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New rare-earth complexes with phosphonium bis(ylide) ligand $[Ph_2P(CH_2)_2]^-$ and the first structural evidence for its bridging coordination mode†

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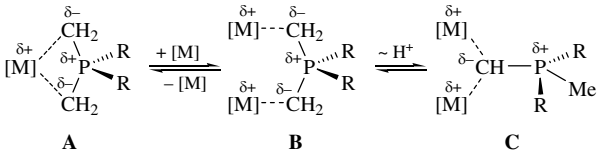
A series of phosphonium bis(ylide) rare-earth complexes of the type Cp*M(byl)$_2$ (M = Sc, Y, Dy, Yb and Lu; byl = $[Ph_2P(CH_2)_2]^-$) has been synthesised and in three cases (Dy, Yb and Lu) structurally characterised revealing realization alongside with the chelating coordination mode for byl, also, for the first time, the bridging mode in dimeric Dy-complex.

Organometallic chemistry of rare-earth (group III and lanthanides) metals has witnessed a spectacular growth in the last decade.[1] Changing the ligand environment of an organometallic complex to modify its properties has been an important strategy for the development of efficient and selective catalysts.[2] We have recently begun systematic investigation of the chelating organophosphorus(V) ligands $[R_2P(X)Z]^-$ (X, Z = S, NR′, CH_2, CHR′, Cp, Ind, Flu; as for X = Z and X ≠ Z) and corresponding rare-earth organometallic complexes in a view of their advances as fine-tunable single-site polymerisation catalysts. Examples in these series of ligands and complexes have been reported previously.[3]

The bis(ylide) ligand $[R_2P(CH_2)_2]^-$ (byl) is, however, the parent one for the whole series; therefore, it has attracted our particular attention. There are many examples of byl-metal complexes known from the literature; their bonding to metals has been studied and discussed.[4] Homoleptic rare-earth byl-complexes remain scarce due to their low resistance to metathesis.[5] These complexes show in solution rapid inter- and intramolecular prototropy, metallotropy and ligand exchange processes between chelating-byl (**A**) and bridging-byl (**B**) and bridging ylidene (**C**) coordination modes (Scheme 1); however, no structural data were given.[6]



A **B** **C**

Scheme 1

The Ln-byl species can be stabilised by introducing a strong donor such as the Cp* ligand;[7] however, among 12e$^-$ Cp*Ln(byl)$_2$ complexes until now only one example (Ln = Lu, byl = $[Me_2P(CH_2)_2]^-$) was described, whereas for Ln(byl)$_3$ no structural data were reported.[8] We synthesised a series of rare-earth species of this type using a simple salt metathesis protocol of $LnCl_3(THF)_n$ with Cp*Na and $Ph_2P(CH_2)_2Li$ in THF at room temperature that gives Cp*Ln(byl)$_2$ complexes as crystalline materials in 70–90% yields.‡

This protocol, however, has brought us success only for the group III (Sc, Y), middle (Dy) and late (Yb, Lu) lanthanides, whereas for early lanthanides (Nd, Sm) no reliable products have been obtained (Scheme 2). Moreover, complexes **1**, **4** and **5** with the elements of smaller ionic radii have significantly higher thermal stability, whereas **2** and particularly **3** decompose rapidly even after a short heating over 60 °C. The 12e$^-$ configuration seems a prerequisite for the stability of at least late Ln-byl complexes.

An NMR study (at room temperature) of diamagnetic **1**, **2** and **5** reveals sharp resonance signals for **1** and **5**, and slightly broadened ones for **2**, revealing the above byl exchange

† This communication is the Part 5 in our series 'Organophosphorus(V) ligands for coordination and organometallic chemistry'. For the previous parts, see ref. 3.

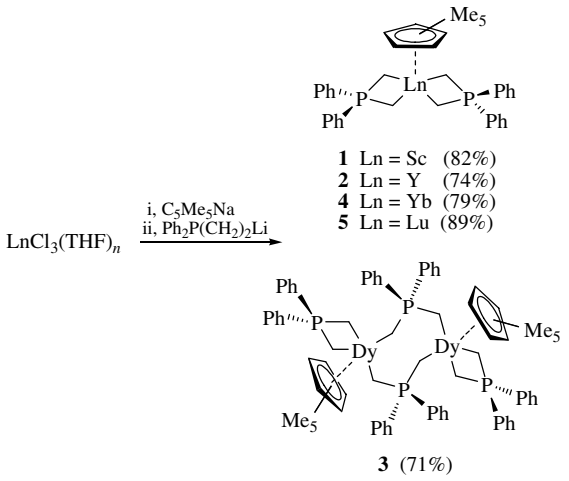
‡ *General procedure for the synthesis of* **1**–**5**: a solution of Cp*Na in THF (0.5 M, 1.5 ml, 750 μmol) was added to a stirred suspension of 750 μmol of $LnCl_3(THF)_n$ (Ln = Sc, Y, Yb or Lu) or $DyCl_3$ in THF (20 ml) at room temperature. After the dissolution of all solids (5–20 min), a solution of $Ph_2P(CH_2)_2Li$ in THF (0.25 M, 6 ml, 1.5 mmol) was added *via* a syringe. The reaction mixture was stirred for additional 1 h that was followed by removal of all volatiles in a high vacuum and extraction of semi-solid residuals with Et_2O (50 ml). The clear solution was syringed through a glass filter and slowly reduced in volume to ~20 ml keeping the solution temperature all the time around room temperature. At the certain moment when the solution becomes slightly cloudy it must be quickly warmed up with a heating gun until it becomes transparent again and allowed to stand for crystallisation at room temperature. After several minutes deposition of colourless (**1**, **2** or **5**), yellow (**3**) or orange (**4**) crystalls occurs. Typically yields vary in all cases between 70 and 90%.

For **1**: ^{1}H NMR (C_6D_6, 300 MHz, 23 °C) δ: 7.61–7.54 (m, 8H, *o*-H_{Ph}), 7.04–6.80 (m, 12H, *p*,*m*-H_{Ph}), 2.06 (s, 15H, Cp*), 0.66 (d, 8H, CH_2P, J_{PH} 10.5 Hz). ^{13}C NMR (C_6D_6, 75.5 MHz, 23 °C) δ: 138.0 (d, P–*ipso*-C_{Ph}, J_{PC} 56 Hz), 130.4 (m, *o*-C_{Ph}), 129.8 (s, *p*-C_{Ph}), 128.1 (m, *m*-C_{Ph}), 117.3 (s, C_5Me_5), 12.5 (s, $C_5\mathit{Me}_5$), 11.8 (d, PCH_2, J_{PC} 38 Hz). ^{31}P NMR (C_6D_6, 121.5 MHz, 23 °C) δ: 17.7.

For **2**: ^{1}H NMR ([$^2H_8$]toluene, 75.5 MHz, 23 °C) δ: 7.80–7.73 (m, 8H, *o*-H_{Ph}), 7.31–7.11 (m, 12H, *p*,*m*-H_{Ph}), 2.27 (s, 15H, Cp*), 0.59 (dd, 8H, CH_2P, J_{PH} 11.1 Hz, J_{YH} 1.4 Hz). ^{13}C NMR ([$^2H_8$]toluene, 75.5 MHz, 23 °C) δ: 130.5 (m, *o*-C_{Ph}), 129.8 (s, *p*-C_{Ph}), 128.0 (m, *m*-C_{Ph}), 116.1 (s, C_5Me_5), 11.7 (s, $C_5\mathit{Me}_5$), 10.3 (d, PCH_2, J_{PC} 36 Hz). ^{31}P NMR ([$^2H_8$]toluene, 121.5 MHz, 23 °C) δ: 18.1 (d, J_{YP} 12 Hz).

For **5**: ^{1}H NMR ([$^2H_8$]toluene, 300 MHz, 23 °C) δ: 7.79–7.72 (m, 8H, *o*-H_{Ph}), 7.13–7.05 (m, 12H, *p*,*m*-H_{Ph}), 2.28 (s, 15H, Cp*), 0.69 (d, 8H, CH_2P, J_{PH} 11.4 Hz). ^{13}C NMR ([$^2H_8$]toluene, 75.5 MHz, 23 °C) δ: 138.7 (d, PC_{Ph}, J_{PC} 58 Hz), 130.5 (m, *o*-C_{Ph}), 129.9 (s, *p*-C_{Ph}), 128.1 (m, *m*-C_{Ph}), 115.3 (s, C_5Me_5), 11.8 (s, $C_5\mathit{Me}_5$), 14.9 (d, PCH_2, J_{PC} 35 Hz). ^{31}P NMR ([$^2H_8$]toluene, 121.5 MHz, 23 °C) δ: 17.0.

Satisfactory elemental analyses were obtained for compounds **1**, **2** and **5**.



Scheme 2 Synthesis of Cp*M(byl)$_2$ complexes.

processes (see Scheme 1), albeit poor solubility of **2** at lower temperatures has prohibited studying this behaviour by NMR spectroscopy in more detail. Chemical shifts in ^{1}H NMR spectra of **2** and **5** are almost identical, while for **1** they are for ~0.3 ppm downfield shifted. The ^{31}P NMR signals appear around δ 17.5 ppm for all complexes. No coordinated THF (or diethyl ether) molecules have been found. Further, significantly lowerer solubility of **3** in benzene points out on its rather not monomeric structure in the solid state. This observation has been confirmed after elucidation of the molecular structures of **3**, **4** and **5**.§ Indeed, **4** and **5** are monomeric in structure with both byl attached to metal in a chelating **A** mode, while Dy-complex **3** is a dimer having two byl attached in a chelating **A** and the other two – in a bridging **B** mode. ORTEP drawing for **3** is given in Figure 1. Complexes of ytterbium (**4**) and lutetium (**5**) are isostructural; therefore, only one of them (**4**) is depicted in Figure 1. Selected bond lengths and angles for **3**–**5** are summarised in Table 1. While C(1)–Ln–C(2) angles for chelating byl are similar for all three complexes, there are striking structural dissimilarities between monomeric complexes **4** and **5** on the one hand and dimeric complex **3** on the other. Thus, all four bond lengths between Dy and coordinated CH_2 groups of both chelating and bridging byl in **3** are very similar, while in **4** and **5** a detailed comparison reveals that one byl is bonded to Yb or Lu slightly weaker than another; moreover, the angles between planes defined by CPC and CLnC atoms for chelating ligands in **4** and **5** are 12.1° and 12.2° for the stronger bonded byl and 35.2° and 34.9° for the weaker bonded one, whereas for chelating byl in **3** this angle is only 3.5°. It seems that in the case of Dy, which has an ion size for ~7% larger than the late lanthanides, the **B**-bridging mode of coordination of one of byl becomes thermodynamically more favourable leading to the formation of dimeric structure and almost planar coordination mode of the second chelating byl, while for smaller Yb and Lu ions both byl prefer **A**-chelating bent coordination mode. This observation can be considered as the first structural evidence of the earlier revealed tendency of Ln-byl complexes for intermolecular ligand exchange processes.

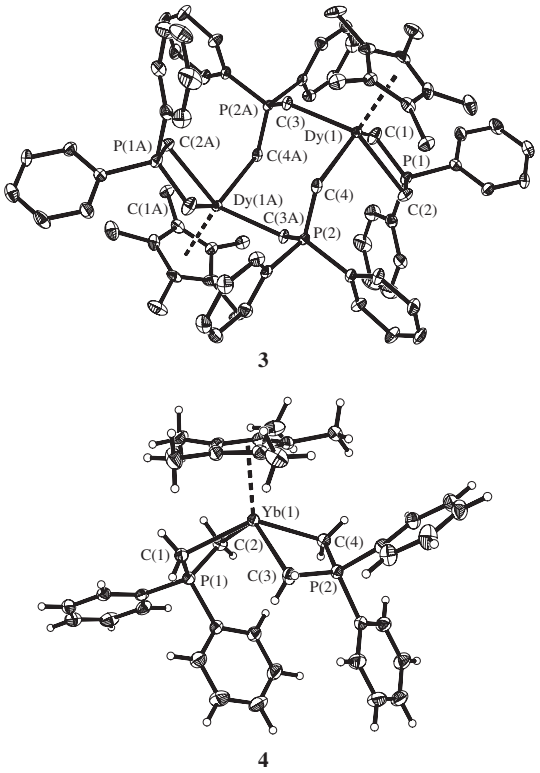


Figure 1 ORTEP drawing of the molecular structures of **3** and **4**. All hydrogen atoms for dimeric structure of **3** are ommited for clarity; 30% probability thermal ellipsoids are presented for all non-hydrogen atoms.

Table 1 Selected bond lengths (Å) and angles (°) for **3**–**5**.

Parameter	**3** (Ln = Dy)	**4** (Ln = Yb)	**5** (Ln = Lu)
Ln(1)–C(1)	2.536(7)	2.497(2)	2.493(2)
Ln(1)–C(2)	2.551(7)	2.544(2)	2.526(2)
Ln(1)–C(3)	2.542(6)	2.480(2)	2.465(2)
Ln(1)–C(4)	2.551(6)	2.484(2)	2.480(2)
Ln(1)–P(1)	3.141(2)	3.051(1)	3.044(1)
Ln(1)–P(2)	—	3.072(1)	3.063(1)
C(1)–Ln(1)–C(2)	67.0(2)	65.83(6)	65.89(7)
C(1)–Ln(1)–C(3)	88.2(2)	90.93(7)	90.70(8)
C(1)–Ln(1)–C(4)	133.6(2)	137.11(7)	136.88(7)
C(3)–Ln(1)–C(4)	87.8(2)	68.64(6)	68.87(7)
C(2)–Ln(1)–C(4)	88.0(2)	91.08(7)	90.87(8)
C(3)–Ln(1)–C(2)	140.3(2)	119.25(8)	119.31(8)
C(1)–P(1)–C(2)	107.9(3)	104.1(1)	103.9(1)
P(1)–C(1)–Ln(1)	92.5(3)	90.5(1)	90.3(1)

§ Data were collected on a STOE IPDS diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at –73 °C. The structures were solved by direct methods and refined by difference Fourier syntheses using the SHELX-97 software package.[9] XP (BRUKER AXS) was used for structure representations.

Crystal data for **3**: $C_{76}H_{86}Dy_2P_4$, M = 1448.33, monoclinic, space group $P2_1/n$, a = 14.198(3), b = 13.948(2) and c = 17.093(4) Å, β = 98.21(2)°, V = 3350.30(13) Å^3, Z = 2, d_{calc} = 1.436 g cm^{-3}, μ(MoKα) = = 2.350 mm^{-1}. Crystal dimensions 0.40×0.30×0.25 mm. Of 5904 symmetry independent reflections, 3612 were observed [$I > 2\sigma(I)$]. The final agreement factors were R_1 = 0.0415 and wR_2 = 0.0723 (all data).

For **4**: $C_{38}H_{43}P_2Yb$, M = 734.74, monoclinic, space group $P2_1/c$, a = 11.8661(4), b = 13.4824(6) and c = 20.8702(7) Å, β = 90.516(3)°, V = 3338.8(2) Å^3, Z = 4, d_{calc} = 1.462 g cm^{-3}, μ(MoKα) = 2.981 mm^{-1}. Crystal dimensions 0.47×0.35×0.20 mm. Of 53397 reflections measured, 7673 were symmetry independent and 6558 were observed [$I > 2\sigma(I)$]. The final agreement factors were R_1 = 0.0170 and wR_2 = 0.0392 (all data).

For **5**: $C_{38}H_{43}P_2Lu$, M = 736.63, monoclinic, space group $P2_1/c$, a = 11.8525(15), b = 13.4791(11) and c = 20.873(3) Å, β = 90.485(11)°, V = 3334.7(7) Å^3, Z = 4, d_{calc} = 1.467 g cm^{-3}, μ(MoKα) = 3.081 mm^{-1}. Crystal dimensions 0.50×0.50×0.40 mm. Of 7651 symmetry independent reflections, 6297 were observed [$I > 2\sigma(I)$]. The final agreement factors were R_1 = 0.0166 and wR_2 = 0.0361.

CCDC 292893–292895 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, 2008.

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References

1 (*a*) F. T. Edelmann, in *Comprehensive Organometallic Chemistry-II*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, vol. 4, p. 11; (*b*) H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865; (*c*) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851; (*d*) S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953; (*e*) Z. Hou and Y. Wakatsuki, in *Science of Synthesis*, eds. R. Noyori and T. Imamoto, Thieme, Stuttgart, 2001, ch. 1, 2.

2 (*a*) F. T. Edelmann, *Top. Curr. Chem.*, 1996, **179**, 247; (*b*) R. Anwander, in *Applied Homogeneous Catalysis with Organometallic Compounds*, eds. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, vol. 2, p. 866; (*c*) *Lanthanides: Chemistry and Use in Organic Synthesis, Topics in Organometallic Chemistry*, ed. S. Kobayashi, Springer, Berlin, 1999, vol. 2; (*d*) W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233–234**, 131.

3 (*a*) K. A. Rufanov, B. Ziemer, M. Hummert and S. Schutte, *Eur. J. Inorg. Chem.*, 2004, 4759; (*b*) K. A. Rufanov, B. Ziemer and M. Meisel, *Dalton Trans.*, 2004, 3808; (*c*) K. A. Rufanov, A. R. Petrov, V. V. Kotov, F. Laquai and J. Sundermeyer, *Eur. J. Inorg. Chem.*, 2005, 3805; (*d*) A. R. Petrov, K. A. Rufanov, B. Ziemer, P. Neubauer, V. V. Kotov and J. Sundermeyer, *Dalton Trans.*, 2007, DOI:10.1039/b710419g.

4 A. Spannenberg, P. Arndt, W. Baumann and U. Rosenthal, *J. Organomet. Chem.*, 2003, **683**, 261 and references cited therein.

5 (*a*) H. Schumann and S. Hohmann, *Chem. Ztg.*, 1976, **100**, 336; (*b*) H. Schumann and F. W. Reier, *J. Organomet. Chem.*, 1982, **235**, 287.

6 K. A. Rufanov, B. Müller, A. Spannenberg and U. Rosenthal, *New J. Chem.*, 2006, 29.

7 (*a*) L. E. Manzer, *Inorg. Chem.*, 1976, **15**, 2567; (*b*) W. K. Wong, H. Chen and F. L. Chow, *Polyhedron*, 1990, **9**, 875; (*c*) M. A. Giardello, V. P. Conticello, L. Brard, M. Sabat, A. L. Rheingold, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10212.

8 H. Schumann, I. Albrecht, F. W. Reier and E. Hahn, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 522.

9 G. M. Sheldrick, *SHELXS 97, Program for Solution of Crystal Structures*, Universität Göttingen, 1997.

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