2</sub>NPh)<sub>2</sub>]; Ln = Y (1), Sm (2), Ho (3), Yb (4), Lu (5)).

#### **Experimental**

All experimental manipulations were carried out under an atmosphere of purified dinitrogen rigorously excluding air and moisture using standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system and a  $-40^{\circ}$ C freezer). Solvents were purified according to conventional procedures and were freshly distilled prior to use. Unless otherwise stated, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker AC-200 instrument operating at 200 and 81.0 MHz, respectively.

The compounds  $LnCl_3(THF)_3$  (8),  $[NPN]Li_2(THF)_2$  (9), and  $KC_8$  (10) were prepared as described in the literature.

MeMgCl (solution in THF), LiAlH<sub>4</sub>, and naphthalene were purchased from Aldrich.

Elemental analyses were performed in the microanalysis laboratory of this department by Mr. P. Borda.

## Preparation of [NPN]LnCl(THF) (Ln = Y, Sm, Ho, Yb, Lu)

General procedure for 1–5: at room temperature, toluene (100 mL) was added to a mixture of  $[NPN]Li_2(THF)_2$  (1.18 g, 2 mmol) and  $LnCl_3(THF)_3$  (2 mmol) and the resulting slurry was heated under reflux overnight. After cooling to room temperature, the mixture was filtered through Celite. The solvent was evaporated to dryness and the residue washed with hexane and dried under vacuum, yielding 1 (0.97 g, 70%), **3** (0.96 g, 68%), **5** (1.12 g, 71%) as white powders, **2** (1.15 g, 75%) as a yellow powder, and **4** (1.18 g, 74%) as an orange powder.

#### [NPN]YCl(THF) (**1**)

EI-MS m/z (%): 593 ([M – Cl]<sup>+</sup>, 10), 558 ([M – THF]<sup>+</sup>, 100). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 298 K)  $\delta$ : 7.92 (m, 2H, PPh *p*-H), 7.40 (m, 4H, NPh *o*-H), 7.15 (m, 6H, NPh *m*-H and PPh *m*-H), 6.80 (m, 2H, NPh *p*-H), 2.93 (m, 4H, THF), 1.60 (m, 2H, PCH<sub>2</sub>Si), 1.00 (m, 2H, PCH<sub>2</sub>Si), 0.76 (m, 4H, THF), 0.30 and 0.24 (s, 12H total, SiCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz, 298 K)  $\delta$ : –27.17 (d,  $J_{P,Y} = 77.1$  Hz). Anal. calcd. for C<sub>28</sub>H<sub>39</sub>ClN<sub>2</sub>OPSi<sub>2</sub>Y: C 53.29, H 6.23, N 4.44; found: C 53.56, H 6.26, N 4.43.

#### [NPN]SmCl(THF) (2)

EI-MS m/z (%): 623 ([M – THF]<sup>+</sup>, 100), 558 ([M – THF – Cl]<sup>+</sup>, 15). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 298 K) & 6.42 (m, 1H, PPh *p*-H), 6.05 (m, 6H, NPh *m*-H and PPh *m*-H), 5.76 (m, 4H, NPh *o*-H), 4.80 (m, 2H, NPh *p*-H), 4.42 (m, 2H, PCH<sub>2</sub>Si), 2.35 and 2.21 (s, 12H total, SiCH<sub>3</sub>), 2.60 (m, 2H, PCH<sub>2</sub>Si), 1.13 (m, 4H, THF), 0.05 (m, 4H, THF). Anal. calcd. for C<sub>28</sub>H<sub>39</sub>ClN<sub>2</sub>OPSi<sub>2</sub>Sm: C 48.56, H 5.68, N 4.04; found: C 48.85, H 5.75, N 4.01.

#### [*NPN*]*HoCl*(*THF*) (**3**)

EI-MS m/z (%): 634 ([M – THF]<sup>+</sup>, 100), 599 ([M – THF – Cl]<sup>+</sup>, 25). Anal. calcd. for C<sub>28</sub>H<sub>39</sub>ClN<sub>2</sub>OPSi<sub>2</sub>Ho: C 47.56, H 5.50, N 3.96; found: C 47.72, H 5.63, N 3.87.

#### [NPN]YbCl(THF) (4)

EI-MS m/z (%): 643 ([M – THF]<sup>+</sup>, 100), 607 ([M – THF – Cl]<sup>+</sup>, 18). Anal. calcd. for C<sub>28</sub>H<sub>39</sub>ClN<sub>2</sub>OPSi<sub>2</sub>Yb: C 47.02, H 5.50, N 3.92; found: C 47.22, H 5.60, N 3.86.

#### [NPN]LuCl(THF) (5)

EI-MS m/z (%): 644 ([M – THF]<sup>+</sup>, 100), 558 ([M – THF – Cl]<sup>+</sup>, 20). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 298 K) δ: 7.90 (m, 2H, PPh *o*-H), 7.41 (m, 4H, NPh *o*-H), 7.15 (m, 6H, NPh *m*-H and PPh *m*-H), 6.81 (m, 2H, NPh *p*-H), 2.98 (m, 4H, THF), 1.58 (m, 2H, PCH<sub>2</sub>Si), 0.97 (m, 2H, PCH<sub>2</sub>Si), 0.69 (m, 4H, THF), 0.32 and 0.25 (s, 12H total, SiCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz, 298 K) δ: –22.70 (s). Anal. calcd. for C<sub>28</sub>H<sub>39</sub>ClN<sub>2</sub>OPSi<sub>2</sub>Lu: C 46.89, H 5.48, N 3.91; found: C 46.63, H 5.90, N 4.02.

#### Methylation of [NPN]YCl(THF) using MeMgCl

To a suspension of [NPN]YCl(THF) (1) (0.63 g, 1 mmol) in toluene (30 mL) was added MeMgCl (0.7 mL, 3.0 M in THF, 2.1 mmol) at room temperature, and the mixture was stirred overnight. After removal of the volatiles, the residue was extracted with hexane-toluene (1:1,  $2 \times 5$  mL), and the mixture was filtered through Celite. Upon cooling to -30°C white crystalline product formulated as [NPN]YMe<sub>2</sub>MgCl(THF) (6) could be obtained in 50% yield (0.34 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 298 K)  $\delta$ : 7.68 (m, 2H, PPh o-H), 7.50 (m, 6H, NPh m-H and PPh m-H), 7.12 (m, 1H, PPh p-H), 6.97 (m, 4H, NPh o-H), 6.85 (m, 2H, NPh p-H), 2.61 (m, 4H, THF), 1.18 (m, 2H, PCH<sub>2</sub>Si), 1.06 (m, 2H, PCH<sub>2</sub>Si), 0.71 (m, 4H, THF), 0.45 and -0.02 (s, 12H total, SiCH<sub>3</sub>), -0.14 (m, 3H, Me), -0.62 (m, 3H, Me).  ${}^{31}P{}^{1}H{}$ NMR ( $C_6D_6$ , 81 MHz, 298 K)  $\delta$ : -46.5(s). Anal. calcd. for C<sub>30</sub>H<sub>45</sub>ClN<sub>2</sub>OPSi<sub>2</sub>MgY: C 52.55, H 6.68, N 4.08; found: C 52.98, H 6.59, N 4.02.

## Reaction of [NPN]YCl(THF) with LiAlH<sub>4</sub>; synthesis of $\{[NPN]AlH(\alpha-H)Li(THF)\}_2$ (7)

To a stirred mixture of [NPN]YCl(THF) (1) (1.26 g, 2 mmol) and LiAlH<sub>4</sub> (0.1 g, 2.6 mmol) was added THF (50 mL) at  $-78^{\circ}$ C. After warming to room temperature, the mixture was stirred overnight. After removal of the precipitate by filtration, the solvent was evaporated to dryness under vacuum, the white residue was extracted with toluene  $(2 \times 15 \text{ mL})$ , and the mixture filtered through Celite. Partial removal of the volatiles and cooling to -30°C to yield (0.58 g, 54%) compound 7 as colorless crystals. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 298 K) & 7.75 (m, 2H, PPh *o*-H), 7.05 (m, 10H, NPh o-H and m-H, and PPh m-H), 6.81 (m, 2H, NPh p-H), 3.61 (m, 4H, THF), 1.68 (m, 2H, PCH<sub>2</sub>Si), 1.25 (m, 4H, THF), 0.95 (m, 2H, PCH<sub>2</sub>Si), 0.52 and -0.21 (s, 12H total, SiCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz, 298 K) δ: -36.01 (q,  $J_{PLi} = 66.4$  Hz). Anal. calcd. for  $C_{28}H_{41}N_2OPSi_2AlLi$ : C 61.97, H 7.61, N 5.16; found: C 61.68, H 7.24, N 5.30.

### Reaction of [NPN]LuCl(THF) with KC<sub>8</sub> and naphthalene (C<sub>10</sub>H<sub>8</sub>); preparation of {[NPN]Lu}<sub>2</sub>( $\mu$ - $\eta^4$ : $\eta^4$ : $\eta^4$ - $C_{10}$ H<sub>8</sub>) (8)

To a mixture of [NPN]LuCl(THF) (5) (1.43 g, 2 mmol), KC<sub>8</sub> (0.27 g, 2 mmol), and naphthalene (0.128 g, 1 mmol) was added toluene at -78°C, leading the immediate development of a purple colour. The mixture was warmed to room temperature and stirred overnight to generate a dark purple colour. After filtration, the volatiles were removed under vacuum, the residue was washed with hexane  $(3 \times 15 \text{ mL})$ , and then the remaining solid was recrystallized from toluene. Compound 8 was obtained as dark red crystals by slowly evaporating the solvent at room temperature. Yield 35% (0.47 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 298 K) δ: 7.25 (m, 4H, PPh o-H), 7.02 (m, 20H, NPh o-H and m-H, and PPh m-H), 6.78 (m, 4H, NPh p-H), 4.12 (m, 4H,  $C_{10}H_8$ ), 2.51 (m, 4H, C<sub>10</sub>H<sub>8</sub>), 1.24 (m, 4H, PCH<sub>2</sub>Si), 0.65 (m, 4H, PCH<sub>2</sub>Si), 0.21 and 0.02 (s, 24H total, SiCH<sub>3</sub>).  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz, 298 K) δ: -9.1 (s). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75.45 MHz, 298 K) δ: 159.7 (m, ipso-C<sub>6</sub>H<sub>5</sub>N), 131.6 (m, o-C<sub>6</sub>H<sub>5</sub>N), 129.6 (s, m/p-C<sub>6</sub>H<sub>5</sub>N), 122.9 (m, ipso-C<sub>6</sub>H<sub>5</sub>P), 120.6 (m, o- $C_6H_5P$ ), 105.8 (m, ipso- $C_{10}H_8$ ), 104.4 (s, m/p- $C_6H_5P$ ), 89.8

	1	4	7	8
Chemical formula	C <sub>28</sub> H <sub>39</sub> ClN <sub>2</sub> OPSi <sub>2</sub> Y	C <sub>28</sub> H <sub>39</sub> ClN <sub>2</sub> OPSi <sub>2</sub> Yb	C <sub>63</sub> H <sub>90</sub> N <sub>4</sub> O <sub>2</sub> P <sub>2</sub> Si <sub>4</sub> Al <sub>2</sub> Li <sub>2</sub>	C <sub>58</sub> H <sub>70</sub> N <sub>4</sub> P <sub>2</sub> Si <sub>4</sub> Lu <sub>2</sub>
FW	631.13	715.27	1177.56	1347.44
Crystal Size (mm)	$0.40\times0.25\times0.10$	$0.30\times0.20\times0.20$	$0.35\times0.20\times0.12$	$0.30\times0.25\times0.10$
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)
<i>T</i> (°C)	-100	-100	-100	-100
λ (Å)	0.71069	0.71069	0.71069	0.71069
a (Å)	15.3199(7)	15.1656(5)	12.8490(9)	10.033(1)
b (Å)	12.0338(5)	12.0402(3)	16.146(2)	11.2951(4)
c (Å)	17.432(1)	17.5551(6)	19.415(2)	13.711(1)
α (°)			68.498(2)	98.892(1)
β (°)	100.906(3)	101.027(3)	121.518 (2)	96.494(2)
γ (°)			66.523(2)	109.255(2)
V (Å <sup>3</sup> )	3155.7(2)	3146.3(2)	3355.5(5)	1426.5(2)
Ζ	4	4	2	1
$D_{\text{calcd.}}$ (g cm <sup>-3</sup> )	1.328	1.510	1.165	1.568
<i>F</i> (000)	1312	1436	1260	674
μ (cm <sup>-1</sup> )	20.84	32.07	2.05	36.21
$2\theta_{\text{max}}$ (°)	55.8	55.8	55.9	56.8
GoF	0.93	0.97	1.37	1.23
$R_1^a$	0.028	0.025	0.039	0.027
$wR_2^{b}$	0.077	0.074	0.107	0.074

Table 1. Crystallographic data for 1, 4, 7, and 8.

 ${}^{a}R_{1} = (|F_{o} - F_{c}| / \Sigma|F_{o}|[I > 3\sigma(I)].$  ${}^{b}wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w F_{o}^{4}]^{1/2} \text{ (all data).}$ 

(s, CH, C<sub>10</sub>H<sub>8</sub>), 31.9 (s, CH, C<sub>10</sub>H<sub>8</sub>), 22.9 (s, SiCH<sub>2</sub>P), 14.8 (s, (CH<sub>3</sub>)<sub>2</sub>Si). Anal. calcd. for C<sub>58</sub>H<sub>70</sub>N<sub>4</sub>P<sub>2</sub>Si<sub>4</sub>Lu<sub>2</sub>: C 51.71, H 5.20, N 4.16; found: C 51.58, H 5.34, N 4.30.

#### X-ray crystallography

Single crystals of compounds 1, 4, 7, and 8 suitable for Xray diffraction studies were selected and mounted on a glass fiber using Paratone oil. The crystallographic data appear in Table 1.<sup>3</sup> All measurements were made on a Rigaku/ADSC CCD area detector at 173 K, with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å), performing 2 $\theta$ - $\omega$  scans. The structures of 1, 4, and 7 were solved by direct methods using SIR97 (11) and 8 by the Patterson method (12) and refined by full-matrix least-squares methods on  $F^2$  for all data. Unless otherwise stated, all nonhydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions with C-H distances of 0.98 Å and the isotropic thermal parameter for each H atom  $(B_{\rm H})$  is equal to 1.2 times  $B_{\rm iso}$  of the atom to which it is bonded. Unmodified statistical weights (w = $1/\sigma^2(F_0^2)$ ) were employed for all structures. The coordinated THF molecules in 1 and 4 were found to be disordered and were subsequently refined isotropically in two separate orientations.

#### **Results and discussion**

A series of complexes of the formula [NPN]LnCl(THF)  $([NPN] = [PhP(CH_2SiMe_2NPh)_2]; Ln = Y (1), Sm (2), Ho$ (3), Yb (4), Lu (5)) were prepared in high yield (>70%) by reaction of [NPN]Li<sub>2</sub>(THF)<sub>2</sub> with LnCl<sub>3</sub>(THF)<sub>3</sub> in molar ratio of 1:1 in toluene under reflux (eq. [1]).



Using THF as the solvent led to lower yields of the products. Compounds 1-5 are moisture sensitive, moderately soluble in toluene and Et<sub>2</sub>O, but very soluble in THF. The

<sup>&</sup>lt;sup>3</sup>Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub\_e.shtml. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Fig. 1. Molecular structure of [NPN]YCl(THF) (1).



Fig. 2. Molecular structure of [NPN]YbCl(THF) (4).



compounds were characterized by elemental analyses, mass spectrometry, and <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy where possible. The most intense peaks observed in the mass spectra correspond to the fragments [NPN]LnCl ([M - THF]<sup>+</sup>) and  $[NPN]Ln ([M - THF - Cl]^+)$ . Although the Sm(III), Ho(III), and Yb(III) derivatives (2, 3, and 4, respectively) are paramagnetic, the samarium derivative [NPN]SmCl(THF) (2) exhibited <sup>1</sup>H NMR signals (although no <sup>31</sup>P NMR resonance could be detected); no diagnostic signals could be detected in both the <sup>1</sup>H and <sup>31</sup>P NMR spectra for compounds **3** and **4**. For complexes 1 and 5, the <sup>1</sup>H NMR spectra each show two signals due to coordinated THF at ca. 2.9 and 0.7 ppm, respectively. More importantly, both diamagnetic derivatives 1 and 5 show very symmetrical NMR patterns in solution suggestive of at least  $C_s$  symmetry; for example, only two environments for the silvlmethyl protons (SiMe2) are observed and the phenyl groups attached to nitrogen are equivalent.

The molecular structures of 1 and 4 were determined by X-ray crystallography and are shown in Figs. 1 and 2, respectively; selected bond distances and angles are given in Tables 2 and 3. These two derivatives are isostructural and isomorphous in the solid state. Both compounds display

**Table 2.** Selected bond distances (Å) and angles (°) for compound **1**.

Bond distances (	Å)		
Y(1) - Cl(1)	2.7561(6)	Y(1) - P(1)	2.9276(6)
Y(1) - N(1)	2.260(2)	Y(1)—N(2)	2.240(2)
Y(1)—O(1)	2.350(2)	P(1)—C(7)	1.826(2)
N(1)—C(13)	1.407(3)	N(2)—C(19)	1.421(3)
Bond angles (°)			
Cl(1)-Y(1)-O(1)	91.54(5)	Cl(1)-Y(1)-P(1)	90.82(2)
Cl(1)-Y(1)-N(2)	94.95(5)	Cl(1)-Y(1)-N(1)	145.98(5)
O(1)-Y(1)-N(2)	94.39(7)	O(1)-Y(1)-N(1)	113.35(6)
N(1)-Y(1)-N(2)	105.30(7)	P(1)-Y(1)-O(1)	171.44(5)
P (1)-Y(1)-N(1)	68.09(5)	P(1)-Y(1)-N(2)	77.20(5)
Y(1)-N(2)-C(19)	117.6(1)	Y(1)-N(1)-C(13)	103.8(1)
Y(1)-P(1)-C(2)	95.06(8)	Y(1)-P(1)-C(1)	109.46(8)
Y(1)-P(1)-C(7)	135.45(8)	C(1)-P(1)-C(2)	103.5(1)

 Table 3. Selected bond distances (Å) and angles (°) for compound 4.

Bond distances (Å	r)		
Yb(1)—Cl(1)	2.7188(9)	Yb(1)—P(1)	2.8809(9)
Yb(1)—N(1)	2.213(3)	Yb(1)—N(2)	2.199(3)
Yb(1)—O(1)	2.325(3)	P(1)—C(7)	1.825(4)
N(2)—C(19)	1.421(5)	N(1)—C(13)	1.412(5)
Bond angles (°)			
Cl(1)-Yb(1)-O(1)	92.67(7)	Cl(1)-Yb(1)-P(1)	90.62(3)
Cl(1)-Yb(1)-N(2)	95.70(8)	Cl(1)-Yb(1)-N(1)	147.55(8)
O(1)-Yb(1)-N(2)	91.9(1)	O(1)-Yb(1)-N(1)	111.2(1)
N(1)-Yb(1)-N(2)	104.7(1)	P(1)-Yb(1)-O(1)	170.01(8)
P(1)-Yb(1)-N(1)	69.68(8)	P(1)-Yb(1)-N(2)	78.38(8)
Yb(1)-N(1)-C(13)	107.6(2)	Yb(1)-N(2)-C(19)	118.3(2)
Yb(1)-P(1)-C(1)	108.8(1)	Yb(1)-P(1)-C(2)	95.7(1)
Yb(1)-P(1)-C(7)	135.3(1)	C(1)-P(1)-C(2)	103.6(2)

five-coordinate environments around the central metals with the coordinated THF occupying the position opposite to the phosphorus atom. Overall, the geometries around each central metal are very similar and can be described as distorted square pyramidal by defining the base of the pyramid by P(1), O(1), N(1), and Cl(1), with N(2) in the apical position. This rather unsymmetrical geometry observed in the solid state cannot account for the solution data; in fact, the solution data are more consistent with a trigonal bipyramidal structure wherein the two amide donors and the chloride occupy the equatorial plane with the phosphine and THF moieties are apical resulting is  $C_s$  molecular symmetry. Presumably the small structural differences between the solid state and in solution are a result of crystal packing in the former.

The Y—Cl (2.7561(6) Å) bond distance in **1** is longer than that reported for the mononuclear diamido complex [DADMB]YCl(THF)<sub>2</sub> (Y—Cl 2.574(2) Å), while Y—N (average 2.250 Å) and Y—O (2.350(2) Å) in compound **1** are comparable to those in compound [DADMB]YCl(THF)<sub>2</sub> (DADMB =  $[6,6'-Me_2-(C_6H_3)_2](2,2'-NSiMe_2-t-Bu)_2$ ) (average Y—N 2.250 Å, average Y—O 2.376 Å) (2). The bond distances Yb—Cl (2.710 Å), Yb—N (average 2.212 Å), and



**Fig. 3.** Molecular structure of  $\{[NPN]AlH(\mu-H)Li(THF)\}_2$  (7). For clarity the Ph groups at N and P are omitted.

Yb—P (2.881 Å) in compound **4** can be compared to other Yb(III) phosphine complexes; for example, in  $Cp_2^*$ YbCl(dmpm), the Yb—Cl bond distance of 2.532 Å is considerably shorter than that found in **4**, while the Yb—P bond length in **4** is slightly shorter than 2.941 Å found in the aforementioned permethylytterbocene derivative (13). The Yb(II) derivative [(Me<sub>2</sub>Si)<sub>2</sub>N]<sub>2</sub>Yb(dmpe) shows Yb—N and Yb—P bond distances of 2.331 and 3.012 Å, respectively, which are both longer than that found in **4** (14).

Attempts to generate metal-carbon bonds by metathesis of the remaining chloride ligands of [NPN]LnCl(THF) have not met with success. Generally mixtures of products are obtained upon addition of RLi (R = Me,  $CH_2SiMe_3$ ) to [NPN]YCl(THF) (1). However, it was found that the addition of MeMgCl to 1 did result in the formation of an adduct of the empirical formula [NPN]YMe<sub>2</sub>MgCl (6). This material is clearly not the expected product, [NPN]YMe(THF). The proposed formulation of 6 is from elemental analyses; while <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy could be obtained, a definitive structure has so far eluded us, as have suitable crystals for single crystal X-ray diffraction studies. From the solution NMR data, it is clear that phosphorus is not bound to Y (no coupling between yttrium-89 and phosphorus-31) and there are two metal-methyl environments. Further speculation on the structure of 6 must await additional data.

Attempts to prepare a hydride of the general formula  $\{[NPN]YH(THF)\}_x$  by the reaction of **1** with LiAlH<sub>4</sub> in THF instead resulted in ligand transfer from yttrium to aluminum and the production in reasonable yield of the air-, moisture-, and slightly light-sensitive dinuclear aluminate **7** (eq. [2]).

The molecular structure of **7** was determined by X-ray crystallography. As shown in Fig. 3, the Al atoms are each coordinated by two amido donors and two hydrides in a distorted tetrahedral coordination mode. Selected bond dis-



tances and angles are given in Table 4. The Li atoms are each coordinated by three atoms (P, O, H) and the angles of P-Li-O (113.7(3)°), P-Li-H (109.5°), and O-Li-H (105.2°) are in agreement with those expected for pseudo-tetrahedral geometries. The average Al—N (1.85 Å), Al—H (1.57 Å), and Li—H (1.84 Å) distances are comparable to those in the related disilylamido aluminate,  $[(Me_3Si)_2N]_2Al(\mu-H)_2Li\cdot2Et_2O$  (Al—N 1.86, Al—H 1.58, and Li—H 1.93 Å) (15). Stoichiometry requires that YClH<sub>2</sub>(THF)<sub>x</sub> also be generated; however, the identity of the yttrium side-product was not pursued.

Recently, we have reported the formation of yttrium and lutetium complexes with polycyclic aromatic compounds that were formulated as  $\{[P_2N_2]Ln\}_2(\mu-\eta^4:\eta^4-C_{10}H_8)$  by reducing  $\{[P_2N_2]LnCl\}_2$  (Ln = Y, Lu) using KC<sub>8</sub> in the presence of aromatic compounds such as naphthalene and anthracene (16). A similar reaction of [NPN]LuCl(THF) with KC<sub>8</sub> and naphthalene resulted in the generation of  $\{[NPN]Lu2_2(\mu-\eta^4:\eta^4-C_{10}H_8)$  (8) in moderate yield (eq. [3]).



Exactly analogous transformations are also evident for the reaction of the holmium and yttrium analogues, although these reactions were not examined in detail. While the lutetium reaction provides proof of concept for this process for some of the lanthanides, it is interesting to note that this kind of reductive process completely fails to provide any kind of isolable product for the samarium and ytterbium derivatives 2 and 4, despite the fact that divalent states are known for these particular lanthanide elements; it is not

**Table 4.** Selected bond distances (Å) and angles (°) for compound **7**.

Bond distances (Å)			
P(1)—Li(1)	2.575(4)	Li(1)—O(1)	1.904(5)
Al(1)—N(1)	1.847(2)	Al(1)—N(2)	1.863(2)
Al(1)—H(79)	1.55	Al(1)—H(80)	1.56
Li(1)—H(80)	1.84		
Bond angles (°)			
H(79)-Al(1)-H(80)	107.0	N(1)-Al(1)-N(2)	116.80(8)
H(79)-Al(1)-N(1)	108.4(5)	H(79)-Al(1)-N(2)	101.0
H(80)-Al(1)-N(2)	111.5	H(80)-Al(1)-N(1)	111.3
P(1)-Li(1)-O(1)	113.7(3)	P(1)-Li(1)-H(80)	109.5
H(80)-Li(1)-O(1)	105.2		

Fig. 4. Molecular structure of  $\{[NPN]Lu\}_2(\mu-\eta^4:\eta^4-C_{10}H_8)$  (8). For clarity the Ph groups at N(2) and P(1) are omitted.



clear if reduction to a putative "Ln(II)[NPN]" species complicates these latter reactions. The <sup>1</sup>H NMR spectroscopic data of **8** show only two sets of signals for the  $C_{10}H_8$  moiety, which indicate that the bridging naphthalene unit is symmetrically bound. In addition, only one signal for its <sup>31</sup>P{<sup>1</sup>H} NMR spectrum also demonstrates equivalent phosphine donors on both Lu(III) centers.

The crystal structure of 8 has been determined and is shown in Fig. 4. Selected bond distances and angles are given in Table 5. The conformation of 8 is very similar to that of compound  $\{[P_2N_2]Y\}_2(\mu-\eta^4:\eta^4-C_{10}H_8).$ Each [NPN]Lu unit binds in an  $\eta^4$  fashion on the opposite sides of the different rings of the naphthalene unit. The naphthalene moiety is distorted slightly with elongated bond lengths, and its rings become nonplanar (16). The average Lu-C (2.59 Å)  $\pi$ -bond distances in compound **8** is found similar to the average  $\pi$ -bond distance of Lu—C(Cp) (2.63 Å) in compound  $(C_5H_5)_2Lu$ -t-Bu(THF) (17). It is interesting to note that the short distance between Lu(1) and C(7) (2.75 Å) appears to indicate a  $\eta^2$ -N,C interaction of the amide in solid state. However, the <sup>13</sup>C NMR spectrum shows no evidence of any asymmetry and both ipso carbons resonate at 159.7 ppm, a shift typical for uncoordinated NPh linkages (2).

**Table 5.** Selected bond distances (Å) and angles (°) for compound **8**.

Bond distances (Å)			
Lu(1) - P(1)	2.7538(8)	Lu(1) - C(7)	2.755(3)
Lu(1) - N(1)	2.214(3)	Lu(1)—N(2)	2.174(3)
Lu(1)—C(26)	2.551(3)	Lu(1)—C(27)	2.614(4)
Lu(1)—C(28)	2.612(4)	Lu(1)—C(29)	2.605(3)
C(25)—C(26)	1.438(5)	C(26)—C(27)	1.426(5)
C(28)—C(29)	1.450(5)	C(27)—C(28)	1.372(5)
C(25)*—C(29)	1.414(5)	C(25)—C(25)*	1.451(6)
Bond angles (°)			
P(1)-Lu(1)-N(1)	72.49(7)	P(1)-Lu(1)-N(2)	80.49(8)
N(1)-Lu(1)-N(2)	113.0(1)	C(7)-Lu(1)-N(1)	30.4(1)
P(1)-Lu(1)-C(26)	85.40(8)	C(7)-Lu(1)-N(2)	115.4(1)
P(1)-Lu(1)-C(27)	113.16(9)	P(1)-Lu(1)-C(28)	141.25(9)
P(1)-Lu(1)-C(29)	135.52(7)	N(1)-Lu(1)-C(26)	129.0(1)
N(1)-Lu(1)-C(28)	130.8(1)	N(1)-Lu(1)-C(27)	151.1(1)
N(1)-Lu(1)-C(29)	99.5(1)	N(1)-Lu(1)-C(26)	129.0(1)
C(7)-Lu(1)-C(28)	106.6(1)	C(7)-Lu(1)-C(27)	95.9(1)
C(7)-Lu(1)-C(29)	80.7(1)	C(7)-Lu(1)-C(26)	136.9(1)
N(2)-Lu(1)-C(26)	107.6(1)	N(2)-Lu(1)-C(27)	95.9(1)
N(2)-Lu(1)-C(28)	108.4(1)	N(2)-Lu(1)-C(29)	138.6(1)
Lu(1)-N(1)-C(7)	96.7(2)	Lu(1)-C(7)-N(1)	53.0(2)
C(25)-C(25)*-C(29)	118.7(4)	C(25)*-C(25)-C(26)	117.4(4)
C(26)-C(25)-C(29)*	123.9(4)	C(25)-C(26)-C(27)	120.8(3)
C(26)-C(27)-C(28)	119.7(3)	C(27)-C(28)-C(29)	119.5(3)

#### Conclusions

The results of this study indicate that the NPN ligand system can be incorporated onto certain Group 3 and lanthanide derivatives to generate five-coordinate, mononuclear complexes. However, these materials are not especially versatile as starting materials for entry into organometallic chemistry as most of the attempts to generate metal–carbon bonds result in mixtures of complexes. The only successful transformation so far is the incorporation of naphthalene under reducing conditions to give a bridging naphthalene unit. Since incorporation of alkyl species has proven difficult, it is likely that the use of these ligand systems with Group 3 and the lanthanides as catalyst precursors for polymerization of  $\alpha$ -olefins will not be optimal.

#### Acknowledgment

Funding was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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