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# Preparation of 2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphacyclobutenes from 2-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethyne and alkyllithiums

**Shigekazu Ito, Hiroki Sugiyama and Masaaki Yoshifuji***

*Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan.*
*E-mail: yoshifj@mail.cc.tohoku.ac.jp*

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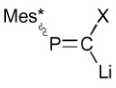
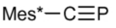
**2-(2,4,6-Tri-*tert*-butylphenyl)-1-phosphaethyne was allowed to react with 0.5 eq. of alkyllithium to afford 2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphacyclobutenes through an intramolecular cyclisation of a 1,3-diphosphabuta-1,3-diene intermediate.**

Kinetically stabilised phosphanylidene carbenoid **1** (Mes* = 2,4,6-tri-*tert*-butylphenyl) is a reactive intermediate containing a low-coordinated phosphorus atom, and thus can be used as a synthon for low-coordinated organophosphorus compounds.[1] We and others have investigated the properties of **1** to show the [1,2]-rearrangement (Fritsch–Buttenberg–Wiechell rearrangement) reaction giving phosphaalkyne **2**.[2] Recently we have reported an unusual reaction of **1** affording a 1,3,6-triphosphafulvene derivative (**3**) including a reaction of **1** with a twofold amount of **2**, which is assumed to be generated under the reaction conditions starting from dibromophosphaethene **4** and *tert*-butyllithium.[3] On the other hand, Niecke and co-workers reported an interesting dimerisation of **1**, where X = Cl, affording 1,3-diphosphacyclobutane-2,4-diyl **5**.[4] Here we report a reaction of **2** with 0.5 eq. of alkyllithium to afford 1,3-diphosphacyclobutene derivatives probably through cyclisation of a 1,3-diphosphabuta-1,3-diene intermediate.



**1**



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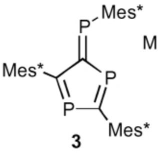

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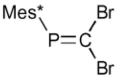

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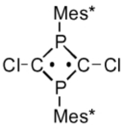
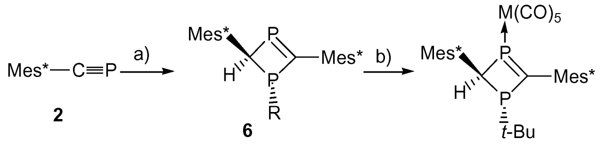


**5**

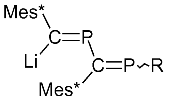
X = Br, Cl  Mes* = 2,4,6-$t$-$Bu_3C_6H_2$

Phosphaalkyne **2** was allowed to react with 0.5 eq. of *tert*-butyllithium followed by quenching with methanol in THF at −78 °C to afford 1,3-diphosphacyclobutene **6a** as a single diastereomer in 41% yield (Scheme 1).† Compound **6a** seemed to be formed by cyclisation of an intermediate **7** affording **8**, which was predicted by theoretical calculations,[5] and **7** might be formed from phosphaethenyllithium [Mes*C(Li)=P–*t*-Bu] and **2**.[6] Lithiated 1,3-diphosphacyclobutene **8a** (R = *t*-Bu) was observed at rt in $^{31}$P NMR spectroscopy [$\delta_P$ = 268.5 (P=C), 87.6 (*t*-BuP), $^2J_{PP}$ = 86.8 Hz]. Either cycloadditions or oligomerisations of **2** has not been reported so far probably due to its bulky Mes* group, in contrast to other phosphaalkynes, whereas Regitz *et al.* prepared 1,3-diphosphacyclobutene **9** by a hydrostannylation[7a] of phosphaalkyne [Ad–C≡P; Ad = 1-adamantyl].[7] 1,3-Diphosphacyclobutene **6a** is stable at rt, and can be handled in the air. The *tert*-butyl group on the phosphorus atom is *trans* to the Mes* group at the 4 position probably to minimize the steric congestion as shown in **10**.[7a] In $^{31}$P NMR spectroscopy, a peak due to the low-coordinated phosphorus atom of **6a** was observed at $\delta_P$ = 308.8 which is comparable to 2-chloro-1,3-diphosphapropene **11** ($\delta_P$ = 302.4),[8] and the phosphorus at the 3 position was observed at $\delta_P$ = 89.2. In $^{13}$C NMR spectroscopy, a peak due to the P=C and the CH carbon atoms in the diphosphacyclobutene ring were observed at $\delta_C$ = 208.6 and 43.7, respectively. 1,3-Diphosphacyclobutene skeleton in **6a** was confirmed by X-ray analysis as shown in Fig. 1.‡



R = $t$-Bu (**a**), $n$-Bu (**b**), $s$-Bu (**c**), Me (**d**)

**Scheme 1** *Reagents and conditions*: (a) i, RLi (0.5 eq.), THF, −78 °C, 10 min; ii, MeOH, rt; (b) M(CO)$_5$(thf) (M = Cr, W), THF, rt, 3 h (R = *t*-Bu).



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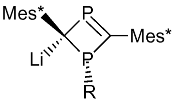

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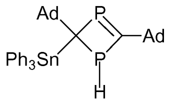
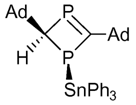


**9**



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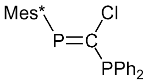
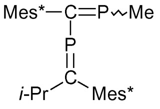


**11**



**12**

Ad = 1-adamantyl

Similarly, phosphaalkyne **2** was allowed to react with *n*- and *s*-butyllithiums to afford the corresponding 1,3-diphosphacyclobutenes **6b**,**c** in 35% and 20% yields, respectively.§ Compound **6c** was also obtained from the reaction of **4** and 3 eq. of *s*-butyllithium in 25% yield together with **3** (15%), and its two diastereomers caused by the *s*-butyl group were identified to take 3,4-*trans* configuration. Moreover, **2** was allowed to react with methyllithium solely to afford the corresponding product **6d** [$\delta_P$ ($CDCl_3$) = 334.0 (P=C), 53.7 (MeP); $^2J_{PP}$ = 86.3 Hz]. Compound **6d** was not so stable at rt to allow its isolation probably due to the poor protecting ability of the methyl group for the 1,3-diphosphacyclobutene skeleton. Previously, Cowley *et al.* reported the reaction of **2** with methyllithium followed by quenching with 2-chloropropane to

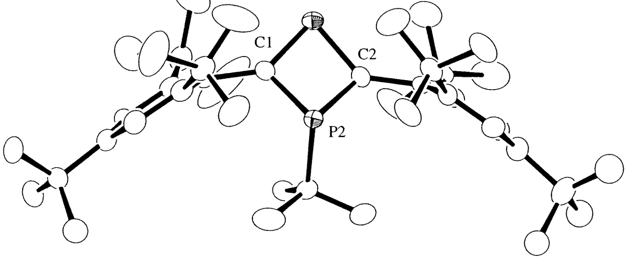


**Fig. 1** Molecular structure of **6a** with the 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. The P1 and P2 atoms are disordered, and the atoms with a predominant occupancy factor (0.86) are shown. The *p*-*tert*-butyl group in the Mes* group on the C2 atom is also disordered, and the atoms with a predominant occupancy factor (0.58), which are refined isotropically, are shown.

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give a 1,3-diphosphabuta-1,3-diene **12**. There is a close resemblance in the $^{31}P\{^{1}H\}$ NMR data between **6d** and **12** [**12**: $\delta_P$ = 337.92, 55.29; $^{2}J_{PP}$ = 87.03 Hz],[9] thus, we believe that 'the structure of **12**' was erroneously reported.

We investigated coordination properties of **6a** on some transition metals. 1,3-Diphosphacyclobutene **6a** was allowed to react with pentacarbonyl(tetrahydrofuran)chromium(0) and -tungsten(0) in THF to afford the corresponding complex **13** and **14** in 61% and 87% yields from **1**, respectively.¶ The coordination at the sp$^2$ phosphorus atom was identified by $^{31}P$ NMR spectrum to be displaying higher chemical shift than that of **6a** together with the observed satellite peaks due to $^{1}J_{PW}$ (for **14**), whereas **9** and **11** coordinate on the tungsten atom at the $\lambda^3\sigma^3$-phosphorus atoms.[7a,8,10]

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## Notes and references

† Data for **6a**: pale green needles (hexane), mp 193–194 °C; $^{31}P$ NMR (162 MHz, $CDCl_3$) $\delta$ = 308.8 (dd, $^{2}J_{PH}$ = 8.7 Hz, $^{2}J_{PP}$ = 94.1 Hz, P=C), 89.2 (dm, $^{2}J_{PP}$ = 94.1 Hz, *t*-BuP); $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 7.39 (1H, s, *m*-Mes*), 7.31 (1H, s, *m*-Mes*), 7.29 (1H, s, *m*-Mes*), 7.24 (1H, s, *m*-Mes*), 4.11 (1H, pt, $^{2}J_{PH}$ = $^{2}J_{PH}$ = 8.7 Hz, C*H*), 1.70 (9H, s, *o*-C*Me*$_3$), 1.63 (18H, s, *o*-C*Me*$_3$), 1.58 (9H, s, *o*-C*Me*$_3$), 1.31 (9H, s, *p*-C*Me*$_3$), 1.30 (9H, s, *p*-C*Me*$_3$), 0.43 (9H, d, $^{3}J_{PH}$ = 11.5 Hz, PC*Me*$_3$); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ = 208.6 (dd, $^{1}J_{PC}$ = 49.6 Hz, $^{1}J_{PC}$ = 37.2 Hz, P=*C*), 152.1 (d, $^{3}J_{PC}$ = 4.4 Hz, *o*-Mes*), 151.5 (d, $^{3}J_{PC}$ = 3.0 Hz, *o*-Mes*), 149.1 (d, $^{3}J_{PC}$ = 5.5 Hz, *o*-Mes*), 146.8 (s, *p*-Mes*), 146.1 (s, *p*-Mes*), 144.7 (d, $^{3}J_{PC}$ = 4.4 Hz, *o*-Mes*), 137.3 (dd, $^{2}J_{PC}$ = 9.6 Hz, $^{2}J_{PC}$ = 3.6 Hz, *ipso*-Mes*), 134.8 (d, $^{2}J_{PC}$ = 4.4 Hz, *ipso*-Mes*), 124.4 (s, *m*-Mes*), 123.8 (s, *m*-Mes*), 121.7 (s, *m*-Mes*), 120.8 (s, *m*-Mes*), 43.7 (dd, $^{1}J_{PC}$ = 32.8 Hz, $^{1}J_{PC}$ = 15.3 Hz, *C*H), 39.4 (s, *o*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 38.9 (dd, $^{1}J_{PC}$ = 52.0 Hz, $^{3}J_{PC}$ = 4.4 Hz, P–*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 37.6 (s, *o*-*C*Me$_3$), 35.1 (s, *p*-*C*Me$_3$), 34.9 (d, $^{5}J_{PC}$ = 8.0 Hz, *o*-C*Me*$_3$), 34.8 (s, *p*-*C*Me$_3$), 34.7 (d, $^{5}J_{PC}$ = 2.9 Hz, *o*-C*Me*$_3$), 33.2 (d, $^{5}J_{PC}$ = 2.2 Hz, *o*-C*Me*$_3$), 33.1 (d, $^{5}J_{PC}$ = 2.2 Hz, *o*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$), 31.6 (s, *p*-C*Me*$_3$), 28.0 (d, $^{2}J_{PC}$ = 13.9 Hz, P–C*Me*$_3$); MS (EI, 70 eV) *m*/*z* 634 ($M^+$).

‡ Crystal data for **6a**: $C_{42}H_{68}P_2$, $M$ = 634.95, triclinic, space group $P\bar{1}$ (#2), $a$ = 13.592(2), $b$ = 14.861(2), $c$ = 10.916(2) Å, $\alpha$ = 98.722(3), $\beta$ = 98.760(2), $\gamma$ = 67.629(9)°, $V$ = 2004.6(5) Å$^3$, $Z$ = 2, $T$ = 110 K, crystal size 0.40 × 0.30 × 0.25 mm$^3$, $\rho$ = 1.052 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 0.134 mm$^{-1}$, $\theta_{max}$ = 27.5°, $F(000)$ = 700, 12670 total reflections, 7888 unique reflections ($R_{int}$ = 0.047), $R1$ = 0.138 [$I > 1\sigma(I)$], $R$w = 0.320 (all data). All non-hydrogen atoms, except the disordered C atoms in the *p*-*tert*-butyl group, were refined anisotropically. All hydrogen atoms were included in calculated positions and refined isotropically, except for the hydrogen atoms directly attached upon the 1,3-diphosphacyclobutene ring and those in the disordered methyl groups, which were not refined. CCDC 184131. See http://www.rsc.org/suppdata/cc/b2/b204142c/ for crystallographic files in CIF or other electronic format.

§ $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **6b**: $\delta$ = 331.9 (d, $^{2}J_{PP}$ = 82.0 Hz, P=C), 70.9 (d, $^{2}J_{PP}$ = 82.0 Hz, *n*-BuP); **6c**: isomer A, $\delta$ = 327.1 (d, $^{2}J_{PP}$ = 82.8 Hz, P=C), 79.0 (d, $^{2}J_{PP}$ = 82.8 Hz, *s*-BuP); isomer B, $\delta$ = 326.6 (d, $^{2}J_{PP}$ = 82.1 Hz, P=C), 78.7 (d, $^{2}J_{PP}$ = 82.1 Hz, *s*-BuP).

¶ Selected data for **13**: yellow needles (hexane), mp > 300 °C; $^{31}P$ NMR (162 MHz, $CDCl_3$) $\delta$ = 285.8 (dd, $^{2}J_{PH}$ = 21.5 Hz, $^{2}J_{PP}$ = 137.2 Hz, P=C), 85.9 (dm, $^{2}J_{PP}$ = 137.2 Hz, *t*-BuP); $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.90 (1H, dd, $^{2}J_{PH}$ = 21.5 Hz, $^{2}J_{PH}$ = 7.7 Hz, C*H*), 0.58 (9H, d, $^{3}J_{PH}$ = 11.9 Hz, PC*Me*$_3$); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ = 208.5 (dd, $^{1}J_{PC}$ = 43.8 Hz, $^{1}J_{PC}$ = 16.8 Hz, P=*C*), 54.0 (dd, $^{1}J_{PC}$ = 23.4 Hz, $^{1}J_{PC}$ = 0.8 Hz, *C*H). FAB-MS *m*/*z* 826 ($M^+$). For **14**: yellow plates (hexane), mp 211–212 °C; $^{31}P$ NMR (162 MHz, $CDCl_3$) $\delta$ = 234.5 (dd, $^{2}J_{PH}$ = 22.7 Hz, $^{2}J_{PP}$ = 141.4 Hz, $^{1}J_{PW}$ (satellite) = 253.8 Hz, P=C), 85.8 (dm, $^{2}J_{PP}$ = 141.4 Hz, *t*-BuP); $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.95 (1H, dd, $^{2}J_{PH}$ = 22.7 Hz, $^{2}J_{PH}$ = 7.6 Hz, C*H*), 0.60 (9H, d, $^{3}J_{PH}$ = 12.0 Hz, PC*Me*$_3$); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ = 201.8 (dd, $^{1}J_{PC}$ = 43.8 Hz, $^{1}J_{PC}$ = 23.4 Hz, P=*C*), 40.3 (dd, $^{1}J_{PC}$ = 59.2 Hz, $^{1}J_{PC}$ = 16.4 Hz, *C*H). FAB-MS *m*/*z* 958 ($M^+$).

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