

The isolation and X-ray crystal structure of $[\text{Li}(\text{Et}_2\text{O})_2(\text{CHPh})\text{PPh}_2]$

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Abstract

The organolithium complex $[\text{Li}(\text{Et}_2\text{O})_2(\text{CHPh})\text{PPh}_2]$ (**1**) has been prepared by lithiation of the corresponding phosphine with *n*-BuLi and recrystallized from Et_2O solution. The structure of **1** was confirmed by X-ray crystallography. Compound **1** crystallizes as a monomer with two molecules of Et_2O coordinated to the lithium metal. Crystal data (Mo $K\alpha$ radiation) at -90°C for **1**: $a = 10.350(1)$ Å, $b = 11.063(1)$ Å, $c = 12.528(1)$ Å, $\alpha = 79.19(1)^\circ$, $\beta = 66.84(1)^\circ$, $\gamma = 77.56(1)^\circ$, triclinic, space group $P\bar{1}$, $R = 0.087$ ($F > 4\sigma(F)$), $wR2 = 0.1611$.

Keywords: Crystal structure; Lithium; Phosphine

1. Introduction

During the last four decades the use of organolithium compounds has increased to the extent that they now play a central role in chemical synthesis [1]. In some respects, organolithium reagents have greater flexibility than the corresponding Grignard reagents since they exhibit higher reactivities and, in many instances, do not require the use of donor solvents for their preparation. The importance of organolithium reagents has led to a considerable interest in their solid state structures. Organolithium complexes of benzyl derivatives, for example, show a wide range of binding modes. Depending on the nature of the solvent and the presence or absence of base stabilization, lithyl compounds of this type have been crystallized as monomers, dimers or polymers [2]. Moreover, the character of the Li–C bonds in benzyl-lithium compounds ranges from partially covalent [3] to ionic [4] depending on the mode of coordination. Further structural diversity is evident from the observation that the lithium atom can adopt η^1 , η^2 or η^3 bonding modes with respect to the alkyl, *ortho* and *ipso* carbon atoms of the benzyl moiety [2b,5].

In this paper we report the synthesis, characterization and X-ray crystal structure of $[\text{Li}(\text{Et}_2\text{O})_2(\text{CHPh})\text{PPh}_2]$, (**1**).

2. Experimental details

All experiments were performed under anaerobic and anhydrous conditions using standard Schlenk techniques or a HE-493 Vacuum Atmospheres drybox. The Et_2O solvent was dried over sodium and distilled from sodium benzophenone ketyl under argon prior to use. $\text{PhCH}_2\text{PPh}_2$ (Aldrich) and *n*-BuLi (Aldrich) were used without purification. NMR spectra were recorded on a GE QE-300 spectrometer (^1H , 300.15 MHz; ^{13}C , 75.48 MHz; ^{31}P , 121.5 MHz). ^1H and ^{13}C NMR spectra are referenced to C_6D_6 which was dried over sodium-potassium alloy and distilled prior to use; ^1H and ^{13}C chemical shifts are reported relative to $\text{Si}(\text{CH}_3)_4$ (0.00 ppm). ^{31}P NMR spectra are referenced to 85% H_3PO_4 .

2.1. Synthesis of $[\text{Li}(\text{Et}_2\text{O})_2(\text{CHPh})\text{PPh}_2]$ (**1**)

n-BuLi (9.1 ml, 2.0 M in hexane solution, 18.2 mmol) was added to $\text{PhCH}_2\text{PPh}_2$ (5 g, 18.2 mmol) in Et_2O solution (75 ml) at 25°C . The reaction mixture assumed an orange color immediately. After being stirred for 4 h at 25°C , the reaction mixture was stored at -20°C . Well-defined single crystals, suitable for X-ray diffraction studies formed over a period of several days. ^1H NMR δ : 7.65 (t, 7.0 Hz, 5H), 7.09 (m, 10H), 3.04 (q, 6.9 Hz, 8H), 2.96 (s, 1H), 0.82 (t, 6.9 Hz, 12H). ^{13}C NMR δ : 152.3 (q), 143.3 (q); 132.7; 132.5; 129.3; 128.2; 127.2; 120.7; 120.5; 114.4; 65.5; 36.9; 14.7. ^{31}P NMR δ : -16.6 .

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2.2. X-ray structure determination of 1

The data collection for the structure determination was performed on a Nicolet P3 diffractometer at -90°C using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Accurate unit cell parameters for **1** were obtained by recentering 41 high angle reflections. Crystal data and the details of data collection and structure refinement are summarized in Table 1. Atomic coordinates and selected bond lengths and angles are presented in Tables 2 and 3 respectively. Throughout the data collection the intensities of four standard reflections were measured every 100 reflections as a check of crystal stability. Significant decay was not observed (decay $< 2.5\%$). A total of 6998 reflections were measured and 5864 reflections were used in the solution and refinement. The data set was corrected for Lorentz and polarization effects as well as for absorption. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with Siemens SHELXL software [6].

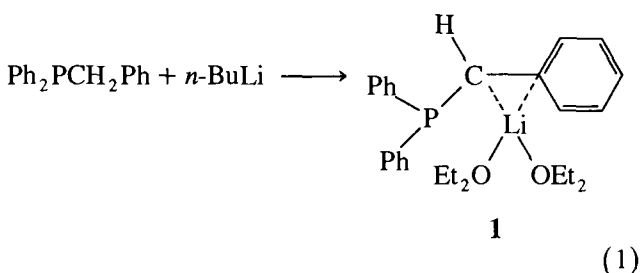
Table 1

Crystal data, data collection, and refinement of the structure of **1**

1	
Formula	$\text{C}_{27}\text{H}_{36}\text{LiO}_2\text{P}$
Formula weight	430.47
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm)	$0.34 \times 0.34 \times 0.15$
a (\AA)	10.350 (1)
b (\AA)	11.063 (2)
c (\AA)	12.528 (2)
α ($^\circ$)	79.19 (1)
β ($^\circ$)	66.84 (1)
γ ($^\circ$)	77.56 (1)
V (\AA^3)	1279.4 (3)
Z	2
d (calc.) (g cm^{-3})	1.117
μ (cm^{-1})	1.27
Scan range ($^\circ$)	4.34–55
Index ranges	$-13 \leq h \leq 2, -14 \leq k \leq 13, -16 \leq l \leq 15$
Refl. coll.	6998
Indep. refl.	5883
Param. refined	334
$R1/wR2, \%$	8.70/16.11

3. Results and discussion

The reaction of $n\text{-BuLi}$ with the benzyl-substituted phosphine $\text{PhCH}_2\text{PPh}_2$ in Et_2O solution at ambient temperature yielded the new lithium complex $[\text{Li}(\text{Et}_2\text{O})_2(\text{CHPh})\text{PPh}_2]$ (**1**) (Eq. (1)).



Upon cooling the reaction mixture to -20°C , yellow crystals of **1** suitable for X-ray crystal structure determination were obtained. Compound **1** crystallizes in the monoclinic space group $P\bar{1}$ with two molecules per unit cell and there are no unduly short interactions between individual molecules (Fig. 1). The lithium atom is bonded in an η^2 fashion to the alkyl carbon atom and the *ipso* ring carbon of the benzyl moiety. The $\text{Li}-\text{C}(7)$ and $\text{Li}-\text{C}(1)$ bond lengths of $2.170(8) \text{ \AA}$ and $2.493(8) \text{ \AA}$ respectively fall within the range which has been found for compounds that feature this type of bonding [2a,3]. There is no interaction between the lithium atom and the *ortho* ring carbons since these distances range from 3.125 \AA to 3.175 \AA for $\text{Li}-\text{C}(2)$ and $\text{Li}-\text{C}(6)$ respectively. The coordination sphere of the lithium metal is completed by two ether molecules and the bond distances for $\text{Li}-\text{O}(1)$ ($1.922(8) \text{ \AA}$) and $\text{Li}-\text{O}(2)$ ($1.894(7)$

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **1** (with ESDs in parentheses)

Atom	x	y	z	U_{eq}
P	1728 (1)	477 (1)	2792 (1)	54 (1)
Li	3802 (7)	-2069 (6)	3034 (6)	65 (2)
C (1)	1633 (4)	-1989 (3)	2596 (3)	47 (1)
C (2)	527 (4)	-2151 (4)	3692 (4)	57 (1)
C (3)	-77 (5)	-3221 (4)	4058 (4)	69 (1)
C (4)	340 (5)	-4170 (4)	3384 (4)	67 (1)
C (5)	1396 (5)	-4051 (4)	2309 (4)	62 (1)
C (6)	2018 (4)	-2985 (4)	1917 (4)	53 (1)
C (7)	2404 (4)	-943 (3)	2186 (4)	52 (1)
C (8)	898 (4)	1534 (3)	1825 (3)	48 (1)
C (9)	484 (5)	1075 (4)	1087 (4)	64 (1)
C (10)	-221 (5)	1845 (5)	406 (5)	78 (2)
C (11)	-539 (5)	3088 (4)	491 (5)	72 (1)
C (12)	-176 (5)	3571 (4)	1228 (4)	68 (1)
C (13)	545 (4)	2812 (4)	1895 (4)	57 (1)
C (14)	3332 (4)	1196 (3)	2386 (3)	51 (1)
C (15)	3232 (6)	2208 (6)	2925 (6)	111 (2)
C (16)	4408 (7)	2777 (6)	2683 (7)	137 (3)
C (17)	5695 (6)	2334 (5)	1903 (6)	88 (2)
C (18)	5809 (5)	1354 (5)	1361 (4)	67 (1)
C (19)	4647 (5)	799 (4)	1604 (4)	58 (1)
O (1)	3348 (3)	-2407 (3)	4693 (3)	76 (1)
C (20)	2803 (6)	-3523 (4)	5347 (4)	95 (2)
C (21)	3305 (5)	-4502 (4)	4542 (4)	78 (1)
C (22)	2511 (8)	-1298 (8)	5604 (7)	170 (4)
C (23)	3508 (9)	-737 (10)	5162 (7)	217 (5)
O (2)	5679 (3)	-2736 (3)	2113 (3)	77 (1)
C (24)	6910 (6)	-2943 (6)	2411 (6)	107 (2)
C (25)	7217 (8)	-1919 (7)	2654 (7)	181 (4)
C (26)	6040 (6)	-2829 (5)	893 (5)	106 (2)
C (27)	6147 (6)	-4105 (5)	677 (6)	130 (2)

Table 3
Selected bond lengths (Å) and angles (°) for **1**

P–C (7)	1.758 (4)	Li–O (2)	1.894 (7)
Li–O (1)	1.922 (8)	Li–C (7)	2.170 (8)
Li–C (1)	2.493 (8)	C (1)–C (2)	1.409 (5)
O (2)–Li–O (1)	114.7 (4)	O (2)–Li–C (7)	119.6 (4)
O (1)–Li–C (7)	125.6 (4)	O (2)–Li–C (1)	125.5 (4)
O (1)–Li–C (1)	109.6 (3)	C (7)–Li–C (1)	35.3 (2)
C (1)–C (7)–P	122.3 (3)	C (7)–C (7)–Li	84.6 (3)
P–C (7)–Li	108.5 (3)		

Å) fall within the range usually observed for solvent stabilized lithium complexes [3]. The fact that **1** is monomeric in the solid state is presumably a consequence of the steric crowding by the phenyl groups on the phosphine fragment. The similar, but less sterically encumbered phosphido compounds [Li(TMEDA)-(CH₂)PPh₂] and [Li(TMEDA)(CH₂)PPhMe] [2b] (TMEDA = Me₂NCH₂CH₂NMe₂) adopt dimeric solid state structures. The non-phosphorus-containing benzyl-lithium compounds such as [Li(Et₂O)₂(CH₂Ph)], [Li(THF)(TMEDA)(CH₂Ph)], and [Li(N₂C₆H₁₂)-(CH₂Ph)] [2a] are polymeric in the solid state. The isolation of monomeric benzyl-lithium compounds has so far been achieved by coordination of bulky bases to the lithium atom as in the case of [Li(sparteine)(CH₂)PPh₂] [2b] or by increasing the steric demand at the α carbon as in [Li(Et₂O)₂CPh₃] [3]. In the case of

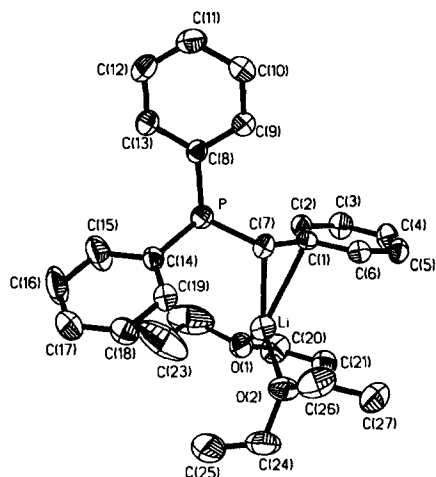


Fig. 1. View of and atom labeling for [Li(Et₂O)₂(CHPh)PPh₂] (**1**). Thermal ellipsoids are at the 30% probability level and hydrogen atoms are omitted for clarity.

1, the monomeric nature of the compound is due to the presence of phenyl substituents on both the α-carbon atom and the phosphorus atom. Finally, the cause of the η²-binding mode for the lithium stems from the replacement of a strong Lewis base by a solvent molecule. Thus, all TMEDA complexes feature η¹ attachment of lithium to the alkyl carbon atom while the Et₂O complexes are η² coordinated.

The elimination of TMEDA as a ligating base is very important for further use of the novel organolithium compound **1**, since one can envision salt elimination reactions with main group halides that are not complicated by the concomitant formation of LiX · TMEDA. The reactivity of the interesting bifunctional reagent **1** toward group 13 halides and organohalides is currently under investigation.

Acknowledgments

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