COMMUNICATION

ChemComm
www.rsc.org/chemcomm

The first structurally authenticated alkali metal 1,3-diphosphaallyl complex [{Bu^{t}C(PMes)$_2$}Li(thf)$_3$] (Mes = 2,4,6-Me$_3$C$_6$H$_2$): an alternative synthetic approach to substituted 1,3-diphosphaallyl complexes

Stephen T. Liddle* and Keith Izod

Chemistry, School of Natural Sciences, University of Newcastle upon Tyne, Newcastle upon Tyne, UK NE1 7RU. E-mail: S.T.Liddle@ncl.ac.uk

Received (in Cambridge, UK) 9th January 2003, Accepted 6th February 2003
First published as an Advance Article on the web 24th February 2003

Reaction of the phosphavinyl Grignard reagent [*Z*-MesP=C(Bu^t)MgBr.OEt$_2$]$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) with MesPCl$_2$ affords the corresponding 1,3-diphosphapropene compound [*Z*-MesP=C(Bu^t)P(X)Mes] (X = Cl, Br); subsequent reaction with two equivalents of elemental lithium in thf affords the title compound [{Bu^{t}C(PMes)$_2$}Li(thf)$_3$], which contains an asymmetric η^1-1,3-diphosphaallyl ligand.

In recent years first-row heteroallyl variants such as 1-azaallyls and amidinates have attracted considerable attention and have found widespread applications as ancillary ligands for main group, lanthanide, and transition metal complexes.[1–3] However, considerably less attention has been paid to heteroallyl systems that incorporate second row elements such as phosphorus (*e.g.* 1-phosphaallyls and 1,3-diphosphaallyls),† even though there has been a prolific development in the field of low-coordinate phosphorus chemistry.[4]

With this in mind, we have recently embarked upon a study of 1,3-diphosphaallyl chemistry. Such a ligand system may be regarded as the 'big-brother' to amidinates and, given that phosphorus is a larger and softer donor than nitrogen, may be expected to confer useful properties on its complexes, such as increased Lewis acidity, and exhibit a greater repertoire of coordination modes. Few examples of 1,3-diphosphaallyl complexes have been reported, all of which are transition metal derivatives. In these cases the parent 1,3-diphosphapropenes were synthesised by: (i) reaction of a phosphaketene (Mes*P=C=O) with a silyl phosphane [Mes*P(H)SiMe$_3$] to afford Mes*P=C(OSiMe$_3$)P(H)Mes* (Mes* = 2,4,6-Bu$^t_3$C$_6$H$_2$), *via* a 1,3-silyl migration,[5] or (ii) dehydrohalogenation of the bis-phosphane H$_2$C{P(Cl)Mes*}$_2$ to give the corresponding chloro-1,3-diphosphapropene.[6] These two routes suffer from the disadvantage that the 2-substituent is limited to OSiMe$_3$ or H; for other substituents (such as *tert*-butyl) a different approach is required. Our attention was drawn to the phosphavinyl Grignard reagents derived from the regio- and stereo-selective 1,2-addition of Grignard reagents across 2,2-dimethylpropylidynephosphine reported by Jones,[7] and by Binger and Regitz.[8] Jones and co-workers have demonstrated the utility of such compounds as ligand transfer reagents with a variety of main group halides, but often observe facile coupling reactions.[9] We reasoned that with suitable protection of the reactive phosphavinyl P=C bond, by a bulky group such as Mes (Mes = 2,4,6-Me$_3$C$_6$H$_2$), chloro-1,3-diphosphapropene compounds with any 2-substituent that stabilises the parent phosphaalkyne would be accessible.

Treatment of a slight excess of MesPCl$_2$ with half an equivalent of the dimer [*Z*-MesP=C(Bu^t)MgBr.OEt$_2$]$_2$ (**1**)[7] in thf at −78 °C yields, after work up, the corresponding 1,3-diphosphapropene [*Z*-MesP=C(Bu^t)P(X)Mes] (**2**) (X = Cl, Br) in essentially quantitative yield. This is confirmed by ^{31}P NMR spectroscopy; the spectrum of **2** in d$_6$-benzene exhibits two pairs of AX doublets in an approximate ratio of 1 : 2 at 262.3 and 81.3 ppm ($^2J_{PP}$ = 47 Hz), and 259.3 and 93.6 ppm ($^2J_{PP}$ = 40 Hz), which are assigned as the bromo and chloro derivatives respectively. The former resonances in each case are clearly due to a phosphavinyl group, whereas the latter are typical for a secondary chloro- or bromo-phosphine; ^{1}H NMR spectroscopy indicates the presence of two derivatives in a 1 : 2 ratio, each exhibiting inequivalent Mes rings. Satisfactory microanalysis were obtained. Whilst it seemed likely that the *Z* isomeric form would be retained, this assignment is not conclusive from ^{31}P spectroscopy alone. To clarify this point, crystals of **2** were grown from a cold (5 °C) solution in diethyl ether, and an X-ray crystallographic study was undertaken.

X-Ray crystallography (Fig. 1)‡ reveals that the *Z* configuration of the P=C bond is retained in the 1,3-diphosphapropene (**2**); the two Mes groups adopt an approximately *syn* orientation with respect to each other. In the crystal examined a competitive refinement indicated that the bromide and chloride components are disordered over the same site in a refined ratio of 0.36:0.64, in agreement with ^{31}P NMR spectroscopy. The C(1)–P(2) bond length of 1.694(2) Å is in good agreement with other localised P=C bond lengths.[4] The C(1)–P(1) bond is somewhat longer at 1.836(2) Å, indicative of a P–C single bond, and is in good agreement with the two P–C$_{ipso}$ bond lengths [P(2)–C(15) 1.837(2); P(1)–C(6) 1.832(2) Å]. The C(15)–P(2)–C(1) bond angle of 109.18(9)° is as expected, and P(1) is distinctly trigonal pyramidal [sum of angles = 314.91°]; C(1) also shows a slight deviation from planarity [sum of angles = 357.39°].

Sonication of a thf solution of **2** with two equivalents of elemental lithium for one hour under an argon atmosphere results in a rapid darkening of the solution from orange to dark red. Work up gives [{Bu^{t}C(PMes)$_2$}Li(thf)$_3$] (**3**) as a red powder in essentially quantitative yield,§ which gives satisfactory microanalysis consistent with the formation of a tris-thf adduct. In d$_8$-thf the ^{31}P and ^{7}Li NMR spectra (relative to aqueous 85% H$_3$PO$_4$ and 1 M LiCl at 0.00 ppm respectively) exhibit single sharp resonances at 109.4 and −0.69 ppm respectively, indicating a symmetrical species in solution; this is further corroborated by the ^{1}H NMR spectrum of **3**, which exhibits a single set of signals for the Mes rings. This could be due to rapid exchange of the lithium between both phosphorus centres, symmetrical η^2-PP or η^3-PCP coordination modes, or formation of solvent separated ion pairs in solution.

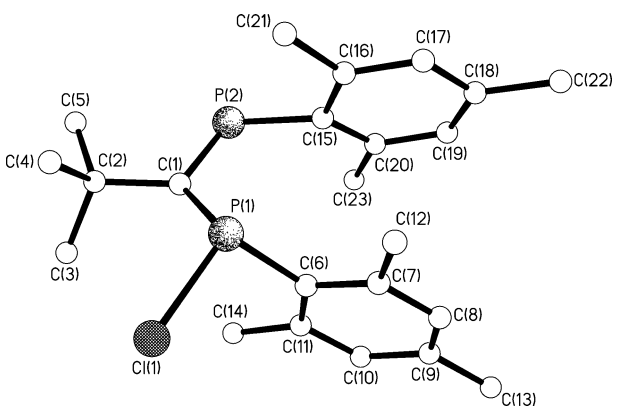

Fig. 1 Molecular structure of **2**. Hydrogen atoms and disordered bromide component are omitted for clarity. Selected bond lengths (Å): P(1)–C(1) 1.836(2), P(1)–C(6) 1.832(2), P(1)–Cl(1) 2.202(2), P(2)–C(1) 1.694(2), P(2)–C(15) 1.837(2), C(1)–C(2) 1.552(3).

DOI: 10.1039/b300272a

Dark red, air- and moisture-sensitive, X-ray quality crystals of **3** were grown from a concentrated diethyl ether solution at 5 °C. The structure of **3** (Fig. 2)‡ consists of a 1,3-diphosphaallyl ligand bonded to a lithium cation in a terminal η^1 manner; the coordination sphere of lithium is completed by three molecules of thf. Although the P–C–P unit in **3** is clearly asymmetric, due to coordination of lithium to one phosphorus centre, the P(1)–C(1) and P(2)–C(1) bond lengths of 1.760(2) and 1.737(2) Å, respectively, lie between the P–C and P=C bond lengths observed in **2**, and are also well within the range observed in structurally characterised 1,3-diphosphaallyl complexes (1.712–1.793 Å).[5,6b,c,e] This indicates extensive delocalisation in the P–C–P unit, an assertion that is supported by the approach of P(1) towards planarity [sum of angles = 353.94°]; C(1) is essentially planar [sum of angles = 359.9°]. The Li(1)–P(1) bond length of 2.562(4) Å is unexceptional, and well within the range of Li–P bond lengths reported to date.[10] The Li–O bond lengths span the range 1.935(5)–1.959(5) Å and are unremarkable in nature. With the exception of the large O(3)–Li(1)–P(1) angle of 125.3(2)°, which is presumably a result of steric repulsion between the *tert*-butyl group and the O(3)-thf, the bond angles at lithium [104.1(2)–107.5(2)°] are close to the tetrahedral ideal. The C(1)–P(2)–C(15) bond angle [106.97(11)°] is marginally compressed from that observed in **2**. The two Mes rings are orientated such that an *ortho* carbon of each ring resides over the centre of the other Mes ring. The C_{ortho}–ring (centroid) distances of 3.469 and 3.452 Å are within the range commonly encountered for π stacking (3.4–3.8 Å),[11] and are suggestive of a π···π slipped stacking interaction.

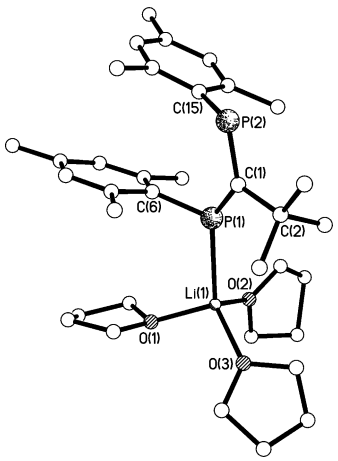

Fig. 2 Molecular structure of **3** with selective labelling. Hydrogen atoms and minor thf disorder components are omitted for clarity. Selected bond lengths (Å): P(1)–C(1) 1.760(2), P(1)–C(6) 1.832(2), P(1)–Li(1) 2.562(4), P(2)–C(1) 1.737(2), P(2)–C(15) 1.838(3), C(1)–C(2) 1.557(4), Li(1)–O(1) 1.935(5), Li(1)–O(2) 1.943(5), Li(1)–O(3) 1.959(5).

We rationalise the terminal η^1 bonding mode of the 1,3-diphosphaallyl ligand on the grounds that lithium is exceptionally hard and polarising, and therefore bonding to a soft delocalised system is disfavoured; the charge localising nature of lithium compared to the heavier alkali metals is well demonstrated by their complexes of the triphenylmethanide anion.[12] However, it may also be that the *anti*,*anti* orientation of the two Mes rings relative to the *tert*-butyl group enforces η^1 coordination. Certainly, a *syn*,*syn* isomer would favour an η^2-PP or an η^3-PCP bonding mode.

We are currently investigating the isomerisation of **2** and **3**, the heavier alkali metal analogues of **3**, and their metathesis chemistry for the synthesis of main group, transition metal, and lanthanide complexes.

We thank The University of Newcastle upon Tyne (Wilfred Hall Fellowship to S. T. L.), the Royal Society (URF to K. I.), Prof. C. Jones (Cardiff) and Prof. F. G. N. Cloke (Sussex) for helpful discussions regarding the synthesis of 2,2-dimethylpropylidynephosphine, and Prof. W. Clegg (Newcastle) for the use of X-ray diffraction facilities.

Notes and references

† Although diphosphinomethanides are often referred to as 'heteroallyl' in nature, and are extensively investigated, they should not be confused with genuine heteroallyl systems.

‡ *Crystal data* for **2**: $C_{23}H_{31}Br_{0.36}Cl_{0.64}P_2$, M = 420.87, triclinic, space group $P\bar{1}$, a = 8.8412(6), b = 9.4818(6), c = 14.4128(10) Å, α = 109.001(2), β = 92.033(2), γ = 98.202(2)°, U = 1126.37(13) Å^3, Z = 2, D_c = 1.241 g cm^{-3}, μ = 0.91 mm^{-1} (MoKα, λ = 0.71073 Å), T = 150 K, R ($F^2 > 2\sigma$) = 0.0307, R_w (F^2, all data) = 0.0815, goodness-of-fit = 1.045 for all 3930 unique data (8092 measured, R_{int} = 0.0189, $2\theta < 50°$, CCD diffractometer) and 245 refined parameters. CCDC 201226. For **3**: $C_{35}H_{55}LiO_3P_2$, M = 592.67, monoclinic, space group $P2_1/c$, a = 11.3121(5), b = 16.3249(7), c = 19.3487(8) Å, β = 105.365(2)°, U = 3445.4(3) Å^3, Z = 4, D_c = 1.143 g cm^{-3}, μ = 0.16 mm^{-1} (MoKα, λ = 0.71073 Å), T = 150 K, R ($F^2 > 2\sigma$) = 0.0492, R_w (F^2, all data) = 0.1370, goodness-of-fit = 1.083 for all 6074 unique data (24775 measured, R_{int} = 0.0326, $2\theta < 50°$, CCD diffractometer) and 389 refined parameters. Programs: standard Bruker AXS control and integration software and SHELXTL.[13] CCDC 201227. See http://www.rsc.org/suppdata/cc/b3/b300272a/ for crystallographic files in CIF or other electronic format.

§ *Spectroscopic data* for **3**: ^{1}H NMR (295 K, 500 MHz, d_8-thf) δ 1.44 (9H, s, C(CH_3)$_3$), 1.65 (12H, m, CH_2-thf), 1.86 (6H, s, *para*-CH_3), 2.21 (12H, s, *ortho*-CH_3), 3.48 (12H, m, OCH_2-thf) and 5.96 (4H, s, *aryl*-C*H*). ^{13}C NMR (295 K, 125 MHz, d_8-thf) δ 20.21 (*ortho*-CH_3), 22.22 (*para*-CH_3), 25.37 (CH_2-thf), 34.96 (t, $^3J_{PC}$ 16.8 Hz, C(CH_3)$_3$), 42.62 (t, $^2J_{PC}$ 28.2 Hz, *C*(CH$_3$)$_3$), 67.49 (OCH_2-thf), 125.79 (*meta*-*C*), 130.20 (*para*-*C*), 139.38 (*ortho*-*C*), 144.96 (d, J_{PC} 25.4 Hz, *ipso*-*C*) and 214.1 (t, J_{PC} 84.2 Hz, PCP). ^{31}P NMR (295 K, 121 MHz, d_8-thf) δ 109.4. ^{7}Li NMR (295 K, 194 MHz, d_8-thf) δ −0.69. Anal. Found: C, 70.89; H, 9.49%. Calc. for $C_{35}H_{55}LiO_3P_2$: C, 70.93; H, 9.35%.

1 C. F. Caro, M. F. Lappert and P. G. Merle, *Coord. Chem. Rev.*, 2001, **219**, 605.
2 T. Schareina and R. Kempe, in *Synthetic Methods of Organometallic and Inorganic Chemistry*, ed. W. A. Herrmann, Thieme, Stuttgart, 2002, vol. 10, p. 1.
3 F. T. Edelmann, *Top. Curr. Chem.*, 1996, **179**, 113.
4 (*a*) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, 1990 and references therein; (*b*) K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998 and references therein.
5 W. Keim, R. Appel, S. Gruppe and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1012.
6 (*a*) H. H. Karsch, F. H. Köhler and H. U. Reisacher, *Tetrahedron. Lett.*, 1984, **25**, 3687; (*b*) R. Appel, W. Schuhn and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 420; (*c*) R. Appel, W. Schuhn and F. Knoch, *J. Organomet. Chem.*, 1987, **319**, 345; (*d*) R. Appel and W. Schuhn, *J. Organomet. Chem.*, 1987, **329**, 179; (*e*) R. Appel, W. Schuhn and M. Nieger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 416.
7 D. E. Hibbs, C. Jones and A. F. Richards, *J. Chem. Soc., Dalton Trans.*, 1999, 3531.
8 J. Renner, U. Bergsträßer, P. Binger and M. Regitz, *Eur. J. Inorg. Chem.*, 2000, 2337.
9 (*a*) C. Jones and A. F. Richards, *J. Chem. Soc., Dalton Trans.*, 2000, 3233; (*b*) C. Jones, J. A. Platts and A. F. Richards, *Chem. Commun.*, 2001, 663; (*c*) C. Jones and A. F. Richards, *J. Organomet. Chem.*, 2001, **629**, 109; (*d*) C. Jones, P. C. Junk, A. F. Richards and M. Waugh, *New J. Chem.*, 2002, **26**, 1209.
10 K. Izod, *Adv. Inorg. Chem.*, 2000, **50**, 33, and references therein.
11 (*a*) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525; (*b*) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
12 (*a*) J. J. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, 1972, **94**, 7333; (*b*) H. Köster and E. Weiss, *J. Organomet. Chem.*, 1979, **168**, 273; (*c*) R. A. Bartlett, H. V. R. Dias and P. P. Power, *J. Organomet. Chem.*, 1988, **341**, 1; (*d*) D. Hoffmann, W. Bauer, P. von R. Schleyer, U. Pieper and D. Stalke, *Organometallics*, 1993, **12**, 1193.
13 G. M. Sheldrick, *SHELXTL user manual, version 5.1*, Bruker AXS Inc., Madison, WI, USA, 1997.