Preparation and Structure of 2,3-Dichloro-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,3-butadiene

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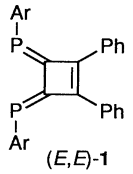
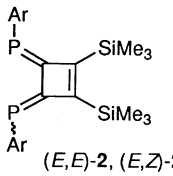
A sterically protected 1,4-diphospha-1,3-butadiene was prepared from the copper-mediated coupling reaction of 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene. The X-ray crystallographic analysis shows that the molecule has a center of symmetry and that each of the bulky phenyl groups tilts almost perpendicularly to the diphosphabutadiene system serving as a good protecting group.

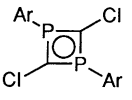
Sterically protected and multiple-bonded organophosphorus compounds are currently of interest.[1] Utilizing the 2,4,6-tri-*t*-butylphenyl group (abbreviated to the Ar group) as a protecting group, we have been successful in isolation and characterization of diphosphenes[2] and phosphaethenes[3] containing low-coordinated phosphorus atom(s) (coordination number 2) as stable molecules. Phosphorus compounds involving conjugated systems[4] such as phosphabutadienes[5] have been isolated and, as a more extended conjugated system, diphosphinidenecyclobutenes have been reported by Appel *et al.* (**1**),[6] Märkl *et al.* (**2**),[7] and ourselves (**2**),[8] involving the 1,4-diphospha-1,3-butadiene or 1,6-diphospha-1,2,4,5-hexatetraene system.



(*E,E*)-**1**



(*E,E*)-**2**, (*E,Z*)-**2**



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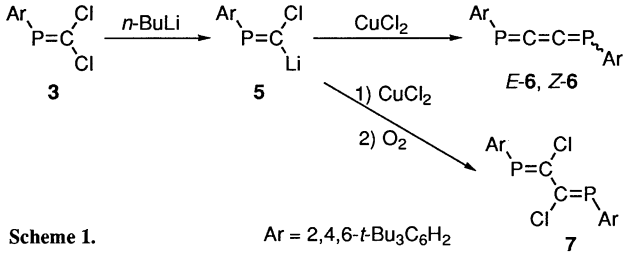
Very recently, Niecke *et al.* reported an interesting reaction of 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**3**) with 0.5 molar equiv. of butyllithium at –100 °C to give a 1,3-diphosphacyclobutane-2,4-diyl **4** and confirmed the structure by the X-ray analysis.[9] On the other hand, we have been interested in 1-chloro-2-phosphaethenyllithium **5** and reported on some reactions with carbonyl compounds.[10] We now report on a different reaction from Niecke's reaction[9] but to give a 1,4-diphospha-1,3-butadiene.[11]

Copper-mediated oxidative coupling reactions have been used for organic synthesis.[12] This method is also useful for preparation of radialenes and cumulenes.[13,14] Thus **3** (105 mg, 0.292 mmol) was allowed to react with an equimolar amount of butyllithium in THF (8 mL) at –78 °C, 0.5 molar equiv. of copper(II) chloride was added to the resulting pale blue solution



Scheme 1. Ar = 2,4,6-*t*-Bu$_3$C$_6$H$_2$

of 1-chloro-2-phosphaethenyllithium **5**[10] at –78 °C, and warmed up immediately to room temperature to give a deep red solution with yellow precipitates of 1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,2,3-butatriene (**6**)[15,16] in 63% yield base on **3** (Scheme 1).[17] However, if oxygen gas (*ca.* 35 mmol) was bubbled through a yellow solution of a mixture of $CuCl_2$ (30.0 mg, 0.61 mmol) and **5** [similarly prepared from **3** (437 mg, 1.22 mmol) and *n*-BuLi (1.22 mmol) in THF (35 mL)] at –78 °C, the mixture became red and turned green upon warming to room temperature to give 2,3-dichloro-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,3-butadiene (**7**) in 23% yield after recrystallization together with *Z*-2-chloro-1-phosphaethene **8** (δ_P = 249.8, 8%). There was no compound **4** observed under our reaction conditions of relatively low concentration. **7**: Mp 253 – 254 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.34 (18H, s, *p*-*t*-Bu), 1.51 (36H, s, *o*-*t*-Bu), and 7.42 (4H, m, *m*-Ar); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 31.3 (s, *p*-C($\underline{C}H_3$)$_3$), 32.7 (brs, *o*-C($\underline{C}H_3$)$_3$), 35.1 (s, *p*-$\underline{C}$(CH$_3$)$_3$), 37.9 (brs, *o*-$\underline{C}$(CH$_3$)$_3$), 122.0 (brs, *m*-Ar), 135.5 (dd, $^1J_{PC}$ = 27.6 Hz, $^4J_{PC}$ = 25.3 Hz, *ipso*-Ar), 151.0 (s, *p*-Ar), 154.0 (brs, *o*-Ar), and 167.4 (dd, $^1J_{PC}$ = 26.5 Hz, $^2J_{PC}$ = 18.0 Hz, P=$\underline{C}$); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 248.0; IR (KBr) 1595 cm^{-1}; UV (hexane) 242 (log ε 4.44) and 366 nm (4.28); MS (70 eV, EI) *m/z* 650 (M^++4; 2), 648 (M^++2; 8), 646 (M^+; 12), 611 (M^+–Cl; 4), 589 (M^+–^{t}Bu; 5), 575 (M^+–2Cl–1; 7), 401 ($ArP_2C_2Cl_2^+$; 90), 335 ($ArPC_2Cl^+$; 14), 299 ($ArPC_2^+$–1; 6), 275 (ArP^+–1; 34), and 57 (^{t}Bu$^+$; 100). Found: *m/z* 646.3373. Calcd for $C_{38}H_{58}{}^{35}Cl_2P_2$: M, 646.3391. The UV-Vis spectrum of **7** indicated that the conjugation in **7** is slightly longer than in (*E,E*)-**2** (λ_{max} 314 nm),[8] indicating the higher planarity of the system.

The structure of **7** was unambiguously determined by X-ray crystallographic analysis. Figure 1 is an ORTEP drawing[18] of

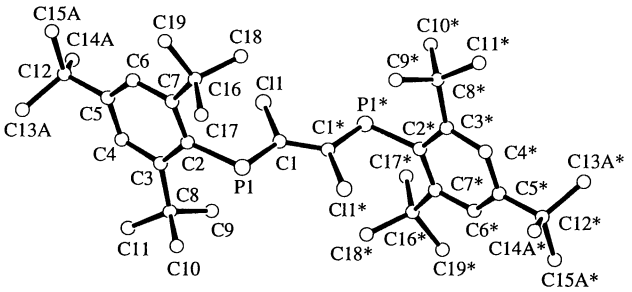
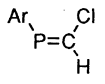


Figure 1. Molecular structure of **7**. Hydrogen atoms are omitted for clarity. As for the disordered carbons, C(13)–C(15), only those with the higher occupancy factor (0.61) are shown. Some important bond lengths(Å) and angles(°): Cl(1)–C(1), 1.744(4), P(1)–C(1), 1.691(4); P(1)–C(2), 1.833(4); C(1)–C(1)*, 1.445(7); C(1)–P(1)–C(2), 102.7(2); Cl(1)–C(1)–P(1), 123.3(2); Cl(1)–C(1)–C(1)*, 113.3(4); P(1)–C(1)–C(1)*, 123.4(4).

the molecular structure for **7**.[19] The molecule has a center of symmetry and the diphosphabutadiene system [P(1), C(1), P(1)*, C(1)*] is almost planar including the chlorine atoms [Cl(1), Cl(1)*] and ipso-carbons of the phenyl rings [C(2), C(2)*] within 0.016(5) Å. Furthermore, the planes of the phenyl rings [C(2)–C(7), C(2)*–C(7)*] take an angle of 90.6° with the phosphabutadiene system plane to release the steric congestion and serve as a good protecting group for the P=C–C=P π-system. A similar phenomenon was observed in 2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethenes.[20] The bond length P(1)-C(1) [1.691(4) Å] for **7** is slightly longer than either 1.660(6) Å in (*E*)-2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethene (*E*-**9**)[20] or 1.674(2) Å for the (*Z*)-derivative (*Z*-**9**).[20] The bond length of C(1)–C(1)* [1.445(7) Å] is shorter than the corresponding bond length of 1.483 ± 0.01 Å in 1,3-butadiene.[21] These features seem to be attributable to delocalization over the planar diphosphabutadiene unit. This is the first X-ray structural analysis of 1,4-diphospha-1,3-butadiene, although the structures of 2,3-diphosphabutadiene[6] and 1,3-diphosphabutadiene[6] were reported by Appel *et al.* Furthermore, the compound **7** did not seem to give the structural isomer **4**, either thermally or photochemically, while Niecke also unsuccessfully attempted to isomerize **4** to **7**.



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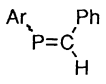
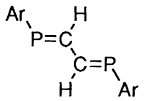


E-**9**, *Z*-**9**



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References and Notes

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