Synthesis and molecular structures of the first phosphoranylidene complexes of rare earth metals†‡

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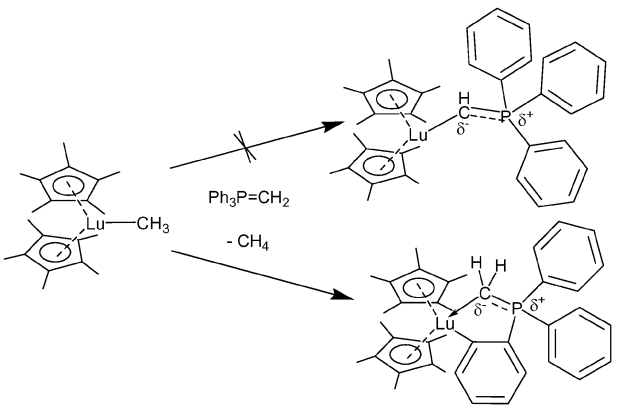
Metallation of the donor-functionalised ylide ligand $Ph_3P{=}CH{-}(o\text{-}CH_3OC_6H_4)$ with homoleptic alkyl and aryl complexes of yttrium and lutetium furnished unprecedented phosphoranylidene complexes, featuring a central $\mu_2\text{-}M_2C_2$ core.



Scheme 1

The organometallic chemistry of rare earth metals, which to date has been dominated by metallocene complexes, has recently received some impetus towards the search for new ligand systems to expand its scope beyond this traditional realm.[1–8] In contrast to main-group[9–11] and transition metals,[12] there are no examples of the activation of the CH protons of ylenes by rare-earth metals. Because the increased Lewis acidity of the lanthanides may lead to reactivity patterns that are different from those for transition metals, we were encouraged to develop new synthetic approaches towards lanthanide complexes of these phosphorus-ylide ligands.

Previously Schumann has found that $Ph_3P{=}CH_2$ and $Ph_3P{=}CHSiMe_3$ simply substitute THF in the complexes $Cp_2LuX(THF)$ (X = Bu^t, Cl),[13] while $(C_5Me_5)_2LuMe$ reacts with *ortho*-metallation of one of the phenyl substituents and formation of a 5-membered cyclic ylide complex,[14–16] rather than in metallation of the $=CH_2$ group (Scheme 1). Similar donor–acceptor adducts were later reported for other rare earth metals.[17]

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‡ Dedicated to Prof. Dmitry A. Lemenovskii on occasion of his 60th birthday

For our study we have chosen the known chelating phosphoranylidene ligand $Ph_3P{=}CH\text{-}(o\text{-}CH_3OC_6H_4)$ **1**,[18] whose structure we determined for comparison purposes (Fig. 1).§

In the early stages of our investigation we attempted to metallate **1** with rather stable $Cp^{\#}{}_2Lu(THF)CH_3$ ($Cp^{\#}$ = [1,3-$(SiMe_3)_2C_5H_3$]) and $M[N(SiMe_3)_2]_3$ (M = Y, Lu) complexes. However, NMR-monitoring of these reactions revealed only the simple substitution of the THF molecule or reversible formation of unstable adducts, similar to those described earlier.[14] The metallation of **1**, however, was not observed. Although the protonolysis of the more reactive homoleptic alkyl- or aryl-complexes of the types $Ln(CH_2SiMe_3)_3(THF)_n$ (n = 2, 3) or $Ln(o\text{-}Me_2NCH_2C_6H_4)_3$ with different CH acids, such as Cp and acetylenes, is well established,[19–21] such reactions have not been reported for phosphoranylidenes.

Initially we discovered that reaction of $Lu(CH_2SiMe_3)_3(THF)_2$ with **1** leads to exhaustive protonolysis. Indeed, NMR monitoring of the reaction mixture revealed the gradual growth of a new broad ^{31}P signal at 12.2 accompanied by the decline of the sharp signal of **1** at 10.8. The reaction, which is complete after 2 d, furnished yellow, microcrystalline material in 46% yield. Single crystals were obtained from a saturated benzene solution that had been standing at 10 °C for several weeks. The broad ^1H resonances for the aromatic protons and the methoxy group suggest that **3** displays a dynamic behaviour in solution and that the ethereal ligands are hemi-labile.[22]

We also studied the metallation of **1** with the thermally more stable and less reactive yttrium complex $Y(o\text{-}Me_2NCH_2C_6H_4)_3$, intending to synthesize heteroleptic mono-ylide complex **4** (Scheme 2). A reaction of equimolar amounts of **1** and the metal complex furnished, after heating at 65 °C for 5 h, unexpectedly a similar product of the exhaustive protonolysis of **1**, namely **5**. This yellow microcrystalline material has very low solubility in common solvents and was characterized by ^1H-, ^{31}P-NMR and elemental analysis and shown to be an analogue of binuclear complex **3**. Recrystallization of **5** from boiling THF furnished, upon slow cooling of the solution, the light yellow complex **5a**. The molecular structures of **3** and **5a** differ only in the number of coordinated THF molecules. Each lutetium atom in **3** is coordinated by only one THF donor ligand and the molecule has a center of inversion, with both lutetium atoms having distorted octahedral coordination geometry. In compound **5a**, by contrast, one yttrium is six-coordinate, bearing one THF ligand, while the other is seven-coordinate, bearing two THF ligands (Fig. 2).[23]

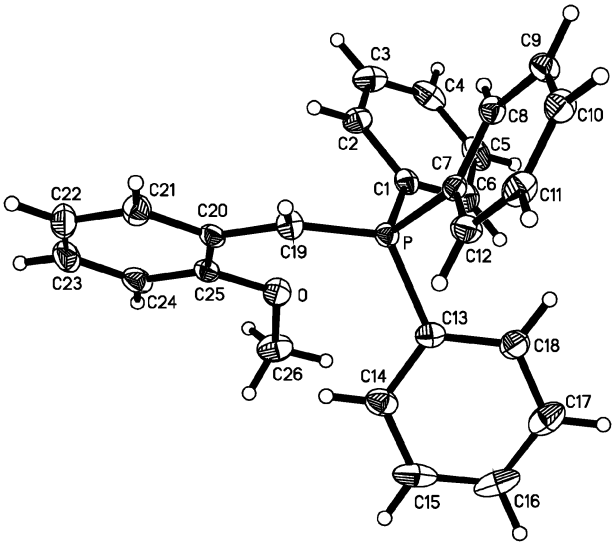


Fig. 1 ORTEP drawing of the molecular structure of **1**; 50% probability thermal ellipsoids are presented.¶

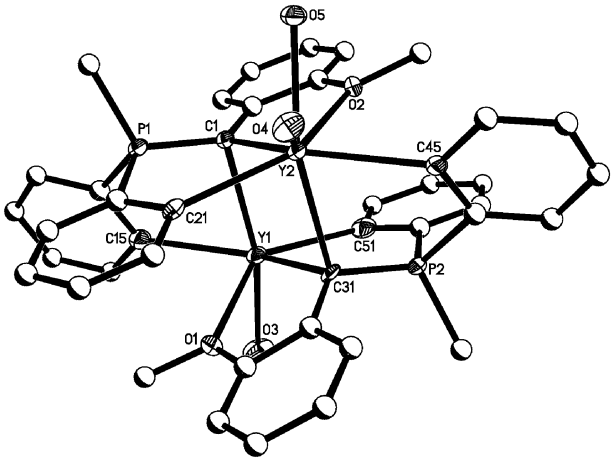


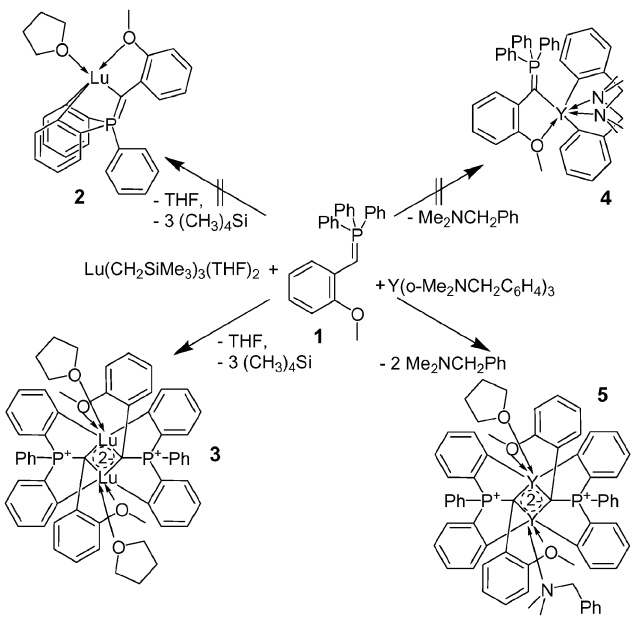
Fig. 2 ORTEP drawing of the molecular structure of **5a**. All hydrogen atoms are omitted; for non-metallated Ph-rings and co-ordinated THF ligands only *ipso*-C and oxygen atoms are shown for clarity. 50% probability thermal ellipsoids are presented only for the labelled atoms.

The difference in bond lengths within the central μ_2-M_2C_2 core is larger for **5a** (Δ = 0.18 Å) than for **3** (Δ = 0.14 Å), but the poor crystal quality of **3** (R_1 = 0.0843) prohibits detailed comparisons of the bond lengths and angles of **3** with those of **1** and **5a**. Selected structural parameters of the structures of the free ligand **1** and of **5a** are given in Table 1.

The shortest Y–C bond in the μ_2-Y_2C_2 core is of 2.396(6) Å long, and it lies in a range typical for neutral, low-coordinated, non-Cp complexes of yttrium with at least two hard-donor ligands.[24a] The THF molecules form strong bonds with the yttrium atoms with a maximum bond length of 2.47 Å, which is a similar value to those found in other Y–THF adducts.[24] One of the Y–O bonds to the methoxy groups is much longer and indicates weaker bonding. The phosphonium centers are nearly tetrahedral with a narrower range of C–P–C angles 110 (±5)° and significantly smaller P–C_{Ylide}–C_{Aryl} angle 119(±1)° than that in the free ligand **1**—112(±8)° and 132°, respectively.

Table 1 Selected bond lengths/Å and angles/° for **1** and **5a**

	1	**5a**
Y–C(shortest)		2.396(6)
Y–C(longest)		2.576(6)
Y–C_{Ph}		2.480(7)–2.572(6)
Y–O_{THF}		2.408(5), 2.450(5), 2.471(4)
Y–O_{OMe}		2.431(4), 2.577(4)
P–C_{Ylide}	1.693(2)	1.701(6), 1.714(6)
P–C_{Ph}	1.818(2)–1.831(2)	1.807(7)–1.851(6)
C_{Ylide}–C_{Aryl}	1.452(2)	1.449(9), 1.455(8)
C_{Aryl}–O_{OMe}	1.382(2)	1.398(7), 1.404(8)
C–P–C	103.4(1)–120.2(1)	104.4(3)–115.4(3)
P–C_{Ylide}–C_{Aryl}	132.0(1)	117.8(4), 119.9(4)
C_{Ylide}–Y–C_{Ylide}		85.4(2), 87.5(2)
Y–C–Y		93.2(2), 93.7(2)



Scheme 2 Synthesis of binuclear phosphoranylidene complexes **3** and **5**.

These new phosphoranylidene complexes of lutetium and yttrium should be important both for our understanding of fundamental bonding concepts of organometallic chemistry and as catalyst precursors. Full details of our results on rare earth complexes in this series will be discussed in a forthcoming paper.

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§ Synthetic and analytical details for the starting reagents are given in the ESI. *Synthesis of* **3**: a 0.5 M benzene solution of $Lu(CH_2SiMe_3)_3(THF)_2$ (5 mL, 2.5 mmol) was slowly added to a stirred solution of **1** (956 mg, 2.5 mmol) in benzene (5 mL) at room temperature. The reaction mixture was then stirred and heated at 45 °C. It gradually changed in colour from orange-red to dark yellow. After 2 d a small amount of precipitate formed that was filtered off and the resulting solution was reduced in volume to approx. 5 mL and very slowly cooled down to 10 °C for crystallization. After several weeks light yellow crystals formed. The product was filtered off, washed with pre-cooled benzene (2 mL) and dried under vacuum. Yield 0.72 g (46%). ^{1}H NMR (300 MHz, C_6D_6, +23 °C): δ 7.89–6.95 (br m, Aryl-groups and solvated C_6H_6), 3.60 (br s, CH_2–O, THF), 2.75 (br s, CH_3–O), 1.70 (br t, CH_2–CH_2–O, THF). ^{31}P NMR (121.5 MHz, C_6D_6, +23 °C): δ 12.2 (br s). Elemental analysis was calculated for $C_{60}H_{56}Lu_2O_4P_2(C_6H_6)_4$, C 64.45%, H 5.15%, Lu 22.35%, observed C 63.92%, H 5.28%, Lu 22.17%. *Synthesis* of **5**: a 0.5 M THF solution of Y(*o*-$Me_2NCH_2C_6H_4)_3$ (5 mL, 2.5 mmol) was added to a stirred solution of **1** (956 mg, 2.5 mmol) in toluene (30 mL). The orange solution was slowly heated to 65 °C and allowed to stir at this temperature for 5 h, while it gradually deepened in colour and a bright yellow precipitate deposited. After slow cooling to room temperature, the dark red solution was decanted and the yellow solid was washed with toluene (2 × 5 mL) and dried under high vacuum. Yield 0.60 g (42%) of $C_{52}H_{40}O_2P_2Y_2(C_4H_8O)(C_9H_{13}N)$. ^{1}H NMR (300 MHz, C_5D_5N, +23 °C): δ 7.89–7.15 (br m, Aryl-groups), 3.65 (br s, CH_2–O, THF), 3.54 (s, Me_2NCH_2), 3.45 (br s, CH_3–O), 2.19 (s, Me_2N), 1.59 (br t, CH_2–CH_2–O, THF). ^{31}P NMR (121.5 MHz, C_5D_5N, +23 °C): δ 36.8. Elemental analysis was calculated for $C_{65}H_{61}NO_3P_2Y_2$, C 68.25%, H 5.37%, N 1.22%, observed C 68.96%, H 5.31%, N 1.22%.

¶ Data were collected on a STOE IPDS diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2 using SHELX-97 software package.[25] *Crystal data:* for **1**: $C_{26}H_{23}OP$, M = 382.41, triclinic, space group $P\bar{1}$, a = 9.746(2) Å, b = 10.046(2) Å, c = 10.715(2) Å, α = 73.76(2)°, β = 85.61(2)°, γ = 89.94(2)°, V = 1004.0(3) Å^3, Z = 2, D_c = 1.265 g cm^{-3}, μ(Mo-Kα) = 0.151 mm^{-1}. T = −123 °C, crystal dimensions 0.76 × 0.40 × 0.08 mm, 6420 reflections were measured, 3401 were symmetry independent and 2577 were observed [$I > 2\sigma(I)$], R_1 = 0.0376 and wR_2 = 0.0945 (all data). CCDC reference number 245413. For **3**: $C_{84}H_{80}Lu_2O_4P_2$, M = 1565.36, monoclinic, space group $P2_1/c$, a = 14.192(5) Å, b = 12.461(4) Å, c = 20.490(5) Å, β = 105.51(3)°, V = 3491.6(18) Å^3, Z = 2, D_c = 1.489 g cm^{-3}, μ(Mo-Kα) = 2.908 mm^{-1}. T = −93 °C, crystal dimensions 0.40 × 0.28 × 0.20 mm, 17113 reflections were measured, 4979 were symmetry independent and 2802 were observed [$I > 2\sigma(I)$], R_1 = 0.0843 and wR_2 = 0.2278 (all data). The intensities were corrected for Lorentz polarization and absorption effects using ABSCOR, a modification of DIFABS (T_{min} = 0.366, T_{max} = 0.558).[26] CCDC reference number 245412. For **5a**: $C_{68}H_{72}O_6P_2Y_2$, M = 1225.02, triclinic, space group $P\bar{1}$, a = 12.513(3) Å, b = 14.455(3) Å, c = 19.023(4) Å, α = 86.89(3)°, β = 75.64(3)°, γ = 70.68(3)°, V = 3144.4(11) Å^3, Z = 2, D_c = 1.294 g cm^{-3}, μ(Mo-Kα) = 1.936 mm^{-1}. T = −73 °C, crystal dimensions 0.45 × 0.25 × 0.20 mm, 40601 reflections were measured, 11055 were symmetry independent and 6310 were observed [$I > 2\sigma(I)$], R_1 = 0.0624 and wR_2 = 0.1511 (all data). CCDC reference number 286123. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514439f.

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