A Lutetium Cyclopentadienyl-Phosphazene Constrained Geometry Complex (CGC): First Isolobal Analogues of Group 4 Cyclopentadienyl-Silylamido CGC Systems[‡]

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Dedicated to Prof. Dr. Herbert Schumann on the occasion of his 70th birthday

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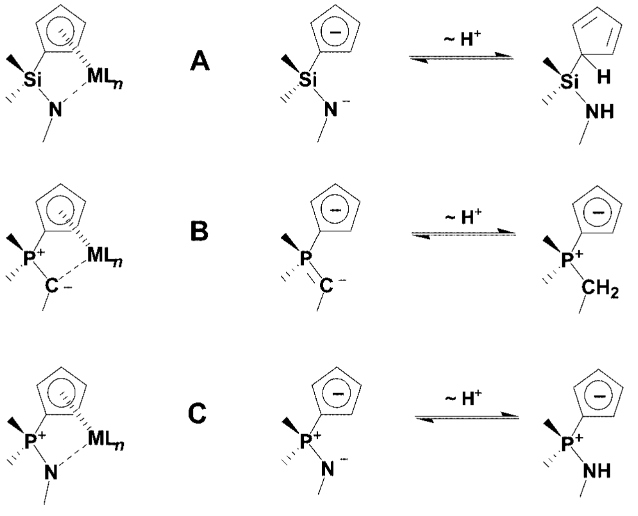
$C_5Me_4HPMe_2$ reacts with 1-adamantyl azide to form the first example of a new family of cyclopentadienylideneaminophosphorane ligands (**1**). Metallation of **1** with $Lu(CH_2SiMe_3)_3(THF)_2$ leads to the first cyclopentadienyl-phosphazene CGC **2**, isolobal to known group 4 cyclopentadienyl-silylamido CGC systems.

Introduction

Linked cyclopentadienyl-silylamido complexes of early transition metals,[1–4] the so-called “constrained-geometry” catalysts[5] (**A**; Scheme 1), have become one of the best developed classes of specially designed organometallics because of their industrial application as single-site olefin polymerisation catalysts.[4–6] Isolobal analogues of ligands **A** are the chelating cyclopentadienyl-phosphoranylidenes (**B**) and cyclopentadienyl-phosphazenes (**C**).[7]

We found that corresponding ligand systems (**B** and **C**, left) do exist in the thermodynamically more stable tautomeric form of cyclopentadienylidene-*P*-carbo- (**B**, right) and *P*-amino-phosphoranes (**C**, right). In the framework of our current studies on coordination and organometallic chemistry of organophosphorus(v) ligands with different O, S, Se, RN and RCH functionalities, synthesis and molecular structures of the type **B** ligand precursors have been recently developed and reported.[8] In this communication we present synthesis of the first example of type **C** ligands and a new CGC lutetium complex thereof along with their crystal structures.



Scheme 1. Isolobally related “constrained-geometry” complexes and corresponding ligand systems.

Results and Discussion

Synthesis of cyclopentadienylidene-phosphorane-C_5Me_4=PMe_2–NHAd (Ad = Adamantyl-1) (**1**) was achieved in 95% yield by the Staudinger reaction of the phosphane $C_5Me_4HPMe_2$, obtained in situ from C_5Me_4HLi and Me_2PCl (Scheme 2), with one equiv. of AdN_3. $^1H/^{13}C$ COSY was used for accurate assignment of all signals. It is

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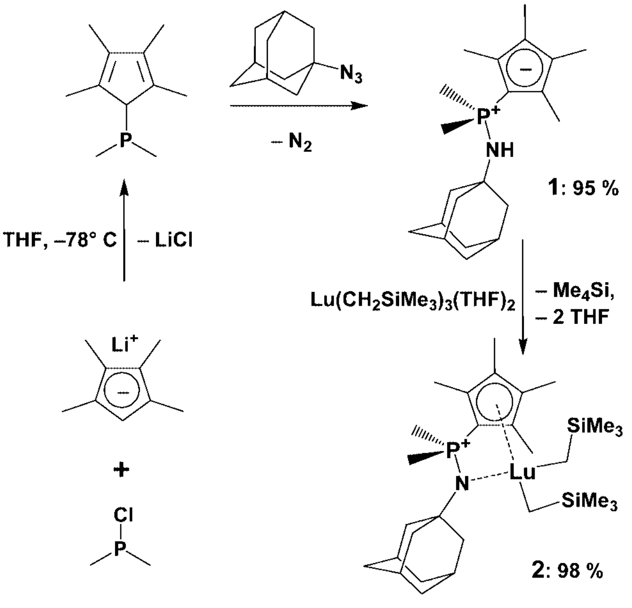
interesting to note that the N*H* proton appears shifted upfield at $\delta = 1.38$ between the adamantyl-group CH_2 multiplets.[9] The highly pure ligand crystallises from THF/hexane mixtures as colourless plates. Simple metallation of **1** with $Lu(CH_2SiMe_3)_3(THF)_2$ in C_6D_6 at r.t. produced a new "constrained-geometry" lutetium complex [η^5:η^1-$C_5Me_4PMe_2NAd$]$Lu(CH_2SiMe_3)_2$ (**2**) in close to quantitative yield.[10]



Scheme 2. Synthesis of **1** and **2**.

Metallation of the ligand **1** ($\delta_P = 17.6$) is accompanied by a shift to $\delta_P = 9.6$. Molecules of THF do not coordinate to Lu in THF-containing solutions of **2**, as confirmed by the ^1H NMR spectrum: one set of signals of THF protons with distinct coupling is observed. Complex **2** is highly soluble in alkanes and crystallises upon slow evaporation of the reaction mixture at r.t. to give large colourless prisms. Both **1** and **2** are thermally rather stable; their molecular structures are shown in Figure 1.

A comparison of these two structures underlines an increase of the aromatic character of the Cp# moiety coordinated to the Lu atom: the difference in C–C bond lengths within the Cp# ring is 0.06 Å for **1** and 0.04 Å for **2**. $P–C_{Me}$ and $N–C_{Ad}$ bonds are only 0.01 Å longer in **2** than in **1**. The $P–C_{Cp}$ bond in **2** is 0.05 Å longer than in **1**, whereas the P–N bond in **2** is almost the same value (0.06 Å) shorter than in **1**. The rather short Lu–N bond (2.28 Å) is much closer to the covalent Lu–N bond lengths (2.21 Å) than to the donor–acceptor ones (2.48 Å) found in the crystal structures of analogous Lu complexes – Cp*Lu(bipy)(NHDip)CH_2SiMe_3 and Cp*Lu(bipy)$(NHDip)_2$.[11] Lu–CH_2 (2.36 Å) and Lu–$Cp^{\#}_{cent}$ (2.33 Å) bond lengths lie in the typical range of Lu σ-alkyl and η^5-Cp* moieties.[11] The 101.2° value of the N–P–C_{Cp} angle is similar to that of N–Si–C_{Cp} in type **A** complexes. In combination with the large radius of Lu, a more open coordination sphere and as a consequence a small but probably nonbonding P···Lu distance (3.08 Å) about 0.7 Å shorter than the sum of the van der Waals radii of these elements (3.80 Å)[12] is observed.

Conclusions

We have introduced the new cyclopentadienyl-phosphazene ligand system **C** and used it for the design of rare earth metal organometallic chelate complexes of the constrained geometry type. A crystal structure analysis of lutetium bisalkyl (**2**) has been presented, confirming that the isolobal relation finds its counterpart in a structural relation to the well-known class of cyclopentadienyl-silylamido complexes of group 4 metals. Systematic synthetic, structural and reactivity aspects of type **B** and **C** ligand systems and a series of new organometallic complexes of *s*-, *p*-, *d*- and *f*-elements will be discussed in a forthcoming full account.[13]

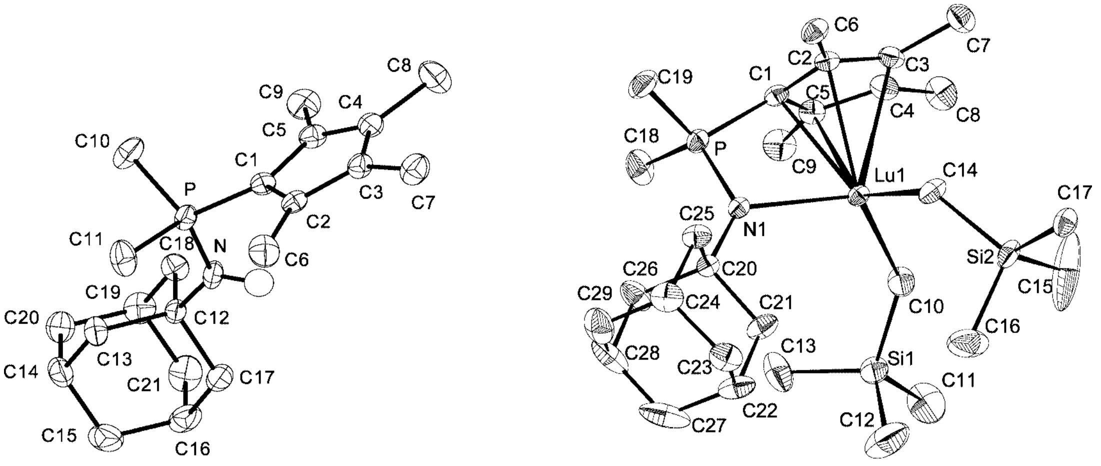


Figure 1. ORTEP illustrations of the ligand **1** (left) and complex **2** (right) showing atom-numbering scheme. Thermal ellipsoids drawn at the 35% probability level. C–*H* hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°] for **1**: C1–C5 1.439(2), C1–C2 1.444(2), C2–C3 1.380(2), P–C1 1.724(2), P–C10 1.803(2), P–N 1.659(1) N1–C12 1.482(2), N–H 0.84(2), P–N1–C12 133.8(1), N–P–C1 108.23(7), N–P–C10 109.63(8). For **2** (right): C1–C5 1.452(6), C1–C2 1.430(6), C2–C3 1.405(6), P–C1 1.774(4), P–C18 1.812(6), P–N1 1.600(3), N1–C20 1.486(5), Lu1–Cp_{cent} 2.343(4), Lu1–N1 2.278(3), Lu1–C10 2.360(4), P–N1–C20 128.2(2), Lu1–N1–C20 128.0(2), P–N1–Lu1 103.7(2), N1–Lu1–C14 109.9(2), N1–Lu1–C10 115.8(2), C14–Lu1–C10 109.9(2).

Supporting Information: Spectra (see footnote on the first page of this article).

Acknowledgments

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[7] *Note:* if [Si and group 4 metal] of type **A** complexes are replaced by [P and group 3 metal] of type **C** ones, not only isolobal but isoelectronic species result. A theoretical investigation of group 4 constrained geometry complexes featuring phosphazene and phosphinimido arms has been recently published. See: L. Truflandier, C. J. Marsden, C. Freund, B. Martin-Vaca, D. Bourissou, *Eur. J. Inorg. Chem.* **2004**, 1939–1947.

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[9] Possible explanation of this phenomenon consists in an effective π-shielding of N*H* proton with the C_5Me_4 group, which was partly confirmed by the X-ray structure of **1**, where this proton was located exactly under the phosphorane C_5-aromatic ring.

[10] **Synthesis of 1**: a solution of Me_2PCl (1.5 g, 15.5 mmol) in THF (10 mL) was added to a stirred suspension of C_5Me_4HLi (1.9 g, 14.7 mmol) in a 1:2 THF/hexane mixture (120 mL) for 0.5 h at –78 °C. The reaction mixture was allowed to stir overnight, warming up to r.t. LiCl was filtered off and all volatiles were removed in vacuo giving $C_5Me_4HPMe_2$ as a light yellow oil (2.2 g, 12.1 mmol, about 83% based on C_5Me_4HLi), which was dissolved in THF (10 mL) and treated with a solution of AdN_3 (2.2 g, 12.4 mmol) in THF (10 mL) at r.t. Thus the obtained yellow solution was allowed to stir with a gas-overpressure controller. During gas (N_2) liberation, the reaction solution gradually deepened in colour and after 4 h became dark brown. To complete the reaction it was warmed up to 50 °C for an additional 30 min. THF was removed in vacuo, yielding a light brown residue, which was treated with hexane (50 mL) and thoroughly washed with the same solvent (4 × 50 mL) to give, after drying in vacuo, a white powder of **1**. Yield 3.8 g (95% based on phosphane, 79% based on C_5Me_4HLi). ^{1}H NMR (300 MHz, C_6D_6, +23 °C): δ = 2.44 (s, 6H, C_5Me_4), 2.39 (s, 6H, C_5Me_4), 1.71 (br. s, 3H, CH_{Ad}), 1.40 [br. d, 6H, N–C(CH_2)$_3$], 1.35 (br. s, 1H, N*H*–Ad), 1.30 (br. m, 6H, CH–CH_2–CH), 1.25 [d, *J*(P,H) = 10 Hz, 6H, Me_2P]. ^{31}P NMR (121.5 MHz, C_6D_6, +23 °C): δ = 17.6 ppm. ^{13}C NMR (75.5 MHz, C_6D_6, +23 °C): δ = 119.7, 117.5 [d, d, *J*(P,C) = 19, *J*(P,C) = 18 Hz, *C*(Me)=*C*(Me)], 77.8 [d, *J*(P,C) = 125 Hz, P-C_{Cp}], 52.4 [d, *J*(P,C) = 4 Hz, P-NH-C_{ad}], 44.7 [d, *J*(P,C) = 4 Hz, N-C(CH_2)$_3$], 36.0 (s, CH-CH_2-CH) 29.9 (s, CH_{Ad}), 19.2 [d, *J*(P,C) = 70 Hz, Me_2P], 14.9 (s, C_5Me_4), 12.1 (s, C_5Me_4). EI-MS: 331, $\mathbf{1}^+$ (36%), 316, $\mathbf{1}^+$ – CH_3 (5%), 286, $\mathbf{1}^+$ – 3 CH_3 (11%), 196, $\mathbf{1}^+$ – Ad (20%). **Synthesis of 2**: a solution of **1** (330 mg, 1 mmol) in C_6D_6 (2 mL) was added to a solution of $Lu(CH_2SiMe_3)_3(THF)_2$ (580 mg, 1 mmol) in C_6D_6 (1 mL) at r.t. The pink-coloured solution obtained in this manner (0.6 mL) was transferred into a WILMAD 505-PS 7 NMR tube with a J. Young teflon valve. The rest of the reaction mixture was left in a glovebox for crystallisation at +25 °C giving, after evaporation of benzene, 540 mg of **2** in the form of colourless crystals in – together with the NMR sample – close to quantitative yield. ^{1}H NMR (300 MHz, C_6D_6, +23 °C): δ = 2.11 (s, 6 H, C_5Me_4), 2.04 (s, 6 H, C_5Me_4), 2.01 (br. s, 3 H, CH_{Ad}), 1.73 [br. d, 6 H, N-C-(CH_2)$_3$], 1.56 (br. m, 6 H, CH-CH_2-CH), 1.15 [d, *J*(P,H) = 13 Hz, 6 H, Me_2P], 0.39 (s, 18 H, Me_3Si), –0.90 (q, ^2J = 20, ^4J = 10 Hz, 4 H, Lu-CH_2-Si). ^{31}P NMR (121.5 MHz, C_6D_6, +23 °C): δ = 9.6. ^{13}C NMR (75.5 MHz, C_6D_6, +23 °C): δ = 123.5, 121.5 [d, d, *J*(P,C) = 14, *J*(P,C) = 13 Hz, *C*(Me)=*C*(Me)], 83.8 [d, *J*(P,C) = 115 Hz, P-C_{ipso}], 54.1 [d, *J*(P,C) = 6 Hz, N-C_{ad}], 47.2 [d, *J*(P,C) = 8 Hz, N-C-(CH_2)$_3$], 38.3 (s, Lu-CH_2-Si), 36.3 (s, CH-CH_2-CH) 30.2 (s, CH_{Ad}), 21.9 [d, *J*(P,C) = 54 Hz, Me_2P], 13.9 (s, C_5Me_4), 11.8 (s, C_5Me_4), 4.9 (s, SiMe_3). EI-MS: 679, $\mathbf{2}^+$ (30%), 665.0, $\mathbf{2}^+$ – CH_2 (10%), 591.0, $\mathbf{2}^+$ – Me_4Si (16%). Satisfactory elemental analyses of **1** and **2** were obtained. General experimental details, NMR and EI-MS spectra as well as references on the syntheses of the starting reagents are collected in the Supporting Information; see also the footnote on the first page of this article.

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[14] **Crystal Data for 1:** $C_{21}H_{34}NP$, *M* = 331.46, orthorhombic, space group *P*21 21 21, *a* = 10.582(2) Å, *b* = 13.135(3) Å, *c* = 13.845(2) Å, *V* = 1924.5(6) Å^3, *Z* = 4, $D_{calcd.}$ = 1.144 g cm^{-3}, μ(Mo-K_α) = 0.144 mm^{-1}. Crystal dimensions 0.52 × 0.40 × 0.28 mm. Data were collected with an area detector using ω-scans at 180(2) K on an IPDS STOE diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and expanded by difference Fourier syntheses using the SHELX-97 software package. G. M. Sheldrick, Program for solution of crystal structures, SHELXS-97; University of Göttingen, **1997**; G. M. Sheldrick, Program for the refinement of crystal structures, SHELXL-97; University of Göttingen, **1997**. 3468 reflections measured, 12951 unique (R_{int} = 0.0332), which were used in all calculations. GoF (on F^2) = 0.995. The final agreement factors were R_1 = 0.0270 [$I > 2.00\sigma(I)$] and wR_2 = 0.0627 (all). For **2**: $C_{29}H_{55}LuNPSi_2$, *M* = 679.86, monoclinic, space group $P2_1/c$, *a* = 15.284(2) Å, *b* = 10.456(1) Å, *c* = 21.092(2) Å, $\alpha = \gamma = 90°$, β = 91.97(2)°, *V* = 3368.7(7) Å^3, *Z* = 4, D_{calcd} = 1.340 g cm^{-3}, μ(Mo-K_α) = 3.066 mm^{-1}. Crystal dimensions 0.32 × 0.20 × 0.16 mm. Data were collected at 180(2) K as above. The structure was solved as above. The intensities were corrected for Lorentz polarisation and absorption effects using ABSCOR, a modification of DIFABS (T_{min} = 0.4404, T_{max} = 0.6398). N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158–166. 6383 reflections measured, 30805 unique (R_{int} = 0.0549), which were used in all calculations. GoF (on F^2) = 1.038. The final agreement factors were R_1 = 0.0398 [$I > 2.00\sigma(I)$] and wR_2 = 0.1034 (all). CCDC-263440 and -263441 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

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