

Protonation of a lanthanum phosphide-alkyl occurs at the P–La not the C–La bond: isolation of a cationic lanthanum alkyl complex

Keith Izod,* Stephen T. Liddle and William Clegg

Chemistry, School of Natural Sciences, University of Newcastle, Bedson Building, Newcastle upon Tyne, UK NE1 7RU. E-mail: k.j.izod@ncl.ac.uk; Fax: +44 (0)191 222 6929; Tel: +44 (0)191 222 7101

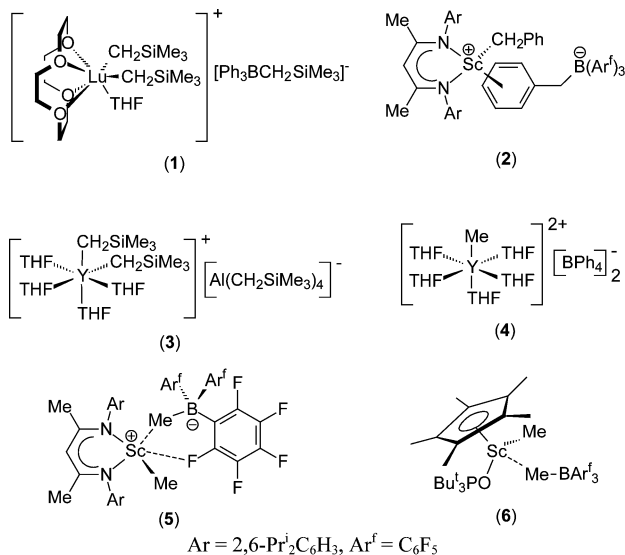
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Protonation of the heteroleptic, cyclometalated lanthanum phosphide complex $[(\text{Me}_3\text{Si})_2\text{CH}](\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2\text{-P})\text{La}(\text{THF})[\text{P}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)(\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2))]$ with $[\text{Et}_3\text{NH}][\text{BPh}_4]$ yields the cationic alkyl lanthanum complex $[(\text{THF})_4\text{La}[\text{P}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)(\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2))]][\text{BPh}_4]$.

Typically, neutral group 3 and lanthanide (rare earth) metal alkyls are less active catalysts for the polymerisation of alkenes than their isoelectronic cationic group 4 analogues.^{1,2} However, recent studies have established that *cationic* group 3 alkyls are highly efficient olefin polymerisation catalysts.^{3–6} In spite of this, there are few examples of well-defined complexes of this type, and only a handful have been isolated and characterised in the solid state.

The synthesis of rare earth metal analogues of cationic group 4 metallocenes (*i.e.* $[\text{Cp}^*\text{LnR}]^+[\text{X}]^-$; Ln = Sc, Y, La, Ce–Lu) is hampered by facile ligand scrambling in complexes of these metals. However, strategies for the synthesis of cationic rare earth metal alkyl complexes which are supported by alternative ligand scaffolds have recently been developed. These alternative supporting ligands include deprotonated aza-crowns,⁷ furyl-substituted cyclopentadienyls,⁸ amidinates,⁵ β -diketiminates,^{4,9} anilido-imines,¹⁰ and amide-functionalised triazacyclononanes;³ in addition, crown ether-stabilised rare earth metal dialkyl cations and an yttrium alkyl dication have very recently been reported.^{11,12}



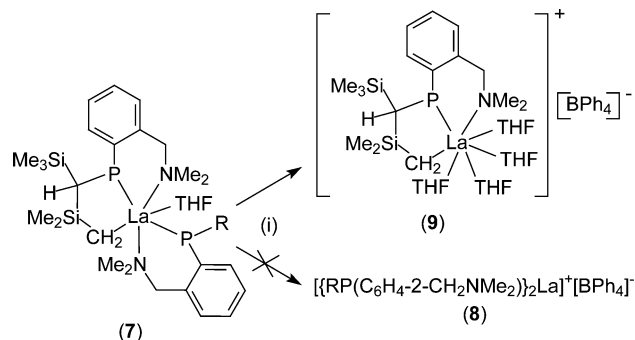
To our knowledge, there are just six examples of crystallographically characterised cationic rare earth metal alkyls with various co-ligands (1–6), all of which contain the relatively small Sc³⁺, Y³⁺ or Lu³⁺ ions;^{4,9,11–13} compounds 2, 5 and 6 exhibit significant cation–anion contacts and so may be regarded as possessing some zwitterionic character.

We recently reported the synthesis, structure and unusual dynamic behaviour of a cyclometalated lanthanum phosphide (7).¹⁴ Although both the phosphide and alkyl donors in this complex may be regarded as soft, we expected that protonation of 7 would occur at the C–La bond to yield a cationic lanthanum bis(phosphide)

complex (8) (Scheme 1). However, we find that treatment of 7 with one equivalent of $[\text{Et}_3\text{NH}][\text{BPh}_4]$ in THF solution results in protonation of the bidentate, monoanionic phosphide ligand, giving the cationic lanthanum phosphide-alkyl complex 9.[†] Although crystalline 9 was isolated in only moderate yield, a ³¹P NMR spectrum of the crude reaction mixture suggests that it is the major phosphorus-containing product, along with the free phosphine byproduct $\{(\text{Me}_3\text{Si})_2\text{CH}\}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\text{PH}$.

The cationic complex 9 is insoluble in hydrocarbons and diethyl ether but is soluble in THF. The NMR spectra of 9 are essentially consistent with the solid state structure. Although 9 is chiral at both the phosphorus and methine carbon atoms the ³¹P{¹H} NMR spectrum of 9 in *d*₈-THF consists of a single broad resonance at 20.6 ppm, suggesting rapid epimerisation of the two diastereomers, possibly due to rapid, reversible inversion at phosphorus associated with “hopping” of the La atom between the two phosphorus lone pairs.¹⁴ In the ¹H NMR spectrum of 9 the diastereotopic protons of the CH₂La group give rise to broad, but well resolved, doublets at –0.68 and –0.66 ppm (²J_{HH} = 4.9 Hz). This contrasts with the ¹H NMR spectrum of 7, in which the corresponding protons are observed as poorly resolved singlets at –1.4 and –1.0 ppm at room temperature [at –56 °C these protons are resolved as a pair of doublets at –1.58 and –1.23 ppm (²J_{HH} = 12.2 Hz)].¹⁴ The CH₂La group gives rise to a broad singlet at 61.58 ppm in the ¹³C{¹H} spectrum [*cf. ca.* 62 ppm for the same carbon atom in 7]; this peak was identified with the aid of a ¹H–¹³C correlation experiment. The observed broadening of this signal may be ascribed to the quadrupolar nature of the adjacent La centre and the dynamic nature of 9.

Compound 9 is initially isolated as an oil, but may be crystallised as the mixed solvate $9 \cdot (\text{THF})_{0.6}(\text{hexane})_{0.2}$ (9a) by layering a concentrated THF solution with *n*-hexane. X-ray crystallography reveals that 9a crystallises as discrete ion pairs with no unusual contacts between the cations and anions (Fig. 1).[‡] A disordered mixture of THF and *n*-hexane is present as solvent of crystallisation; there is also minor disorder in two of the THF ligands. The lanthanum atom in the cation is coordinated by the N, P and alkyl C atoms of a tridentate aminophosphide-alkyl ligand and by the O atoms of four molecules of THF; the geometry about the metal is best described as distorted pentagonal bipyramidal with two THF molecules in the apical positions [O(1) and O(2)]. The La–P, La–C and La–N distances of 2.956(2), 2.485(9) and 2.754(6) Å, respectively, in 9a are somewhat shorter than the corresponding



Scheme 1 (i) $[\text{Et}_3\text{NH}][\text{BPh}_4]$, THF; R = CH(SiMe₃)₂.

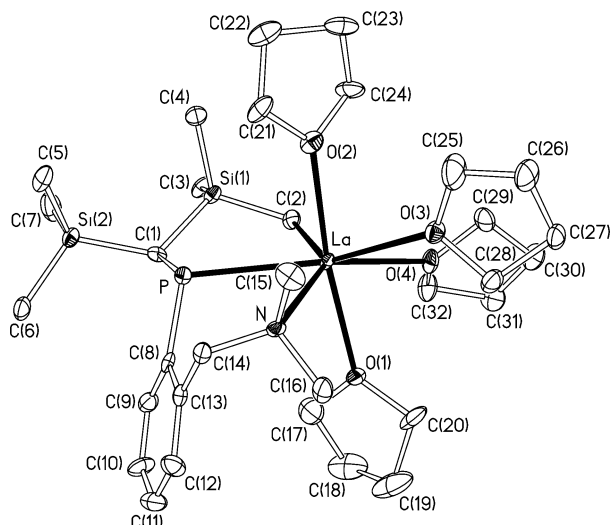


Fig. 1 Molecular structure of the cation of **9a** with 30% probability ellipsoids and with H atoms and minor THF disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): La–P 2.956(2), La–N 2.754(6), La–C(2) 2.485(9), La–O(1) 2.541(6), La–O(2) 2.521(6), La–O(3) 2.690(6), La–O(4) 2.634(5), P–C(1) 1.860(8), P–C(8) 1.799(9), C(2)–Si(1) 1.849(9), C(2)–La–P 71.60(19), N–La–P 69.33(15).

distances in **7** [2.9919(10), 2.522(4) and 2.773(3) Å, respectively],¹⁴ consistent with the presence of a positive charge on the complex cation in **9a**. As expected, the La–O(THF_{apical}) distances [2.541(6) and 2.521(6) Å] are significantly shorter than the La–O(THF_{equatorial}) distances [2.690(6) and 2.634(5) Å].

The La–C distance in **9a** [2.485(9) Å] compares with La–C distances of 2.515(9) Å in {(Me₃Si)₂CH}₃La¹⁵ and 2.55(2)–2.68(4) Å in {(Me₃Si)₂CH}₃LaClLi(pmdeta);¹⁶ the La–P distance in **9a** compares with La–P distances of 3.165(6) Å in (Ph₂P)La{N(SiMe₃)₂}₂(OPPh₃)₂¹⁷ and 3.141(4) Å in the ate complex (Pr₂N)₂La{μ-P(C₆H₄-2-OMe)₂}₂Li(THF).¹⁸ The C–La–P and N–La–P bite angles of the ligand in **9a** [71.60(19) and 69.33(15)°, respectively] are similar to those in the neutral precursor **7** [75.2(10) and 70.53(7)°, respectively]. The crystal structure is racemic, one particular diastereomer of the cation and its inversion partner being present in equal proportions.

In summary, protonation of **7**, a lanthanum complex containing both a tridentate, dianionic CPN- and a bidentate, monoanionic PN-ligand, occurs at the phosphorus of the PN-ligand rather than the carbon of the CPN-ligand, yielding a cationic lanthanum alkyl complex. We are currently studying the reactions of **9** with unsaturated inorganic and organic substrates.

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Notes and references

† A solution of **7** (1.49 g, 1.73 mmol) in THF (20 ml) was added to a cold (–78 °C) slurry of [Et₃NH][BPh₄] (0.73 g, 1.73 mmol) in THF (10 ml). The solution was allowed to warm to room temperature and was stirred for 1 h. Volatiles were removed *in vacuo* to afford a sticky red oil, which was washed with diethyl ether (20 ml). The oil was dissolved in THF (10 ml),

filtered, carefully layered with *n*-hexane (15 ml), and stored at –30 °C for 12 weeks to give **9a** as yellow blocks. A further batch of **9a** was obtained by the addition of a large excess of *n*-hexane to the mother liquor. Combined yield of crystalline material: 0.95 g, 51%. Satisfactory microanalysis could not be obtained due to the highly air- and moisture-sensitive nature of **9a**. ¹H NMR (500 MHz, *d*₈-THF): δ –0.68 (d, 1H, ²J_{HH} = 4.9 Hz, CH₂La), –0.66 (d, 1H, ²J_{HH} = 4.9 Hz, CH₂La), 0.04 (s, 9H, SiMe₃), 0.09 (s, 3H, SiMe₂), 0.11 (s, 3H, SiMe₂), 1.75 (m, 16H, THF), 2.04 (s, br, 3H, NMe₂), 2.18 (s, 3H, NMe₂), 3.09 (m, 1H, CH₂N), 3.59 (m, 16H, THF), 4.13 (m, 1H, CH₂N), 6.73 (m, 1H, ArH), 6.78 (t, 4H, *p*-BPh), 6.91 (t, 8H, *m*-BPh), 7.06 (m, 1H, ArH), 7.16 (m, 1H, ArH), 7.31 (s, br, 8H, *o*-BPh), and 7.54 (m, 1H, ArH). ¹¹B{¹H} NMR (160.4 MHz, *d*₈-THF) δ –3.4. ³¹P{¹H} NMR (202.4 MHz, *d*₈-THF): δ 20.6 (s, br).

‡ Crystal data for C₃₂H₆₂LaNO₄PSi₂·BC₂₄H₂₀[–]·0.6C₄H₈·0.2C₆H₁₄. **9a**: *M*_r = 1125.6, monoclinic, *P*₂₁/*n*, *a* = 15.7843(15), *b* = 20.861(2), *c* = 17.8375(17) Å, β = 93.678(2)°, *U* = 5861.5(10) Å³, *Z* = 4, μ (Mo–Kα) = 0.842 mm^{–1}, *T* = 150 K. 25268 data, 7640 unique (*R*_{int} = 0.093). w*R*(*F*²) = 0.181 for all data, conventional *R* = 0.079 for *F* values of 5761 reflections with *F*_o² > 2σ(*F*_o²). CCDC 234580. See <http://www.rsc.org/suppdata/cc/b4/b404188g/> for crystallographic data in .cif or other electronic format.

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