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Reactions of bulky alkyl lithium reagents with a phosphaalkyne ($P{\equiv}CBu^t$): synthesis and structural characterisation of a mixed valent phosphorus cage compound, $P^{III}\{\mu\text{-}C(H)(Bu^t)\}_2\{\mu\text{-}C(H)(SiMe_3)Si(Me)_2C(H)_2\}P^V{=}C(SiMe_3)_2$, and a phosphaalkenyl-substituted η^3-azaallyl-lithium complex, $[Li(tmeda)\{C(SiMe_3)(2\text{-}NC_5H_3Me\text{-}6)[P{=}C(Bu^t)(SiMe_3)]\}]$

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Abstract

The reactions of the phosphaalkyne, $P{\equiv}CBu^t$, with the bulky alkyl lithium reagents, $[LiCH_{3-n}(SiMe_3)_n]$ $n = 1$–3 and $[LiC(SiMe_3)_2(2\text{-}NC_5H_3Me\text{-}6)]$, have been investigated. These have led to unexpected results which include the formation of the mixed valent phosphorus cage compound, $P^{III}\{\mu\text{-}C(H)(Bu^t)\}_2\{\mu\text{-}C(H)(SiMe_3)Si(Me)_2C(H)_2\}P^V{=}C(SiMe_3)_2$, and the phosphaalkenyl-substituted η^3-azaallyl-lithium complex, $[Li(tmeda)\{C(SiMe_3)(2\text{-}NC_5H_3Me\text{-}6)[P{=}C(Bu^t)(SiMe_3)]\}]$, both of which have been crystallographically characterised. A mechanism for the formation of each complex has been discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphaalkyne; Alkyl lithium; Phosphaalkenyl; Cage compound; Crystal structure

1. Introduction

We have recently shown that 1,2-additions of Grignard reagents across the triple bond of phosphaalkynes regioselectively leads to the high yield formation of stable phosphavinyl Grignard reagents, e.g. *Z*-$[CyP{=}C(Bu^t)MgCl(OEt_2)]$ (**1**) Cy = cyclohexyl [1]. The use of these as transfer reagents in the formation of both main group and transition metal complexes is being systematically explored. This study has highlighted the synthetic versatility of the phosphavinyl ligand as it can behave similarly to normal vinyl groups, as in $[CyIn\{C(Bu^t){=}PCy\}_2]$ [2] and $[Me_2Sn\{C(Bu^t){=}PCy\}_2]$ [3], or it can undergo facile coupling reactions at metal centres to give strained metallo-organophosphorus cage compounds such as $[Bu^tC(\mu\text{-}PCy)_2\{\mu\text{-}AlC(Bu^t){=}PCy\}CBu^t]$ [2]. In addition, oxidative coupling of the phosphavinyl fragment can occur to give metal free organophosphorus systems such as the endo:endo-1,3-diphosphabicyclo[1.1.0]butane, $Cy_2P_2C_2Bu^t_2$ [4]. We have had little success utilising **1** as a transfer reagent in the formation of lanthanide complexes and saw phosphavinyl lithium reagents as more appropriate for this purpose.

A handful of phosphavinyl lithium reagents are known, e.g. $[Mes^*P{=}C(SiMe_3)Li]$ $Mes^* = C_6H_2Bu^t_3$-2,4,6 [5]; but they are all very thermally unstable, are generated in-situ and always incorporate the bulky supermesityl group (Mes*) as either the phosphorus or carbon substituent. In this context, it is noteworthy that only one such compound, *Z*-$[Mes^*P{=}C(Cl)\{Li(DME)_2\}]$ [6], has been structurally characterised but this is unstable in the solid state at room temperature. One logical route to a wider variety of phosphavinyl lithium reagents is the 1,2-addition of alkyl lithium reagents to phosphaalkynes (cf. the for-

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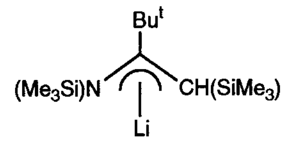
mation of **1**). This has been previously attempted and in one case, the addition of MeLi to P≡CMes*, has led to the species, [MeP=C(Mes*)(Li)] (**2**), though this was only stable in solution and was poorly characterised [7]. We believed that the use of bulkier alkyl lithium reagents in similar reactions could lead to more stable phosphavinyl lithium complexes. The silyl substituted methyl lithium reagents, [$LiCH_{3-n}(SiMe_3)_n$] (**3**), $n = 1$–3 and [$LiC(SiMe_3)_2(2\text{-}NC_5H_3Me\text{-}6)$] (**4**), seemed ideal for this purpose. Despite this, the possibility of further reactivity of any generated phosphavinyl lithium reagents could not be ruled out given the work of Lappert et al. who have shown that the reaction of **3** with nitriles, N≡CR, can lead to lithium η^3-azaallyl or β-diketiminato complexes, e.g. **5** and **6**, depending on the nature of the nitrile substituent [8]. Both these ligand systems have been widely exploited as transfer reagents in the formation of metal complexes [8]. In the case of **5**, the intermediate in its formation is thought to be the 1,2-addition product [$LiN{=}C(Bu^t)\{CH(SiMe_3)_2\}$], which undergoes a 1,3-silicotropic rearrangement. It is worth noting that a reverse addition, i.e. C–Li bond formation, was observed in the preparation of **2** because of the reverse polarity of phosphaalkynes, $^{\delta+}P{\equiv}C^{\delta-}$, relative to nitriles, $^{\delta-}N{\equiv}C^{\delta+}$ [9]. Herein, we report the unexpected outcomes of the reactions of **3** and **4** with P≡CBu^t.



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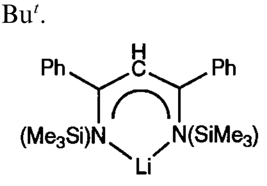

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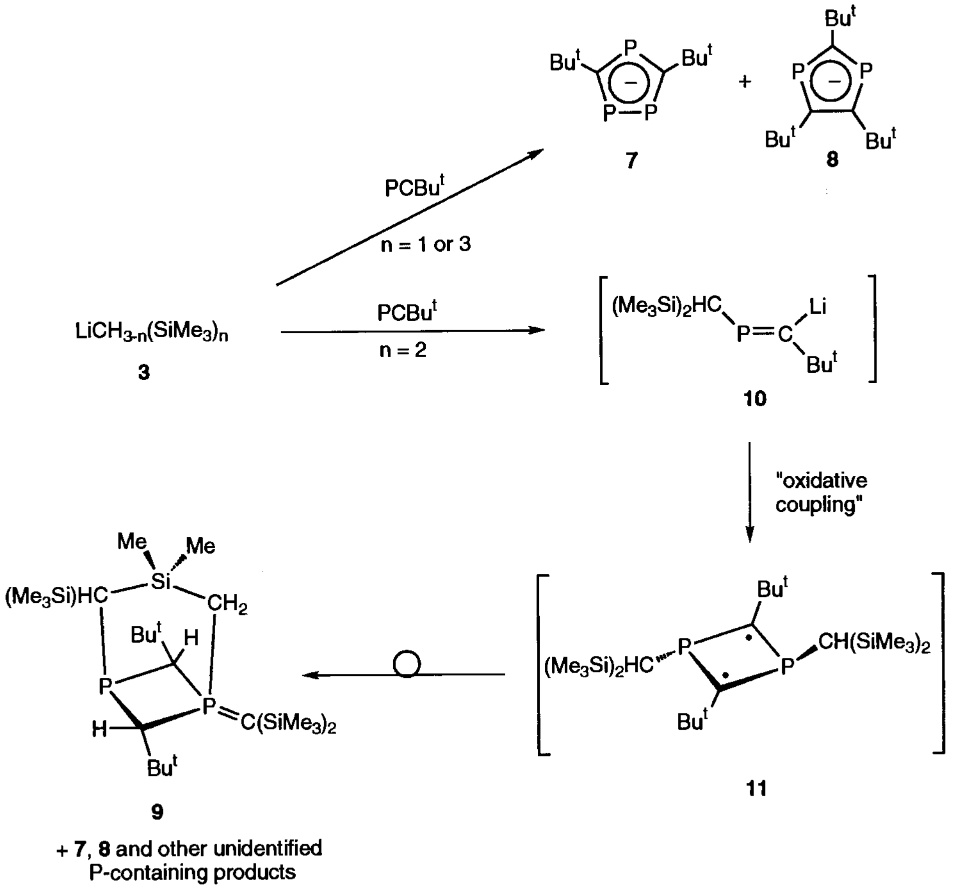
2. Results and discussion

The reaction of **3**, $n = 1$ or 3, with either one equivalent or an excess of P≡CBu^t led to product mixtures containing the previously reported di- and tri-phospholyl ring anions, **7** and **8**, as the major components as determined by ^{31}P-NMR analyses of the reaction solutions (Scheme 1). Presumably, when the reaction is carried out in a 1:1 stoichiometry, a proportion of the lithium alkyl starting material remains unreacted. These results are not surprising as the reactions of electropositive metals and their complexes with P≡CBu^t have led to **7** and **8** via P≡CBu^t bond cleavage and reductive coupling reactions on several previous occasions [10].



Scheme 1.

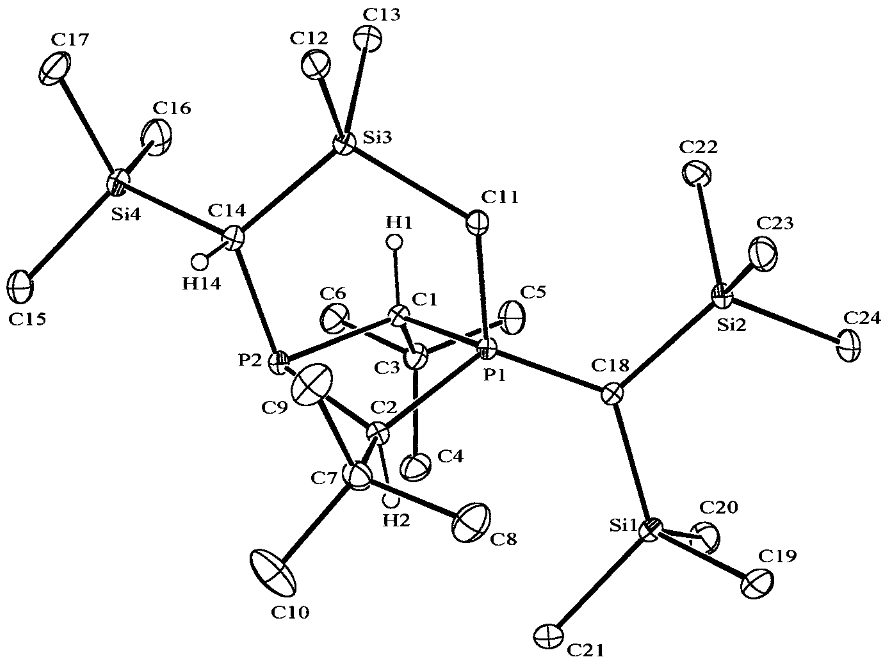


Fig. 1. Molecular structure of **9**. Selected bond lengths (Å) and angles (°): P(1)–C(18) 1.690(2), P(1)–C(11) 1.816(2), P(1)–C(1) 1.879(2), P(2)–C(14) 1.862(2), P(2)–C(1) 1.892(2), P(2)–C(2) 1.915(2), Si(3)–C(14) 1.882(2), Si(3)–C(11) 1.898(2), C(18)–P(1)–C(11) 113.22(11), C(18)–P(1)–C(2) 121.68(11), C(11)–P(1)–C(2) 104.73(11), C(18)–P(1)–C(1) 125.71(11), C(11)–P(1)–C(1) 99.73(10), C(2)–P(1)–C(1) 86.95(10), C(14)–P(2)–C(1) 100.97(10), C(14)–P(2)–C(2) 106.96(10), C(1)–P(2)–C(2) 84.19(10), P(1)–C(1)–P(2) 91.38(10), P(1)–C(2)–P(2) 92.21(10), C(14)–Si(3)–C(11) 109.64(10), P(2)–C(14)–Si(3) 115.16(11), P(1)–C(11)–Si(3) 118.59(12).

The by-products in the present reactions are probably derived from the likely generated radicals, $^{\bullet}CH_{3-n}(SiMe_3)_n$, $n = 1$ or 3, though no efforts were made to identify them.

Of greater interest was the reaction of **3**, $n = 2$, with $P{\equiv}CBu^t$ which in the 1:1 stoichiometery gave a moderate yield (64%) of the novel mixed valent phosphorus cage compound **9** (Scheme 1), though a number of other unidentified phosphorus containing products and small quantities of **7** and **8** (ca. 5% of each) were also formed. When an excess of the phosphaalkyne was used in this reaction, **9** was formed in lower yield along with significant amounts of **7** and **8**. In addition, when the analogous sodium or potassium alkyls, $[MCH(SiMe_3)_2]$, M = Na or K, were reacted with one equivalent of $P{\equiv}CBu^t$, no formation of **9** was observed and again the major products were **7** and **8**. It is not known why these differences occur.

All attempts to elucidate the mechanism of formation of **9** have proved fruitless and therefore this can only be tentatively speculated upon. It does, however, seem likely that an initial 1,2-addition reaction occurs to give the phosphavinyl lithium reagent, **10**. Perhaps, this then undergoes an oxidative coupling reaction to give the 1,3-diphosphacyclobutane-2,4-diyl, **11**. Closely related diradical compounds, e.g. $(Mes^*)PC^{\bullet}(Cl)P(Mes^*)C^{\bullet}(Cl)$, that are stable crystalline materials have been prepared, for example, by the reaction of $Mes^*P{=}C(Cl)(Li)$ with BuLi [11]. If **11** is formed in the present reaction, a reduction must occur and perhaps this can be partly explained by the formation of **7** and **8** as by-products. However, the yield of **9** dictates the formation of at least one other lithium-containing by-product that could not be identified despite many attempts. Finally, the diradical **11**, could be sufficiently reactive to allow the migration of one methine proton from a $CH(SiMe_3)_2$ group to one radical carbon centre followed by an insertion of a silyl C–H bond from the other $CH(SiMe_3)_2$ group into a P–C bond of the four membered ring. Unfortunately the formation of **9** is rapid, even at −50 °C, so neither **10** or **11** could be observed when the reaction was followed by ^{31}P-NMR spectroscopy.

The formation of **9** was confirmed by spectroscopic studies and an X-ray crystal structure analysis. Its $^{31}P\{^1H\}$-NMR spectrum consists of two signals at 38.2 and −17.7 ppm with a mutual $^2J_{PP}$ coupling of 16 Hz. This value is low for a two-bond coupling but is consistent with the acute CPC angles and resulting high degree of *p*-character to the bonds within the four membered ring system. Its ^{1}H-NMR spectrum is as expected and exhibits two distinct $SiMe_3$ resonances for the $CH(SiMe_3)_2$ substituent suggesting that this group does not rotate freely around the P–C bond as would be expected if this bond is double. The protons attached to the carbon centres of the PCPC ring were also observed and showed couplings to both the phosphorus centres. Finally, the APCI mass spectrum of **9** displayed the molecular ion as its base peak.

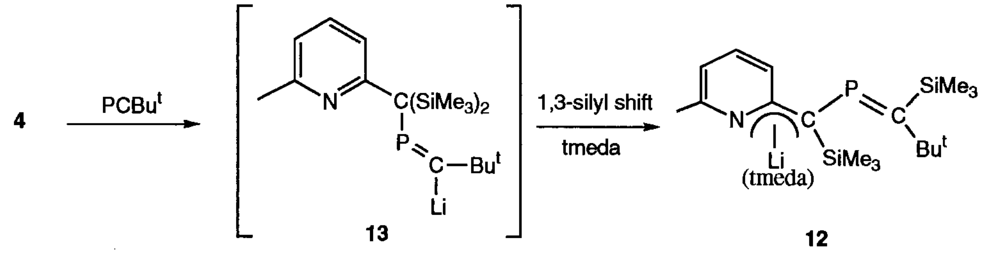
The molecular structure of **9** is depicted in Fig. 1 and shows it to contain a diphosphabicyclo[3.1.1]heptane cage core. All the bond lengths within this core are normal for single bonded interactions and the angles within the PCPC ring are acute, varying between ca. 84 and 92°. The co-ordination geometries of C(1) and C(2) are distorted tetrahedral and there is a close cross ring P···P interaction of 2.6982(11) Å. One of the phosphorus centres, P(2), is in the + 3 oxidation state whilst the other, P(1) is ylidic and in the + 5 oxidation state. This is confirmed by the P(1)–C(18) bond length, 1.690(2) Å, which is in the normal region for phosphorus ylides (average P=C length 1.725 Å [12]). In addition, the geometry about C(18) is slightly distorted trigonal planar (Σ angles = 359.99°).

Considering the ylidic nature of **9**, it was thought of sufficient interest to investigate its reactivity toward several aldehydes and ketones in Wittig reactions in order to attempt the formation of its phosphine oxide analogue. Unfortunately, under all conditions employed intractable mixtures of products were obtained and this avenue was abandoned.

The bis-silylated alkyl lithium reagent **4** is closely related to **3**. Its chemistry and that of its unmethylated analogue, $[\mathrm{LiC(SiMe_3)_2(2\text{-}NC_5H_4)}]$, have been extensively investigated and both have been found to be effective transfer reagents in the formation of a variety of metal complexes [13]. In these the alkyl ligands display excellent stabilising properties that revolve around their steric bulk and their ability to act as intramolecular N-donors. It was thought that these properties might prove beneficial in the stabilisation of phosphavinyl lithium reagents. Accordingly, **4** was reacted with one equivalent of P≡CBu^t in diethyl ether at − 78 °C. There was an immediate colour change to deep green which was accompanied by a signal appearing at 301 ppm in the ^{31}P-NMR spectrum of the reaction mixture. Upon warming to room temperature the solution changed to a purple colour and the signal at 301 ppm was replaced by one at 262 ppm. Work-up of the reaction mixture and treatment with an excess of tmeda yielded the phosphaalkenyl substituted η^3-azaallyl complex (**12**) in good yield (74%) (Scheme 2). It is believed that the mechanism of this reaction involves an initial 1,2-addition of **4** across the phosphaalkyne triple bond to give **13**. This intermediate probably gives rise to the ^{31}P-NMR signal at 301 ppm. If this is so, the addition is of a similar regiochemistry to that seen in the formation of **2** but opposite to related 1,2-additions to nitriles because of the aforementioned reverse polarity of phosphaalkynes. Since **13** rapidly converts to **12** at room temperature, it was not possible to isolate it in the solid state. This conversion seems to involve a 1,3-silyl shift very similar to those observed by Lappert et al. in the reactions of nitriles with bulky alkyl lithium reagents [8]. However, in this case an η^3-2-phosphaallyl complex is not formed as might be expected. Instead, the negative charge on the ligand appears to be stabilised over an η^3-azaallylic fragment involving the pyridyl ligand (vide infra). The related reaction of the mono-silylated alkyl lithium reagent, $[\mathrm{LiCH(SiMe_3)(2\text{-}NC_5H_3Me\text{-}6)}]$, with P≡CBu^t was carried out but this led to a number of very air sensitive phosphorus-containing products that could not be identified.

Complex **12** also proved to be very air and moisture sensitive in solution and the solid state. Its ^{31}P{^{1}H}-NMR spectrum displayed a singlet at 262 ppm, which is in the region normally seen for phosphaalkenes [9]. The ^{1}H-NMR spectrum exhibited two distinct SiMe$_3$ resonances and the base peak in the APCI mass spectrum of the compound corresponded to the phosphorus-containing ligand.

An X-ray crystal structure analysis was required to confirm the proposed formula of **12** (Fig. 2). This showed it to be monomeric with the lithium centre chelated by a molecule of tmeda and sitting above a planar azaallylic unit to which it is η^3-ligated. This co-ordination mode is commonly seen in lithiated silyl substituted picolines, e.g. $[\mathrm{Li(tmeda)\{C(SiMe_3)_2(2\text{-}NC_5H_4)\}}]$ (**14**) [14] and the geometry of the azaallylic fragment in **12** is similar to that in the previously reported complexes. Most notably, C(6) displays a distorted trigonal planar geometry (Σ angles = 340.49°) and the bond lengths from C(6), C(7) and N(1) to Li(1) [2.345(4), 2.515(4) and 2.129(4) Å, respectively] are close to the analogous bonds in similar complexes, e.g. **14** [2.43(2), 2.46(2) and 1.96(2) Å] [14]. Interestingly, the P(1)–C(1) distance [1.7101(18) Å] is slightly longer than



Scheme 2.

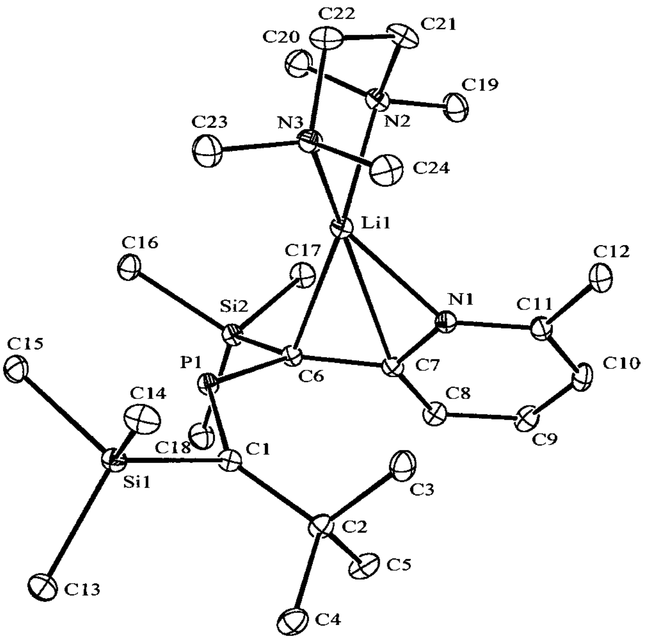


Fig. 2. Molecular structure of **12**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.710(2), P(1)–C(6) 1.759(2), P(1)–Li(1) 2.892(3), Si(1)–C(1) 1.878(2), Li(1)–C(6) 2.345(4), Li(1)–C(7) 2.515(4), N(1)–Li(1) 2.026(4), C(6)–C(7) 1.476(3), N(1)–C(7) 1.365(2), Li(1)–N(2) 2.123(4), Li(1)–N(3) 2.129(4), C(1)–P(1)-C(6) 124.03(9), P(1)–C(1)–Si(1) 108.07(10), P(1)–C(6)–C(7) 131.29(13), Si(2)–C(6)–P(1) 109.19(10), Si(2)–C(6)–C(7) 118.01(13), C(6)–C(7)–N(1) 116.56(16), Li(1)–C(7)–C(6) 66.14(12), Li(1)–C(7)–N(1) 53.54(12).

normal localised P=C bond lengths (ca. 1.67 Å) [9] and the P(1)–C(6) distance [1.7592(18) Å] is short for a P–C single bond. The latter observation is not surprising as both centres are sp^2-hybridised. Moreover, the slightly abnormal length of the P(1)–C(1) bond could indicate that there is some delocalisation over the C(1)P(1)C(6)C(7) fragment though this cannot be great as the fragment is not planar. There is, however, a long interaction between P(1) and Li(1) of 2.892(3) Å.

3. Conclusion

In conclusion, we have investigated the reactions of the phosphaalkyne, $P{\equiv}CBu^t$, with the bulky alkyl lithium reagents **3** and **4**. These have shown very different outcomes to the corresponding reactions with nitriles and have given rise to a novel mixed valent diphosphorus cage compound **9** and a phosphaalkenyl substituted alkyl lithium reagent **12**. Considering the versatility that lithiated silyl substituted picoline ligands have found in organometallic synthesis it seems likely that complex **12**, which is a phosphaalkenyl functionalised example of such compounds, should prove to be equally versatile as a transfer reagent in the formation of transition and lanthanide metal complexes. We are currently investigating this possibility and will report on it in a future publication.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. The solvents Et_2O, hexane and DME were distilled over either potassium or Na–K alloy then freeze/thaw degassed prior to use. ^1H- and ^{31}P-NMR spectra were recorded on either a Bruker DPX400 or a JEOL Eclipse 300 spectrometer in C_6D_6 and were referenced to the residual ^1H resonances of the solvent used (^1H-NMR) or to external 85% H_3PO_4, 0.0 ppm (^{31}P-NMR). Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points (m.p.) were determined in sealed glass capillaries under argon, and are uncorrected. The starting materials $P{\equiv}CBu^t$ [15], $LiCH(SiMe_3)_2$ [16] and $HC(SiMe_3)_2(2\text{-}NC_5H_3Me\text{-}6)$ [13b] were prepared by literature procedures. All other reagents were used as received.

4.1. *$P\{\mu\text{-}C(H)(Bu^t)\}_2\{\mu\text{-}C(H)(SiMe_3)Si(Me)_2\text{-}C(H)_2\}P{=}C(SiMe_3)_2$ (9)*

To a stirred solution of $LiCH(SiMe_3)_2$ (0.50 g, 3.0 mmol) in Et_2O (20 ml) at −78 °C was added neat $P{\equiv}CBu^t$ (0.48 ml, 0.29 g, 2.9 mmol) over 5 min. An orange solution resulted, which on warming to room temperature (r.t.) became deep red. This solution was stirred for 16 h after which time volatiles were removed in vacuo. Extraction of the foamy residue into DME (5 ml) and slow cooling to −30 °C afforded colourless crystals of **9**. (0.48 g, 64%); M.p. (dec.) 184–186 °C; ^1H-NMR (400 MHz, C_6D_6, 298 K) δ 0.09 (s, 9H, $SiMe_3$), 0.19 (s, 3H, SiMe), 0.28 (s, 3H, SiMe), 0.47 (s, 9H, $SiMe_3$), 0.51 (s, 9H, $SiMe_3$), 1.02 (s, 9H, Bu^t), 1.16 (s, 9H, Bu^t), 1.61 (v.tr., 1H, PCHP, $^2J_{PH}$ 15 Hz), 2.13 (v.tr., 1H, PCHP, $^2J_{PH}$ 12 Hz), 2.43 (d, 1H, SiCHP, $^2J_{PH}$ 11 Hz), 3.10 (unresolved m., 2H, CH_2); $^{31}P\{^1H\}$-NMR (145 MHz, C_6D_6, 298 K): δ −17.6 (d, P(2), $^2J_{PP}$ 16 Hz), 38.3 (d, P(1), $^2J_{PP}$ 16 Hz); APCI/MS *m/z* 519 ([M^+], 100%); IR (Nujol) ν cm^{-1}: 1719(w), 1672(w), 1251(s), 1032(s), 844(s).

4.2. *$[Li(tmeda)\{C(SiMe_3)(2\text{-}NC_5H_3Me\text{-}6)[P{=}C\text{-}(Bu^t)(SiMe_3)]\}]$ (12)*

Bu^nLi (2.40 ml of a 1.65 M soln., 4.0 mmol) was added over 5 min to an ice-cold solution of $CH(SiMe_3)_2(2\text{-}NC_5H_3Me\text{-}6)$ (1.0 g, 4.0 mmol) in Et_2O.

The resulting solution was stirred for 4 h and then cooled to − 78 °C. $P\equiv CBu^t$ (0.64 ml, 0.40 g, 4.0 mmol) was added neat to this solution over 5 min. A dark green solution resulted which was warmed to r.t. over which time it turned a purple colour. This solution was stirred overnight, volatiles removed in vacuo to yield a purple oil. This was extracted into hexane–ether 50:50 (8 ml) and tmeda added to the point of crystallisation. Filtration and slow cooling of the filtrate to − 30 °C afforded crystalline **12** (1.40 g, 74%); m.p. 48–52 °C; ^{1}H-NMR (400 MHz, C_6D_6, 298 K) δ 0.52 (s, 9H, $SiMe_3$), 0.61 (s, 9H, $SiMe_3$), 1.32 (s, 9H, Bu^t), 1.41 (s, 3H, Me), 2.01 (br. s, 12H, NMe), 2.06 (s, 4H, CH_2), 6.12–7.04 (m, 3H, Ar); $^{31}P\{^1H\}$-NMR (145 MHz, C_6D_6, 298 K): δ 262(s); APCI/MS m/z 352 ([MH^+] –Li(tmeda), 100%), 117 (tmedaH^+); IR (Nujol) ν cm^{-1}: 1574(m), 1260(s), 1019(m), 804(m).

4.3. Crystallographic studies

All crystallographic measurements were made using an Enraf–Nonius CAD4 diffractometer. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares (SHELX97) [17] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model) (Table 1).

Table 1
Summary of crystallographic data for compounds **9** and **12**

	9	**12**
Formula	$C_{24}H_{56}P_2Si_4$	$C_{24}H_{49}LiN_3PSi_2$
M_r	518.99	473.75
a (Å)	9.862(3)	9.315(2)
b (Å)	29.991(4)	11.325(3)
c (Å)	10.970(4)	115.874(2)
α (°)	90	75.56(2)
β (°)	102.606	85.63(2)
γ (°)	90	66.05(3)
V (Å^3)	3166.2(16)	1481.4(5)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
λ (Å)	0.71073	0.71073
T (K)	150(2)	150(2)
Z	4	2
Size	$0.3\times0.3\times0.3$	$0.3\times0.3\times0.2$
Colour	Colourless	Green
μ (mm^{-1})	0.300	0.189
$F(000)$	1144	520
Reflections collected	6039	5667
R_{int}	0.0368	0.0399
Unique reflections	5697	5314
Parameters varied	288	294
R [$I>2\sigma(I)$]	0.0463	0.0394
R_w (all data)	0.1346	0.1161

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **9** and **12** have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 169738 for compound **9** and CCDC no. 169739 for compound **12**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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References

[1] D.E. Hibbs, C. Jones, A.F. Richards, J. Chem. Soc. Dalton Trans. (1999) 3531.

[2] C. Jones, A.F. Richards, J. Organomet. Chem. 629 (2001) 109.

[3] C. Jones, A.F. Richards, J. Chem. Soc. Dalton Trans. (2000) 3233.

[4] C. Jones, J.A. Platts, A.F. Richards, Chem. Commun. (2001) 663.

[5] M. van der Sluis, J.B.M. Wit, F. Bickelhaupt, Organometallics 15 (1996) 174.

[6] E. Niecke, M. Nieger, O. Schmidt, D. Gudat, W.W. Schoeller, J. Am. Chem. Soc. 121 (1999) 519.

[7] A.M. Arif, A.R. Barron, A.H. Cowley, S.W. Hall, J. Chem. Soc. Chem. Commun. (1988) 171.

[8] (a) P.B. Hitchcock, M.F. Lappert, M. Layh, D.-S. Liu, R. Sablong, T. Shun, J. Chem. Soc. Dalton Trans. (2000) 2301;
(b) P.B. Hitchcock, M.F. Lappert, D.-S. Liu, J. Chem. Soc. Chem. Commun. (1994) 2637, and references therein.

[9] K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy, Wiley, Chichester, 1998 and references therein.

[10] (a) R. Bartsch, J.F. Nixon, Polyhedron 8 (1989) 2407;
(b) A.H. Cowley, S.W. Hall, Polyhedron 8 (1989) 849.

[11] E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W.W. Schoeller, Angew. Chem. Int. Ed. Engl. 34 (1995) 555.

[12] Value determined from a survey of the Cambridge Structural Database.

[13] (a) P.C. Andrews, D.R. Armstrong, C.L. Raston, B.A. Roberts, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (2001) 996;
(b) T. Anker, C.L. Raston, B.W. Skelton, A.H. White, Organometallics 19 (2000) 4437;
(c) T. Anker, C.L. Raston, J. Organomet. Chem. 200 (1995) 289 and references therein.

[14] (a) D. Cogan, R.I. Papasergio, C.L. Raston, A.H. White, J. Chem. Soc. Chem. Commun. (1984) 1708;
(b) R.I. Papasergio, B.W. Skelton, P. Twiss, A.H. White, J. Chem. Soc. Dalton Trans. (1990) 1161.

[15] G. Becker, G. Gresser, W. Uhl, Z. Naturforsch. 36b (1981) 16.

[16] P.J. Davidson, D.H. Harris, M.F. Lappert, J. Chem. Soc. Dalton Trans. (1976) 2268.

[17] G.M. Sheldrick, SHELX-97, University of Göttingen, 1997.