Synthesis and Structural Study of the First 1-Phosphaallyl Anion

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Received December 18, 1992

The allyl anion (I) and, in particular, the metal-stabilized η^3-complexes are among the best explored carbanion systems.[1] In contrast, little is known about the phosphaallylic systems in which one carbon atom is replaced by a twofold coordinated phosphorus center (II, III) (Scheme I). While the 2-phosphaallyl complexes are unknown, 1-phosphaallyl complexes has been obtained recently by Mathey et al.[2] However, no spectroscopic evidence or even isolation of a free phosphaallyl anion has been reported so far.

Herein we report on the synthesis and X-ray analysis of the first 1-phosphaallyl system (Scheme II). Thus, treatment of a solution of 3.2 mmol of tolan in 5 mL of (dme) dimethoxyethane with an equimolar amount of lithium arylphosphide **1**, dissolved in 7 mL of dme, at ambient temperature produced a deep red-colored solution, whose ^{31}P-NMR spectrum showed two resonance signals (δ 31.5, **2**, and 65.2, **3**). After the solution was stirred for several hours the high-field signal was completely transformed into the low-field one. With the addition of 10 mL of pentane, compound **3** precipitated as a red microcrystalline solid. The isolation of the extremely moisture- and air-sensitive product (mp 132 °C) has been achieved by filtering off and drying under vacuum (yield 75%).[3]

Support for the constitution of **3** as the 1-phosphaallyl anion $[\mathrm{ArylPC(Ph)C(H)Ph}]^-$ was gained from two well-separated resonances for the carbon atoms of the PCC moiety in the ^{13}C-NMR spectrum (δ 155.0 ($^1J_{\mathrm{CP}}$ = 40.4 Hz), 34.7 ($^2J_{\mathrm{CP}}$ = 10.2 Hz)), and the relatively high-field shift in the ^{31}P-NMR spectrum. However, the exact geometry of the anion as well as the coordination of the cation only became apparent after a single-crystal X-ray diffraction study had been carried out.[4]

In crystalline **3** the isolated ion pair, $[\mathrm{ArylPC(Ph)C(H)Ph}]^-[\mathrm{Li(dem)_3}]^+$, is evident from the shortest distance between the metal (Li) and P(1) (5.99 Å), which lies outside the sum of the van der Waals radii. This is a consequence of the nearly spherically coordination of the lithium atom by three dme molecules.[5] In the anion, the central P1–C1–C2 skeleton and all atoms directly adjacent to this moiety (C3, H1, C9, C13) lie in a plane (Figure 2). The aromatic ring substituents at P1 and C1, which are *trans* to each other, are orthogonal to this plane, thus

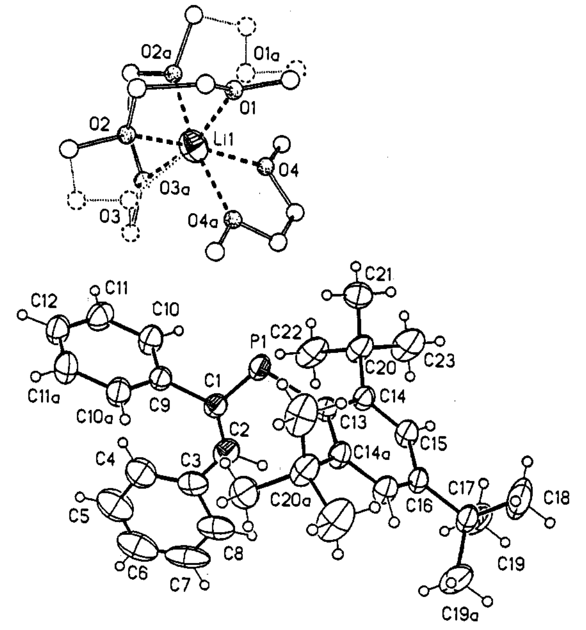


Figure 1. Structure of **2** showing the allylic system with ellipsoids at the 50% probability level.

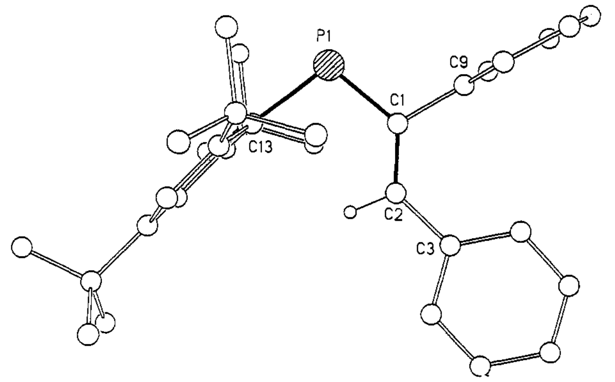
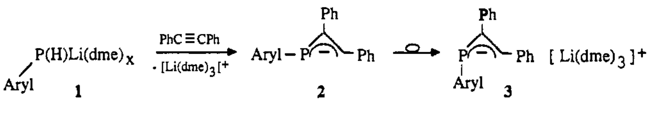


Figure 2. Structure of **3** showing the anion. Important bond lengths (Å) and angles (deg): P1–C1 1.757(6), P1–C13 1.879(7), C1–C2 1.366(6), C1–C9 1.501(9), C2–C3 1.466(9); C13–P1–C1 102.1(3), P1–C1–C2 128.7(6), P1–C1–C9 109.4(3), C2–C1–C9 121.8(6), C1–C2–C3 132.0(7).

Scheme I

(I) (II) (III)

Scheme II



1 **2** **3**

(Aryl = 2,4,6-tBu$_3$C$_6$H$_2$)

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[1] (a) Wilke, G.; et al. *Angew. Chem.* **1966,** *78,* 157–175; *Angew. Chem., Int. Ed. Engl.* **1966,** *5,* 150–164. (b) Studiengesellschaft Kohle. Belg. Pat. 651 596, 1964.

[2] (a) Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Organometallics* **1988,** *7,* 955–963. (b) Mercier, F.; Mathey, F. *Organometallics* **1990,** *9,* 863–864. (c) Hugel-Le Goff, C.; Mercier, F.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1989,** *363,* 325–333. (d) Mercier, F.; Ricard, L.; Mathey, F. *Polyhedron* **1990,** *23,* 2859–2861. (e) Mercier, F.; Hugel-Le Goff, C.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1990,** *389,* 389–397.

[3] Anal. Calcd. for $C_{44}H_{70}LiO_6P$: C, 72.10; H, 9.63. Found: C, 72.35; H, 10.15.

[4] The crystals obtained by crystalisolation from dme at room temperature are monoclinic, space group $C2/m$ (No. 12) with a = 28.046(3) Å, b = 11.412(2) Å, c = 19.913(3) Å, β = 122.47(1)°, V = 5377(1) Å, Z = 4, D_{calc} = 1.072 mg m^{-3}, μ(Cu Kα) = 0.81 mm^{-1}, $F(000)$ = 1900. A total of 2938 symmetry-independent reflections ($2\theta_{\max}$ = 100°, ω-scans) were recorded on an Enraf–Nonius CAD4 diffractometer at T = 193 K. Of these, 2642 reflections with $|F| > 3\sigma(F)$ were used for the structure solution (Direct Methods) and refinement (341 parameters) using the SHELXTL-Plus program system. Non-hydrogen atoms were refined anisotropically (full-matrix least squares), H atoms using a riding model. R = 0.083 (R_w = 0.098, $w^{-1} = \sigma^2(F) + 0.0005F^2$). An extinction correction was applied. Two of the coordinated and one free dme molecule were disordered.

[5] The coordination of lithium by three dme molecules is known: Baker, T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983,** *105,* 6763. Altwood, J. L.; Rogers, R. D.; Vann Bynum, R. *Cryst. Struct. Commun.* **1984,** *40,* 1812. Schumann, H.; Nickel, S.; Hahn, E.; Heeg, M. J. *Organometallics* **1985,** *4,* 800. Schumann, H.; Nickel, S.; Loebel, J.; Pickardt, J. *Organometallics* **1988,** *7,* 2004.

0002-7863/93/1515-6989$04.00/0

minimizing steric repulsions between these groups. In contrast to this, the two phenyl groups adopt a *cis* conformation, with the phenyl ring at C2 in a coplanar arrangement with respect to the P1-C1-C2-plane. The bond length P1-C1 (1.757 Å) is significant shorter than a normal P-C single bond[6] as it is found for P1-C13 (1.879 Å), while the C1-C2 double bond (1.366 Å) is slightly elongated as compared to a similar substituted ethene (1.32 Å[7]). These findings agree with a description as a delocalized 4-electron 3-center π-system in the form of a 1-phosphaallylic anion. The bond lengths within the central skeleton are quite similar to that found in the transition-metal η^3-1-phosphaallyl complex **4**, $(CO)_3Co(\eta^3\text{-}PhPCHCH_2)$ (PC 1.76 Å, C–C 1.42 Å).[2e] However, the P1-C1-C2 angle in **3** is significantly widened (128.7°) compared to **4** (112°), which may be attributed to the *endo* position of the aryl substituent. The C1-C9 (1.501 Å) and C2-C3 bond distances (1.466 Å) lie in the normal range of C–C single bonds.[6] The shortening of the latter is in accord with a weak π-interaction between the allylic and the aromatic systems.

The proven *endo* conformation of **3** in the solid state, which probably exists also in solution, suggests the constitution of the intermediate **2** as the thermodynamically less favored *exo* isomer.

Acknowledgment. We are indebted to the Fonds der Chemischen Industrie for generous support.

Supplementary Material Available: Tables of crystal data, final atomic coordinates, anisotropic displacement parameters, and bond lengths and angles, structural diagrams (14 pages); listing of final observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(6) Rademacher, P. Grösse und Gestalt von Molekülen. In *Strukturen organischer Moleküle*; Klessinger, M., Ed.; Verlag Chemie: Weinheim, 1987; Vol. 2, pp 55–60.

(7) *International Tables for Crystallography*; Verlag Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, pp 685–706.