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Air-stable helical bis(cyclopentadienylphosphazene) complexes of divalent ytterbium[†]

Alex R. Petrov,^{*a*} Konstantin A. Rufanov,^{*b*} Noa K. Hangaly,^{*a*} Michael Elfferding,^{*a*} Klaus Harms^{*a*} and Jörg Sundermeyer^{*a*}

^a Fachbereich Chemie der Philipps-Universität Marburg, 35032 Marburg, Germany.

Fax: +49 6421 28 25711; e-mail: jsu@staff.uni-marburg.de

^b Chemical Diversity Research Institute, 114401 Khimki, Moscow Region, Russian Federation.

Fax: +7 495 626 9780; e-mail: kruf@iihr.ru

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Two homoleptic Yb^{II} constrained geometry complexes [Yb{ $\eta^5, \eta^1-R_2P(C_5Me_4)NAd$ }_2] [R = Me (3), Ph (4); Ad = 1-adamantyl] derived from *P*-amino(cyclopentadienylidene)phosphoranes (CpPN) R₂P(C₅Me₄)NHAd [R = Me (1), Ph (2)] were found to be remarkably stable towards dioxygen, as shown by NMR spectroscopy and further confirmed by the crystal structure analysis of 4 and discussed in terms of efficient steric shielding and electronic stabilization of the Yb^{II} metal centre by this CpPN ligand type.

In the course of systematic studies of ambident organophosphorus(V) donor ligands of the general type $[R_2P(X)Z]^-(X, Z = S, NR', CH_2, CHR', Cp, Ind, Flu; as for X = Z and X \neq Z)$, we recently focused on the coordination chemistry of *P*-amino(cyclopentadienylidene)phosphoranes $R_2P(C_5R'_4)NHR''$ (CpPN ligand type).¹

Taking into consideration the general concept that threevalent complexes on the basis of monoanionic CpPN type ligands are isolobal, in case of group III metals even isoelectronic, with tetravalent group IV transition metal complexes of dianionic CpSiN type ligands (Figure 1), which became one of the best developed classes of complexes bearing chelating cyclopentadienyl(amido) ligands of the early transition metals,² the so-called 'constrained geometry catalysts' (CGC).³



Figure 1 Isolobal relationship between complex families.

We were interested in investigating the ability of CpPN ligands to stabilize divalent lanthanide ions in a solid state for further applications as the components of luminescent materials.⁴

Recently, we have reported the synthesis and crystal structure of the constrained geometry CpPN lutetium complex [$\{\eta^5, \eta^1-Me_2P(C_5Me_4)NAd\}Lu(CH_2SiMe_3)_2$] (Ad = 1-adamantyl).^{1(c)} The ligand Me_2P(C_5Me_4)NHAd **1** was synthesized by the Staudinger reaction of AdN₃ and Me_2P–C₅Me₄H according to the procedure reported previously.^{1(c),(d)} Analogously, the new CpPN ligand Ph_2P(C_5Me_4)NHAd **2** was synthesized from the phosphane precursor Ph_2P–C_5Me_4H (Scheme 1). As anti-



Scheme 1 Synthesis of the CpPN ligand 2.

cipated, the reactivity of the diphenylphosphane towards AdN_3 is considerably lower than that of the dimethylphosphane. After the optimisation of reaction conditions (toluene, 110 °C, 14 h), bright yellow crystalline compound **2** was isolated in 50% yield.[‡]

Unlike 1, compound 2 is only slightly air-sensitive, and it can be stored under aerobic conditions in a matter of days. Furthermore, the ³¹P NMR characterization of compound 2 showed three isomeric forms **2a–c**, which are not observed for ligand 1.^{1(d)} The (cyclopentadienylidene)phosphorane **2a** form is the predominant one (79% estimated by ³¹P NMR); it crystallized from the isomeric mixture and was characterized by X-ray structure analysis (Figure 2).[§] Minor tautomers **2b** and **2c** are assigned to P-allylic and P-vinylic bonded cyclopentadienyl-(imino)phosphoranes, respectively.^{1(d)} All these isomers lead to only one ³¹P NMR signal upon metalation and back again to the three ³¹P NMR signals in the thermodynamic equilibrium upon reprotonation.

The orange crystals of **2** suitable for X-ray structure determination were obtained by crystallization from a saturated hexane solution at room temperature. Ligand **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two almost identical independent molecules (I and II). For one of them (II), a disordered model for the N–Ad group has been refined as two sites with 62÷38 occupancy. The observed small differences in bond lengths and angles in the molecules are

[†] Part 6 in the series 'Organophosphorus(V) ligands for coordination and organometallic chemistry'. For part 5, see ref. 1(*e*).

[‡] For procedures and characteristics of products, see Online Supplementary Materials.



Figure 2 Molecular structure of ligand **2**. The thermal ellipsoids are drawn at the 50% probability level. Molecule I is presented. All hydrogen atoms, except for H(1) have been omitted for clarity. Selected bond lengths (Å) and angles (°): N–P 1.667(4), P–C_{cp} 1.706(3), P–C_{Ph} 1.815(4) and 1.824(3), N–C_{Ad} 1.489(5); C_{cp}–P–N 118.3(2), C_{Ph}–P–C_{Ph} 102.1(2), P–N–C_{Ad} 125.9(3).

predominantly a result of packing effects. Therefore, only molecule I is shown in Figure 2.

The divalent ytterbium complexes were synthesized *via* the salt metathesis route starting from $[YbI_2(thf)_2]$ and the potassium salts of CpPN ligands 1 and 2, which were obtained by deprotonation with benzyl potassium [BnK] in THF (Scheme 2).

Because of the low solubility of starting $[YbI_2(thf)_2]$ and [BnK] in other common organic solvents, the syntheses were performed in THF. After filtration of precipitated KI and subsequent crystallization from diethyl ether solutions, deep red crystalline solids were obtained in 82 and 60% yields, respectively.[‡]

Unexpectedly, the complexes are stable towards dioxygen: they can be handled in air and, in the solid state, they do not change for months.^{II} Both **3** and **4** show high solubility in aromatic and polar solvents such as THF and pyridine, but they are



Scheme 2 Synthesis of the ytterbium(II) complexes.

[§] X-ray diffraction data were collected on a STOE IPDS2 diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 173(2) K. The structures were solved by direct methods and refined by difference Fourier syntheses using SIR92¹⁶ and SHELXL-97¹⁷ software package. Programme Diamond 3.0a¹⁸ was used for structure representations.

Crystal data for **2**: C₃₁H₃₈NP, *M* = 455.59, triclinic, space group: PĪ, *a* = 11.696(1), *b* = 13.415(1) and *c* = 17.197(1) Å, *α* = 69.970(7)°, *β* = = 78.667(7)°, *γ* = 80.750(8)°, *V* = 2472.5(4) Å³, *Z* = 4, *d*_{calc} = 1.224 g cm⁻³, μ (MoK*α*) = 0.131 mm⁻¹. Crystal dimensions: 0.22×0.08×0.06 mm. 19230 reflections collected, 8679 independent reflections and 2956 with *I* > 2*σ*(*I*). Final agreements factors were *R*₁ = 0.0473 (observed reflections) and *wR*₂ = 0.0729 (all data). For one of the two independent molecules a disordered model for the N-adamantyl group has been refined.

Crystal data for 4: $C_{66}H_{84}N_2OP_2Yb_2$, M = 1156.33, monoclinic, space group P2/n, a = 21.486(1), b = 11.545(1) and c = 23.604(1) Å, $\beta = 106.194(3)^\circ$, V = 5622.8(4) Å³, Z = 2, $d_{calc} = 1.366$ g cm⁻³, μ (MoK α) = 1.764 mm⁻¹. Crystal dimensions: 0.24×0.24×0.15 mm. 78030 reflections collected, 10932 independent reflections and 8915 with $I > 2\sigma(I)$. Final agreements factors were $R_1 = 0.0258$ and $wR_2 = 0.0598$ (all data).

CCDC 764288 and 721138 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

sparingly soluble in Et_2O or DME and insoluble in alkanes. Whereas complex **3** can be purified by crystallization from Et_2O solutions, complex **4** crystallizes from the same solvent with half a molecule of non-coordinated diethyl ether as $4 \cdot 1/2Et_2O$. Prolonged drying in a vacuum (10⁻³ mbar) or heating in toluene leads to the formation of the solvent-free powdery compound.

The ¹H NMR spectra of complexes **3** and **4** are similar. In the aliphatic region, four sharp resonances of the methyl groups at the Cp ring were observed. Moreover, the presence of two doublets assigned to the Me₂P group in **3** and two sets of resonances of *o*-Ph protons in **4** point out the asymmetric coordination mode of the ligands at the metal centre. The asymmetric arrangement was also verified by the presence of five coupled resonances for the Cp ring carbon atoms and two sets of resonances for R₂P groups in the ¹³C NMR spectra. The ³¹P NMR resonances were found at 0.5 (**3**) and 3.1 ppm (**4**), respectively, in the characteristic region of *P*-cyclopentadienyl-iminophosphoranes [*cf.* Me₂P(=NR)C₅Me₄H, R = SiMe₃, 2,6-di-isopropylphenyl].^{1(d)}

The multinuclear NMR spectroscopy of **3** and **4** clearly indicates that both complexes of the bidentate CpPN ligands are best described as derivates of divalent ytterbocene and the bonding between nitrogen and the metal centre is weak. A further insight into the bonding situation was gained by X-ray diffraction analysis.

Large deep red crystals of **4** suitable for X-ray structure determination were grown by cooling a saturated diethyl ether solution to -10 °C. Complex **4** crystallizes with 1/2 molecule of Et₂O per ytterbium complex (**4**·1/2Et₂O) in the monoclinic space group *P2/n*.[§] Two independent molecules in the unit cell can be best described as a distorted tetrahedron with ytterbium atoms located on the crystallographic *C*₂ axis. Both ligands in each molecule adopt a chiral helical arrangement around the ytterbium atom. The two independent molecules are the rotational Δ - and Λ -enantiomers. The molecular structure of the Δ -enantiomer is presented in Figure 3. The selected bond lengths and angles are given in Table 1. The observed small differences in bond lengths and angles in the molecules predominantly result from packing effects.

The average bond lengths of P–C_{Cp} [1.758(3) and 1.763(3) Å] are longer than those in the free ligand [1.706(3) Å], while the P–N bonds are essentially shorter [for **4**, 1.597(2) and 1.596(2) Å; for **2**, 1.667(4) Å].

The average dihedral N–Yb–N' and Z–Yb–Z' angles in **4** (Z = centroid of Cp ring) are 125.0(1) and 132.6(1)°, respectively. Although both Cp rings are carrying four methyl groups, the structures are less strained than in a related sterically hindered molecule, $[{\eta^5-Bu_2^tC_5H_3}_2Yb(dme)]$,⁵ with a Z–Yb–Z' angle of 143.2(1)°. This can be explained by the constraints within our



Figure 3 Molecular structure of complex $4 \cdot 1/2$ Et₂O. The thermal ellipsoids are drawn at the 50% probability level. The Δ -enantiomer is presented; the Et₂O molecules in the unit cell are not depicted. View along the C_2 -axis (left) and the side-view (right); all hydrogen atoms and Ph groups, except for their *ipso*-carbon atoms, have been omitted for clarity.

[¶] No changes have been observed after storing complexes **3** and **4** at room temperature without any precaution over period of more than 6 months, that was confirmed by repeated NMR and elemental analyses.

Table 1 Selected bond lengths (Å) and angles (°) for the $\Delta\text{-}$ and $\Lambda\text{-}enantiomers of <math display="inline">4\cdot 1/2\,Et_2O.$

Δ -enantiomer		Λ -enantiomer	
Yb(1)-N(1)	2.537(2)	Yb(2)–N(2)	2.618(2)
N(1) - P(1)	1.597(2)	N(2)–P(2)	1.596(2)
P(1)-C(1)	1.758(3)	P(2)-C(32)	1.763(3)
Yb(1)–Z(1)	2.622(1)	Yb(2)–Z(2)	2.563(1)
N(1)-Yb(1)-C(1)	60.2(1)	N(2)-Yb(2)-C(32)	59.6(1)
N(1)-Yb(1)-Z(1)	85.2(1)	N(2)-Yb(2)-Z(2)	85.2(1)
N(1)-P(1)-C(1)	103.1(1)	N(2)-P(2)-C(32)	102.7(1)
N(1)-Yb(1)-N(1)'	122.1(1)	N(2)-Yb(2)-N(2)'	127.8(1)
Z(1)-Yb(1)-Z(1)'	133.6(1)	Z(2)-Yb(2)-Z(2)'	131.5(1)

CpPN chelate ligand and by the helical configuration of both.

The molecular bonding distances and angles of the CpPN ligand are closely related to those found in the structure of the $[\{\eta^5, \eta^1-Me_2P(C_5Me_4)NAd\}Lu(CH_2SiMe_3)_2]$ complex.^{1(c)} However, a further investigation into the ligand bonding mode, by comparison of Lu³⁺ and Yb²⁺ complexes, reveals characteristic differences. Although the ionic radius of ytterbium(II) (0.159 Å)⁶ is larger than that of lutetium(III), the average Yb-N bond length is significantly greater [2.578(4) Å] than that of the corresponding Lu–N bond in the lutetium complex $[\{\eta^5, \eta^1\}$ $Me_2P(C_5Me_4)NAd Lu(CH_2SiMe_3)_2$ [2.278(3) Å]. On the one hand, the value is better comparable with those found in closely related ytterbocenes with σ -donating nitrogen ligands (e.g., 2.486, 2.514 Å in $[\{\eta^{5}-1,3-(Me_{3}Si)_{2}C_{5}H_{3}\}_{2}Yb(Phen)],^{7}$ 2.544, 2.586 Å in $[\{\eta^5-C_5Me_5\}_2Yb(py)_2]^8$ and av. 2.579 Å in $[\{\eta^5,\eta^1 C_5H_4(CH_2)_2NMe_2\}_2Yb]^9$). On the other hand, the average Yb-Z distance of 2.593(2) Å is unexpectedly long and falls out of the range typical of ytterbocenes. For instance, in ytterbocenes with the polysubstituted cyclopentadienyl ligands, the Yb-Z distance of av. 2.466(3) Å was found in $[\{\eta^5-C_5Me_5\}_2Yb(py)_2]^8$ and 2.443(2) Å in $[\{\eta^5-C_5Me_5\}_2Yb(terpy)]^{.10}$ Note that the Yb–Z distances in complexes with a non-substituted Cp moiety are, in general, significantly shorter; the distance of only 2.408(1) Å was found in $[\{\eta^5\text{-}C_5H_5\}_2Yb(dme)]^{11}$ and av. 2.376(2) Å in $[{\eta^5-C_5H_5}_2Yb(thf)]$.¹² The elongation of the Yb-Z distance in the structure of complex 4 can be attributed to the significant electron withdrawing -I and/or -M effects of the iminophosphorane moiety. The comparison of the average $P{-}C_{\rm Ph}$ bond length [av. 1.835(3) Å] in 4 with the closely related $Ph_2P(C_5H_4)Me$ $(av. 1.808 \text{ Å})^{13}$ and $Ph_3P(C_5H_4)$ (av. 1.806 Å)¹⁴ is in accordance with this assumption.

Thus, not only steric but also electronic effects of the CpPN ligands are responsible for the unique stability of the above compounds with respect to dioxygen. The ligands reveal an ambident character; the monoanionic charge is partially localized on the Cp ring, as well as on the nitrogen atom of the phosphazene unit (Scheme 3). Due to the negative-hyperconjugative stabilizing effect¹⁵ of the phosphorus(V) σ^* orbitals and the characteristic charge distribution, CpPN ligands can be considered as much weaker donors than classical ligands [C₅R₅]⁻ or [NPR₃]⁻, which are well established in lanthanide chemistry.

Both the weaker donor character and charge distribution lead to less polar metal carbon and metal nitrogen bonds and a less



electron-rich Yb^{II} central atom, thus, to compounds that are less susceptible toward protolytic and oxidative degradation. These properties render the CpPN building unit an ideal spectator ligand for functionalized lanthanide complexes such as heteroleptic amides and alkyls.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.06.004.

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Scheme 3 Valence bond description of the title complexes.

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