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X-ray and multinuclear NMR study of the mixed aggregate $[(Ph_2P(O)N(CH_2Ph)CH_3)\cdot LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}_2\text{-}4\text{-}CH_3)\cdot C_7H_8]_2$: a model for the directed metalation of phosphinamides ☆

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Abstract

The addition of $LiBu^n$ to a toluene solution of $Ph_2P(O)N(CH_2Ph)CH_3$ **1** and 2,6-di-*tert*-butyl-4-methylphenol **5** leads to the formation of the mixed dimer $[(Ph_2P(O)N(CH_2Ph)CH_3)\cdot LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}_2\text{-}4\text{-}CH_3)\cdot C_7H_8]_2$ **6**. The single crystal X-ray structure shows that two lithium aryloxide moieties dimerize giving rise to a Li_2O_2 core in which each lithium atom is additionally coordinated to a phosphinamide **1** ligand. The multinuclear magnetic resonance study (^1H, ^7Li, ^{13}C, ^{31}P) indicates that the solid-state structure is preserved in toluene solution. Complex **6** may be considered as a model for the pre-complexation step preceding the metalation of phosphinamides by an organolithium base.

Keywords: Phosphinamides; Phenolate; X-ray; Multinuclear magnetic resonance; ^{31}P; ^7Li coupling; CIPE

1. Introduction

Directed deprotonation of organic compounds by organolithium bases and subsequent addition of an electrophile represents a very efficient strategy for the regio- and stereoselective functionalization of a great variety of substrates [1]. The mechanism of the lithiation step has been interpreted in two ways. In one hypothesis, substrate and base forms a complex through lithium coordination to the lone pairs of the directing group. This complexation brings the carbanion moiety in close proximity (complex-induced proximity effect, CIPE) [2] to the acidic hydrogen, thus facilitating the metalation. The alternative explanation assigns to the directing group the role of stabilizing the transition state for the deprotonation rather than that of pre-complexation, so that the transfer of a particular hydrogen to the base is kinetically enhanced [3].

In the course of our studies on the synthetic applications of *N*-alkyl-*N*-benzyldiarylphosphinamides we have reported that their lithiation in THF at −90 °C in the presence of HMPA (hexamethylphosphoramide) or DMPU (*NN*′-dimethylpropyleneurea), followed by addition of an electrophile afforded tetrahydrobenzo [*c*][1,2]aza-1λ^5-phospholes **2** with very high regio- and stereocontrol (Scheme 1) [4]. These dearomatized products arise from an anionic cyclization reaction involving a benzylic anion. In absence of coordinating solvents, products **3** and **4** derived from the electrophilic quench of *ortho* and benzylic anions, respectively, were also obtained [5]. NMR monitoring of the dearomatization reaction revealed the formation of a pre-lithiation

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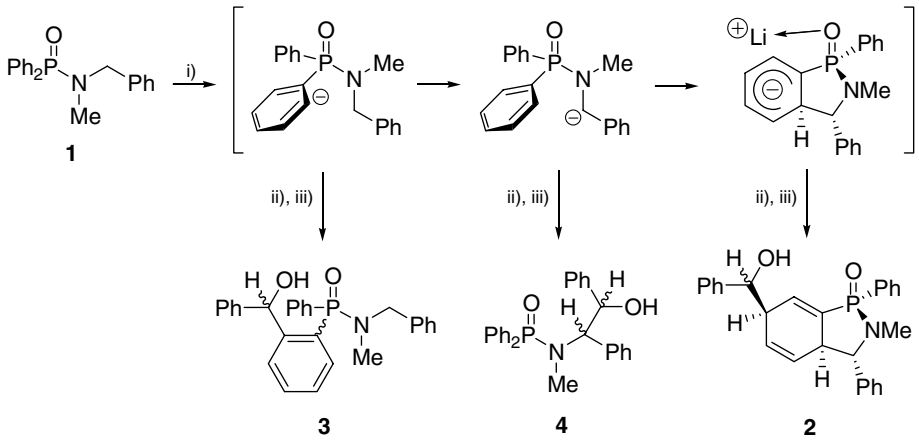


Scheme 1. Anions generated in the lithiation of **1** and subsequent reaction with benzaldheyde, followed by hydrolysis. Reaction condition: (i) $LiBu^s$, −90 °C, 30 min, THF; (ii) PhCHO −90 °C, 2 h; (iii) H_2O, 0 °C.

complex in the reaction pathway between the base ($LiBu^s$) and the phosphinamide [6].

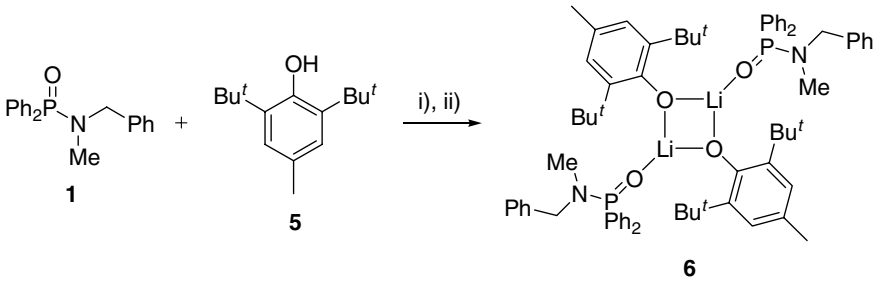
The ability of phosphorus (V) Lewis bases R_3PX to coordinate lithium centres is well established [7]. Most structural work has focused on phosphine oxides [8] and phosphoramides [9]. In a synthetic, rather than a structural context, HMPA has also been used widely as a modulator of the chemical behaviour of organolithium compounds [10]. In contrast, the possibility of using phosphinamides as donors in s-block chemistry remains virtually unexplored. Only one complex showing a phosphinamide coordinated to a lithium cation has been reported. This structural fragment was part of a bimetallic complex $[NiLiCl(C_{10}H_{23}NOP)_2(C_{10}H_{24}NOP)]$ containing both phosphinamide and phosphinamidate ligands [11]. In this paper we describe the synthesis, isolation, X-ray and NMR structural identification of the first structurally characterized example of a lithium complex $[(Ph_2P(O)N(CH_2Ph)CH_3)\cdot LiO\text{-}(C_6H_2\{C(CH_3)_3\}_2CH_3)]_2$ **6** where a phosphinamide, namely *N*-benzyl-*N*-methyldiphenylphosphinamide **1**, acts as Li-ligand exclusively in its neutral form. Compound **6** may be considered as a structural model for the formation of a pre-complex in the directed lithiation of substrates containing a P=O group.

2. Results and discussion

All attempts to crystallize a complex between phosphinamide **1** and $LiBu^s$ under synthetically meaningful reactions conditions (THF, −90 °C) failed. Even at −90 °C, and in absence of coordinating co-solvents (HMPA, DMPU) the phosphinamide is deprotonated in a few hours [6]. The use of $LiBu^n$ as a base has the additional drawback of favouring the competing process of attack to the phosphinamide linkage leading to lithium butyldiphenylphosphine oxide. We reasoned that lithium 2,6-di-*tert*-butyl-4-methylphenolate could be a representative sterically demanding weak base suitable to interact with the PO linkage of **1** that could favour the isolation of stable complexes. The treatment of a 1:1 toluene solution of $Ph_2P(O)N(CH_2Ph)CH_3$ **1** and 2,6-di-*tert*-butyl-4-methylphenol **5** with equimolar amounts of *n*-buthyllithium (hexane solution) at −30 °C lead to the quantitative formation of complex **6** (Scheme 2).

When the solution reached room temperature a white precipitate was obtained which dissolved upon heating. From the resulting solution a crop of X-ray quality colourless crystals of **6** could be isolated.

Single-crystal X-ray analysis of **6** confirms the expected dimeric lithium aryloxide complex coordinated



Scheme 2. Reaction condition: (i) $LiBu^s$, −30 °C to RT, toluene; (ii) gentle warming followed by storage at −20 °C for 24 h.

by neutral phosphinamide ligands (Fig. 1(a)). The crystal lattice also contains toluene solvent molecules. Selected interatomic distances and angles are collected in Fig. 1. The planar Li_2O_2 core contains small Li–O–Li and large O–Li–O bond angles [Li(1)–O(2)–Li(1a) 82.4(2); O(2)–Li(1)–O(2a) 97.6(2)°] and the Li–OAr bond lengths [Li(1)–O(2) 1.887(4) and Li(1)–O(2a) 1.848(4) Å] are similar to those found in analogous lithium phenolates, e.g., $[Li(O\text{-}2,6\text{-}^tBu_2C_6H_3)(THF)_2]_2$ [av. Li–O 1.848 Å] [12], $[Li(O\text{-}2,6\text{-}^tBu_2C_6H_3)(OEt)_2]_2$ [av. Li–O 1.875 Å] [13], $[Li(OPh)(OEt)_2]_2$ [av. Li–O 1.875 Å] [14], and $[Li(O\text{-}2,6\text{-}^tBu_2C_6H_3)(py)_2]_2$ [av. Li–O 1.851 Å] [15]. The phosphinimide ligand is coordinated to the three-coordinate lithium centre in an approximately linear fashion [Li(1)–O(1)–P(1) angle 168.3(2)°], with the P(1)–O(1) bond length [1.489(1) Å] little changed upon complexation (mean P–O bond length in similar uncomplexed molecules from the Cambridge Structural Database, 1.482 [16,17]). The amide substituents of the phosphinamide ligands adopt a *transoid* arrangement about the central metal-oxygen core and N(1) is pyramidal (sum of angles around N(1) = 349°) with the lone pair adopting an antiperiplanar conformation with respect to the P–O bond (Fig. 1(b)). In spite of the apparent availability of the lone pair on N(1), no interaction between nitrogen and lithium occurs. This is unsurprising given the 'ylidic' polar nature of the P–O bond in **1** and the well-documented proclivity for this functional group to coordinate to lithium [7].

In order to elucidate the solution structure of **6** a multinuclear magnetic resonance study in toluene was undertaken. All NMR spectra were measured at 0 °C.

^1H and ^{13}C NMR: Coordination of **1** to the highly crowded lithium aryloxide is readily deduced from the changes in chemical shifts and coupling constants observed in the NMR spectra. A selection of ^1H and ^{13}C NMR data of **1** and the phosphinamide moiety of **6** is given in Table 1.

Most of the proton and carbon signals of **6** shift to higher field with respect to the free ligand. In the ^1H NMR spectrum the largest shielding is observed for the methylene group H-3 ($\Delta\delta_H = -0.29$ ppm; $\Delta\delta_X = \delta(\text{complex}) - \delta(\text{ligand})$), the methyl H-8 ($\Delta\delta_H = -0.13$) and the *ortho* protons H-10 of the *P*-phenyl rings ($\Delta\delta = -0.31$ ppm). In contrast, the *ortho* carbons C-10 also show a slight deshielding effect upon complexation ($\Delta\delta_C = +0.19$ ppm) [18].

^{31}P and $^{6/7}Li$ NMR: The ^{31}P NMR spectrum of complex **6** exhibits one resonance at $\delta_P = 32.03$ ppm ($\Delta\delta_P = -2.89$ ppm) with an unusual line shape: a sharp triplet is overlapped to a broad doublet (Fig. 2(a)). The triplet arises from the coupling of one ^{31}P nucleus to the ^6Li isotope of one lithium atom ($^2J(^{31}P,^6Li) = 4.5$ Hz). The apparent doublet is the result of the $^{31}P,^7Li$ coupling. Similar line shapes have been occasionally observed in the ^{13}C [19] and ^{31}P [20] NMR spectra of organolithium compounds. These uncommon line shapes have been explained in terms of relaxation effects

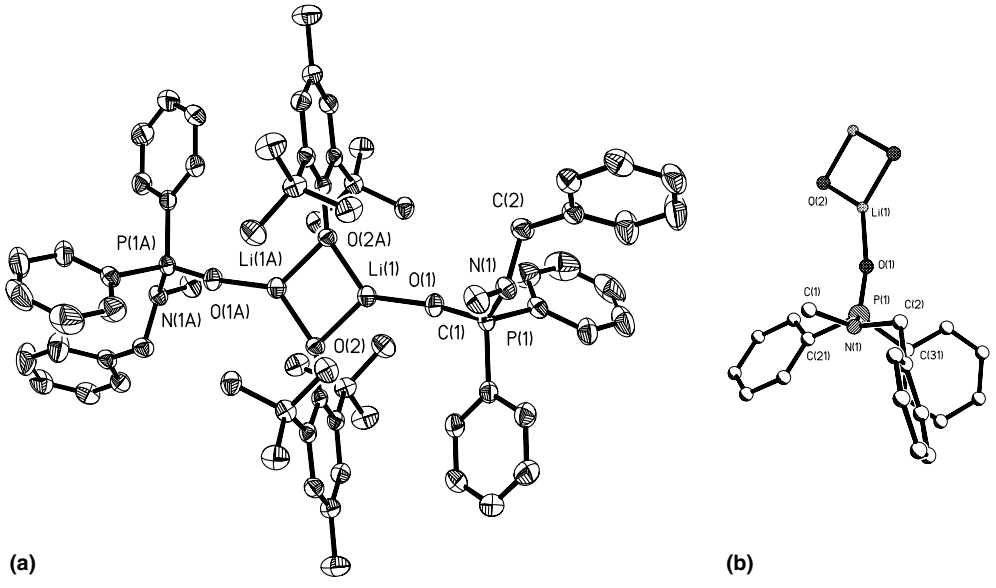
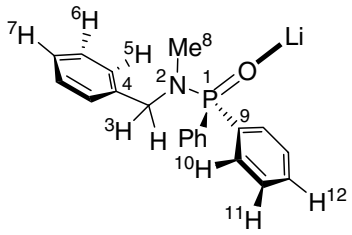


Fig. 1. (a) Molecular structure of $[(Ph_2P(O)N(CH_2Ph)CH_3)\cdot LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}_2\text{-}4\text{-}CH_3)\cdot C_7H_8]_2$ **6** (thermal ellipsoids at the 50% probability level, hydrogen atoms and toluene solvent omitted for clarity). (b) View down a P–N bond in **6**, highlighting the antiperiplanar conformation of the nitrogen lone pair with respect to P–O bond. Selected bond lengths (Å) and angles (°): Li(1)–O(2) 1.887(4); Li(1)–O(2a) 1.848(4); O(1)–Li(1) 1.825(4); P(1)–O(1) 1.489(1); P(1)–N(1) 1.653(2); P(1)–C(21) 1.798(2); P(1)–C(31) 1.805(2); N(1)–C(1) 1.472(3); N(1)–C(2) 1.481(3); Li(1)–O(2)–Li(1a) 82.4(2); O(2)–Li(1)–O(2a) 97.6(2); N(1)–P(1)–O(1) 117.58(9); O(1)–P(1)–C(21) 111.59(9); O(1)–P(1)–C(31) 109.44(9); P(1)–O(1)–Li(1) 168.3(2); C(2)–N(1)–C(1) 112.1(2); C(2)–N(1)–P(1) 117.9(1).

Table 1
Selected ^{1}H and ^{13}C NMR δ (ppm) and $^{n}J_{PC}$ (Hz) of **1** and the phosphinamide moiety of **6** in toluene-d_8 at 0 °C

	Site	**1**			**6**		
		δ (^{1}H)	δ (^{13}C)	$^{n}J_{PC}$	δ (^{1}H)	δ (^{13}C)	$^{n}J_{PC}$
	3	4.03	52.80	3.0	3.74	52.80	2.4
	4		138.06	6.0		136.94	7.2
	5	7.38	128.21		7.02	127.91	
	6	7.19	128.27		7.02	128.50	
	7	7.11	127.00		7.02	127.25	
	8	2.36	33.19	3.0	2.23	32.86	2.1
	9		133.32	126.8		130.14	134.6
	10	8.02	132.40	9.0	7.71	132.59	9.5
	11	7.11	128.20	12.0	7.15	128.46	12.8
	12	7.11	131.07	2.4	7.02	131.68	2.3

and the magnitude of the scalar coupling [21]. As expected, ^{7}Li decoupling of the ^{31}P NMR spectrum (Fig. 2(b)) gives rise to a singlet. The triplet of the ^{31}P, ^{6}Li isotopomer (7.4%) lies buried at the base of the signal corresponding to the much more abundant $^{31}P,^{7}Li$ isotopomer. This is another illustrative example of the usefulness of $^{31}P\{^{7}Li,^{1}H\}$ in the structural analysis of lithium organophosphorus compounds [20e].

The $^{6/7}Li$ NMR spectra of **6** show the same trends found in the ^{31}P spectrum, i.e., only one signal is detected at δ 1.96 ppm. The coupling to only one phosphorus nucleus is clearly observed for both isotopes ($^{2}J(^{31}P,^{7}Li) = 11.6$ Hz, Fig. 2(c); $^{2}J(^{31}P,^{6}Li) = 4.4$ Hz, Fig. 2(e); ratio $\gamma^{7}Li/\gamma^{6}Li = 2.64$). This coupling disappears when the spectrum is acquired under ^{31}P decoupling, as shown for ^{7}Li in Fig. 2(d).

2.1. Solution structure and aggregation state

Although the preceding NMR data clearly establishes that only one nucleus of ^{31}P is coupled to one $^{6/7}Li$ nucleus in complex **6**, the aggregation state in solution cannot be unambiguously deduced. The coupling observed would be consistent either with a monomeric species or any other structure having alternate (Ar)O–Li bonds (linear oligomers, cyclic dimer, cyclic trimer, etc.). However, additional information useful for the identification of the aggregation state can be obtained from NOE measurements and competitive complexation experiments.

The NOEs observed in the g-ROESY spectrum of **6** are consistent with the information derived from the ^{31}P, $^{6/7}Li$-coupling constants and evidence the proximity between the ligand **1** and the aryloxide fragments. Thus, the benzylic and *ortho* protons of the *P*-phenyl ring of **1** interact dipolarly with the methyl protons of the *t*-butyl moiety of the aryloxide fragment (Fig. 3). Although these NOEs do not resolve the question of the aggregation state, they confirm that the ligands **1** and ArO^{-} coordinated to the lithium cation are spatially close.

Support for the proposed solution aggregation state ($n = 2$) was obtained from ^{31}P NMR spectra of a new

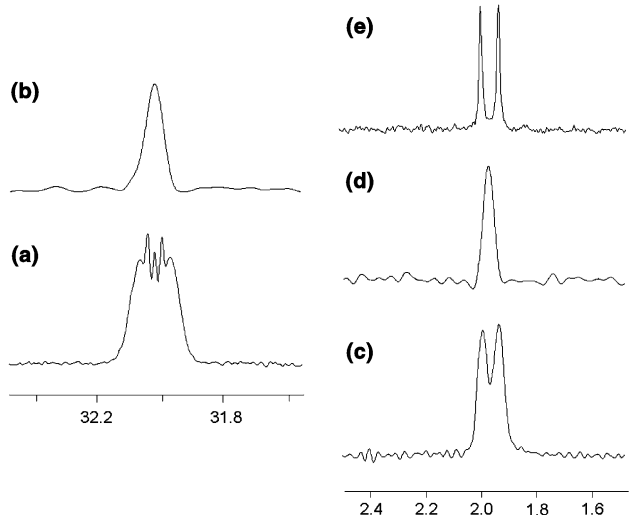


Fig. 2. (a) $^{31}P\{^{1}H\}$ (202.46 MHz), (b) $^{31}P\{^{7}Li,^{1}H\}$, (c) $^{7}Li\{^{1}H\}$ (194.37 MHz), (d) $^{7}Li\{^{31}P,^{1}H\}$, (e) $^{6}Li\{^{1}H\}$ (73.60 MHz) spectrum of **6** in toluene-d_8, natural isotope abundance at 0 °C.

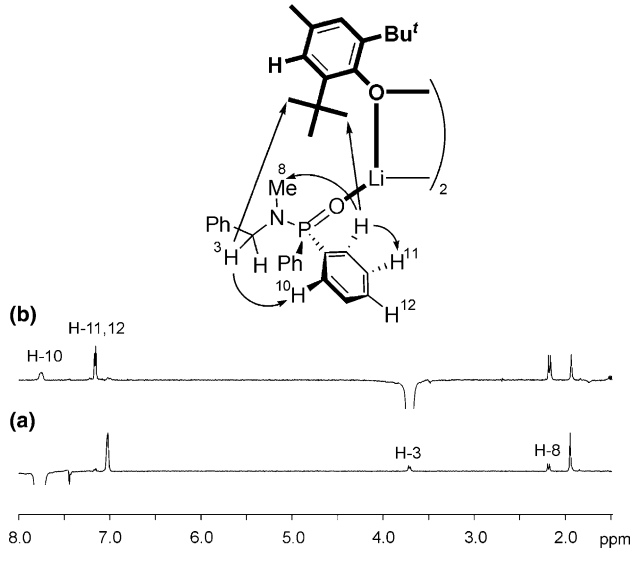


Fig. 3. Selected rows from the 2D ROESY spectrum (500.13 MHz) of complex **6** measured in toluene-d_8 at 0 °C: (a) *ortho*; (b) benzylic protons. See Table 1 for the numbering scheme used.

sample of **6** prepared in toluene by using a ratio **1**:**5** of 1.5:1. In this way, the complex **6** will be formed and will coexist with an excess of 0.5 equiv of the starting phosphinamide in a non coordinating solvent such as toluene. The variable temperature ^{31}P spectra (see supporting information) of this new sample indicate that the signal due to **6** does not show any significant change in the presence of an excess of **1** with respect to the sample devoid of free phosphinamide. Considering the coordinating ability of the PO linkage of **1** two potential effects may be envisaged upon further coordination of **1**–**6**. Firstly, the deaggregation of any possible higher aggregate would be favoured, and secondly, a new coupling would be detected in the ^{31}P and/or $^{7/6}Li$ NMR spectra [22]. Taken together with previous investigations into the solution structure of organolithium compounds [7], these observation suggests that: (i) no equilibria between different aggregation states operate, even in the presence of excess ligand; (ii) **6** is unlikely to be a two-coordinate monomer ($n = 1$) since coordination of the excess ligand would occur; (iii) complex **6** is unlikely to exist in solution in a higher aggregation state (i.e., $n = 3, 4$, etc.) than is observed in the solid state, especially in the presence of excess Lewis base. Thus, the lack of coordination of free **1**–**6** strongly suggests that the dimeric structure observed in the solid state is maintained in solution and that this structure is highly compact thus blocking the approach of a new ligand to the coordination sphere of a lithium cation.

The coordination of the bulky phosphinamide **1** to lithium 2,6-di-*tert*-butyl-4-methylphenolate to give complex **6** indicates that the formation of a similar complex with a less sterically demanding metalating reagent such as $LiBu^s$ would be an even more favourable process. NMR studies carried out on the lithiation of **1** in THF solution have shown the existence of these types of pre-metalation complexes [6]. Hence, complex **6** can be considered as a model for pre-complexes present during the initial steps of the lithiation of **1**.

In conclusion, a new mixed aggregate $[(Ph_2P(O)N(CH_2Ph)CH_3)\cdot LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}_2\text{-}4\text{-}CH_3)\cdot C_7H_8]_2$ **6** has been synthesized and characterized. The dimeric structure found in the solid state is preserved in toluene solution. The lithium aryloxide moiety gives rise to a dimer having a Li–O–Li–O four-membered ring in which each lithium atom is coordinated to one molecule of phosphinamide. This novel species supports the interpretation of the deprotonation of phosphinamide **1** through a lithium base in terms of the CIPE model.

3. Experimental

All compounds were treated as air-sensitive and moisture-sensitive, accordingly all reactions and manipulations were carried out in an atmosphere of dry, pure N_2 or argon gas, using standard procedures. Solvents were fresh distilled over Na/K alloy. Phosphinamide **1** was prepared as described elsewhere [4b], the highly crowded phenol 2,6-di-*tert*-butyl-4-methylphenol was obtained commercially and pre-dried prior to use. $LiBu^n$ was obtained from Aldrich and used as received.

NMR studies: All multinuclear NMR experiments were performed on a Bruker Avance 500 MHz spectrometer equipped with a third radio frequency channel. A 5 mm direct triple probe head $^1H/^{31}P$, BB was used. The inner coil was tuneable in the frequency range of ^{31}P–^{109}Ag nuclei. $^{6/7}Li$ spectra were acquired in natural abundance. The pulse widths for the 90° pulses and operating frequencies were: 85 μs (^1H, 500.13 MHz), 15.7 μs (^7Li, 194.37 MHz), 31 μs (^{31}P, 202.46 MHz) and 21 μs (^6Li, 73.60 MHz). The attenuation levels used were 15 dB for the proton channel and 0 dB for the heteronuclei. The spectral references used were, 85% H_3PO_4 for ^{31}P and 1M LiBr in D_2O for $^{6/7}Li$. A set of two complementary $^{31}P/^7Li$ selective band pass/stop frequency filters were used for the acquisition of the $^{31}P\{^7Li,^1H\}$ NMR spectrum. Selected spectral parameters were as follows.

One-dimensional ^1H NMR: 32*K* data points; spectral width, 4000 Hz. ^{13}C NMR: 32*K* data points; spectral width 18 000; exponential multiplication with a line broadening factor of 0.6 Hz. ^{31}P NMR: 32 *K* data points; spectral width 6000; exponential multiplication with a line broadening factor of 1 Hz. $^{6/7}Li$ NMR: 16*K* data points; spectral width 600; exponential multiplication with a line broadening factor of 0.4 Hz. Exponential multiplication of the FID (LB = 1) was applied to ^{13}C and ^6Li previous to the Fourier transformation. Gaussian multiplication (GM) was applied to ^7Li and ^{31}P, (LB = −3, GB = 0.1 for ^{31}P, and LB = −4, GB = 0.1 for ^7Li). Two-dimensional phase sensitive g-ROESY: spin-lock field of 2.5 KHz, mixing time of 200 ms and 256 increments, final matrix of 2048 × 1024 apodized by a sine squared of factor 2 in both dimensions prior to Fourier transformation.

NMR sample preparation, sample preparation: dry toluene-d_8 (0.5 ml) was added to a mixture of *P*-diphenyl(*N*-benzyl-*N*-methyl)-λ^5-phosphinamide **1** (30 mg, 93.5×10^{-2} mmol) and 2,6-di-*tert*-butyl-4-methylphenol (20.6 mg, 93.5×10^{-2} mmol) in a 5 mm NMR tube. To this solution was added dropwise *n*-butyllithium (1.6 M hexane solution, 64 μl, 10.3 mmol) at −30 °C. The concentration of the sample was 0.19 M.

X-ray data for **6**: $C_{42}H_{51}Li_1N_1O_2P_1$, colourless block of dimensions $0.25 \times 0.10 \times 0.10$ mm^3, triclinic, $P-1$, $a = 10.1350(5)$, $b = 13.3260(7)$, $c = 14.0970(6)$ Å, $\alpha = 87.831(3)$, $\beta = 83.845(3)$, $\gamma = 78.379(3)°$, $V = 1853.9(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.146$ g cm^{-3}. Data collected on a Nonius Kappa CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å), $T = 170(2)$ K, $\theta_{max} = 27.50°$, 10 198 reflections measured of which 7296 independent ($R_{int} = 0.0247$), $\mu = 0.109$ mm^{-1} (no absorption

correction). Structure solved by direct methods (SHELXS-86) [23] and refined on F^2 by full-matrix least-squares (SHELXL-97) [24], 433 parameters, $R_1 = 0.0612$ (5815 data $I > 2\sigma(I)$), $wR_2 = 0.1646$ (all data). All non hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with a riding refinement.

3.1. Synthesis of 6

To a toluene solution containing 2,6-di-*tert*-butyl-4-methylphenol (0.14 g, 0.62×10^{-3} mol) and *P*-diphenyl(*N*-benzyl-*N*-methyl)-λ^5-phosphinamide **1** (0.2 g, 0.62×10^{-3} mol), was added dropwise *n*-butyllithium (1.6 M hexane solution, 0.4 ml, 0.68×10^{-3} mol) at −30 °C. The solution was stirred during 60 min affording a white precipitate. The precipitate was dissolved upon heating. From the resulting solution a crop of X-ray quality colourless crystals **6** could be isolated after storage at −20 °C during 24 h. ^{1}H NMR (C_7D_8, 0 °C) δ 1.86 (s, 18H), 2.21 (d, 3H, J_{PH} 11.2 Hz), 2.58 (s, 3H), 3.76 (d, 2H, J_{PH} 8.6 Hz), 7.14–6.94 (m, 11H, ArH), 7.33 (s, 2H, ArH), 7.71 (m, 4H, ArH); ^{13}C NMR (C_7D_8, 0 °C) δ 21.52 (CH_3), 31.88 (CH_3), 32.86 (CH_3, J_{PC} 3.0 Hz), 35.48 (C), 52.80 (d, CH_2, J_{PC} 3.0 Hz), 118.83 (C_{ipso}), 125.50 (CAr), 127.25 (CAr), 127.90 (CAr), 128.46 (d, CAr, J_{PC} 12.8 Hz), 128.49 (CAr), 130.14 (d, C_{ipso}, J_{PC} 134.6 Hz), 131.68 (d, CAr, J_{PC} 2.3 Hz), 132.59 (d, CAr, J_{PC} 9.5 Hz), 136.94 (C_{ipso}), 138.06 (d, C_{ipso}, J_{PC} 6.0 Hz), 164.67 (C_{ipso}); ^{31}P NMR (C_7D_8, 0 °C) δ 32.03; ^{7}Li NMR (C_7D_8, 0 °C) δ 1.96 (d, J_{PLi} 11.6 Hz); ^{6}Li NMR (C_7D_8, 0 °C) δ 1.96 (d, J_{PLi} 4.4 Hz).

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 229362. Copies of this information may be obtained free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (int code) +44-(1223)336-033 or email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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