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ortho-Lithiated benzyl diorganophosphines $[o\text{-}(R_2PCH_2)C_6H_4Li(Et_2O)]$, R = Ph, Me. Synthesis, structural characterization, and reactions

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Abstract

(*o*-Lithiobenzyl)dimethylphosphine, $[o\text{-}(Me_2PCH_2)C_6H_4Li(Et_2O)]_2$ (**7**), is shown by crystal structure analysis to be dimeric, the two lithium atoms bridging the phenyl *ortho*-carbon atoms in a four-membered ring structure. A distorted tetrahedral coordination sphere at lithium is completed by coordination of one phosphino group and a molecule of diethylether (triclinic, space group $P\bar{1}$, $a = 10.986(3)$, $b = 11.160(3)$, $c = 12.368(4)$ Å, $\alpha = 86.04(2)$, $\beta = 89.51(2)$, $\gamma = 83.04(2)°$, $Z = 2$). $[o\text{-}(Me_2PCH_2)C_6H_4Li(Et_2O)]_2$ (**7**) cleanly reacts in donor solvents like diethylether to the thermodynamically more stable (α-lithiobenzyl)dimethylphosphine $[Me_2PCHLi(Et_2O)C_6H_5]_2$ (**9**) with the same overall composition. Crystal structure analysis of the latter shows each lithium atom to be now bonded in an η^2 fashion to the $C_{benzyl}\text{–}C_{ipso}$ bond of one anion, the diethylether molecule, and to the phosphino group of the second anion thereby resulting in a dimeric structure with a central six-membered ring (triclinic, space group $P\bar{1}$, $a = 8.482(3)$, $b = 9.388(3)$, $c = 9.482(3)$ Å, $\alpha = 95.42(2)$, $\beta = 91.36(2)$, $\gamma = 104.20(2)°$, $Z = 1$). (*o*-Lithiobenzyl)diphenylphosphine undergoes the same reaction to the corresponding α-lithiobenzylphosphine upon addition of strong donors like *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (tmeda). Upon addition of Cp_2TiCl_2, (*o*-lithiobenzyl)diphenylphosphine reacts to form 1,2-bis[*o*-(diphenylphosphino)phenyl]ethane, $[o\text{-}(Ph_2P)C_6H_4CH_2]_2$ (**10**), the formation of which is thought to proceed by oxidation of the anion $[o\text{-}(Ph_2PCH_2)C_6H_4]^-$ by Cp_2TiCl_2 to the radical which undergoes a 1,3 shift of the diphenylphosphino group from the sp^3 benzyl carbon atom to the sp^2 *ortho*-carbon atom of the phenyl ring to form the more stable benzyl radical. Dimerization of the latter ultimately leads to $[o\text{-}(Ph_2P)C_6H_4CH_2]_2$ (**10**) whose molecular structure was determined in the solid state (monoclinic, space group $P2_1/n$, $a = 12.217(2)$, $b = 8.382(1)$, $c = 15.004(2)$ Å, $\beta = 90.81(1)°$, $Z = 2$). The same reaction occurs upon oxidation of (*o*-lithiobenzyl)diphenylphosphine with ferricinium tetrafluoroborate, $[Cp_2Fe]^+BF_4^-$, thus corroborating the proposed reaction sequence with the transition metal species acting solely as oxidizing agents. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium organyls; Anionic benzyl phosphines; Crystal structure elucidation

1. Introduction

(*o*-Lithiobenzyl)diorganophosphines, $[o\text{-}(R_2PCH_2)\text{-}C_6H_4Li]$, R = Ph, Me, are valuable starting materials for the preparation of metal complexes of the potentially bidentate anionic *o*-(phosphinomethyl)phenyl ligands [1,2]. Their potential as transition metal ligands has already been explored to a large extent [3] but their main group metal complexes have only recently been investigated in more detail [1,2,4]. They are conveniently prepared by kinetically controlled bromine–

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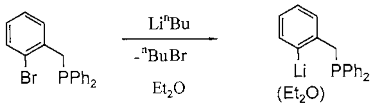
lithium exchange of the corresponding *o*-bromobenzyl compounds with lithium organyls at low temperatures (Eq. (1)) [1,2]. Solid [*o*-(Ph_2PCH_2)C_6H_4Li(Et_2O)] (**1**), prepared in diethylether was found to contain one molecule of Et_2O [1]. Its insolubility in etheral and other polar but aprotic solvents prevented any further characterization by spectroscopic means, as well as a determination of its molecular structure. In particular, it was not possible to assess the degree of aggregation of **1** in the solid state as well as the presence or absence of phosphine coordination to lithium [1]. In a similar way (*o*-lithiobenzyl)dimethylphosphine, [*o*-(Me_2PCH_2)-C_6H_4Li], can be prepared in pentane and was found to be only scarcely soluble in this solvent [2]. Likewise, the degree of association could not be determined nor could phosphine coordination to lithium be ascertained for this lithiated phosphine [2].



1

(1)

We now found that upon dissolution of [*o*-(Me_2PCH_2)C_6H_4Li] in Et_2O the dimeric monoetherate [*o*-(Me_2PCH_2)C_6H_4Li(Et_2O)]$_2$ is formed which contains a central four-membered ring and phosphine coordination to lithium, as could be ascertained by an X-ray structure analysis on crystals grown rapidly from solution. After prolonged standing of the etheral solution crystals of the same overall composition form but could be shown by structure determination to contain the dimeric α-lithiated species [$Me_2PCHLi(Et_2O)C_6H_5$]$_2$. A similar reaction is found for the diphenyl compound **1** upon addition of the strong donor *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) leading to the monomeric tmeda-containing species [Ph_2PCHLi-(tmeda)C_6H_5] (**2**). Furthermore, we also report a second completely different reaction of **1**, eventually leading to 1,2-bis[*o*-(diphenylphosphino)phenyl]ethane, [*o*-(Ph_2P)-$C_6H_4CH_2$]$_2$, which is observed when **1** is reacted with titanocene dichloride, Cp_2TiCl_2, or ferricinium tetrafluoroborate, $[Cp_2Fe]^+BF_4^-$.

2. Experimental

All experiments were performed under rigorous exclusion of atmospheric oxygen and moisture under an atmosphere of purified dry argon using standard Schlenk techniques. Solvents were dried under argon over sodium or sodium–potassium alloy and freshly distilled prior to use. Reagents and starting materials: Ph_2PCl (Chempur), PBr_3 (Aldrich), *o*-bromo-toluene (Merck, Acros), *o*-bromo-benzylbromide (Merck), Li^{n}Bu (2 and 2.5 M solution in pentane or hexane, Aldrich), Cp_2TiCl_2 (Aldrich), $[Cp_2Fe]^+BF_4^-$ (Aldrich). (*o*-Bromo-benzyl)diphenylphosphine, *o*-(Ph_2PCH_2)-C_6H_4Br, was prepared from Ph_2PCl and the Grignard reagent of *o*-bromo-benzylbromide [1]. (*o*-Bromo-benzyl)dimethylphosphine [2] was prepared by the photochemical reaction of PBr_3 and *o*-bromo-toluene and subsequent two fold P-methylation with MeMgBr, as described previously [5]. [*o*-(Ph_2PCH_2)C_6H_4Li(Et_2O)] (**1**) was prepared according to Abicht and Issleib from *o*-bromo-benzyldiphenylphosphine and Li^{n}Bu in diethylether [1]. Instruments: NMR spectra: JEOL JMN-GX-400. ^{1}H-NMR: internal C_6H_6 or external hexamethyldisilane, HMDS, as standard; ^{13}C-NMR: external tetramethylsilane, TMS; ^{31}P-NMR: external 85% H_3PO_4; ^{7}Li-NMR: external 1 M LiBr in D_2O. Chemical shifts are in ppm with negative signs referring to high field. ^{1}H and ^{13}C chemical shifts are reported relative to TMS while those of ^{31}P and ^{7}Li are reported relative to the standards mentioned above. FT-IR spectra: Mattson Polaris. The elemental analysis was performed by the microanalytical laboratory of the University of Konstanz on a Heraeus CHN-O-Rapid instrument. Melting points were determined in sealed capillaries in a Büchi 530 apparatus and are uncorrected.

2.1. Methylation of [*o*-(Ph_2PCH_2)C_6H_4Li(Et_2O)] (**1**)

To 1.5 g (4.2 mmol) of **1** suspended in 50 ml of Et_2O the twofold molar quantity of MeI was added at −10°C under stirring. Stirring was continued for 3 h whereupon the mixture was allowed to warm to room temperature (r.t.). The resulting white precipitate **3** was filtered off, washed twice with Et_2O and recrystallized from EtOH–Et_2O. Yield: 1.69 g (3.9 mmol, 92.8%). M.p. 218–221°C. ^{1}H-NMR ($CDCl_3$, RT): δ 4.65 (d, PCH_2, $^2J(PH) = 15.2$ Hz), 2.69 (d, PMe, $^2J(PH) = 13.4$ Hz), 1.79 (d, Me, $^5J(PH) < 1$ Hz).

2.2. Reaction of [*o*-(Ph_2PCH_2)C_6H_4Li] upon addition of tmeda

To 1.35 g (3.8 mmol) of *o*-(Ph_2PCH_2)C_6H_4Br dissolved in 40 ml of benzene the equimolar amount of a 2 M solution of Li^{n}Bu in hexane was added at r.t. In contrast to the synthesis of **1** in ether [1], under these conditions the ether-free *o*-lithiated compound is formed. Stirring was continued for 2 h at r.t. whereupon an equimolar amount of tmeda (0.6 ml) was added. After an additional 3 h of stirring at r.t., the twofold molar quantity of MeI (1.25 ml) was added and the stirring continued for 90 min. The resulting white suspension was filtered off, washed first with benzene and then with ether and recrystallized from CH_2Cl_2–Et_2O. The resulting mixture of salts **3** and **4** was characterized by ^{1}H-NMR. ^{1}H-NMR of **4** ($CDCl_3$, RT): δ 5.35 (m, CH), 1.83 (dd, CMe, $^3J(HH) = 7.2$ Hz,

^3J(PH) = 19.8 Hz). From the intensities of the respective ^{1}H-NMR signals of **3** and **4** the amount of **4** formed is estimated to be about 5–10%.

*2.3. Synthesis of [$Ph_2PCHLi(tmeda)C_6H_5$] (**2**)*

In a 100 ml round-bottom flask 3.25 g (9.2 mmol) of *o*-(Ph_2PCH_2)C_6H_4Br was dissolved in 40 ml of Et_2O. At r.t. 4.6 ml of a 2 M solution of Li^{n}Bu in hexane (9.2 mmol) was added dropwise. Stirring was continued for 2 h and the resulting precipitate was filtered off and washed twice with 20 ml of Et_2O and 10 ml of methyl ^{t}butyl ether (mtbe), respectively. Subsequently, 5 ml of tmeda (3.9 g, 33.5 mmol) in 15 ml of mtbe was added. A clear red solution formed which was concentrated in vacuo and cooled to − 35°C whereupon very small red crystals formed which were not suitable for X-ray structure analysis. They could be filtered off and stored under pentane. Further recrystallization experiments from mtbe resulted only in deep-red oils. According to the ^{1}H-NMR spectrum, the crystals formed under these conditions do not contain mtbe but 1 to 1.5 equivalents of tmeda per lithium atom. ^{1}H-NMR (C_6D_6, RT): δ 7.76–7.84 (m, *m*-H(phenyl)), 7.13–7.17 (m, *m*-H(benzyl), *p*-H(phenyl)), 7.03–7.08 (m, *o*-H(benzyl/phenyl)), 6.41 (t, *p*-H(benzyl), ^3J(HH) = 7.0 Hz)), 3.21 (d, CH, ^2J(PH) = 7.7 Hz), 1.95 (br. s., CH_2(tmeda)), 1.87 (br. s., Me(tmeda)). ^{13}C-NMR (C_6D_6, RT): δ 154.4 (d, C1(benzyl), ^2J(PC) = 23.2 Hz), 148.5 (d, C1(phenyl), ^1J(PC) = 13.4 Hz), 132.5 (d, C2(phenyl), ^2J(PC) = 18.3 Hz), 130.2 (s, C3(benzyl)), 126.5 (s, superposition with benzene signals possible), 118.1 (d, C2(benzyl), ^3J(PC) = 16.5 Hz), 112.0 (d, C4(benzyl), ^5J(PC) = 2.5 Hz), 57.3 (s, CH_2(tmeda)), 45.4 (s, Me(tmeda)), 44.4 (d, LiCH, ^1J(PC) = 10.5 Hz). ^{31}P-NMR (C_6D_6, RT): δ − 18.3 (s). ^{7}Li-NMR (C_6D_6, RT): δ 0.19 (s).

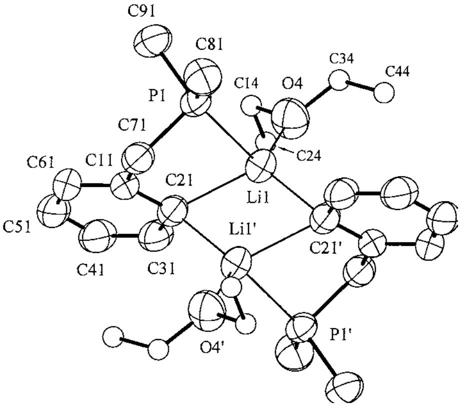


Fig. 1. Molecular structure of one of the two crystallographically independent dimers in the crystal structure of **7** and numbering scheme adopted. Primed atoms are related to those without a prime by a center of inversion. (ORTEP-III; displacement ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity; of the disordered ethyl carbon atoms only one alternative is shown with arbitrary radii).

Deuteration of **2**: To a small amount of **2** a drop of MeOD was added in an NMR tube. ^{1}H-NMR of $Ph_2PCHDC_6H_5$ (C_6D_6, RT): δ 7.34–7.41 (m, 4H), 7.03–7.20 (m, 11H), 3.2 (br. s., CHD, 1H).

*2.4. Synthesis of [o-(Me_2PCH_2)C_6H_4Li] (**6**) and [o-(Me_2PCH_2)$C_6H_4Li(Et_2O)$]$_2$ (**7**)*

In a 100 ml round-bottom flask 6.9 g (30 mmol) of *o*-(Me_2PCH_2)C_6H_4Br was dissolved in 75 ml of hexane. The solution was cooled to 0°C and 15 ml of a 2 M solution of Li^{n}Bu in hexane (30 mmol) was slowly added dropwise under stirring. A colorless to slightly yellow precipitate formed which was filtered off after 2 h, washed once with 8 ml of hexane and dried in vacuo. To the solid 25 ml of toluene was added and the resulting suspension was stirred for 20 min. Only very little substance dissolved and the precipitate was filtered again. Yield of the ether-free compound **6**: 3.9 g (24.9 mmol, 83%). 5–7 ml of ether was added to **6** prepared in this way and the resulting approximately saturated solution was stirred for 10 min. and filtered. Upon cooling to 4°C single crystals of the monoetherate **7** formed in the course of a few hours which proved to be suitable for X-ray diffraction. Rapid crystallization is essential as prolonged standing of solutions of **7** results in increased formation of the rearrangement product **9** (see Section 2.5). Yield: 1.5 g (3.2 mmol, 21.3%). Upon cooling of the etheral solution to − 30°C the yield may be increased up to 5.2 g (11.2 mmol, 74.6%). ^{1}H-NMR (C_6D_6, RT): δ 8.29 (br. s. H3), 7.23 (br. s., H5), 7.0–7.15 (m, H4,6), 3.13 (q, $CH_2(Et_2O)$, ^3J(HH) = 7.0 Hz), 2.89 (br. s., PCH_2), 0.95 (t, $CH_3(Et_2O)$, ^3J(HH) = 7.0 Hz), 0.92 (br. s., PCH_3). ^{13}C-NMR (C_6D_6, RT): δ 182.4 (s, C2), 151.8 (s, C1), 143.9 (s, C3), 126.1 (d, C6, ^3J(PC) = 3.7 Hz), 125.7 (s, C5), 123.5 (s, C4), 65.4 (s, $CH_2(Et_2O)$), 46.5 (s, PCH_2), 14.8 (s, $CH_3(Et_2O)$), 12.4 (d, PCH_3, ^1J(PC) = 6.2 Hz). ^{31}P-NMR (C_6D_6, RT): δ − 44.4 (s). ^{7}Li-NMR (C_6D_6, RT): δ 1.33 (s). The ^{1}H- and ^{13}C-NMR atom numbering follows the crystallographic numbering scheme. See Fig. 1 for details.

Deuteration of **7**: To a small amount of etheral solution of **7** MeOD was added. The solvent was removed in vacuo, and the precipitate was extracted with $CDCl_3$. ^{1}H-NMR of *o*-(Me_2PCH_2)C_6H_4D ($CDCl_3$, RT): δ 7.09–7.15 (m, Ph, 1H), 6.85–6.90 (m, Ph, 3H), 2.65 (s, CH_2), 0.91 (d, CH_3, ^2J(PH) = 2.9 Hz).

*2.5. Synthesis of [$Me_2PCHLi(Et_2O)C_6H_5$]$_2$ (**9**)*

An approximately saturated solution of **7** in Et_2O was prepared as described in Section 2.4. The solution was kept at r.t. for 1 week. After cooling to 4°C crystals of **9** formed which were suitable for X-ray structure determination. ^{1}H-NMR (C_6D_6, RT): δ 7.12 (dd, H3,5, ^3J(HH) = 7.1 Hz, ^3J(HH) = 7.1 Hz), 6.91 (d, H2,6,

^3J(HH) = 8.1 Hz), 6.50 (t, H4, ^3J(HH) = 7.1 Hz), 3.13 (q, $CH_2(Et_2O)$, ^3J(HH) = 7.0 Hz), 2.35 (d, PCH, ^2J(PH) = 5.1 Hz), 1.17 (s, PCH_3), 0.95 (t, $CH_3(Et_2O)$, ^3J(HH) = 7.0 Hz). ^{13}C-NMR (C_6D_6, RT): δ 152.9 (d, C1, ^2J(PC) = 7.5 Hz), 129.6 (s, C3), 119.5 (d, C2, ^3J(PC) = 16.2 Hz), 112.8 (s, C4), 66.1 (s, $CH_2(Et_2O)$), 43.4 (s, PCH), 16.9 (s, PCH_3), 14.9 (s, $CH_3(Et_2O)$). ^{13}C-NMR (C_6D_6, RT, ^{1}H coupled (DEPT)): δ 152.9 (weak s), 129.6 (m, C3, ^1J(CH) = 152 Hz), 119.5 (m, C2, ^1J(CH) = 151 Hz), 112.8 (dt, C4, ^1J(CH) = 160 Hz, ^3J(CH) = 8 Hz), 66.1 (t, $CH_2(Et_2O)$, ^1J(CH) = 142 Hz), 43.4 (d, PCH, ^1J(CH) = 139 Hz), 16.9 (q, PCH_3, ^1J(CH) = 122 Hz), 14.9 (q, $CH_3(Et_2O)$, ^1J(CH) = 126 Hz). ^{31}P-NMR (C_6D_6, RT): δ − 60.8 (s). ^{31}P-NMR (C_7D_8, 212 K): δ − 61.5 (br. s.). ^{7}Li-NMR (C_6D_6, RT): δ 0.59 (br. s.). ^{7}Li-NMR (C_7D_8, 212 K): δ 0.62 (br. s.).

Deuteration of **9**: To a small amount of **9** a drop of MeOD was added in an NMR tube. ^{1}H-NMR of $Me_2PCHDC_6H_5$ (C_6D_6, RT): δ 2.49 (br. s., CHD, 1H), all other peaks are identical with those in $Me_2PCH_2C_6H_5$; compare δ 2.51 (s, CH_2, 2H) for $Me_2PCH_2C_6H_5$ under identical conditions.

2.6. Reaction of [o-(Ph_2PCH_2)C_6H_4Li(Et_2O)] (1) to [o-(Ph_2P)$C_6H_4CH_2$]$_2$ (10)

2.6.1. Reaction of 1 with Cp_2TiCl_2

To 4.33 g (17.38 mmol) of Cp_2TiCl_2 dissolved in 200 ml of THF a suspension of 6.19 g (17.38 mmol) of **1** in 20 ml of Et_2O was added in small portions at − 30°C whereupon the color of the mixture changed from red to red–black. The mixture was allowed to warm to r.t. and stirring was continued for 2 days. The solvents were removed in vacuo and 50 ml of toluene was added to the remaining residue. The undissolved solid was filtered off. It contained substantial amounts of unreacted Cp_2TiCl_2. The filtrate was concentrated in vacuo and dissolved again in 20 ml of toluene under warming. Upon cooling **10** crystallized as clear colorless crystals, which were recrystallized from toluene. Yield: 2.01 g (3.65 mmol, 42.0% with respect to Li). M.p. 191°C. $C_{38}H_{32}P_2$. Elemental analysis (550.626): C observed 82.87, calculated 82.89; H observed 5.87, calculated 5.86. ^{1}H-NMR (C_6D_6, RT): δ 6.86–7.40 (m, Ph), 3.44 (s, CH_2). ^{13}C-NMR (C_6D_6, RT): δ 147.11 (d, J(PC) = 25.8 Hz), 137.84 (d, J(PC) = 11.9 Hz), 135.99 (d, J(PC) = 11.9 Hz), 134.36 (d, J(PC) = 20.4 Hz), 126.78–134.22 (m, Ph), 37.2 (d, CH_2, ^3J(PC) = 23.6 Hz). ^{31}P-NMR (C_6D_6, RT): δ − 15.06 (s). IR (KBr, cm^{-1}): 3056 s, 2998 s, 2940 sh, 2859 m, 1964 w, 1895 w, 1829 w, 1582 m, 1466 s, 1432 s, 1327 w, 1304 w, 1279 w, 1181 w, 1158 w, 1092 m, 1069 w, 1026 w, 999 w, 764 sh, 745 s, 695 s, 552 w, 486 s.

2.6.2. Reaction of 1 with $[Cp_2Fe]^+BF_4^-$

A solution (3.9 g, 11 mmol) of *o*-(Ph_2PCH_2)C_6H_4Br was dissolved in 50 ml of Et_2O. After cooling with ice, 4.8 ml (12 mmol) of a 2.5 M solution of Li^{n}Bu in hexane was added dropwise. After 2.5 h the resulting precipitate was filtered off and added to a suspension of 5.25 g (19.25 mmol) of $[Cp_2Fe]^+BF_4^-$ in 30 ml of Et_2O. The reaction mixture turned orange and warmed up noticeably. It was filtered after 3 days. The filtrate was hydrolyzed with water and extracted with Et_2O. After drying the etheral phase with Na_2SO_4, the solvent was removed in vacuo leaving 1.8 g of oily residue. ^{31}P-NMR (C_6D_6, RT): δ − 14.9 (s, **10**) and − 9.4 (s, $Ph_2PCH_2C_6H_5$). The intensity ratio of 100 (2P):43 (1P) indicated that 2/3 of the starting material **1** had reacted.

2.7. X-ray structure analyses

Suitable single crystals of **7** and **9** (from Et_2O) were mounted under argon on glass fibers in an inert oil drop at − 70°C. Single crystals of **10** (from toluene) were mounted in a sealed glass capillary. The crystals were examined directly on the four-circle diffractometer (Enraf–Nonius CAD4) with graphite-monochromated Mo–K$_\alpha$ radiation (λ = 0.71069 Å). The crystal systems indicated by a preliminary search and indexing procedures were checked for higher metrical symmetry by reduced-cell calculations (DELOS [6], LePage [7]). Exact cell dimensions were determined by refinement of the Bragg angles of 25 selected high-angle reflections from various parts of reciprocal space carefully centered on the diffractometer. Lp and linear decay corrections were applied. For **7** absorption was corrected empirically on the basis of ψ scans around the diffraction vectors of 6 reflections near χ = 90° which served to evaluate the transmission curves (T_{min}: 0.87, T_{max}: 1.00). For **9** and **10** no absorption correction was deemed necessary. All structures were solved by direct methods (SHELXS-86 [8]). Refinement was done with anisotropic displacement parameters for the non-H atoms. In **7** the severely disordered ether carbon atoms in both crystallographically independent molecules were refined in two alternative positions with an occupation ratio of 70:30 with isotropic displacement parameters and C–C and C–O bonds restrained to 1.54 and 1.45 Å, respectively. The hydrogen atoms in **7** could be found in difference Fourier syntheses with the exception of those at the ether molecules which were calculated at idealized geometrical positions. The methyl groups at phosphorus were refined as rigid groups while some of the phenyl H atoms were refined freely with isotropic displacement parameters. The ether hydrogen atoms were included as fixed-atom contributions into structure factor calculations. For **9** and **10** all hydrogen atoms were located. For **9** the hydrogen atoms at the anion were refined freely with individual isotropic displace-

Table 1
Crystal structure data for compounds **7**, **9**, and **10**

	7	**9**	**10**
Crystals	Yellow prisms	Yellow prisms	Colorless prisms
Crystal size (mm)	$0.15\times0.25\times0.3$	$0.2\times0.2\times0.25$	$0.15\times0.2\times0.3$
Formula	$C_{26}H_{44}Li_2O_2P_2$	$C_{26}H_{44}Li_2O_2P_2$	$C_{38}H_{32}P_2$
M_r (g mol^{-1})	464.43	464.43	550.58
T (K)	198(2)	198(2)	293(2)
Crystal sytem	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	10.986(3)	8.482(3)	12.217(2)
b (Å)	11.160(3)	9.388(3)	8.382(1)
c (Å)	12.368(4)	9.482(3)	15.004(2)
α (°)	86.04(2)	95.42(2)	90
β (°)	89.51(2)	91.36(2)	90.81(1)
γ (°)	83.04(2)	104.20(2)	90
V (Å^3)	1501.6(7)	727.8(4)	1536.3(4)
Z	2	1	2
D_{calc} (g cm^{-3})	1.027	1.060	1.190
μ (Mo–K$_\alpha$) (cm^{-1})	1.6	1.7	1.6
$F(000)$ (e)	504	252	580
Scan type	θ–2θ	θ–2θ	θ–2θ
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.646	0.649	0.649
hkl range	$+14, \pm14, \pm15$	$+8, -12$–$+11, \pm12$	$+15, +10, \pm19$
Reflections measured	7153	3167	3671
Independent reflections	6795	2941	3511
R_{int}	0.019	0.011	0.017
Reflections with $I>2\sigma(I)$	3875	2489	2646
Refined parameters	320	193	245
(shift/error)$_{max}$	0.03	0.00	0.00
$R(F)/wR(F^2)$ all data [a]	0.068/0.211	0.036/0.107	0.036/0.105
Goodness-of-fit on F^2	1.04	1.04	1.04
$\Delta\rho_{fin}$ (max./min.) (eÅ^{-3})	0.48/−0.40	0.23/−0.26	0.22/−0.22

[a] $w=1/[\sigma^2(F_o^2)+(X\cdot P)^2+Y\cdot P)$, $P=[\max(F_o^2 0)+2F_c^2]/3$ where for **7**: $X=0.0964$, $Y=0.7065$; for **9**: $X=0.0607$, $Y=0.151$; and for **10**: $X=0.0513$, $Y=0.3021$.

ment parameters, all others were kept constant. For **10** all hydrogen atoms were refined isotropically.

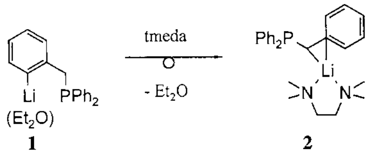
Scattering factors for neutral spherical atoms were those given by Cromer and Waber [9]; for the hydrogen atoms a bonded spherical atom model was used [10]. Corrections for $\Delta f'$ and $\Delta f''$ were applied to all atoms except hydrogen [11]. Refinement program: SHELXL-93 [12]. Other programs used included ORTEP-III [13] (structure drawings) and PLATON [14].

Crystal data and numbers pertinent to data collection and structure refinement are summarized in Table 1. Tables 2–4 contain the atomic coordinates. Important bond distances and angles are summarized in Tables 5–7. See also Section 5.

3. Results and discussion

3.1. 1,3-Proton shift of [o-(Ph_2PCH_2)$C_6H_4Li(Et_2O)$] (**1**) and synthesis of [$Ph_2PCHLi(tmeda)C_6H_5$] (**2**)

The *ortho*-lithiated benzyl phosphine [*o*-(Ph_2PCH_2)$C_6H_4Li(Et_2O)$] (**1**) is easily prepared according to Eq. (1) in diethylether [1]. It is virtually insoluble in polar aprotic solvents, which has prevented its further characterization as yet. In the solid state or as a suspension in diethylether **1** is stable as is shown by derivatization with methyl iodide which exclusively yields the *ortho*-methylated phosphonium iodide **3**. However, compound **1** rearranges upon addition of the strong donor tmeda to the thermodynamically more stable α-lithiated tmeda-containing compound [$Ph_2PCHLi(tmeda)C_6H_5$] (**2**) (Eq. (2)). The characterization of this reaction is based primarily on derivatization reactions. In particular, treatment of the reaction mixture with MeI after various periods of time yields the *o*-methylated phosphonium iodide **3** and the α-methylated one **4**, clearly resulting from methylation of educt **1** and reaction product **2**, respectively (Scheme 1). The salts **3** and **4** were characterized by ^{1}H-NMR. Longer reaction times and especially reaction in etheral solvents leads to an increase in the α-lithiated species formed. Thus, after addition of tmeda the reaction in benzene (under exclusion of ether) results in the formation of only 5–10% of **4** after 3 h, while the reaction to the α-lithiated species with tmeda in methyl ^{t}butyl ether (mtbe) as the solvent is essentially complete after this time (see Section 2). Under the latter conditions, the deuteration of the reaction mixture with MeOD allowed only the detection of the α-deuterated benzylphosphine $Ph_2PCHDC_6H_5$ by ^{1}H-NMR. A reaction similar to that in Eq. (2) has been described previously for (*ortho*-lithiophenyl)dimethylphosphine, [*o*-(Me_2P)-C_6H_4Li], which slowly forms the thermodynamically more stable methyllithio compound, the phosphinomethanide [$LiCH_2PMePh$] [15].



1 **2**

(2)

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters for **7** [a]

Atom	*x*/a	*y*/b	*z*/c	*U*(eq)
P1	0.53800(8)	0.39371(8)	0.73507(6)	0.0521(3)
O4	0.6683(3)	0.6621(3)	0.5950(2)	0.0852(11)
C11	0.3162(3)	0.5139(3)	0.6659(2)	0.0532(10)
C21	0.3671(3)	0.5742(3)	0.5755(2)	0.0566(10)
C31	0.3038(3)	0.6884(4)	0.5457(3)	0.0670(11)
C41	0.1997(4)	0.7396(4)	0.5980(3)	0.0794(16)
C51	0.1547(4)	0.6773(5)	0.6855(3)	0.0832(16)
C61	0.2125(3)	0.5648(4)	0.7202(3)	0.0697(13)
C71	0.3756(3)	0.3904(3)	0.7049(3)	0.0582(11)
C81	0.5864(4)	0.2349(3)	0.7784(3)	0.0758(16)
C91	0.5260(4)	0.4596(4)	0.8655(3)	0.0734(15)
C14 [b]	0.642(2)	0.7354(17)	0.6837(15)	0.138(7)
C14B [b]	0.6026(7)	0.7694(7)	0.6427(6)	0.103(2)
C24 [b]	0.599(2)	0.8579(19)	0.6282(19)	0.147(8)
C24B [b]	0.5865(9)	0.8712(9)	0.5595(8)	0.143(3)
C34 [b]	0.7994(14)	0.6092(18)	0.6164(15)	0.134(7)
C34B [b]	0.7951(8)	0.6606(8)	0.6083(7)	0.125(3)
C44 [b]	0.8590(15)	0.6779(14)	0.5195(12)	0.093(4)
C44B [b]	0.8677(9)	0.5754(9)	0.5493(8)	0.139(3)
Li1	0.5723(5)	0.5335(5)	0.5608(4)	0.0553(17)
P2	0.24701(8)	−0.05464(8)	−0.12718(8)	0.0595(3)
O5	−0.0342(3)	0.1352(2)	−0.2224(2)	0.0883(12)
C12	0.2153(3)	0.1251(3)	0.0188(2)	0.0555(10)
C22	0.0888(3)	0.1243(3)	0.0353(2)	0.0498(10)
C32	0.0265(4)	0.2376(3)	0.0572(3)	0.0618(12)
C42	0.0799(5)	0.3423(4)	0.0606(3)	0.0796(16)
C52	0.2023(5)	0.3401(4)	0.0395(4)	0.0913(19)
C62	0.2705(4)	0.2322(4)	0.0201(3)	0.0774(16)
C72	0.2929(3)	0.0080(4)	−0.0024(3)	0.0731(14)
C82	0.3444(4)	−0.2002(4)	−0.1212(4)	0.0912(18)
C92	0.3274(4)	0.0312(4)	−0.2301(4)	0.0909(17)
C15 [b]	0.0184(6)	0.2568(5)	−0.2285(5)	0.0800(15)
C15B [b]	−0.1092(14)	0.0992(14)	−0.3052(11)	0.090(4)
C25 [b]	−0.0848(8)	0.3506(8)	−0.2147(7)	0.122(3)
C25B [b]	−0.0459(13)	−0.0069(13)	−0.3506(11)	0.080(4)
C35 [b]	−0.0491(6)	0.1060(6)	−0.3293(5)	0.0936(18)
C35B [b]	−0.076(2)	0.2568(16)	−0.228(2)	0.164(9)
C45 [b]	−0.1091(7)	−0.0085(6)	−0.3219(6)	0.0976(19)
C45B [b]	0.039(2)	0.315(2)	−0.241(2)	0.179(10)
Li2	0.0110(5)	0.0236(5)	−0.0963(4)	0.0527(17)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Split model of disordered ethyl groups.

Table 3
Fractional atomic coordinates and equivalent isotropic displacement parameters for **9** [a]

Atom	*x*/a	*y*/b	*z*/c	*U*(eq)
P	0.33612(5)	0.31754(4)	0.57813(4)	0.0389(1)
O	0.80440(14)	0.69245(14)	0.80988(12)	0.0540(4)
C1	0.35821(18)	0.58045(15)	0.75810(14)	0.0347(4)
C2	0.3988(2)	0.66525(18)	0.89160(16)	0.0446(5)
C3	0.3638(2)	0.79969(19)	0.9226(2)	0.0536(6)
C4	0.2850(3)	0.85917(19)	0.8231(2)	0.0579(6)
C5	0.2418(3)	0.7802(2)	0.6925(2)	0.0556(7)
C6	0.2754(2)	0.64403(18)	0.65998(17)	0.0447(5)
C7	0.40848(19)	0.44591(15)	0.72738(15)	0.0379(5)
C8	0.1325(3)	0.2077(2)	0.6174(3)	0.0640(8)
C9	0.4507(3)	0.1796(2)	0.6023(2)	0.0582(7)
C10	0.8770(2)	0.5968(3)	0.8849(2)	0.0679(7)
C11	0.8618(3)	0.4568(3)	0.7947(2)	0.0719(8)
C12	0.8294(3)	0.8362(3)	0.8831(2)	0.0747(8)
C13	0.7749(3)	0.9350(2)	0.7895(3)	0.0815(8)
Li	0.6271(3)	0.6055(3)	0.6720(3)	0.0452(8)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Fractional atomic coordinates and equivalent isotropic displacement parameters for **10** [a]

Atom	*x*/a	*y*/b	*z*/c	*U*(eq)
P	0.76192(3)	0.18190(5)	0.01120(3)	0.0442(1)
C1	0.95931(12)	−0.0338(2)	−0.03451(10)	0.0429(5)
C11	0.77123(11)	−0.03257(18)	0.03731(10)	0.0408(4)
C12	0.86475(12)	−0.11586(18)	0.01010(9)	0.0406(4)
C13	0.87236(16)	−0.2782(2)	0.02848(12)	0.0537(6)
C14	0.79142(18)	−0.3577(2)	0.07265(13)	0.0625(7)
C15	0.69947(16)	−0.2767(2)	0.09985(13)	0.0604(6)
C16	0.68981(13)	−0.1150(2)	0.08238(12)	0.0516(5)
C111	0.69926(12)	0.17298(19)	−0.10049(10)	0.0450(5)
C112	0.61934(15)	0.0637(2)	−0.12547(11)	0.0540(6)
C113	0.57603(19)	0.0616(3)	−0.21092(13)	0.0661(7)
C114	0.6128(2)	0.1680(3)	−0.27307(14)	0.0760(9)
C115	0.6923(2)	0.2760(3)	−0.25025(16)	0.0846(9)
C116	0.73538(18)	0.2797(3)	−0.16453(15)	0.0665(7)
C121	0.65010(12)	0.25064(19)	0.08167(10)	0.0429(4)
C122	0.54826(13)	0.2986(2)	0.04983(11)	0.0493(5)
C123	0.47203(16)	0.3642(2)	0.10706(13)	0.0595(6)
C124	0.49659(17)	0.3828(3)	0.19587(13)	0.0641(7)
C125	0.59779(18)	0.3374(3)	0.22823(13)	0.0673(7)
C126	0.67381(16)	0.2724(2)	0.17191(12)	0.0586(6)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Isolation of **2** was only partly successful. Attempts to recrystallize **2** from mtbe mostly gave deep-red oils. In some cases, red crystals formed which were not suitable for crystal structure determination. In any case, a full set of NMR spectra of **2** could be obtained in benzene (see Section 2). They indicated the absence of ether (mtbe or Et_2O) while the content of tmeda varied between 1 and 1.5 per mole lithium. However, the spectra were not conclusive with regard to the exact structure of **2** (degree of aggregation; phosphine coordination to lithium). Thus the monomeric structure of **2**, as it is proposed by the formula in Eq. (2), is based only on circumstantial evidence. In simple benzyl lithium compounds [16] the lithium atom often adopts an η^2 bonding mode with respect to the alkyl and *ipso* carbon atoms of the benzyl moiety. Also the monomeric phosphino-substituted benzyl lithium compound $[Ph_2PCHLi(Et_2O)_2C_6H_5]$ (**5**), which is closely related to **2**, was shown to contain this type of lithium coordination, the remaining coordination sites at lithium being occupied by two molecules of diethyl ether [17]. No phosphine coordination to lithium is observed in **5**. Both of these structural aspects are discussed in more detail together with the structure of the α-lithiated P-dimethyl compound $[Me_2PCHLi(Et_2O)C_6H_5]_2$ (below). It should be mentioned at this point, that **5** was prepared directly by lithiation of the benzyl-substituted phosphine $Ph_2PCH_2C_6H_5$ in diethylether. Thereby the *ortho*-lithiated species **1** is not expected to form.

Clearly, these experiments do not allow a clear-cut conclusion with regard to the nature (structure, degree of association) of **1**. However, it is plausible to assume that the strong donor tmeda breaks up an oligomeric or polymeric structure, which may be responsible for the general unsolubility of **1**, thereby rendering it more soluble. An oligomerization of **1** may occur via lithium phosphorus bonds, but we do not have any direct evidence for that. In any case, the composition of **1** (one equivalent of ether per lithium organyl) indicates a coordinative unsaturateness of lithium (compare the composition of **5**) which might be compensated for by lithium phosphorus bonds.

Table 5
Selected bond distances (Å), angles (°), and dihedral angles (°) for both crystallographically independent molecules of **7** with estimated standard deviations in parentheses

Bond distances			
Li1–P1	2.624(5)	Li2–P2	2.667(6)
Li1–O4	1.952(6)	Li2–O5	1.956(6)
Li1–C21	2.253(6)	Li2–C22	2.270(6)
Li1–C21′	2.190(6)	Li2–C22′	2.179(6)
P1–C71	1.831(4)	P2–C72	1.836(4)
P1–C81	1.832(4)	P2–C82	1.831(5)
P1–C91	1.816(4)	P2–C92	1.826(5)
C11–C71	1.501(5)	C12–C72	1.509(5)
C11–C21	1.411(4)	C12–C22	1.404(5)
C21–C31	1.403(5)	C22–C32	1.405(5)
C31–C41	1.390(6)	C32–C42	1.373(6)
C41–C51	1.367(6)	C42–C52	1.365(8)
C51–C61	1.379(7)	C52–C62	1.374(6)
C61–C11	1.398(5)	C62–C12	1.405(6)
Bond angles			
C21–Li1–C21′	114.2(3)	C22–Li2–C22′	114.1(1)
C21–Li1–P1	80.8(2)	C22–Li2–P2	82.6(2)
C21′–Li1–P1	111.0(2)	C22′–Li2–P2	110.9(2)
C21–Li1–O4	116.4(3)	C22–Li2–O5	109.8(3)
C21′–Li1–O4	117.7(3)	C22′–Li2–O5	125.9(3)
P1–Li1–O4	110.6(2)	P2–Li2–O5	104.5(2)
Li1–P1–C71	93.2(2)	Li2–P2–C72	92.3(2)
Li1–P1–C81	134.8(2)	Li2–P2–C82	137.1(2)
Li1–P1–C91	118.9(2)	Li2–P2–C92	116.4(2)
C71–P1–C81	101.5(2)	C72–P2–C82	101.1(2)
C71–P1–C91	100.4(2)	C72–P2–C92	101.5(2)
C81–P1–C91	100.3(2)	C82–P2–C92	100.7(2)
Li1–C21–Li1′	65.8(2)	Li2–C22–Li2‘	65.9(2)
P1–C71–C11	110.7(2)	P2–C72–C12	112.0(2)
C11–C21–C31	113.8(3)	C12–C22–C32	113.8(3)
C21–C31–C41	124.4(3)	C22–C32–C42	125.0(4)
C31–C41–C51	119.2(4)	C32–C42–C52	119.3(4)
C41–C51–C61	119.7(4)	C42–C52–C62	119.3(4)
C51–C61–C11	120.3(3)	C52–C62–C12	120.9(4)
C61–C11–C21	122.4(3)	C62–C12–C22	121.6(3)
Dihedral angles			
C11–C61/Li1,C21,Li1′,C21′	84.6(2)	C12–C62/ Li2,C22,Li2′,C22′	78.2(2)
O4,Li1,P1/Li1,C21,Li1′,C21′	74.1(3)	O5,Li2,P2/ Li2,C22,Li2′,C22′	77.2(3)

Table 6
Selected bond distances (Å), angles (°), and dihedral angles (°) for **9** with estimated standard deviations in parentheses

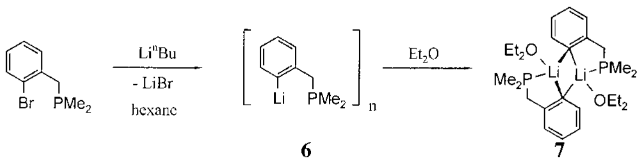
Bond distances			
Li–P′	2.548(3)	Li–O	1.934(3)
Li–C7	2.189(3)	Li–C1	2.405(3)
P–C7	1.762(2)	P–C8	1.848(3)
P–C9	1.827(2)	C1–C7	1.436(2)
C1–C2	1.417(2)	C2–C3	1.373(2)
C3–C4	1.379(3)	C4–C5	1.374(3)
C5–C6	1.385(3)	C6–C1	1.412(2)
C7–H7	0.90(2)		
Bond angles			
P′–Li–C7	121.9(1)	P′–Li–O	116.6(1)
C7–Li–O	121.6(2)	Li′–P–C7	120.8(1)
Li′–P–C8	117.0(1)	Li′–P–C9	108.8(1)
C7–P–C8	107.2(1)	C7–P–C9	101.1(1)
C8–P–C9	98.4(1)	Li–C7–P	108.6(1)
P–C7–C1	124.1(1)	P–C7–H7	117(1)
C1–C7–H7	112(1)		
Dihedral angles			
P′,Li,C7/C7,P,C7′,P′	149.2(2)	Li,C1,C7/C1,C7,P	74.1(2)
Li,C1,C7/C1–C6	87.1(1)	P,C7,C1/C1–C6	13.7(2)

Table 7
Selected bond distances (Å), angles (°), and dihedral angles (°) for **10** with estimated standard deviations in parentheses

Bond distances			
P–C11	1.843(2)	P–C111	1.834(2)
P–C121	1.832(2)	C1–C12	1.509(2)
C1–C1′	1.534(2)	C11–C12	1.405(2)
C11–C16	1.394(2)	C12–C13	1.391(2)
C13–C14	1.371(3)	C14–C15	1.379(3)
C15–C16	1.385(2)	C111–C112	1.387(2)
C111–C116	1.389(3)	C112–C113	1.380(3)
C113–C114	1.371(3)	C114–C115	1.368(3)
C115–C116	1.383(3)	C121–C122	1.386(2)
C121–C126	1.393(2)	C122–C123	1.389(3)
C123–C124	1.371(3)	C124–C125	1.376(3)
C125–C126	1.377(3)		
Bond angles			
C11–P–C111	100.26(7)	C11–P–C121	103.20(7)
C111–P–C121	103.60(7)	C12–C1–C1′	111.2(1)
P–C11–C12	118.1(1)	P–C11–C16	123.0(1)
C12–C11–C16	118.9(1)	C11–C12–C13	118.7(1)
C1–C12–C11	122.2(1)	C1–C12–C13	119.0(1)
Dihedral angles			
C111–P–C11–C12	87.4(1)	C121–P–C11–C12	−165.9(1)
C11–C16/C12, C1,C1′,C12′	87.8(1)	C111–C116/C121 –C126	73.4(1)

3.2. Synthesis and molecular structure of [*o*-(Me$_2$PCH$_2$)C$_6$H$_4$Li(Et$_2$O)]$_2$ (7)

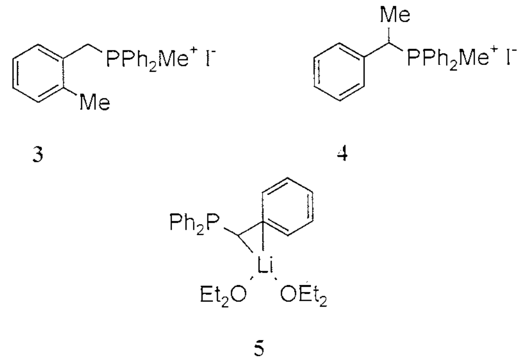
The dimethyl-substituted compound corresponding to **1**, [*o*-(Me$_2$PCH$_2$)C$_6$H$_4$Li] (**6**), may be conveniently prepared in unpolar solvents like pentane or hexane (Eq. (3)) [2]. Therefore, the lithium organyl **6** does not contain coordinated ether molecules. Its scarce solubility in unpolar solvents including aromates prevents the further characterization of **6**. Addition of diethyl ether to **6** affords the monoetherate **7** (Eq. (3)), which, unlike **1**, is sufficiently soluble not only in ether but also in benzene or toluene to allow for the recording of NMR spectra. Indicative with regard to the molecular structure of **7** should be the ^{31}P and ^{7}Li resonances. At room temperature they appear as singlets at δ (^{31}P) = −44.4 ppm and δ (^{7}Li) = 1.33 ppm, respectively. Upon cooling to −70°C, essentially no change is observed in the ^{31}P-NMR spectra. It should be noted that in simple lithium monophosphinomethanides, i.e. phosphines that are lithiated at the carbon atom in the α-position to the phosphino group, temperature-dependent equilibria between monomeric and dimeric species were found. In particular, [(tmeda)LiCH$_2$PMe$_2$]$_2$ [18,19], [(tmeda)LiCH$_2$PMePh]$_2$ [19], [(sparteine)LiCH$_2$-PMePh]$_2$ [19], and [(tmeda)LiCH$_2$PPh$_2$]$_2$ [19–21], which are dimeric in the solid (see below) were found by cryoscopy to be monomeric in benzene at 5°C and ca. 0.5 mol l^{-1} [19]. This was confirmed by the lack of ^{7}Li–^{31}P coupling in the respective NMR spectra at this temperature [19,20]. In contrast to **7**, in the above-mentioned lithium phosphinomethanides ^{7}Li–^{31}P coupling is present below −70°C which supports the presence of dimers with Li–P bonding [19]. While no indication for a dimer or oligomer formation of **7** could be found in solution, it is also dimeric in the solid state as could be shown by X-ray structure determination on single crystals grown rapidly from etheral solutions.



6 **7**

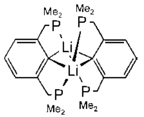
(3)

In the solid state **7** is dimeric, each unit cell in space group $P\bar{1}$ containing two crystallographically independent dimers with crystallographically imposed inversion



3 4 5

Scheme 1.



8

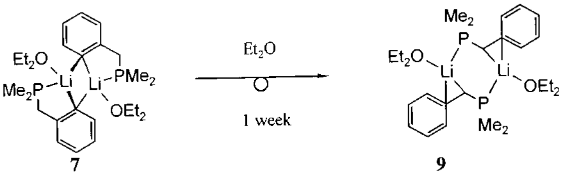
Scheme 2.

symmetry. They differ in small but significant details, which will be commented on below. Fig. 1 shows a view of the molecular structure of one of the dimers, Table 5 summarizes important bond distances and angles for both crystallographically independent molecules. Dimerization of **7** is brought about by double-bridging of the carbanionoid (metalated) carbon atoms of two different phenyl rings by two lithium atoms resulting in the formation of a Li,C,Li,C four-membered ring characteristic for this kind of dimeric metalated aromates. Metalation indeed occurred at the carbon atom *ortho* to the phosphinomethyl substituent. A distorted tetrahedral coordination geometry at each lithium atom is completed by one molecule of diethyl ether and one phosphine phosphorus atom, the latter resulting in the formation of two five-membered chelate rings (Fig. 1). It is particularly noteworthy that the overall composition of **7** is exactly identical to that of **1**, i.e. both lithium organyls contain exactly one molecule of ether per lithium atom. It is therefore tempting to speculate that **1** might have the same dimeric structure as **7** in the solid state, as well as phosphine coordination to lithium.

Some further aspects in the molecular structure of **7** deserve comment. From a structural (and chemical) point of view the organolithium compound [*o,o′*-$(Me_2PCH_2)_2C_6H_3Li]_2$ (**8**) (Scheme 2) [22] is probably most closely related to **7**, while the classic dimeric structure of phenyl lithium·tmeda, $[(tmeda)LiPh]_2$ [23], may serve for a comparison of the basic structural features [24]. In **7** the central Li,C,Li,C four-membered ring is exactly planar due to the crystallographically imposed inversion symmetry. Also, in **8** the central ring was found to be essentially planar within standard deviations [22]. However, in $[(tmeda)LiPh]_2$ a noticeably folded (146.6°) four-membered ring (with crystallographically imposed 2 (C_2) symmetry) was observed [23]. In all three structures the phenyl rings are not strictly perpendicular with respect to the central Li,C,Li,C ring (see Table 5 for the dihedral angles in **7**) [25]. Therefore, this cannot be entirely due to the Li–P bonds which in **7** and **8** serve as an additional link between the phenyl rings and lithium. As was already pointed out for **8**, we rather think that these differences from a strictly perpendicular arrangement are the result of packing forces [22]. Due to their known inherent weakness, the additional Li–P bonds in **7** and **8** should only play a minor role in determining the dihedral angles between the phenyl rings and the central Li,C,Li,C ring. Quite interestingly, both in **7** and **8** not only the dihedral angles between the phenyl rings and the central Li,C,Li,C rings but also the Li–P bond lengths are found to be significantly different between the crystallographically independent dimers occurring in both structures [22]. In **7** the Li–P bonds are 2.624(5) and 2.667(6) Å in the different dimers which is in the normal range for phosphines coordinated to lithium [26]. Quite interestingly, the phosphine coordination to lithium as part of five-membered chelate rings in **7** (Fig. 1) has two immediate effects on the molecular structure. The Li–C bonds which are part of the five-membered rings (Li1–C21 2.253(6), Li2–C22 2.270(6) Å) are consistently longer than the unbridged ones (Li1–C21′ 2.190(6), Li2–C22′ 2.179(6) Å). Furthermore, the five-membered ring formation is certainly responsible for deviations from perfectly tetrahedral geometries at phosphorus and lithium. In particular, the lone pair at phosphorus, assumed to be at the fourth empty tetrahedral site, does not point directly to lithium as may be inferred from the grossly different Li–P–C_{Me} angles (Table 5). At the lithium atom the dihedral angles between the planes P,Li,O and C,Li,C,Li (74.1(3)/77.2(3)°) deviate noticeably from a perpendicular arrangement typical for a perfect tetrahedron. All other bond lengths and angles in **7**, in particular the Li–C and Li–O bonds (Table 5), do not deviate from standard values in similar compounds. It should be mentioned, however, that the intraring angles in the phenyl rings are significantly smaller than the sp^2 standard at the metalated (*ortho*) carbon atoms C21/C22 in **7** (113.8(3)/113.8(3)°). This effect, which is attributed to the low electronegativity of lithium and subsequent rehybridization of the metalated carbon atom, has been discussed in detail elsewhere [27].

3.3. 1,3-Proton shift of [o-$(Me_2PCH_2)C_6H_4Li(Et_2O)]_2$ (7) and molecular structure of $[Me_2PCHLi(Et_2O)C_6H_5]_2$ (9)

Prolonged standing (7 to 10 days) of etheral solutions of the *ortho*-lithiated species **7** results in the formation of a different compound of the same overall composition (**9**; Eq. (4)). This process is best monitored by ^{31}P-NMR. The ^{31}P resonance of **7** at -44.4 ppm disappears and a new singlet at -60.8 ppm forms at the expense of the former. The other NMR spectra also undergo changes but these are less pronounced (see Section 2). Virtually no change is observed in the ^{7}Li spectra. For **7**, a broad singlet at 1.33 ppm is observed, while the ^{7}Li resonance of **9** is a broad singlet at 0.59 ppm. Unfortunately, the lack of discernable coupling in the ^{31}P- and ^{7}Li-NMR spectra of **9** again does not allow clues with regard to the bonding of these nuclei. Also at -60°C no ^{7}Li–^{31}P coupling is observed. This precludes any evidence from NMR data for monomer/dimer equilibria in solution at different temperatures. Only the pronounced high-field shift of the ^{31}P resonance on going from **7** to **9** points to a noticeably higher charge near this nucleus. Deuteration of **9** with MeOD yields $Me_2PCHDC_6H_5$ thus proving that the α-lithiated benzyl phosphine was formed in a clear-cut rearrangement reaction. The rearrangement is essentially complete after 7 days, and no by-product seems to be formed.



(4)

Unequivocal proof of the chemical composition and the structure of **9** comes from a structure determination which was obtained on single crystals grown from etheral solution kept at 4°C for 10 days (Fig. 2, Table 6). As Fig. 2 shows, **9** has exactly the same chemical composition as **7** (one molecule ether per lithium atom) but instead of the *ortho* position of the benzyl ring it is now the methylene (α) carbon at phosphorus which is deprotonated, i.e. **9** is the phosphinobenzylide $[Me_2PCHLi(Et_2O)C_6H_5]_2$. Furthermore, the structure determination shows that **9** is dimeric in the solid state. Thus, in etheral solution **7** slowly but cleanly reacts to the thermodynamically more stable α-lithiated species, as was already observed for the analogous P-diphenyl compound [*o*-$(Ph_2PCH_2)C_6H_4Li(Et_2O)$] (**1**). In contrast to **1**, the P-dimethyl compound **7** reacts already in ether, i.e. also in the absence of stronger donors as tmeda which were necessary to induce the 1,3 H shift in **1**, as was shown above. The reason for this is certainly the much better solubility of **7** in ether as compared to the virtual insolubility of **1** in this solvent. It should be noted at this point that experiments to synthesize **9** in analogy to **5** (vide supra) directly from dimethyl benzyl phosphine and ^{n}butyl lithium in diethyl ether or mtbe in the absence of tmeda were not satisfactory in our hands. The desired α-lithiated benzyl phosphine **9** was formed with maximum yields of about 35% but could not be isolated from the reaction mixtures due to product mixtures resulting from predominant cleavage of the phosphorus benzyl bonds leading to benzyl lithium, $PMe_2{}^{n}Bu$, and butane [28,29].

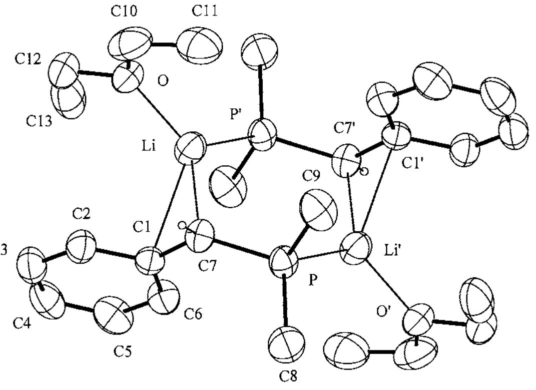


Fig. 2. Molecular structure of **9** in the crystal and atomic numbering scheme adopted. Primed atoms are related to those without a prime by a center of inversion. (ORTEP-III; displacement ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity except those at the benzylic C atoms which are drawn with arbitrary radius).

In the solid state the C_{benzyl}-C_{ipso} bond (C7–C1 in Fig. 2; d(C7–C1) = 1.436(2) Å) of the phosphinobenzylide anion in **9** is coordinated in an η^2 fashion to the lithium atom. As is usually found in benzyl lithium structures containing η^2-coordinated benzyl anions [16a,c,e,f], the bonds between lithium and C_{benzyl} and C_{ipso} are grossly different in length (2.189(3) and 2.405(3) Å, respectively), the shorter ones being formed to the benzylic carbon atom. Despite the different Li–C bond lengths, the lithium atom is placed fairly symmetrically above the benzylic system, as is evident from the dihedral angle between the planes Li,C7,C1 and the phenyl ring (atoms C1–C6) which is 87.1(1)°. The plane P,C7,C1 is slightly tilted with respect to the phenyl ring, however (dihedral angle 13.7(2)°). The carbanionoid benzylic carbon atom C7 is slightly pyramidalized as the sum of the angles (excluding the lithium atom) of 353.1° shows. Pyramidalization of the benzylic carbon atom in benzyl lithium compounds has been shown previously to depend strongly on the mode of coordination to lithium. The pyramidalization is largest when lithium is η^1-bonded only to C_{benzyl}, but less so when being η^2-bonded to C_{benzyl}-C_{ipso}, and virtually absent when the benzylic bond is coordinated by two lithium atoms from both sides, a situation where the benzylic carbon atom has an approximate trigonal bipyramidal environment [16].

In addition to the benzyl bond, each lithium atom is coordinated to the phosphino group of a second benzyl anion whereby the dimeric nature of **9** results. The lithium phosphorus bond (2.548(3) Å) is rather short for phosphine coordination to lithium [26]. One molecule of diethyl ether completes the coordination sphere of lithium. Dimeric **9** may be described as a six-membered ring structure if only the bond Li–C7 is considered part of the ring. The entire molecule has crystallographic inversion symmetry as the unit cell of **9** (space group $P\bar{1}$) contains two monomers. This implies that the P–C_{benzyl} bonds of the two benzyl anions are arranged in a strictly antiparallel (head-to-tail) fashion with respect to each other and form a strictly planar tetragon. The entire six-membered ring has a chair conformation, the angle of fold along the lines P′...C7 and C7′...P (i.e. the dihedral angle between the planes C7,Li,P′ and C7,P,C7′,P′) being 149.2(2)°.

A comparison of the molecular structure of **9** with those of other benzyl lithium compounds with heteroatom-substituted benzylic carbon atoms reveals interesting differences. A η^2 coordination of the benzylic C_{benzyl}–C_{ipso} bond by lithium is most often observed, but higher and lower hapticities have also been found. If we concentrate here first on benzyl anions with silicon [16d,19,30–32], phosphorus [17,33], and sulfur substitution [30,34] at C_{benzyl}, it is remarkable that in the fairly large number of structurally characterized silyl-substituted benzyl lithium compounds hapticities larger than η^1 are almost always observed, with the η^2 coordination of the C_{benzyl}–C_{ipso} bond to lithium as the most common feature. On the other hand, only two examples of α-lithiated benzyl sulfides have been structurally characterized to date [30,34]. In both of these cases a η^1 (C_{benzyl}) coordination of the ligand to the metal was observed. When comparing **9** with the analogous α-lithiated P-diphenyl compound $[Ph_2PCHLi(Et_2O)_2C_6H_5]$ (**5**) [17] as one of the few other α-lithiated benzylphosphines structurally characterized as yet, the similarities in the η^2 coordination of the benzyl bond to lithium and the differences in the phosphine coordination to lithium are immediately evident. With regard to the first, both in **5** and in **9** the C_{benzyl}–C_{ipso} bonds are complexed by lithium, the Li–C_{ipso} bonds being noticeably longer than Li–C_{benzyl} (d(Li–C_{benzyl}) = 2.170(8) and d(Li–C_{ipso}) = 2.493(8) Å in **5**). With regard to the latter, it was already mentioned above that **5** is monomeric and does not show phosphine coordination to lithium. As a consequence, in **5** two molecules of ether coordinate to lithium, whereas in **9** the additional phosphorus coordination to lithium allows only one ether molecule to be bonded. The reason for the monomeric nature of **5** certainly lies in the reduced donor capability of the diphenyl phosphino group in **5** as compared to the dimethyl-substituted phosphorus atom in **9**. Quite interestingly, however, in the lithium phosphinomethanides $[(tmeda)LiCH_2PMe_2]_2$ [18,19], $[(tmeda)LiCH_2PMePh]_2$ [19], $[(sparteine)LiCH_2PMePh]_2$ [19], and $[(tmeda)LiCH_2PPh_2]_2$ [19–21] mentioned above, which bear only hydrogen atoms in addition to the phosphino substituent at the lithiated α-carbon atom, the phosphino groups were always found to coordinate to lithium in the solid state, irrespectively of the other substituents at phosphorus (methyl vs. phenyl). They all have dimeric, six-membered ring structures, the dimerization being brought about by Li–CH_2 and Li–P bonds in a head-to-tail arrangement of the phosphinomethanides, quite similar to the situation in **9**. Thus the impossibility of a delocalization of the negative charge at the carbanionoid carbon in the phosphinomethanides, as compared to the benzylides **5** and **9**, results in an increased donor character of the phosphino group which overcompensates the known reduction in donor character as caused by phenyl substituents at phosphorus. Also $[(THF)LiCH_2PPh_2]_x$, (THF = tetrahydrofuran), which has recently been shown to form a polymeric structure in the solid, contains Li–P bonds [35]. A comparison of this compound with the closely related tmeda-containing lithium phosphinomethanides mentioned before, immediately makes clear that the additional donor molecules often exert a crucial influence especially on the aggregation, the overall connectivity pattern, and the conformation in lithium organyls. This is especially true for the hapticities of the lithium coordination, particularly good examples being, among others, the various lithium benzyls, which have been structurally characterized [16].

Despite these words of caution, a comparison of the solid-state structure of **9** with that of the analogous nitrogen compound $[Me_2NCHLi(Et_2O)C_6H_5]_2$ [36] should finally be done. In the latter, in stark contrast to **9**, the lithium atom bridges the (incompletely pyramidalized) anionic benzyl carbon atom and the nitrogen atom in an intramolecular η^2 fashion. A dimeric structure results again, but this is formed through an additional lithium contact to C_{benzyl} of a neighboring benzyl anion. Thus, the structure of $[Me_2NCHLi(Et_2O)C_6H_5]_2$ clearly reflects the superior donor capability of nitrogen over phosphorus to lithium. Similar results have been found for α-lithiated ethers [37].

3.4. *Reaction of [o-(Ph_2PCH_2)$C_6H_4Li(Et_2O)$] (**1**) to [o-(Ph_2P)$C_6H_4CH_2$]$_2$ (**10**)*

During attempts to synthesize early transition metal complexes of the *o*-(phosphinomethyl)phenyl ligand, we reacted Cp_2TiCl_2 with two equivalents of [*o*-(Ph_2PCH_2)$C_6H_4Li(Et_2O)$] (**1**) in tetrahydrofuran (Eq. (5), upper part). The reaction mixture immediately turned from red to black and after work-up, substantial amounts of unreacted Cp_2TiCl_2 could be recovered. Some 40% of **1** had reacted to form 1,2-bis[*o*-(diphenylphosphino)phenyl]ethane, [*o*-(Ph_2P)C_6H_4-CH_2]$_2$ (**10**). The large amounts of unreacted Cp_2TiCl_2 and the black by-products formed immediately suggested an oxidizing reaction of Cp_2TiCl_2 which thereby is reduced to lower-valent species not identified further. It is plausible that in a two-electron reduction $TiCp_2$ forms initially which then decomposes further but a reduction via Cp_2TiCl cannot be excluded. After the *o*-(diphenylphosphinomethyl)phenyl anion is oxidized to the corresponding radical, this rearranges in a 1,3 shift of the Ph_2P group from the sp^3 benzyl carbon atom to the sp^2 *ortho*-carbon atom of the phenyl ring whereby the more stable benzyl radical forms which then eventually dimerizes to **10** (Eq. (5)). 1,3 shifts of carbanions of the type shown in Eq. (6) have been observed previously especially for X = NR, O, S; M = Li, Na, with a variety of groups E undergoing the 1,3 shift [38]. For X = CR_2, M = Li a shift of a carbamoyl group is reported [39], while for X = CH_2 and M = MgX the groups $SiMe_3$ and $P(O)Ph_2$ were found to shift [40], the latter being probably the systems most closely related to ours.

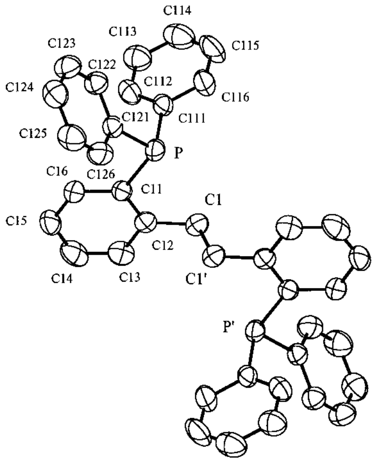
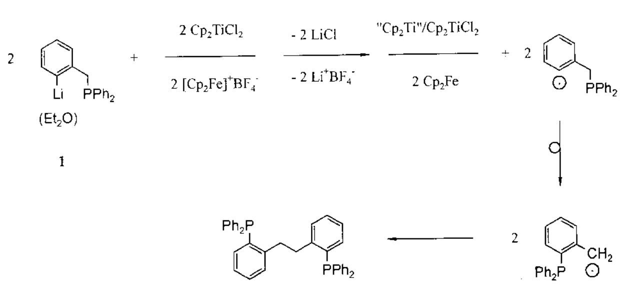
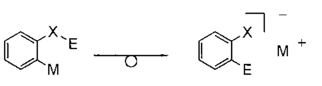


Fig. 3. Molecular structure of **10** in the crystal and atomic numbering scheme adopted. Primed atoms are related to those without a prime by a center of inversion. (ORTEP-III; displacement ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity).



(5)



(6)

Independent proof of the proposed oxidation/1,3 shift sequence comes from reaction of **1** with the ferricinium cation $[Cp_2Fe]^+BF_4^-$ (Eq. (5), lower part) which is known to be of approximately equal oxidizing power as Cp_2TiCl_2. Reaction of equimolar amounts of **1** and $[Cp_2Fe]^+BF_4^-$ and aqueous work-up led to the formation of **10** in about 70% yield while one third of **1** was recovered as benzyl diphenyl phosphine. Thus, any mechanism involving species with titanium carbon bonds can definitely be excluded [41].

3.5. Molecular structure of [o-(Ph$_2$P)C$_6$H$_4$CH$_2$]$_2$ (10)

Proof of the identity of **10** was obtained by a crystal structure determination (Fig. 3; Table 7). It crystallizes in space group $P2_1/n$ with two formula units in the unit cell. That means that **10** has crystallographically imposed inversion symmetry which implies that the conformation about the central ethane C–C bond is strictly *anti*-periplanar with regard to the phenyl substituents. It also implies that the phenyl rings at the ethane backbone are parallel with respect to each other and their phosphino substituents point away from each other. These phenyl rings are in a virtually perpendicular orientation with respect to the central C_{ipso}–C1–C1′–C'_{ipso} framework (Fig. 3) as is evident from the dihedral angle between the planes C11–C16 and C12,C1,C1′,C12′ which is 87.8(1)° (see also the torsion angles in Table 7). They do not bisect exactly the angle at phosphorus opened by its two phenyl rings (C111–P–C121) as the torsion angles C111–P–C11–C12 (87.4(1)°) and C121–P–C11–C12 (–165.9(1)°) show. The ethane C–C bond length (1.534(2) Å) is virtually unperturbed and also the bond angles at C1 (C12–C1–C1′ 111.2(1)°) do not show major deviations from the standard value.

4. Conclusions

In summary, we have shown that *ortho*-lithiated benzyl phosphines, formed by kinetically controlled bromine lithium exchange, react easily to the thermodynamically more stable α-lithiated species (metalation at the benzyl carbon atom) in polar solvents. This implies that some solvent-induced separation between the lithium cation and the anionic benzyl phosphine seems to favor the reaction, or, in other words, a simple 1,3-proton shift which includes reorientation of Li^+ is the energetically most favorable mechanism. A different, though conceptually related reaction, is observed when *o*-(diphenylphosphinomethyl)phenyl anions in the form of their lithium compounds are oxidized by Cp_2TiCl_2 or $[Cp_2Fe]^+BF_4^-$ to the respective radicals which leads to a 1,3 shift of the entire phosphino substituent at the benzyl carbon atom under formation of the more stable benzyl radical which subsequently dimerizes to 1,2-bis[*o*-(diphenylphosphino)phenyl]-ethane, [*o*-(Ph$_2$P)C$_6$H$_4$CH$_2$]$_2$.

The reported structure determinations of *ortho*- and α-lithiated benzyl phosphines allow a noticeably more detailed insight into the principles governing their molecular structures, especially with regard to phosphine coordination to lithium and degree of association. The rapid reaction from *ortho*- to α-lithiated benzyl phosphines in strong donor solvents explains why attempts to synthesize other *ortho*-metalated benzyl phosphines from the respective lithium precursors often resulted in inseparable product mixtures.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 148 385 (**7**), 148 384 (**9**), 148 383 (**10**). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union

Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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