Reactions of Dichlorocarbene with Sterically Protected 1-Phosphaallene and 1,3-Diphosphaallene

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Dichlorocarbene reacted with sterically protected 1-phosphaallene and 1,3-diphosphaallene to give a methylene-phosphirane and a methylene-diphosphirane, respectively; the former phosphirane was converted to 1-phosphabutatriene with butyllithium and the structure of the latter diphosphirane was determined by X-ray crystallography.

Sterically protected phosphorus-containing multiple bonded compounds are currently of interest. We have recently reported that dichlorocarbene reacts with diphosphenes to give diphosphiranes, which can be converted to 1,3-diphosphaallenes.[1,2] Dichlorocarbene also reacts with phosphaethylenes to give phosphiranes which can be converted to 1-phosphaallenes.[3]

We now report our preliminary results on the reactions of dichlorocarbene with phosphaallene compounds, a 1-phosphaallene and a 1,3-diphosphaallene.

The reaction of dichlorocarbene generated by the Makosza method[3] with 3,3-diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaallene **1**[4] gave the methylenephosphirane **2** in 35% yield (m.p. 175–176 °C, ^{31}P NMR δ_P −93.4) together with 2,2-dichloro-1-(2,4,6-tri-*tert*-butylphenyl)phosphaethylene (m.p. 155–158 °C, δ_P 231.0) in 10% yield as a by-product with 34% recovery of the starting phosphaallene **1**. Furthermore, **2** was converted with 1.2 equiv. of butyllithium in tetrahydrofuran (THF) at −78 °C to the 1-phosphabutatriene **3**[5] in 68% yield (m.p. 153—154 °C, δ_P 157.0).[†] One carbon atom was formally inserted in the P=C bond to extend the cumulative double bond system.

Dichlorocarbene reacted with the 1,3-diphosphaallene **4**[6] to give the methylenediphosphirane **6** as pale-yellow crystals in 34% yield (m.p. 145–147 °C, δ_P −44.6).[‡] The reaction may

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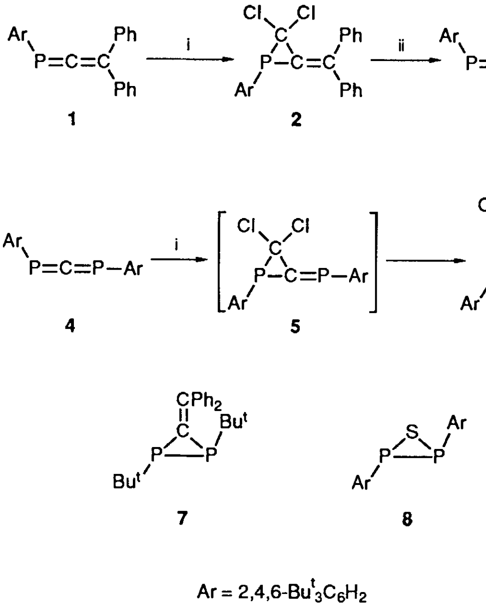
[†] When 2.2 equiv., of Bu^tLi was used the following *tert*-butylated phosphines were obtained as products: $ArP(H)C\equiv CCPh_2Bu^t$ (15% yield, δ_P −100.7, d, *J* 244.1 Hz) and $ArP(Bu^t)C\equiv CCHPh_2$ (10% yield, δ_P −25.6).

[‡] Compound **6**: ^1H NMR ($CDCl_3$) δ 1.26 (18H, s, *p*-Bu^t), 1.51 (36H, s, *o*-Bu^t) and 7.23 (4H, br s, Ar); ^{13}C NMR ($CDCl_3$) δ 31.19 (*p*-Me), 33.40 (t, *J* 5.7 Hz, *o*-Me), 34.61 (*p*-CMe_3), 38.22 (*o*-CMe_3), 119.55 (t, *J* 17.5, C-4), 122.24 (*m*-Ar), 132.38 (t, *J* 42.0, *ipso*-Ar), 144.69 (t, *J* 76.2, C-3), 149.99 (*p*-Ar) and 157.39 (t, *J* 5.43, *o*-Ar); UV (hexanes) λ_{max}/nm 310 (log ε 4.03) and 257sh (4.29). Satisfactory elemental analyses were obtained.



Scheme 1. *Reagent and conditions*: i, [PhCH$_2$NEt$_3$]Cl, 50% aq. NaOH, CHCl$_3$, hexane; ii, Bu^{n}Li, THF, −78 °C

proceed *via* a phosphinidenephosphirane **5** as an intermediate followed by cleavage of the P–CCl$_2$ bond to form a phosphorus analogue of trimethylenemethane[7] leading to the thermodynamically stable **6**. The structure of **6** (Fig. 1) was unambiguously established by X-ray crystallographic analysis.§

The atoms C(7), P(1), P(2) and C(25) are coplanar within 0.08 Å with a dihedral angle C(7)–P(1)–P(2)–C(25) of 172.1 °. The two benzene rings bonded to P(1) and P(2) make angles of 78.4 and 26.6° respectively with this plane. The bond angles P(2)–P(1)–C(7)) and P(1)–P(2)–C(25) are 87.4(2) and 124.3(2)°, respectively. These values indicate that the overall molecular conformation of **6** is greatly different from those of the related compounds **7**[9] and **8**,[10] where an approximate or a crystallographic two-fold axis bisects the central three-membered ring and the corresponding P–P–C angles range from 99.9(2) ° for **8** to 104.8(3) ° for **7**.

The atoms C(3), C(4), Cl(5) and Cl(6), are coplanar within 0.02 Å and this plane is bent by 20.4° (8.2° in **7**) at C(3) out of the three-membered ring plane. This bending and the large contraction of the P(2)–P(1)–C(7) bond angle is due to the steric repulsions between C(4) and Cl(5), and the *o-tert*-butyl group on C(8), and between the *o-tert*-butyl groups on C(12) and C(26). The *o-tert*-butyl group on C(26) has many short contacts with the diphosphirane ring, resulting in abnormal opening of the P(1)–P(2)–C(25) and P(2)–C(25)–C(26) bond angles. The bond length P(1)–P(2) [2.277(2) Å] is significantly longer than that [2.195(4) Å] in **8**, resulting in the slight opening of P(1)–C(3)–P(2) [78.9(3)°] and contraction of P(1)–P(2)–C(3) [50.4(2)°] and P(2)–P(1)–C(3) [50.7(2)°] in **6** compared with the corresponding angles [75.2(3), 52.6(3) and 52.2(3)°] in **8**. The lengthening of the P(1)–P(2) bond probably reflects the large steric repulsion in **6**.

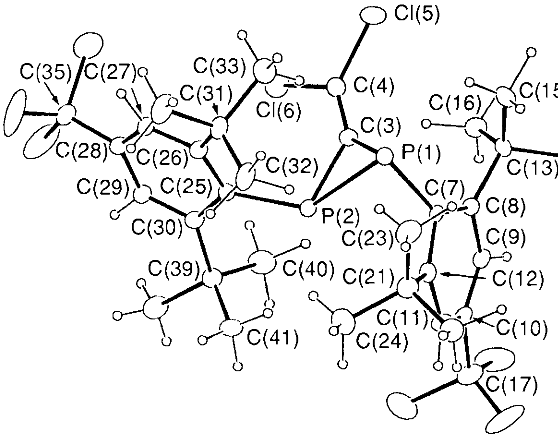


Fig. 1 ORTEP drawing[8] of the molecular structure of the methylenediphosphirane **6**. Some important bond lengths (Å) and angles (°): P(1)–P(2), 2.277(2); P(1)–C(3), 1.789(7); P(1)–C(7), 1.875(6); P(2)–C(3), 1.795(6); P(2)–C(25), 1.860(6); C(3)–C(4), 1.325(10); P(2)–P(1)–C(3), 50.7(2); P(1)–P(2)–C(3), 50.4(2); P(1)–C(3)–P(2), 78.9(3); P(2)–P(1)–C(7), 87.4(2); P(1)–P(2)–C(25), 124.3(2); C(3)–P(1)–C(7), 101.8(3); C(3)–P(2)–C(25), 104.6(3); P(1)–C(7)–C(8), 122.5(4); P(1)–C(7)–C(12), 117.1(4); P(2)–C(25)–C(26), 128.9(5); P(2)–C(25)–C(30), 109.8(5).

Intramolecular short contacts induce the deformation of the phenyl group to the boat form, which is commonly observed for Ar–P containing compounds.[11] The deformations of the Ar groups in **6** are 14.0 and 12.6°, defined by the angles between the planes [C(7), C(8), C(12)] and [C(8), C(9), C(11), C(12)] and the planes [C(25), C(26), C(30)] and [(C26), C(27), C(29), C(30)], respectively.

This work was supported in part by Grants-in-Aid for Scientific Research (No. 02403008 and 02247104) from the Ministry of Education, Science and Culture, Japanese Government and the Asahi Glass Foundation. The authors thank the Research Centre for Protein Engineering, Institute for Protein Research, Osaka University, for computer calculations, Tosoh Akzo Co., Ltd. for donating organolithium reagents and Shin-Etsu Chemical Co., Ltd. for organosilicon compounds.

Received, 10th September 1990; Com. 0/04105J

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§ *Crystal data* for **6**: C$_{38}$H$_{58}$Cl$_2$P$_2$, M_r = 647.74. Orthorhombic, space group *Pbca*, a = 45.851(7), b = 18.417(4), c = 9.365(4) Å, U = 7907(3) Å^3, Z = 8, D_c = 1.088 g cm^{-3}, μ = 2.65 cm^{-1}. 7004 Reflections with $2\theta \leqslant 50.0°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo-Kα radiation. Of these, 4538 with $F > 3\sigma(F)$ were judged as observed. The structure was solved using SHELX86.[12] The hydrogen atoms of the *p-tert*-butyl groups could not be located because of large thermal motion. Full-matrix least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic for hydrogen converged to R = 0.072.[13] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.