Isolation and Characterisation of the First Stable Diphospha-allene: *P,P′*-Bis(2,4,6-tri-t-butylphenyl)-1,3-diphospha-allene

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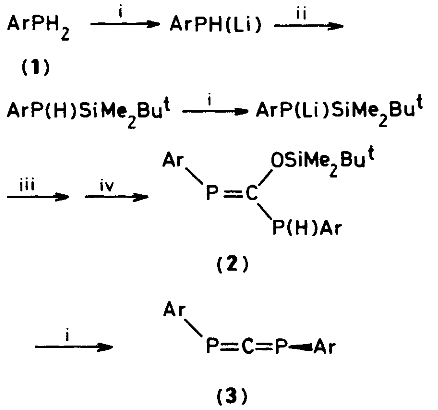
The diphospha-allene, *P,P′*-bis(2,4,6-tri-t-butylphenyl)-1,3-diphospha-allene (**3**), was isolated and characterised as a stable compound for the first time.

There is a great deal of interest at present in phosphorus compounds in low co-ordination states.[1] We and others have recently reported on the preparation of some unusual phosphorus compounds, using the 2,4,6-tri-t-butylphenyl moiety as a protecting group for reactive sites such as –P=P–,[2] –P=P(S)–,[3] –P=P(O)–,[4] –P=C<,[5] –P=C=O,[6] –P=C=N–,[7] –P=As–,[8] *etc.*

We report here the isolation and characterisation of the first example of a stable diphospha-allene, *P,P′*-bis(2,4,6-tri-t-butylphenyl)-1,3-diphospha-allene (**3**), prepared by the route in Scheme 1.



Scheme 1. i, BuLi; ii, Me$_2$Bu^{t}SiCl; iii, CO$_2$; iv, H$_2$O. Ar = 2,4,6-Bu$^t_3$C$_6$H$_2$.

2,4,6-Tri-t-butylphenylphosphine[5] (**1**) (2.17 mmol) in tetrahydrofuran (THF) (40 ml) was allowed to react successively with butyl-lithium (2.39 mmol in hexane), t-butyldimethylchlorosilane (2.57 mmol), and then butyl-lithium (2.81 mmol) under argon at room temperature. Dry carbon dioxide gas was bubbled through the resulting red solution at −78 °C and the solvent was evaporated. Column chromatography (silica gel, pentane) of the residue afforded the phosphinomethylenephosphine (**2**) in 81% yield as a stable compound.† Based on spectroscopic data, (**2**) was tentatively assigned the structure with the aryl and silyloxy groups *cis*, by analogy with *Z*-α-(t-butyldimethylsilyloxybenzylidene)-2,4,6-tri-t-butylphenylphosphine.[5] The phosphine (**2**) (0.19 mmol) in THF (8 ml) was treated with butyl-lithium (0.29 mmol) at room

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† (**2**): m.p. 166—168 °C; ^{1}H n.m.r. (CDCl$_3$) δ 7.39 (d, $^4J_{PH}$ 2.2 Hz, 2H, ArH), 7.28 (d, $^4J_{PH}$ 1.1 Hz, 2H, ArH), 5.80 (dd, $^1J_{PH}$ 219.3 Hz, $^3J_{PH}$ 21.5 Hz, 1H, PH), 1.60 (s, 18H, *o*-Bu^t), 1.37 (s, 18H, *o′*-Bu^t), 1.29 (s, 9H, *p*-Bu^t), 1.26 (s, 9H, *p′*-Bu^t), 0.49 (s, 9H, Bu^{t}Si), and 0.19 (s, 6H, MeSi); ^{31}P n.m.r. (CDCl$_3$) δ_P (from ext. 85% H$_3$PO$_4$) 167.6 (dd, $^2J_{PP}$ 26.9 Hz, $^3J_{PH}$ 22.0 Hz, –P=) and −44.7 (dd, $^1J_{PH}$ 219.7 Hz, $^2J_{PP}$ 26.9 Hz, >PH) p.p.m.; ^{13}C-{^{1}H} n.m.r. (Cdcl$_3$) δ 191.8 (dd, $^1J_{P=C}$ 96.2 Hz, $^1J_{P-C}$ 40.3 Hz, P=C–P) p.p.m.; i.r. (KBr) ν (P–H) 2350 cm^{-1}; u.v. (hexane) λ_{max} (ε) 245 (16 500) and 292sh nm (810); M^+; *m/z* 696.4987, C$_{43}$H$_{74}$OSiP$_2$ requires 696.4984.

temperature under argon, and the mixture was stirred for 18 h at 35 °C. Evaporation, column chromatography (silica gel, pentane) of the residue, and recrystallisation from pentane gave (**3**) in 73% yield [m.p. 206—207 °C; ^{1}H n.m.r. (CDCl$_3$) δ 7.36 (d, $^{4}J_{\mathrm{PH}}$ 1.3 Hz, 4H, ArH), 1.33 (s, 36H, *o*-Bu^{t}), and 1.28 (s, 18H, *p*-Bu^{t}); ^{31}P n.m.r. (CDCl$_3$) δ_{P} 142.7 (s) p.p.m.; ^{13}C-{^{1}H} n.m.r. (CDCl$_3$) δ 276.2 (t, $^{1}J_{\mathrm{PC}}$ 58.1 Hz, P=*C*=P) and 129.5 (dd, $^{1}J_{\mathrm{PC}}$ 73.7 Hz, $^{3}J_{\mathrm{PC}}$ 27.9 Hz, ipso-ArC);‡ u.v. (hexane) λ_{max} (ε) 262 (48 600) and 358 nm (1 300); *M*$^{+}$; *m/z* 564.3977, $C_{37}H_{58}P_2$ requires 564.4012].

The compound (**3**) thus obtained is slightly yellow and stable to air and moisture.

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‡ Other ^{13}C-{^{1}H} n.m.r. signals due to (**3**) are as follows: δ 153.2 (s, *p*-Ar), 149.6 (s, *o*-Ar), 121.7 (s, *m*-Ar), 38.0 (s, *o*-*C*Me$_3$), 34.8 (s, *p*-*C*Me$_3$), 33.2 (pseud. t, *J* 4.1 Hz, *o*-C*Me*$_3$), and 31.4 (s, *p*-C*Me*$_3$).

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