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Alkali-Metal-Mediated Coupling of a Phosphorus-Substituted Alkene. Structural Characterization of Dilithium 1,1,4,4-Tetrakis(diphenylphosphino)butane-1,4-diide

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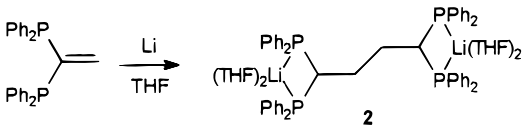
Summary: The butane-1,4-diide salt $\{(THF)_2Li(Ph_2P)_2CCH_2\}_2$ *is obtained by treatment of* $(Ph_2P)_2C{=}CH_2$ *with lithium in THF; hydrolysis of this salt yields the novel tetraphosphine* $\{(Ph_2P)_2CHCH_2\}_2$.

While the reduction of silicon- and aryl-substituted alkenes, alkynes and dienes by alkali metals to give 1,2- and 1,4-diide salts has been known for some years, it is only recently that these salts have received much attention.[1] Such dianions are useful intermediates in both organic and organometallic synthesis and often exhibit unusual structural features, although, in lithium complexes of these dianions, a Li−C contact is typically maintained with the carbanion center.[2] A more diverse structural chemistry is exhibited by phosphorus-stabilized carbanions such as the phosphinomethanides, $[R_2C{-}PR_2]^-$, and diphosphinomethanides, $[RC(PR_2)_2]^-$, which may bind as η^1, η^2, or η^3 ligands via their phosphorus and/or carbanion centers.[3] However, despite this structural diversity there has been no investigation into the potential of phosphorus-substituted alkenes as precursors to phosphorus-stabilized diide salts. We now report the first instance of an alkali-metal-induced coupling of a phosphorus-substituted alkene to give a 1,4-diide salt and also its hydrolysis to a novel tetraphosphine.

Scheme 1



Treatment of the vinylidene phosphine $(Ph_2P)_2C{=}CH_2$ (**1**)[4] with an excess of lithium powder in THF gave, after 1 h, the bis(diphosphinomethanide) $\{(THF)_2Li(Ph_2P)_2CCH_2\}_2$ (**2**) in quantitative yield (Scheme 1).[5] A single peak at 17 ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution after this time (cf. −3.9 ppm for **1**), verifying complete conversion of **1** into **2**. The ^1H NMR spectrum of **2** exhibits, in addition to signals due to the phenyl rings and coordinated THF, a multiplet at δ 1.91 which collapses to a singlet upon ^{31}P decoupling at δ 17, assigned to the protons in the newly formed ethylene bridge. In contrast to **3** (see below), the phenyl rings in **2** are nondiastereotopic due to the planarity of the ligand at the carbanion centers.

Recrystallization of **2** from 10:1 toluene/THF solution gave small crystals suitable for a synchrotron X-ray diffraction study.[6] This confirmed that the alkene had undergone a radical coupling reaction to yield a 1,4-diide salt (Figure 1). The molecule has exact inversion symmetry; each lithium atom is in a distorted-tetrahedral environment, coordinated at an end of the diide ligand by two phosphorus atoms and two molecules of THF. In contrast to the related 1,4-diide $[(Et_2O)_2LiPh_2CCH_2]_2$ (Li−C(1) = 2.28 Å),[1e] there are no significant interactions between the lithium atoms and the carbanion centers C(1) in **2**; C(1) is almost perfectly planar (sum of angles around C(1) 359.9°), and the Li−C(1)

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(5) To a suspension of Li powder (14 mg, 2.07 mmol) in THF (10 mL), under argon, was added a solution of $(Ph_2P)_2C{=}CH_2$ (410 mg, 1.034 mmol) in THF (5 mL). This mixture was ultrasonically treated for 1 h. Excess Li was removed by filtration, and the solvent was removed in vacuo. The resulting oily solid was washed with light petroleum ether (bp 40−60 °C, 2 × 10 mL) and then recrystallized from cold (−30 °C) toluene/THF (10:1 ratio) as orange plates. Isolated yield: 435 mg, 76.9%. ^1H NMR (500 MHz, $[D_8]$THF, 25 °C): δ 1.75 (m, 16H, THF), 1.91 (m, 4H, CH_2), 3.58 (m, 16H, THF), 6.80−7.14 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR (125.6 MHz, $[D_8]$THF, 25 °C): δ 25.5 (THF), 34.5 (CH_2), 67.3 (THF), 124.1, 127.8, 132.3 (Ph), 148.1 (*ipso*-Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $[D_8]$THF, 25 °C, 85% H_3PO_4, external): δ 17. Due to the air-sensitive nature of **2**, satisfactory C, H analysis could not be obtained.

(6) Crystal data for **2**: $C_{68}H_{76}Li_2O_4P_4$, M_r = 1095.1; triclinic, $P\bar{1}$, a = 11.314(2) Å, b = 12.268(3) Å, c = 12.857(3) Å, α = 114.754(4)°, β = 109.517(6)°, γ = 93.354(6)°, V = 1485.8(6) Å^3, Z = 1, T = 160 K, D_c = 1.224 g cm^{-3}, λ = 0.6875 Å (synchrotron radiation), μ = 0.18 mm^{-1}. Data were collected on a Bruker AXS SMART CCD diffractometer. Refinement on F^2 for all 3825 unique data (5024 measured, R_{int} = 0.055) gave R_w = 0.241 (on F^2); conventional R = 0.090 on F values of 3291 reflections with $F_o^2 > 2\sigma(F_o^2)$, difference map within ±0.55 e Å^{-3}. Programs were standard control software, SHELXTL (Bruker AXS Inc., Madison, WI, Version 5.1, 1998), and local programs.

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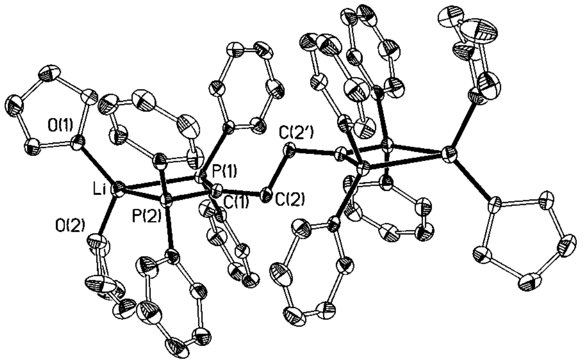

Figure 1. Molecular structure of **2** with 40% probability ellipsoids and with key atoms labeled (H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Li−P(1) = 2.542(6), Li−P(2) = 2.559(6), P(1)−C(1) = 1.739(3), P(2)−C(1) = 1.749(3), Li−O(1) = 1.894(7), Li−O(2) = 1.918(6), C(1)−C(2) = 1.535(4), C(2)−C(2′) = 1.527(6); P(1)−C(1)−P(2) = 107.92(17), P(1)−C(1)−C(2) = 127.3(2), P(2)−C(1)−C(2) = 124.7(2), P(1)−Li−P(2) = 67.14(14), C(1)−C(2)−C(2′) = 115.7(3).

distance is 3.147 Å. The binding mode at each end of the diide ligand is typical of diphosphinomethanide complexes, such as the lithium bis(phosphino)methanide $\{(Ph_2P)_2CH\}Li(tmeda)$.[7] The Li−P and P−C(1) bond lengths in **2** (average 2.551 and 1.744 Å, respectively) are close to the corresponding distances (2.582 and 1.722 Å) reported for $\{(Ph_2P)_2CH\}Li(tmeda)$.

Polyphosphines are of immense interest as ligands for the synthesis of polynuclear transition-metal complexes and other complexes with potential applications in catalysis. However, examples of nontripodal tetraphosphines are relatively rare, despite recent reports of their use in the preparation of bimetallic complexes which are effective in the catalytic hydroformylation of alkenes,[8] and synthetic routes to such ligands are often quite complicated.

In contrast, the novel tetraphosphine $\{(Ph_2P)_2CHCH_2\}_2$ (**3**) is obtained in high yield from the hydrolysis of **2**, providing a facile route to a potentially binucleating polyphosphine.[9] The ^1H and ^{13}C NMR spectra of **3** are as expected, with a large number of signals in the aromatic region due to the diastereotopic phenyl rings. The backbone proton NMR signals of **3** can be treated as part of a complex AA′MM′M″M‴XX′X″X‴ (A, M = ^1H, X = ^{31}P) spin system, which was partially analyzed with the aid of $^1H\{^{31}P\}$ and selective $^1H\{^1H\}$ decoupling experiments to yield the coupling constants given below.[9] The aromatic proton resonances clearly showed the diastereotopic nature of the phenyl groups arising from prochirality of the CH backbone carbons and had δ 7.03 (o-Ph_A), 7.15 (o-Ph_B), 7.14 (m-Ph_A), 7.11 (m-Ph_B), 7.19 (p-Ph_A), and 7.20 (p-Ph_B); the relative assignments of the A and B phenyl rings were obtained from a 2D proton COSY experiment. The diastereotopic nature of the phenyl rings is further revealed by their ^{13}C resonances, which were assigned by a 2D H/C correlation experiment. Owing to tight coupling of the geminally related ^{31}P nuclei, it was possible to determine only the sums of certain $^{31}P-^{13}C$ coupling constants.

The two ends of **3** resemble the important bis(phosphine) ligand bis(diphenylphosphino)methane. There are few examples of polyphosphines in which there is a similar arrangement of donor atoms: the tetraphosphine $(Ph_2P)_2CHCH(PPh_2)_2$ has been isolated as a low-yield product (10−15%) from the oxidation of $Li[HC(PPh_2)_2]$ by iodine,[10] while the complex $\{(CO)_4Mo\}_2\{\mu\text{-}(Ph_2P)_2C{=}CHCH{=}C(PPh_2)_2\}$ has been isolated in 16% yield from the photoinduced coupling of an η^2-bound bis(diphenylphosphino)acetylene ligand,[11] and the same ligand has been isolated as a byproduct of the synthesis of tris(diphenylphosphino)ethene.[12] An example of a tetraphosphinoallene has also been reported.[13]

The chemistry of **2**, **3**, and related compounds is currently under investigation.

Supporting Information Available: Tables giving details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles (6 pages). This information immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(9) To a solution of **2** (320 mg, 0.29 mmol) in diethyl ether (5 mL) was added oxygen-free water (5 mL). This mixture was stirred for 1 min. After standing for 5 min, colorless crystals of **3** were deposited in the organic layer. These were isolated by filtration and dried under vacuum. Yield: 179 mg, 80.7%. Anal. Calcd for $C_{52}H_{46}P_4$: C, 78.58; H, 5.83. Found: C, 78.38; H, 5.77. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.42 (m, $^3J(P,H) = 9.5$ Hz, 4H, CH_2), 2.63 (m, $^2J(P,H) = 6.3$ Hz, 2H, CH), 7.03−7.20 (40H, diastereotopic Ph). $^{13}C\{^1H\}$ NMR (125.6 MHz, $CDCl_3$, 25 °C): δ 31.5 (m, $J(P,C) = 10.0, 5.0$ Hz, CH_2), 33.6 (t, $J(P,C) = 28.7$ Hz, CH), 128−137 (diastereotopic Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4, external): δ −4.5 EIMS (70 eV): m/z (%) 794.2463 (0.4) [M^+; calcd for $C_{52}H_{46}P_4$ 794.2550], 793.2453 (0.1) [$M^+ - H$; calcd for $C_{52}H_{45}P_4$ 793.24718], 717 (2) [$M^+ - Ph$], 609 (100) [$M^+ - PPh_2$], 532 (70) [$M^+ - PPh_2 - Ph$], 423 (35) [$M^+ - (PPh_2)_2$], 347 (90) [$M^+ - (PPh_2)_2 - Ph$], 239 (55) [$M^+ - (PPh_2)_3$], 183 (65) [PPh_2], 108 (65) [PPh].

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