Formation of 6,8-di-*tert*-butyl-3,4-dihydro-4,4-dimethyl-1-phosphanaphthalene by the reaction of 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene with butyllithium

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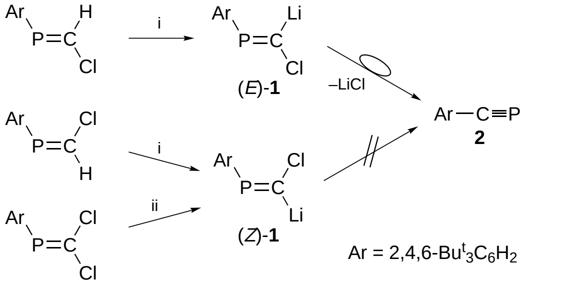
Sterically crowded 1-bromo-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyllithium gave 6,8-di-*tert*-butyl-3,4-dihydro-4,4-dimethyl-1-phosphanaphthalene by intramolecular insertion of an intermediary phosphinidene carbene species into one of the C–H bonds of the two *o-tert*-butyl groups.

Compounds containing multiple bonds of heavier main group elements such as phosphorus are of current interest.[1] The 2,4,6-tri- *tert*-butylphenyl group (hereafter abbreviated to Ar) is one of the typical and powerful bulky protecting groups for such bonds and by utilizing this substituent we have prepared various types of low coordinated tervalent phosphorus compounds such as diphosphenes[2] and phosphacumulenes.[3]

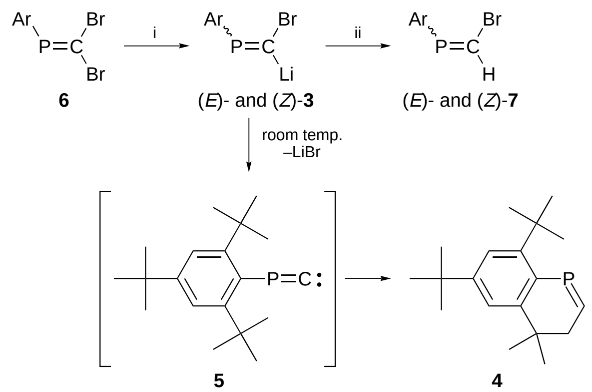
Recently, we and others have reported on the conversion of (*E*)-1-chloro-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyllithium [(*E*)-**1**] to 2-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethyne **2** (Scheme 1),[4] as well as on the synthetic application of (*E*)- and (*Z*)-**1** as a building block having a phosphorus–carbon double bond.[5,6] Although formation and some reactions of the bromo analogue **3** have been described in the literature,[6,7] C–H insertion reactions involving the phosphinidene carbenoid have not been reported. We report here the formation of 6,8-di-*tert*-butyl-3,4-dihydro-4,4-dimethyl-1-phosphanaphthalene **4** *via* (2,4,6-tri-*tert*-butylphenyl)phosphinidene carbene **5**.

2,2-Dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene[6,8] **6** was allowed to react with butyllithium in THF at −78 °C to give 1-bromo-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyllithium **3**.[8] Quenching of the resulting solution of **3** with MeOH at −78 °C gave (*E*)- and (*Z*)-2-bromo-1-phosphaethenes **7** in 2 and 58% yields, respectively, after column chromatographic treatment (Scheme 2). In a separate experiment, ^{31}P NMR spectroscopy of the resulting solution at 210 K showed the formation of (*E*)- and (*Z*)-phosphaethenyllithiums in a 1 : 5 peak ratio [(*E*)-**3** : δ_P ([$^2H_8$]THF) 369.7; (*Z*)-**3** : δ_P 254.6].‡

When the mixed solution of (*E*)- and (*Z*)-**3** was warmed to room temperature, it turned violet, and the 3,4-dihydro-1-phosphanaphthalene derivative **4** was obtained in 17% yield after work up with silica-gel column chromatography.§ The formation of **4** is explicable by intramolecular insertion of an intermediary phosphinidene carbene **5** into one of the C–H



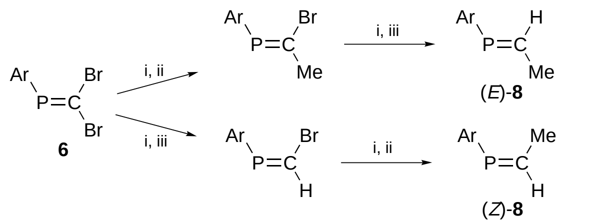
Scheme 1 *Reagents and conditions*: i, Bu^{t}Li or Bu^{s}Li, THF, −78 °C; ii, Bu^{n}Li, THF, −78 °C



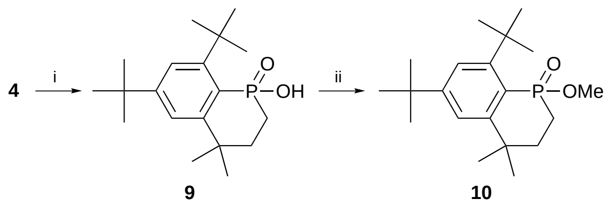
Scheme 2 *Reagents and conditions*: i, Bu^{n}Li, THF, −78 °C; ii, MeOH, −78 °C

bonds of the two *o-tert*-butyl groups, although attempts to trap the carbene with cyclohexene and tetracyanoethene failed. An analogous intramolecular C–H insertion reaction of alkylidene carbenoid has been reported by Köbrich in the reaction of 1-chloro-2,7-dimethylocta-1,6-diene with butyllithium to give 1-methyl-3-isobutenylcyclopent-1-ene.[9] Compound **4** was also obtained from the chloro congener (*Z*)-**1** in Et_2O in a very low yield (1%), probably because of accompanying complicated reactions, although no formation of **4** was detected from (*Z*)-**1** in THF under similar conditions. In contrast to (*E*)-**1**, which gave the phosphaethyne **2** but not **4** as mentioned above, the 1-bromo-2-phosphaethenyllithium **3** did not afford **2**. These facts may indicate that the carbene **5** is smoothly generated from the bromo derivative **3**, because of the better leaving ability of bromide ion, to give **4** in a better yield, compared to either (*Z*)-**1** or (*E*)-**1**. Nevertheless, these results do not mean that phosphinidene carbenes should not isomerise to phosphaethynes. Competitive formation of phosphaethynes may accompany intra- and/or inter-molecular C–H insertion reactions if phosphinidene carbenes bear substituents which retard intramolecular C–H insertion reaction, since theoretical investigation (at the MP4/6-31G** level) has shown that the linear HPC and HCP isomers represent the transition state and the energy minimum, respectively, on the energy surface of the singlet ground state.[10]¶

The UV spectrum of **4** was compared with those of 1-phosphapropenes (*E*)- and (*Z*)-**8**, which were prepared by the method shown in Scheme 3.‖ Although the three compounds exhibit absorption maxima at a similar wavelength of *ca.* 300 nm, the molar absorption coefficient of the dihydrophosphanaphthalene **4** is about ten times larger than those of (*E*)- and (*Z*)-**8**.§ This fact probably indicates that the phosphorus–carbon double bond in **4** is nearly coplanar with the aromatic ring (Ar) while the double bond systems in (*E*)- and (*Z*)-**8** are not coplanar with the Ar ring. In fact, X-ray crystallographic analysis of (*E*)- and (*Z*)-2-phenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethenes, the phenyl analogues of



Scheme 3 *Reagents and conditions*: i, Bu^{n}Li, THF, −78 °C; ii, MeI, −78 °C; iii, MeOH, −78 °C



Scheme 4 *Reagents and conditions*: i, 1 M HCl aq., Et_2O–EtOH (5 : 1), air, room temp.; ii, CH_2N_2, Et_2O, room temp.

(*E*)- and (*Z*)-**8**, shows that the phosphorus–carbon double bonds for those are nearly perpendicular to the aromatic rings of the Ar groups to avoid steric congestion.[11] Attempted X-ray analyses of **4**, however, have been unsuccessful because of difficulties in obtaining a suitable single crystal.

When compound **4** was allowed to react with hydrochloric acid in Et_2O–EtOH, phosphinic acid **9** was obtained in 30% yield (Scheme 4),§ indicating that there is enough room around the phosphorus atom for the approach of water or oxygen.†† However, attempted reaction of **4** with $M(CO)_5$(thf) (M = Cr, W) in THF at room temperature resulted in the decomposition of **4**, which may indicate that the end-on coordination site in **4** is blocked by the *o*-*tert*-butyl groups. Furthermore, attempted reaction of **4** with either $PtCl_2(PPh_3)_2$ and $N_2H_4{\cdot}H_2O$ at 60 °C for side-on coordination or $Cr(CO)_6$ in refluxing dioxane for π-complex formation was not successful and resulted in the decomposition of **4**.

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Footnotes and References

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‡ Attempted selective generation of (*E*)-**3** by deprotonation of (*E*)-ArP=C(H)Br with butyllithium resulted in bromine–lithium exchange to give ArP=CH_2 after quenching with water.

§ *Selected spectroscopic data* for **4**: colourless crystals, mp 122–125 °C (decomp.); δ_H (600 MHz, $CDCl_3$) 1.34 (9 H, s, Bu^t), 1.35 (6 H, s, C*Me*$_2$), 1.63 (9 H, br s, Bu^t), 2.47 (2 H, dd, $^3J_{PH}$ 16.9, $^3J_{HH}$ 6.4, CH_2), 7.40 (1 H, d, $^4J_{HH}$ 2.0, arom.), 7.42 (1 H, dd, $^4J_{PH}$ 2.2, $^4J_{HH}$ 2.0, arom.), 8.03 (1 H, dt, $^2J_{PH}$ 36.7, $^3J_{HH}$ 6.4, P=CH); δ_C (150 MHz, $CDCl_3$) 28.8 (C*Me*$_2$), 31.2 (C*Me*$_3$), 33.2 (d, J_{PC} 14.4, C*Me*$_3$), 35.2 (*C*Me$_3$), 35.9 (d, *J* 3.2, *C*Me$_2$), 37.7 (*C*Me$_3$), 41.8 (d, *J* 12.7, CH_2), 119.2 (arom., CH), 121.4 (d, *J* 7.2, arom., CH), 131.6 (d, *J* 53.9, arom., CP), 148.8 (d, *J* 4.3, arom.), 152.2 (d, *J* 2.9, arom.), 153.1 (d, *J* 16.5, arom.), 168.3 (d, *J* 34.1, P=C); δ_P (81 MHz, $CDCl_3$) 210.8 (dt, $^2J_{PH}$ 36.7, $^3J_{PH}$ 16.9); ν_{max}(KBr)/cm^{-1} 1597; λ_{max}(hexane)/nm (log ε) 240 (3.86), 301 (3.84); *m/z* (70 eV) 288 (M$^+$, 100), 273 (M$^+$ − Me, 25), 57 (Bu$^+$, 16); Found: 288.2011. Calc. for $C_{19}H_{29}P$: 288.2007. For (*E*)-**8**: colourless crystals, mp 62–65 °C; δ_H (200 MHz) 1.33 (9 H, s, *p*-Bu^t), 1.50 (18 H, d, $^5J_{PH}$ 0.6, *o*-Bu^t), 2.14 (3 H, dd, $^3J_{PH}$ 25.3, $^3J_{HH}$ 8.4, Me), 7.39 (2 H, d, $^4J_{PH}$ 1.2, *m*-Ar), 7.44 (1 H, dq, $^2J_{PH}$ 25.4, $^3J_{HH}$ 8.4, P=CH); δ_C(50 MHz) 19.9 (d, *J* 30.8, Me), 31.4 (*p*-C*Me*$_3$), 32.5 (d, *J* 7.4, *o*-C*Me*$_3$), 34.9 (*p*-*C*Me$_3$), 38.2 (d, *J* 0.7, *o*-*C*Me$_3$), 121.5 (d, *J* 1.4, *m*-Ar), 139.9 (d, *J* 55.3, *i*-Ar), 149.2 (*p*-Ar), 153.5 (d, *J* 1.7, *o*-Ar), 175.1 (d, *J* 33.4, P=C); δ_P 250.3 (dq, $^2J_{PH}$ 25.4, $^3J_{PH}$ 25.3); λ_{max} (hexane)/nm (log ε) 210 (4.40), 240 (4.18), 300 (3.07); *m/z* 304 (M$^+$, 100); Found: 304.2317. Calc. for $C_{20}H_{33}P$: 304.2320. For (*Z*)-**8**: colourless crystals, mp 37–39 °C; δ_H (200 MHz) 1.28 (3 H, dd, $^3J_{PH}$ 18.1, $^3J_{HH}$ 7.8, Me), 1.33 (9 H, s, *p*-Bu^t), 1.49 (18 H, d, $^5J_{PH}$ 0.6, *o*-Bu^t), 7.23 (1 H, dq, $^2J_{PH}$ 39.0, $^3J_{HH}$ 7.8, P=CH), 7.40 (2 H, d, $^4J_{PH}$ 1.0, *m*-Ar); δ_C (50 MHz) 19.7 (d, *J* 19.2, Me), 31.3 (*p*-C*Me*$_3$), 32.5 (d, *J* 7.5, *o*-C*Me*$_3$), 34.9 (*p*-*C*Me$_3$), 37.9 (d, *J* 1.1, *o*-*C*Me$_3$), 121.5 (d, *J* 1.0, *m*-Ar), 149.5 (*p*-Ar), 150.0 (d, *J* 62.6, *i*-Ar), 153.7 (d, *J* 1.6, *o*-Ar), 167.2 (d, *J* 41.3, P=C); δ_P 250.3 (dq, $^2J_{PH}$ 39.0, $^3J_{PH}$ 18.1); λ_{max} (hexane)/nm (log ε) 213 (4.39), 240 (4.20), 300 (2.92). For **9**: colourless crystals, mp 280 °C (decomp.); δ_H (200 MHz) 1.31 (9 H, s, Bu^t), 1.39 (6 H, s, C*Me*$_2$), 1.64 (9 H, s, Bu^t), 2.0–2.3 (4 H, m, CH_2CH_2), 2.6–4.5 (OH),†† 7.34 (1 H, dd, $^4J_{PH}$ 5.2, $^4J_{HH}$ 2.0, arom.), 7.55 (1 H, dd, $^4J_{PH}$ 3.7, $^4J_{HH}$ 2.0, arom.); δ_P 44.6 [t, J_{PH} 20.6 when δ_H(OH) 4.5], 45.0 [br, when δ_H(OH) 2.6];‡‡ ν_{max}(KBr)/cm^{-1} 1173 (P=O), 941 (P–O); *m/z* 322 (M$^+$, 43), 307 (M$^+$ − Me, 100). For **10**: colourless oil; δ_H (600 MHz) 1.30 (9 H, s, Bu^t), 1.36 (3 H, s, Me), 1.40 (3 H, s, Me), 1.61 (9 H, s, Bu^t), 1.90 (1 H, m, PCH), 2.05–2.21 (3 H, m, CH*H*CH_2), 3.70 (3 H, d, $^3J_{PH}$ 10.9, OMe), 7.35 (1 H, dd, $^4J_{PH}$ 5.0, $^4J_{HH}$ 1.9, arom.), 7.55 (1 H, dd, $^4J_{PH}$ 3.8, $^4J_{HH}$ 1.9, arom.); δ_C (150 MHz) 22.1 (PCH_2*C*H_2), 31.0 (C*Me*$_3$), 32.3 (Me), 32.8 (C*Me*$_3$), 33.3 (Me), 34.6 (d, *J* 5.6, PCH_2), 35.1 (*C*Me$_3$), 37.9 (d, *J* 7.3, C*Me*$_2$), 38.6 (d, *J* 3.2, *C*Me$_3$), 50.2 (d, *J* 6.4, OMe), 122.7 (d, *J* 58.0, arom., CP), 123.3 (d, *J* 12.0, arom., CH), 124.0 (d, *J* 11.5, arom., CH), 153.3 (d, *J* 12.1, arom.), 153.6 (arom.), 155.2 (d, *J* 6.3, arom.); δ_P 42.7; ν_{max} (KBr)/cm^{-1} 1213 (P=O), 1032 (P–O); *m/z* 336 (M$^+$, 54), 307 (M$^+$ − Me, 100); Found: 336.2216. Calc. for $C_{20}H_{33}O_2P$: 336.2218.

¶ The conversion of (*E*)-**1** to **2** might proceed in a concerted fashion involving elimination of the chlorine atom accompanied with the migration of the Ar group.

∥ Compound **8** has already been described by Märkl and Bauer as a mixture of (*E*)- and (*Z*)-isomers (ref. 12).

†† Compound **9** was further converted to the corresponding methyl phosphinate **10** by the addition of a diazomethane–diethyl ether solution (91% yield).§

‡‡ Both ^{31}P and ^{1}H NMR chemical shifts vary depending on the moisture in the sample solution. In dry $CDCl_3$, δ_P 44.6 and δ_H(OH) 4.5, whereas in wet $CDCl_3$, δ_P 45.0 and δ_H(OH) 2.6.

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