

Note

Synthesis and crystal structure of the heteroleptic lanthanum(III) bis-diphosphinomethanide complex $[\text{La}\{\text{CH}(\text{PPh}_2)_2\}_2(\text{I})(\text{THF})_2]$

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Abstract

Treatment of $\text{CH}_2(\text{PPh}_2)_2$ with *n*-BuLi/*t*-BuOK in diethyl ether affords the potassium diphosphinomethanide complex $[\text{K}\{\text{CH}(\text{PPh}_2)_2\}(\text{OEt}_2)_{0.5}]$ (**1**) in high yield. Metathesis of two equivalents of **1** with $\text{LaI}_3(\text{THF})_4$ yields the heteroleptic bis-diphosphinomethanide complex $[\text{La}\{\text{CH}(\text{PPh}_2)_2\}_2(\text{I})(\text{THF})_2]$ (**2**). X-ray crystallography shows the diphosphinomethanide ligands in **2** adopt different coordination modes in the solid state; one adopts a κ^2 -PP mode with no La–C contact, and the other adopts an η^3 -PCP mode, thus giving an eight-coordinate lanthanum centre.

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1. Introduction

The nature and reactivity of metal alkyls is of fundamental importance due to their implicit roles in catalysis [1]. However, their reactive nature often renders the isolation and study of such species inherently difficult [2]. Consequently, a number of strategies to stabilise the reactive carbanion centre have been developed which employ sterically demanding groups to block decomposition routes, and/or groups which may electronically stabilise the carbanion charge by delocalisation and/or negative hyperconjugation. Classes of ligands which employ these tactics and have proven particularly effective, thus giving rise to unusual metal coordination environments and oxidation states, include: bis- and tris-substituted trimethylsilylmethanides [3,4], bis-iminophosphoranomethanides [5], and bis-diphosphinomethanides [6]. Of these, the latter are of interest because they are closely related to popularly employed heteroallyl ligands, such as guanidates [7] and amidinates [8], although they are not themselves true heteroallyls since

the two P-centres are $\lambda^3\sigma^3$ in nature, unlike the $\lambda^3\sigma^3/\lambda^3\sigma^2$ combination in diphosphaallyls [9]. However, the directly bonded carbon and phosphorus centres in diphosphinomethanides are valence isoelectronic and have similar Pauling electronegativities of 2.55 and 2.19, respectively [10]. Thus, the two centres can compete as nucleophiles for metals giving rise to a number of coordination modes, such as κ^2 -PP (**I**), η^3 -PCP (**II**), and κ^2 -PP- κ^1 -C (**III**) [11], Chart 1.

The application of diphosphinomethanides has proven particularly worthwhile in f-block chemistry with the successful synthesis of lanthanide complexes such as $[\text{M}\{\text{CH}(\text{PPh}_2)_2\}_3]$ ($\text{M} = \text{La}$ [12], Sm [13]), $[\{\text{Sm}(\text{CH}(\text{PMe}_2)_2)_3\}_2]$ [14], $[\text{YbI}_2\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)_2\}_2\{\text{Li}(\text{THF})\}_2]$ [15], $[\text{Sc}\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)_3\}]$ [15], $[\text{Lu}\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)_3(\text{THF})\}]$ [15], $[\text{La}\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)_4\text{Li}\}]$ [15], and $[\text{Lu}\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)_3(\text{OSiMe}_3)\}[\text{Li}(\text{THF})_4]]$ [16]. We were interested to determine whether the diphosphinomethanide ligand $\text{CH}(\text{PPh}_2)_2$ is bulky enough to facilitate only double substitution at a lanthanide metal centre to enable the preparation of heteroleptic lanthanide alkyls. Herein, we report the synthesis of the potassium ligand transfer reagent $[\text{K}\{\text{CH}(\text{PPh}_2)_2\}(\text{OEt}_2)_{0.5}]$ (**1**), and its use

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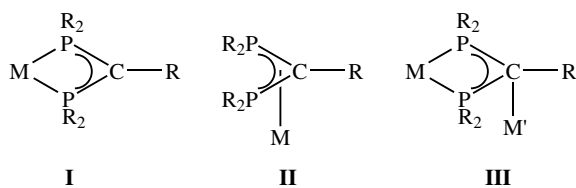
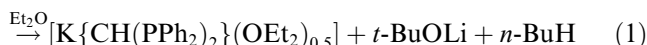
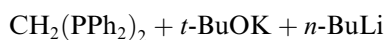


Chart 1.

in the synthesis of the heteroleptic complex $[\text{La}\{\text{CH}(\text{PPh}_2)_2\}_2(\text{I})(\text{THF})_2]$ (**2**), which exhibits two different diphosphinomethanide coordination modes in the solid state (**I** and **II**).

2. Results and discussion



A straightforward addition of *n*-BuLi in hexanes to a slurry of $\text{CH}_2(\text{PPh}_2)_2$ and *t*-BuOK in diethyl ether at room temperature affords the potassium complex $[\text{K}\{\text{CH}(\text{PPh}_2)_2\}(\text{OEt}_2)_{0.5}]$ (**1**) in high yield as a tan powder, Eq. (1). Compound **1** is essentially insoluble in diethyl ether, which facilitates its separation from the *t*-BuOLi by-product. The formation of **1** is readily apparent from inspection of its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in d_8 -THF, which exhibits a sharp singlet at 0.62 ppm (cf. ~ -21 ppm for $\text{CH}_2(\text{PPh}_2)_2$ [17]; this value compares with a chemical shift of -2.85 ppm reported for $[\text{K}\{\text{CH}(\text{PPh}_2)_2\}]$ in benzene/THF [12]. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are as expected and confirm the presence of half an equivalent of diethyl ether per molecule, which we find is not removed by prolonged exposure to vacuum. Despite numerous attempts we were unable to grow single crystals of **1**, but the above method affords spectroscopically pure material suitable for further use.

A salt metathesis reaction between two equivalents of **2** and $\text{LaI}_3(\text{THF})_4$ in diethyl ether/THF affords the heteroleptic lanthanum bis-diphosphinomethanide complex $[\text{La}\{\text{CH}(\text{PPh}_2)_2\}_2(\text{I})(\text{THF})_2]$ (**2**, Scheme 1). The use of lanthanum triiodide is preferential to lanthanum trichloride since iodide is more easily displaced from the coordination sphere of lanthanum than chloride [18]; reactions proceed cleanly at room temperature over a few hours and elevated temperatures which may encourage ligand redistribution reactions are avoided. The asymmetry of the two $\text{CH}(\text{PPh}_2)_2$ ligands of **2** observed in the solid state (see

below) is lost in solution, as evidenced by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum which exhibits a single resonance at -8.14 ppm (cf. 0.84 ppm for the closely related compound $[\text{La}\{\text{CH}(\text{PPh}_2)_2\}_3]$ [12]). The ^{31}P NMR signal for **2** is broad (fwhm ~ 300 Hz), which we ascribe to the presence of the quadrupolar La centre (^{139}La $I = 7/2$, 99.91% natural abundance) and to a dynamic exchange process involving switching of coordination modes of the diphosphinomethanide ligands; we note that a similar exchange phenomenon was observed for the homoleptic complex $[\text{Sc}\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)_3\}]$ [15]. Unfortunately, due to its low solubility we were unable to perform variable temperature NMR studies on **2**. In accord with the ^{31}P NMR spectrum, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** exhibit a single equivalent set of ligand resonances. Compound **2** may be recrystallised from THF in reasonable yield as single crystals of the solvate $2 \cdot 2\text{THF}$ suitable for X-ray diffraction (see Chart 1).

X-ray crystallography reveals that $2 \cdot 2\text{THF}$ crystallises as discrete monomers, along with two molecules of THF of crystallisation, containing an eight-coordinate lanthanum centre (Fig. 1). Selected bond lengths and angles for $2 \cdot 2\text{THF}$ are given in Table 1. The lanthanum atom is bound by a terminal iodide [I(1)], the oxygen atoms of two THF molecules [O(1) and O(2)], a diphosphinomethanide ligand in a κ^2 -PP mode [P(1) and P(2), mode I], and a second diphosphinomethanide ligand in an η^3 -PCP mode [P(3), C(26), and P(4), mode II]. The La(1) bond distances to I(1), O(1), and O(2) of 3.1518(6), 2.544(4), and 2.515(4) Å, respectively, are unexceptional [18]. The La–P bond lengths in $2 \cdot 2\text{THF}$ span the range 2.9949(14)–3.1694(13) Å, which is intermediate for diphosphinomethanide La–P contacts; for example, La–P bond lengths span the ranges 2.940(1)–3.035(1) and 3.039(2)–3.234(2) Å in

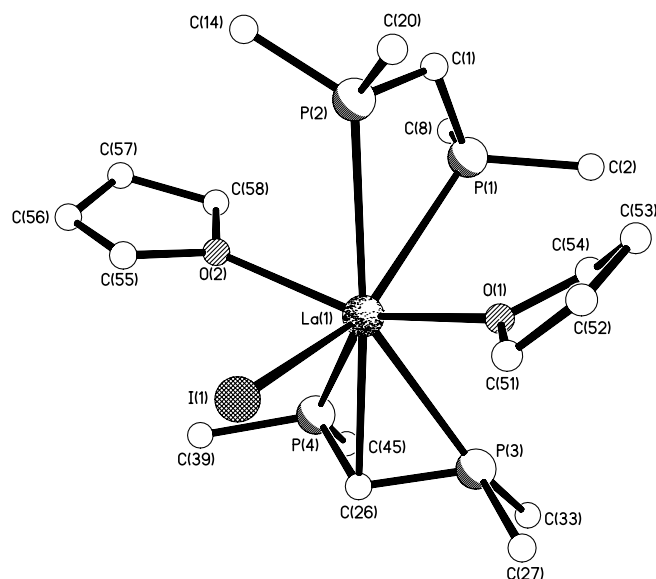
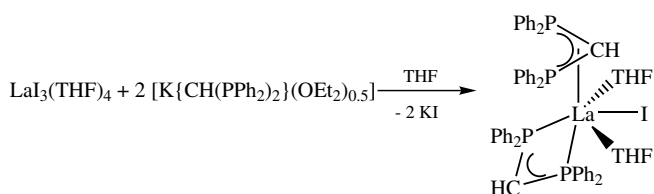


Fig. 1. Molecular structure of $2 \cdot 2\text{THF}$; non-*ipso* aryl carbon atoms of the diphosphinomethanide ligands, hydrogen atoms, and THF of crystallisation omitted for clarity.



Scheme 1. Synthesis of **2**.

Table 1
Selected bond lengths (Å) and angles (°) for **2** · 2THF

La(1)–P(1)	3.1355(13)	La(1)–P(2)	3.1694(13)
La(1)–P(3)	3.0359(13)	La(1)–P(4)	2.9949(14)
La(1)–I(1)	3.1518(6)	La(1)–C(26)	2.805(5)
La(1)–O(1)	2.544(4)	La(1)–O(2)	2.515(4)
C(1)–P(1)	1.733(5)	P(1)–C(2)	1.848(5)
P(1)–C(8)	1.847(5)	C(1)–P(2)	1.737(5)
P(2)–C(14)	1.853(5)	P(2)–C(20)	1.840(5)
C(26)–P(3)	1.772(5)	P(3)–C(27)	1.832(5)
P(3)–C(33)	1.837(5)	C(26)–P(4)	1.768(5)
P(4)–C(39)	1.835(5)	P(4)–C(45)	1.830(5)
O(2)–La(1)–O(1)	149.10(13)	O(2)–La(1)–C(26)	100.71(14)
O(1)–La(1)–C(26)	106.95(14)	O(2)–La(1)–P(4)	73.30(10)
O(1)–La(1)–P(4)	137.49(10)	C(26)–La(1)–P(4)	35.30(11)
O(2)–La(1)–P(3)	130.29(10)	O(1)–La(1)–P(3)	80.50(10)
C(26)–La(1)–P(3)	35.04(11)	P(4)–La(1)–P(3)	57.01(4)
O(2)–La(1)–P(1)	90.80(12)	O(1)–La(1)–P(1)	85.97(11)
C(26)–La(1)–P(1)	122.30(10)	P(4)–La(1)–P(1)	100.42(4)
P(3)–La(1)–P(1)	98.52(4)	O(2)–La(1)–I(1)	85.89(12)
O(1)–La(1)–I(1)	80.92(10)	C(26)–La(1)–I(1)	89.55(10)
P(4)–La(1)–I(1)	109.01(3)	P(3)–La(1)–I(1)	107.86(3)
P(1)–La(1)–I(1)	147.97(3)	O(2)–La(1)–P(2)	72.81(10)
O(1)–La(1)–P(2)	80.47(10)	C(26)–La(1)–P(2)	172.09(11)
P(4)–La(1)–P(2)	136.81(4)	P(3)–La(1)–P(2)	147.84(4)
P(1)–La(1)–P(2)	54.44(3)	I(1)–La(1)–P(2)	94.42(3)
P(1)–C(1)–P(2)	112.5(3)	P(4)–C(26)–P(3)	108.8(3)

[La{CH(PPh₂)₂}₃] [12] and [La{C(PMe₂)₂(SiMe₃)₄Li}] [15], respectively. Unsurprisingly, the La–P bonds for the κ^2 -PP ligand are longer than for the η^3 -PCP ligand, consistent with the absence of a La–carbanion contact in the former. The La(1)–C(26) distance in **2** · 2THF is 2.805(5) Å (8-coordinate La) and compares with an average La–C distance of 2.863 Å in [La{CH(PPh₂)₂}₃] (9-coordinate La) [12]. Inspection of the bond lengths of the two PCP core frameworks, Fig. 2, reveals significant structural differences consistent with the differing coordination modes. The

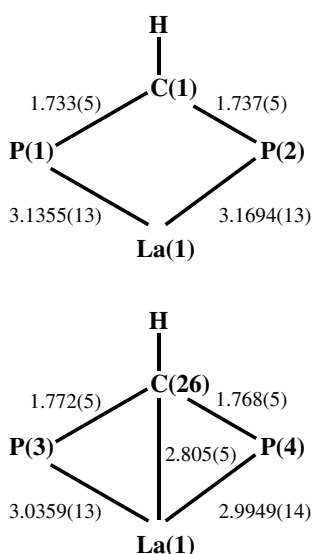


Fig. 2. Observed bond lengths for the core PCP unit of both diphosphinomethanide ligands in the crystal structure of **2** · 2THF.

κ^2 -PP ligand exhibits short C(1)–P(1) and C(1)–P(2) bond lengths of 1.733(5) and 1.737(5) Å consistent with charge delocalisation from the C(1) carbanion centre to P(1) and P(2) (average κ^2 -PP ligand P–C_{ipso} bond length = 1.847 Å). However, the coordination of lanthanum to C(26) localises the carbanion charge resulting in longer C(26)–P(3) and C(26)–P(4) bond lengths of 1.772(5) and 1.768(5) Å, respectively (average η^3 -PCP ligand P–C_{ipso} bond length = 1.818 Å). The extent of delocalisation of the carbanion charges is also reflected by the sums of angles at C(1) [359.9°] and C(26) [ignoring the La-contact, 347.5°].

3. Conclusions

Utilisation of the potassium diphosphinomethanide ligand transfer reagent **1**, which employs the bulky [−]CH(PPh₂)₂ ligand, has enabled the synthesis and characterisation of the di-substituted, heteroleptic bis-diphosphinomethanide iodide complex **2** by a metathesis salt elimination strategy. X-ray crystallography shows that the two diphosphinomethanide ligands adopt two different coordination modes in the solid state, namely κ^2 -PP and η^3 -PCP. This presents a rare opportunity to directly observe and compare the structural consequences for the PCP core which result from the different coordination modes adopted by the [−]CH(PPh₂)₂ ligand in the same molecule.

4. Experimental

4.1. General comments

All manipulations were carried out using Schlenk techniques under an atmosphere of dry nitrogen. Light petroleum (b.p. 40–60 °C), diethyl ether and THF were distilled from sodium–potassium alloy or potassium under dry nitrogen and stored over a potassium mirror (activated 4 Å molecular sieves for THF). Deuterated THF was distilled from a potassium mirror and degassed by three freeze–pump–thaw cycles and was stored over activated 4 Å molecular sieves. (Ph₂P)₂CH₂ and *n*-BuLi (2.5 M solution in hexanes) were purchased from Aldrich and used as supplied. *t*-BuOK was purchased from Aldrich and baked at 150 °C for 2 h prior to use. LaI₃(THF)₄ was prepared as described previously [18].

¹H, ¹³C, and ³¹P NMR spectra were recorded at 295 K on a JEOL Lambda 500 spectrometer operating at 500.16, 125.65, and 202.35 MHz, respectively; chemical shifts are quoted in ppm and are relative to Si(CH₃)₄ (¹H and ¹³C), and external 85% H₃PO₄ (³¹P), respectively. Elemental microanalyses were carried out by the Microanalysis Service, London Metropolitan University, UK.

4.2. Preparation of [K{CH(PPh₂)₂}₂(OEt₂)_{0.5}] (**1**)

n-BuLi (12.20 ml, 29.19 mmol) was added to a cold (0 °C) slurry of CH₂(PPh₂)₂ (11.22 g, 29.19 mmol) and

t-BuOK (3.27 g, 29.19 mmol) in diethyl ether (50 ml) to give an orange-red solution and a tan coloured precipitate. After stirring for 20 h light petroleum (40 ml) was added and the mixture allowed to settle. The solid was isolated by filtration, washed with light petroleum (3 × 20 ml) and diethyl ether (50 ml), and dried in vacuo to afford **1** as a tan coloured powder. Yield: 13.41 g, 87%. ¹H NMR (*d*₈-THF): δ 1.02 (t, 3H, OCH₂CH₃), 1.59 (t, 1H, ²J_{PH} = 8.99 Hz, P₂CH), 3.29 (q, 2H, OCH₂CH₃), 6.86 (m, 4H, *para*-CH), 6.96 (m, 8H, *ortho*-CH) and 7.46 (m, 8H, *meta*-CH). ¹³C{¹H} NMR (*d*₈-THF): δ 15.07 (OCH₂CH₃), 18.44 (t, J_{PC} = 14.26 Hz, CP₂), 65.61 (OCH₂CH₃), 124.60 (*para*-C), 126.67 (*meta*-C), 131.39 (*ortho*-C) and 152.44 (*ipso*-C). ³¹P{¹H} NMR (*d*₈-THF): δ 0.62 (s).

4.3. Preparation of [La{CH(PPh₂)₂}₂(I)(THF)₂] · 2THF (2 · 2THF)

A solution of **1** (1.29 g, 2.81 mmol) in THF (15 ml) was added dropwise to a cold (0 °C) slurry of LaI₃(THF)₄ (1.13 g, 1.40 mmol) in diethyl ether (10 ml). Once the addition was complete the mixture was allowed to warm to room temperature and stirred for 18 h. The solution was filtered and volatiles were removed in vacuo to give a sticky yellow solid. The solid was extracted into THF (5 ml), filtered, and stored at 5 °C for 24 h to give a crop of pale yellow crystals of 2 · 2THF suitable for an X-ray diffraction study. Yield (based on La): 2.49 g, 67%. Crystalline samples of 2 · 2THF lose THF of crystallisation upon extended exposure to vacuum as evidenced by CHN microanalysis and the decomposition of crystalline samples to a yellow powder. Anal. calcd. for C₅₈H₅₈ILaO₂P₄: C, 59.20; H, 4.97. Found: C, 58.58; H, 4.71%. ¹H NMR (*d*₈-THF): δ 1.65 (m, 16H, OCH₂CH₂), 2.60 (t, 2H, ²J_{PH} = 4.80 Hz, P₂CH), 3.52 (m, 16H, OCH₂CH₂) 7.06 (m, 8H, *ortho*-CH), 7.16 (m, 8H, *ortho*-CH), 7.37 (m, 8H, *para*-CH) and 7.57 (m, 16H, *meta*-CH). ¹³C{¹H} NMR (*d*₈-THF): δ 18.75 (t, J_{PC} = 7.52 Hz, CP₂), 25.66 (OCH₂CH₂), 67.60 (OCH₂CH₂), 127.43 (*para*-C), 127.73 (*meta*-C), 131.73 (*ortho*-C) and 142.57 (*ipso*-C). ³¹P{¹H} NMR (*d*₈-THF): δ -8.14 (s, br).

4.4. Crystal structure determination of 2 · 2THF

Data were collected at 150 K on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal data: C₅₈H₅₈ILaO₂P₄ · 2C₄H₈O, *M* = 1320.94, pale yellow blocks, crystal size 0.20 × 0.20 × 0.20 mm, monoclinic, space group *P*2₁/*c*, *a* = 15.4830(16), *b* = 17.0131(8), *c* = 23.836(4) Å, $\beta = 101.927(10)^\circ$, *V* = 6143.3(12) Å³, *Z* = 4, $\mu = 1.348 \text{ mm}^{-1}$, *R* (*F*; *F*² > 2 σ) = 0.0473, *R*_w (*F*²; all data) = 0.0718, *S* = 1.082 for 10747 unique, absorption corrected data and 693 parameters; final difference map extremes +2.977 and -2.575 e Å⁻³. Programs: Nonius COLLECT (diffractometer control), Nonius EVALCCD (data integration), and SHELXTL (structure solution and refinement).

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Appendix A. Supplementary material

Crystallographic data for the structural analysis of 2 · 2THF have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 295061 for compound 2 · 2THF. Copies of this information are available free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or [www:http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.02.012.

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