The structure of 2-(diphenylphosphino)phenyllithium: the significance of P–Li bonding

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Abstract

The solid state structure of 2-(diphenylphosphino)phenyllithium·Et$_2$O has been determined by a single crystal X-ray diffraction study. The crystal consists of dimeric aggregates in which the Li atoms are solvated by an additional diethyl ether molecule. The compound retains the dimeric structure in an apolar solvent (toluene) but in THF it exists in monomeric form. *Ab initio* calculations indicate a small but significant influence of P–Li interaction on the stability and structure of P-containing organolithium compounds.

Introduction

In the course of a study of aryllithium compounds with an α- or β-heteroatom [1] we became interested in the structure of 2-(diphenylphosphino)phenyllithium (**1**). Our interest was mainly forcused on the P–Li interaction since information on this subject is scarce. A search in the Cambridge Crystallographic Database [2] revealed a number of compounds exhibiting short P · · · Li distances but, with one exception, all of these compounds are either lithium-phosphides (LiPR$_2$) or lithium-phosphinomethanides (LiCH$_2$PR$_2$) in which the partly negatively charged phosphorus atoms obviously interact with lithium. The only compound in which a lithium atom interacts with a "neutral" phosphorus atom is a γ-P-functionalised lithium alkoxide (**2**) [3]. The lack of information on dative P · · · Li bonding is mainly due to the smallness of the energy involved in such interactions. Some relevant observations are:

(i) Experimental enthalpies for solvation of alkyllithium compounds by sulfides and phosphines are low compared with the enthalpies of solvation by the corresponding ethers and amines [4].

(ii) In 1978 Abicht and Issleib stated: "Auf Grund der größeren Polarisierbarkeit des Phosphors ist eine Stabilisierung der o-Lithiobenzyldiphenylphosphin (3) durch P-Koordination nicht zu diskutieren, während die Chelatisierung im Fall analoger Stickstoffverbindungen von entscheidender Bedeutung ist" [5].

These features encouraged us to study the structure of 2-(diphenyl-phosphino)phenyllithium (1) on an experimental as well as a theoretical level in order to assess the extent of P · · · Li interaction in this compound.

| 1 | 2 | 3 |
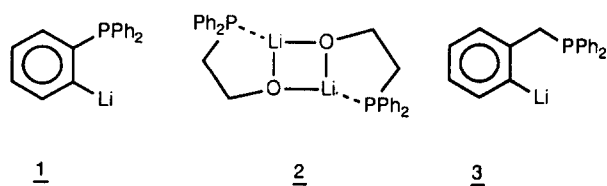
Results and discussion

The crystal structure of 2-(diphenylphosphino)phenyllithium · Et₂O

2-(Diphenylphosphino)phenyllithium was prepared by lithium-bromine exchange between BuLi and 1-bromo-2-(diphenylphosphino)benzene in diethyl ether [6]. The lithium compound crystallized as an etherate with a lithium/ether ratio of 1/1. The structure of this etherate was determined by single crystal X-ray diffraction, and is depicted in Fig. 1. Fractional coordinates with isotropic thermal parameters, selected bond distances/angles and the lithium coordination geometry are presented in Tables 1, 2, and 3, respectively.

The unit cell contains four independent, isostructural, centrosymmetric dimers. Each lithium atom is solvated by an ether ligand, and the O–Li bond distances are in the range 1.905(5)–1.947(6) Å (average 1.925(6) Å). The 2-(diphenyl-phosphino)phenyl anions are isostructural with triphenylphosphine as a neutral ligand (three nearly perpendicular phenyl rings) and bridge asymmetrically between

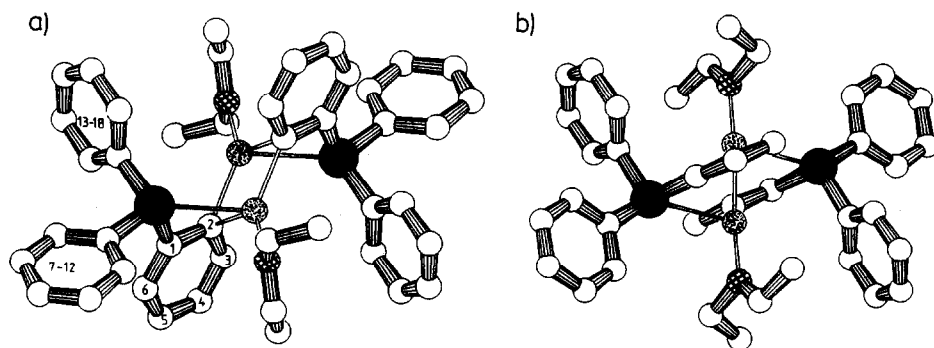Fig. 1. (a) The structure of [2-(diphenylphosphino)phenyllithium]₂·[Et₂O]₂. (b) View along the aryl-ring planes showing the asymmetric bridging. Lithium, phosphorus and oxygen atoms are indicated by speckled, black, and chequered spheres, respectively.

Table 1

Final coordinates and equivalent isotropic thermal parameters for 2-(diphenylphosphino)phenyllithium · Et$_2$O ^{a}

Atom	x	y	z	U_{eq}
P(1)	0.2674(1)	0.0270(1)	0.4367(1)	0.023(4)
C(11)	0.2881(3)	0.0451(2)	0.5369(2)	0.020(2)
C(12)	0.3940(3)	0.0177(2)	0.5645(2)	0.022(2)
C(13)	0.4140(2)	0.0333(2)	0.6420(2)	0.026(2)
C(14)	0.3389(3)	0.0721(2)	0.6867(2)	0.026(2)
C(15)	0.2391(3)	0.0985(2)	0.6564(2)	0.027(2)
C(16)	0.2119(3)	0.0842(2)	0.5803(2)	0.026(2)
C(17)	0.1375(4)	0.0754(2)	0.4157(2)	0.020(2)
C(18)	0.0169(3)	0.0444(2)	0.3975(2)	0.025(2)
C(19)	−0.0768(3)	0.0840(2)	0.3814(2)	0.029(2)
C(110)	−0.0516(2)	0.1563(2)	0.3842(2)	0.029(2)
C(111)	0.0673(3)	0.1880(2)	0.4026(2)	0.029(2)
C(112)	0.1607(3)	0.1480(2)	0.4181(2)	0.027(2)
C(113)	0.2034(3)	−0.0696(2)	0.3976(2)	0.026(2)
C(114)	0.1379(3)	−0.1064(2)	0.4331(2)	0.033(2)
C(115)	0.0893(3)	−0.1793(2)	0.3994(3)	0.044(2)
C(116)	0.1088(2)	−0.2162(2)	0.3295(2)	0.053(2)
C(117)	0.1748(3)	−0.1812(2)	0.2934(4)	0.048(2)
C(118)	0.2232(4)	−0.1085(2)	0.3278(2)	0.038(2)
Li(1)	0.5048(6)	0.0631(3)	0.4992(3)	0.031(2)
P(2)	0.8002(1)	0.07261(7)	0.06328(8)	0.0207(4)
C(21)	0.7710(3)	−0.0281(2)	0.0277(2)	0.018(2)
C(22)	0.8600(2)	−0.0610(2)	−0.0112(2)	0.023(2)
C(23)	0.8364(3)	−0.1389(2)	−0.0387(2)	0.027(2)
C(24)	0.7392(3)	−0.1786(2)	−0.0268(2)	0.029(2)
C(25)	0.6575(2)	−0.1430(2)	0.0130(2)	0.025(2)
C(26)	0.6723(3)	−0.0668(2)	0.0404(2)	0.023(2)
C(27)	0.6941(4)	0.0961(2)	0.1274(2)	0.022(2)
C(28)	0.5840(4)	0.1215(2)	0.1115(2)	0.020(2)
C(29)	0.5037(2)	0.1318(2)	0.1596(2)	0.023(2)
C(210)	0.5342(3)	0.1156(2)	0.2251(2)	0.028(2)
C(211)	0.6444(3)	0.0899(2)	0.2415(2)	0.027(2)
C(212)	0.7254(3)	0.0811(2)	0.1940(2)	0.026(2)
C(213)	0.7278(4)	0.1021(2)	−0.0138(2)	0.021(2)
C(214)	0.6611(3)	0.0538(2)	−0.0795(2)	0.028(2)
C(215)	0.6102(3)	0.0791(2)	−0.1358(2)	0.031(2)
C(216)	0.6223(3)	0.1534(2)	−0.1268(2)	0.031(2)
C(217)	0.6883(3)	0.2024(2)	−0.0619(2)	0.035(2)
C(218)	0.7416(3)	0.1767(2)	−0.0060(2)	0.028(2)
Li(2)	1.1080(7)	0.0152(4)	0.0653(4)	0.025(2)
P(3)	0.7882(1)	0.48533(7)	0.07060(8)	0.0221(4)
C(31)	0.7551(3)	0.4475(2)	−0.0303(2)	0.022(2)
C(32)	0.8520(3)	0.4645(2)	−0.0622(2)	0.033(2)
C(33)	0.8272(4)	0.4349(2)	−0.1404(2)	0.039(2)
C(34)	0.7216(4)	0.3919(2)	−0.1812(2)	0.038(2)
C(35)	0.6301(3)	0.3762(2)	−0.1460(2)	0.032(2)
C(36)	0.6465(3)	0.4048(2)	−0.0701(2)	0.029(2)
C(37)	0.6688(3)	0.4373(2)	0.0997(2)	0.022(2)
C(38)	0.6830(3)	0.3653(2)	0.0982(2)	0.028(2)
C(39)	0.5976(2)	0.3261(2)	0.1200(2)	0.034(2)
C(310)	0.5006(3)	0.3582(2)	0.1452(2)	0.035(2)

Table 1 (continued)

Atom	x	y	z	U_{eq}
C(311)	0.4854(3)	0.4296(2)	0.1467(2)	0.031(2)
C(312)	0.5694(3)	0.4692(2)	0.1240(2)	0.025(2)
C(313)	0.7426(3)	0.5785(2)	0.0911(2)	0.022(2)
C(314)	0.6824(3)	0.6055(2)	0.0382(2)	0.026(2)
C(315)	0.6511(2)	0.6765(2)	0.0569(2)	0.029(2)
C(316)	0.6824(3)	0.7225(2)	0.1293(2)	0.034(2)
C(317)	0.7430(4)	0.6963(2)	0.1825(2)	0.036(2)
C(318)	0.7753(3)	0.6252(2)	0.1643(2)	0.028(2)
Li(3)	0.9950(5)	0.4501(4)	0.0226(3)	0.035(2)
P(4)	0.1909(1)	0.40625(7)	0.45034(8)	0.0239(4)
C(41)	0.2119(3)	0.4995(2)	0.4448(2)	0.025(2)
C(42)	0.1283(3)	0.5454(2)	0.4775(2)	0.028(2)
C(43)	0.1370(3)	0.6151(2)	0.4675(2)	0.033(2)
C(44)	0.2153(4)	0.6361(2)	0.4273(2)	0.035(2)
C(45)	0.2952(3)	0.5893(2)	0.3976(2)	0.035(2)
C(46)	0.2940(3)	0.5203(2)	0.4063(2)	0.031(2)
C(47)	0.3060(2)	0.3603(2)	0.4012(2)	0.025(2)
C(48)	0.4290(3)	0.3700(2)	0.4313(2)	0.028(2)
C(49)	0.5132(3)	0.3395(2)	0.3900(2)	0.032(2)
C(410)	0.4742(3)	0.2983(2)	0.3166(2)	0.034(2)
C(411)	0.3527(3)	0.2864(2)	0.2853(2)	0.035(2)
C(412)	0.2679(3)	0.3169(2)	0.3271(2)	0.031(2)
C(413)	0.2613(3)	0.4157(2)	0.5454(2)	0.025(2)
C(414)	0.3433(3)	0.4740(2)	0.4909(2)	0.033(2)
C(415)	0.3991(2)	0.4746(2)	0.6610(2)	0.043(2)
C(416)	0.3722(3)	0.4168(2)	0.6858(4)	0.045(2)
C(417)	0.2877(3)	0.3578(2)	0.6404(2)	0.041(2)
C(418)	0.2324(2)	0.3578(2)	0.5715(2)	0.036(2)
Li(4)	−0.0305(5)	0.4604(3)	0.4366(3)	0.039(2)
O(5)	0.5108(2)	0.1652(2)	0.5080(2)	0.044(2)
C(51)	0.5199(4)	0.1744(2)	0.4359(2)	0.059(2)
C(52)	0.6466(3)	0.1889(2)	0.4306(2)	0.041(2)
C(53)	0.5051(3)	0.2291(3)	0.5616(3)	0.091(4)
C(54)	0.5083(3)	0.2206(2)	0.6348(4)	0.059(2)
O(6)	1.0589(3)	−0.0102(1)	0.1532(2)	0.030(1)
C(61)	1.0318(3)	−0.0854(2)	0.1496(2)	0.036(2)
C(62)	0.9327(3)	−0.0942(2)	0.1912(2)	0.040(2)
C(63)	1.1326(4)	0.0345(2)	0.2214(2)	0.046(2)
C(64)	1.1589(4)	0.1097(2)	0.2183(2)	0.050(2)
O(7)	1.0044(4)	0.3550(2)	0.0368(2)	0.046(2)
C(71)	1.0243(4)	0.2902(2)	−0.0179(2)	0.046(2)
C(72)	0.9767(3)	0.2935(2)	−0.0918(2)	0.052(2)
C(73)	1.0331(3)	0.3519(4)	0.1122(4)	0.075(2)
C(74)	1.1588(5)	0.3700(4)	0.1423(3)	0.083(2)
O(8)	−0.1140(2)	0.4191(2)	0.3341(2)	0.036(1)
C(81)	−0.1979(4)	0.3542(2)	0.3185(2)	0.051(2)
C(82)	−0.1581(3)	0.2861(2)	0.2692(4)	0.059(2)
C(83)	−0.1280(3)	0.4484(2)	0.2739(2)	0.042(2)
C(84)	−0.0348(2)	0.5122(2)	0.2908(2)	0.047(2)

[a] The first digit in the atom label is the molecule number and the second digit is the atom number which is given in Fig. 1a.

Table 2

Selected bond distances (Å) and angles (degrees) in 2-(diphenylphosphino)phenyllithium·Et$_2$O [a]

X	1	2	3	4
P(X)–C(X1)	1.838(6)	1.835(6)	1.831(6)	1.833(6)
P(X)–C(X7)	1.830(5)	1.839(5)	1.843(6)	1.839(6)
P(X)–C(X13)	1.828(4)	1.840(6)	1.834(6)	1.831(6)
C(X1)–C(X2)	1.417(5)	1.414(5)	1.407(5)	1.418(5)
C(X2)–C(X3)	1.416(5)	1.420(5)	1.420(5)	1.412(6)
C(X3)–C(X4)	1.392(5)	1.387(5)	1.375(6)	1.387(5)
C(X4)–C(X5)	1.373(4)	1.375(5)	1.392(6)	1.376(6)
C(X5)–C(X6)	1.393(5)	1.387(5)	1.381(5)	1.387(6)
C(X6)–C(X1)	1.390(5)	1.397(5)	1.393(4)	1.392(5)
C(X1)–P(X)–C(X7)	104.0(2)	102.0(2)	104.4(2)	102.7(2)
C(X1)–P(X)–C(X13)	103.9(2)	104.0(2)	104.8(2)	104.4(2)
C(X7)–P(X)–C(X13)	102.7(2)	102.2(2)	101.9(2)	100.1(2)
C(X1)–C(X2)–C(X3)	112.7(4)	112.5(4)	113.0(4)	113.1(4)
C(X2)–C(X3)–C(X4)	123.9(4)	123.9(4)	124.0(5)	123.9(4)
C(X3)–C(X4)–C(X5)	120.3(4)	120.5(5)	120.0(4)	120.1(5)
C(X4)–C(X5)–C(X6)	119.3(4)	119.3(4)	119.2(5)	119.4(5)
C(X5)–C(X6)–C(X1)	119.2(4)	119.1(4)	119.4(4)	119.5(4)
C(X6)–C(X1)–C(X2)	124.5(4)	124.7(4)	124.4(4)	123.9(5)

[a] The four crystallographic independent dimers are designated by the molecule number: X. The first digit of the atom label is the molecule number and the second digit represents the atom numbering which is given in Fig. 1a.

the lithium atoms, as can be seen clearly in Fig. 1b. One of the lithium atoms is almost coplanar with the aryl-plane, whereas the other lies out of this plane. The average angle between the C–Li bonds and the aryl-plane is 14.0(2)° for the nearly in-plane lithium atoms and 43.6(3)° for the out-of-plane lithium atoms, and so this dimeric structure can be regarded as a stack of two separate monomers. This may also be evident from a small difference between C–Li bond distances within a "monomeric unit" (varying from 2.158(6)–2.174(6) Å, average 2.168(6) Å) and C–Li

Table 3

The Li coordination geometry in 2-(diphenylphosphino)phenyllithium·Et$_2$O [a]

X	1	2	3	4
C(X2)–Li(X)	2.234(6)	2.234(6)	2.193(5)	2.210(6)
C(X2)′–Li(X)	2.174(6)	2.158(6)	2.169(6)	2.169(6)
P(X)–Li(X)	2.694(6)	2.738(5)	2.689(6)	2.752(6)
O(X + 4)–Li(X)	1.913(5)	1.905(5)	1.936(6)	1.947(6)
Li(X)–Li(X)′	2.425(7)	2.390(8)	2.336(7)	2.424(7)
C(X2)–Li(X)–C(X2)′	113.0(4)	114.5(3)	114.9(3)	112.8(3)
C(X2)–Li(X)–P(X)	65.8(2)	65.3(2)	66.4(2)	65.4(2)
C(X2)–Li(X)–O(X + 4)	119.9(4)	110.4(3)	120.2(4)	125.2(4)
P(X)–Li(X)–O(X + 4)	96.7(3)	109.1(2)	100.2(3)	108.3(3)

[a] The four crystallographic independent dimers are designated by the molecule number: X. The first digit of the atom label is the molecule number and the second digit represents the atom numbering which is given in Fig. 1a.
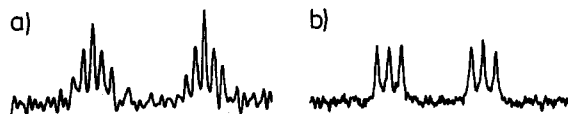
Fig. 2. The ^{13}C NMR signal for the lithiated carbon in (a) dimeric and (b) monomeric [^{6}Li]-2-(diphenyl-phosphino)phenyllithium.

bond distances between monomeric units (varying from 2.193(5)–2.234(6) Å, average 2.218(6) Å). This stacking is analogous to that of two dimers to give a tetramer observed in the structure of 2,6-dimethoxyphenyllithium [1c].

The most stable geometry for an aryllithium dimer is a structure in which the Li · · · Li vector is perpendicular on the plane of bridging aryl groups. However, the bridging aryl groups in the present structure make an average angle of 68.2(5)° with the C(*ipso*)–Li–C(*ipso*)′–Li′ plane. The twisting in the crystal structure may be a consequence of the creation of a favourable P · · · Li interaction, but repulsion between the participating moieties could also be responsible for the distortion of this crowded dimer. The P–Li distances in 2-(diphenylphosphino)phenyllithium (1) are in the range of 2.694(6) to 2.752(6) Å (average 2.718(6) Å) and are only slightly longer than the P–Li distances in 2 (average 2.651(6) Å). This is probably due to the rigidity of the anion and repulsive interactions between the bulky diphenylphosphino substituent and the ether ligand.

The structure of 2-(diphenylphosphino)phenyllithium in solution

The structure of 2-(diphenylphosphino)phenyllithium (1) in solution was studied by NMR spectroscopy. Crystals of the 96% ^{6}Li enriched etherate (1/1) were dissolved in toluene. At −20°C, the ^{13}C signal of the lithiated carbon atom is split into two quintets with integration ratios 1/2/3/2/1 and a ^{13}C–^{6}Li-coupling constant of 8.3 Hz (Fig. 2a), indicative of a dimeric organolithium species. The appearance of a pair of quintets is due to the additional ^{13}C–^{31}P-coupling of 99.9 Hz, which is extremely large; the magnitude of the comparable $^2J(^{13}C–^{31}P)$ coupling in triphenylphosphine is 19.7 Hz [7]; this anomaly will be discussed in a forthcoming publication. An upfield shift observed for the proton resonances of diethyl ether ($\delta = 2.87$ and 0.72 ppm) indicates Li–ether bonding. Thus, the dimeric solid state structure is maintained in solution under these conditions. The ^{6}Li and ^{31}P spectra in the temperature range −50 to +20°C each consists of a single sharp signal. The absence of P–Li-coupling suggests that P–Li bonding is of minor importance in the solution structure. Probably a fast exchange between P–Li coordination bonds within the dimeric species prevents observation of P–Li-coupling.

In ·THF at −65°C, the signal for the lithiated carbon atom is split into two triplets with a ^{13}C–^{6}Li-coupling constant of 14.0 Hz (indicative of a monomeric species) and a ^{13}C–^{31}P-coupling constant of 106.8 Hz (Fig. 2b). The ^{6}Li and ^{31}P spectra in the temperature range of −50 to +20°C each consists of a single sharp signal. Thus, in THF the dimer breaks down into a monomeric species in which P–Li interaction is negligible.

The P–Li interaction in β-P-aryllithium compounds

Short P–Li distances in the X-ray structure of 2-(diphenylphosphino)phenyl-lithium · etherate do not indicate the existence of a P–Li bonding interaction, since

Table 4

Calculated bond distances (Å) and angles (degrees) for molecules 4–13. The atom numbering is shown in eq. 1 and formula for compound 8

formula	4	5	6	7	8	9	10	11	12	13
X	N	P	N	P	–	–	N	N	P	P
C1–C2	1.396	1.406	1.461	1.416	1.412	1.409	1.401	1.390	1.413	1.418
C2–C3	1.388	1.391	1.392	1.395	1.387	1.386	1.388	1.384	1.386	1.386
C3–C4	1.380	1.377	1.385	1.379	1.384	1.383	1.383	1.387	1.382	1.380
C4–C5	1.391	1.392	1.388	1.395	–	–	1.462	1.484	1.882	1.877
C5–C6	1.382	1.379	1.386	1.378	2.141	2.122	2.138	2.133	2.197	2.339
C6–C1	1.406	1.410	1.427	1.434	1.813	1.806	1.810	1.864	1.795	1.777
C–X	1.500	1.876	1.483	1.882	2.328	2.271	2.249	2.445	2.288	2.319
C–Li	1.985	2.015	–	–	–	–	–	–	–	–
H–Li	1.963	2.620	–	–	–	–	–	–	–	–
Li···Li	–	–	–	–	–	–	3.250	2.062	3.463	2.517
X–Li	–	–	–	–	–	–	–	–	–	–
X–H	1.010	1.418	1.009	1.444	–	–	1.006	1.009	1.426	1.417
C2–C1–C6	114.7	115.0	111.7	111.7	115.0	114.5	116.4	116.2	115.6	113.5
C1–C2–C3	124.5	123.4	124.1	124.6	122.7	123.1	122.1	122.8	122.2	123.3
C2–C3–C4	118.6	119.4	121.1	120.3	119.9	119.9	119.7	119.0	120.2	120.5
C3–C4–C5	119.5	119.4	118.0	118.4	119.7	119.4	119.9	120.2	119.6	118.8
C4–C5–C6	120.5	120.5	119.8	120.3	–	–	117.8	115.1	117.1	117.5
C5–C6–C1	122.2	122.3	125.3	124.6	–	–	–	87.3	–	78.0
C1–C2–X	115.3	114.6	119.4	116.5	–	–	113.4	112.7	100.3	103.3
C2–X–Li	83.1	71.2	–	–	–	–	–	–	–	–
C2–X–H	112.0	104.6	112.1	110.1	–	–	–	–	–	–
Li–C1–Li'	–	–	–	–	65.9	64.7	63.5	70.0	62.8	59.4
Li–H–Li'	–	–	–	–	79.9	77.9	76.8	82.0	79.2	81.5
C2–C1–Li	84.9	102.0	–	–	–	–	–	–	–	–
Symmetry	C_s	C_s	C_s	C_s	C_{2v}	C_{2v}	C_{2v}	C_{2v}	C_{2v}	C_{2v}
Energy (SV 3-21G)	–290.95960	–575.78135	–283.44336	–568.30652	–244.213321	–244.20408	–353.65395	–353.71344	–923.33861	–923.35238

these atoms are expected anyway to be close in such a rigid molecule. Likewise, NMR evidence does not give a conclusive answer: the absence of a ^{6}Li–^{31}P-coupling in the dimeric as well as in the monomeric species suggests fast intramolecular exchange of P–Li coordination bonds (for the dimer) or negligible P–Li interaction. Thus we decided to carry out an *ab initio* study on the system, including comparison with the results of such a study on the nitrogen analogue, for which intramolecular N–Li coordination is definitely established.
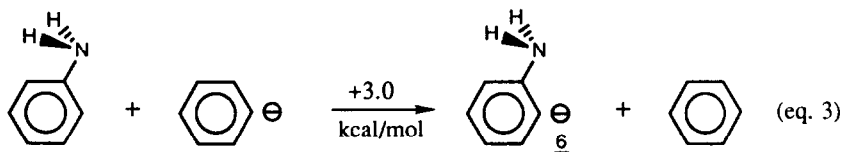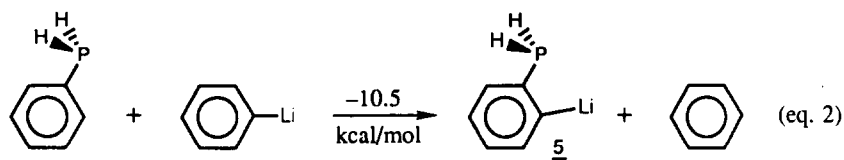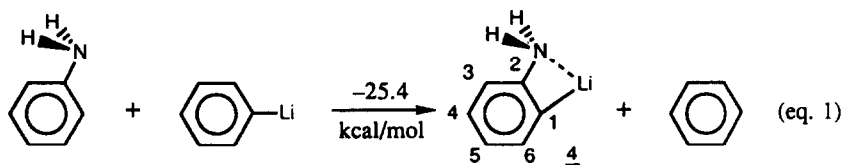
The structures of 2-aminophenyllithium and 2-phosphinophenyllithium were optimized at a SV 3-21G level with C_s-symmetry restriction (geometry information in Tab. 4). The Li atom in 2-aminophenyllithium (4) is bridging the negatively charged C(*ipso*) atom and the NH$_2$-substituent. Extreme bending of Li towards the NH$_2$-substituent can be prohibited only by trisolvation of Li by water molecules [1e]. The Li atom in 2-phosphinophenyllithium (5) is only slightly bent towards the PH$_2$-substituent, indicating little P–Li interaction.

4   5
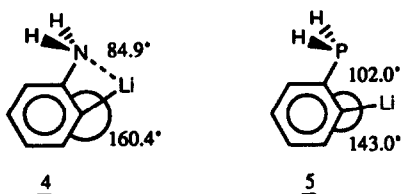
The relative stability of β-heteroatom-substituted aryllithium compounds was evaluated by consideration of some isodesmic reactions. Equations 1 and 2 show that *ortho*-lithiation of aminobenzene and phosphinobenzene by phenyllithium is exothermic by 25.4 and 10.5 kcal/mol, respectively. The stabilizing influence of the *ortho*-substituent is due to Li $\cdots$ heteroatom interactions and/or electronic effects (i.e. the effect of the substituent on the negative charge in the aryl σ-system). In this respect, calculations on the deprotonated anionic species (6 and 7) are worthwhile since only the influence of electronic effects are operative in such models. Equations 3 and 4 reveal a slight destabilizing influence of the *ortho*-NH$_2$ substituent and a considerable stabilizing influence of the *ortho*-PH$_2$ substituent on the anionic species. Therefore, the P–Li interaction in 2-phosphinophenyllithium is only partially responsible for stabilization of the lithium compound, whereas N–Li coordination in 2-aminophenyllithium is the main stabilizing factor. Similar results have been obtained for the comparable set of *ortho*-OH and *ortho*-SH substituted species [1e].

The Li $\cdots$ heteroatom interaction was also studied for a dimeric model, a mixed aggregate of the di-*ortho*-substituted aryllithium species and lithium hydride. The Li atoms in such a model are involved in three-center-two-electron bonding and are better positioned for efficient interaction with the β-heteroatoms. Two different conformers were studied at an SV 3-21G level (geometry information in Tab. 4). A conformation with both lithium atoms in the aryl plane (C_{2v}), in which the Li-heteroatom distance is short, and a conformation with the Li $\cdots$ Li vector perpendicular to the aryl plane in which Li $\cdots$ heteroatom interactions are virtually ruled out. The energy differences between the two conformers of the phenyllithium–LiH dimer have been calculated for a reference. This mixed dimer prefers a perpendicular conformation (8), which is 5.8 kcal/mol lower in energy than the planar conformer (9). However, for 2,6-diaminophenyllithium–LiH the planar con-

$$\xrightarrow{\begin{array}{c}-25.4\\ \text{kcal/mol}\end{array}} \quad \underline{4} \quad (\text{eq. 1})$$

$$\xrightarrow{\begin{array}{c}-10.5\\ \text{kcal/mol}\end{array}} \quad \underline{5} \quad (\text{eq. 2})$$

$$\xrightarrow{\begin{array}{c}+3.0\\ \text{kcal/mol}\end{array}} \quad \underline{6} \quad (\text{eq. 3})$$

$$\xrightarrow{\begin{array}{c}-8.0\\ \text{kcal/mol}\end{array}} \quad \underline{7} \quad (\text{eq. 4})$$

$$\underline{8} \xrightarrow{+5.8 \text{ kcal/mol}} \underline{9}$$

$$\underline{10} \xrightarrow{-37.3 \text{ kcal/mol}} \underline{11}$$

$$\underline{12} \xrightarrow{-8.6 \text{ kcal/mol}} \underline{13}$$
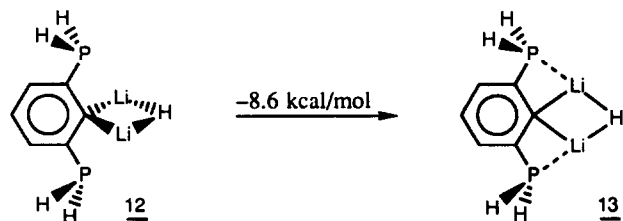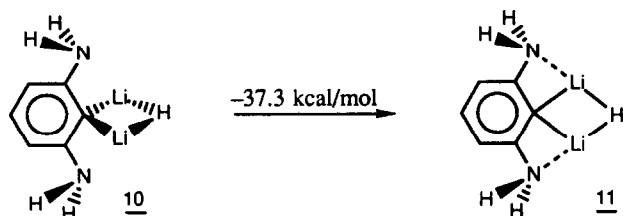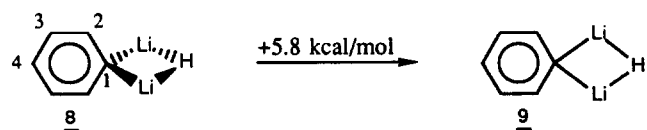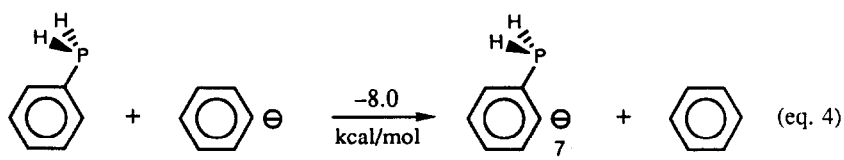
formation (11) is calculated to be 37.3 kcal/mol more stable than the perpendicular conformation (10). The large energy difference between the two conformations is contributed to efficient intramolecular N–Li coordination in the planar species. The energy difference of 8.6 kcal/mol between the two conformations of 2,6-diphosphinophenyllithium–LiH (12 and 13) is much smaller, but still indicates a significant stabilizing effect of the intramolecular P–Li interaction. Both substituted aryllithium dimers were also optimized with C_2 symmetry restriction. The aminosubstituted dimer tends to be planar (C_{2v}) but diphosphinophenyllithium–LiH prefers a conformation in which both Li atoms are positioned slightly out of the aryl plane. The angle between the CLi_2H-plane and the aryl plane is 31.3°, and both phosphino substituents are rotated about the C–P axis in order to direct the phosphorus lone pair towards the Li atoms.

Calculations on the monomeric model compounds indicate that the P–Li bonding interaction is negligible compared with N–Li interaction. However, the intramolecular P–Li interaction in dimeric organolithium compounds may influence the structure and stability of P-containing lithium compounds to a significant extent.

Experimental

General conditions. All experiments involving organolithium compounds were carried out under nitrogen by Schlenk techniques. Solvens were freshly distilled from sodium/benzophenone prior to use.

1-Bromo-2-(diphenylphosphino)benzene

A solution of ^{n}BuLi (1.6 M in hexane, 37 ml, 59.2 mmol) was added slowly (1 ml/min) to a well-stirred solution of dibromobenzene (15 g, 63.6 mmol) in 250 ml of Et_2O/THF (1/1) at −115/−110°C. The mixture was subsequently stirred at the same temperature for 40 min, during which a white precipitate gradually separated. Chlorodiphenylphosphine (10.8 ml; 60.0 mmol) was slowly added at a −110/−105°C and the resulting white suspension stirred for 15 min. The mixture was then allowed to warm to 20°C and 200 ml of saturated aqueous NH_4Cl was added. The layers were separated and the aqeuous layer extracted twice with Et_2O. The combined organic layers were dried ($MgSO_4$) and the solvent evaporated, to leave a yellowish oil which slowly solidified. Recrystallization from dry ethanol afforded large white crystals (14.5 g, 67%). The crystals were crushed and kept under vacuum (0.05 mmHg) for several hours in order to remove traces of ethanol.

^{1}H NMR (CDCl$_3$): δ 6.87–6.95 (m, 1H); 7.21–7.26 (m, 2H); 7.41 and 7.44 (two sharp signals, 10H); 7.64–7.71 (m, 1H). ^{13}C NMR (CDCl$_3$): 127.9; 129.2 ($J = 7.0$ Hz); 129.5; 130.4 ($J = 30.8$ Hz); 130.6; 133.4 ($J = 2.3$ Hz); 134.4 ($J = 20.2$ Hz); 134.9 ($J = 0.6$ Hz); 136.3 ($J = 10.8$ Hz); 139.4 ($J = 12.0$ Hz).

2-(Diphenylphosphino)phenyllithium

A solution of ^{n}BuLi (1.6 M in hexane, 1.0 ml, 1.6 mmol) was added to one equivalent of 1-bromo-2-(diphenylphosphino)benzene (0.54 g, 1.6 mmol) in 5 ml of diethyl ether at room temperature [6]. After 10 min the crystalline product was isolated, washed twice with diethyl ether, and dried *in vacuo*. Yield: 0.42 g, 78%.

^{1}H NMR (THF-d_8, 20°C): δ 7.85 (d, $J = 6.8$, 1H); 7.12–7.30 (m, 10H); 6.61–6.64 (m, 3H); 3.36 (q, $J = 7.0$, 4H); 1.10 (t, $J = 7.0$, 6H). ^{13}C NMR (THF-d_8,

−65°C): numbering as in Fig. 1a, C1 148.9 (17.0 Hz), C2 209.6 (106.8 Hz), C3 141.5 (36.7 Hz), C4 122.4 (< 1 Hz), C5 123.6 (< 1 Hz), C6 129.3 (6.7 Hz), phenyl groups 127.3 (< 1 Hz), 128.2 (5.2 Hz), 134.4 (17.6 Hz), 144.3 (20.7 Hz). ^{13}C NMR (toluene-d_8, −20°C): numbering as in Fig. 1a, C1 150.3 (16.1 Hz), C2 200.0 (99.9 Hz), C3 (143.3 (31.1 Hz), C4 125.7 (< 1 Hz), C5 126.1 (< 1 Hz), C6 130.0 (7.8 Hz), phenyl groups 128.7 (< 1 Hz), 129.2 (< 10 Hz), 134.2 (17.7 Hz), 121.2 (20.3 Hz).

A THF solution of 2-(diphenylphosphino)phenyllithium slowly decomposes and turns blood-red at −20°C. Decomposition is much slower when the lithium compound is dissolved in toluene or benzene, but is accelerated by the addition of highly polar cosolvents such as HMPT. The NMR spectra reveal several modes of decomposition processes of the lithium compound, but it is not clear what reactions are involved.

X-Ray diffraction study of [2-(diphenylphosphino)phenyllithium] · Et_2O

Good quality crystals were obtained by carrying out the synthesis described above with a dilute solution of 1-bromo-2-(diphenylphosphino)benzene in diethyl ether. A rod-shaped crystal (0.8 × 0.3 × 0.2 mm), mounted under nitrogen in a Lindemann glass capillary, was used for data collection on an Enraf–Nonius CAD4 diffractometer with Zr-filtered Mo-K_α radiation (λ-0.71073 Å). Cell parameters were derived from the least-squares fitting of the setting angles of 18 reflections with 6.3 < θ < 11.4°. Crystal data: triclinic; cell parameters: a = 11.226(1), b = 19.225(1), c = 19.397(1) Å, α = 107.80(1), β = 99.58(1), γ = 93.26(1)°; V = 3904(1) Å^3; space group $P\bar{1}$; ($C_{18}H_{14}PLi)_2(C_4H_{10}O)_2$; Z = 4; D_{calcd} = 1.110 g/cm^3. The intensity data of 12140 unique reflections were collected at −170°C within one half of the reflection sphere with θ to 25.4° (0 ⩽ h ⩽ 13, −23 ⩽ k ⩽ 23 and −15 ⩽ l ⩽ 15). Three reference reflections were measured every 50 reflections and showed no significant variation. After correction for Lorentz-polarization effects 6917 reflections survived for which l ⩾ 2.5σ(I).

The space group was assumed to be $P\bar{1}$ and this was confirmed by the successful refinement. The structure was solved by direct methods and subsequent Fourier analysis. The hydrogen atoms were introduced in calculated positions with C–H = 1.00 Å. All hydrogen atoms were refined riding on their carrier atoms. One overall isotropic thermal parameter was refined for the hydrogen atoms of each molecule. The blocked full-matrix least-squares refinement on F converged to $R(F)$ = 0.068, $R(wF)$ = 0.066 with w = 1/σ^2(F). The average and max, shift/error ratios in the final cycles are 0.008 and 0.014. Final residual electron density: −0.25 < ρ < 0.20 e/Å^3.

The scattering factors were taken from Cromer and Mann [8]. Calculations were performed with SHELX-76 (refinement) [9], SHELX-86 (direct methods) [10] and EUCLID (illustrations and molecular geometry) [11] on a MicroVAX computer. Tables of hydrogen atom coordinates, thermal parameters, and structure factors, and a complete list of bond lengths and angles are available from the authors.

NMR-measurements

Spectra were recorded on a Bruker AC200 (^{1}H frequency: 200 MHz) and a Bruker WP300 spectrometer (^{1}H frequency: 300 MHz). Deuterated solvents were dried over sodium sand and stored under nitrogen. Chemical shifts for ^{13}C and ^{1}H spectra are given in ppm relative to TMS. Solvent signals were used to reference ^{13}C

spectra internally: chloroform-d_1 ($\delta = 77.0$ ppm); toluene-d_8 (CD_3, $\delta = 20.4$ ppm); THF-d_8 (β-CD_2, $\delta = 25.2$ ppm). Samples of organolithium compounds used for the NMR studies were enriched with 96% ^{6}Li in order to simplify splitting of the ^{13}C signal of the lithiated carbon by C–Li coupling.

Ab initio *calculation*

These were carried out with the program GAMESS [12]. All geometries corresponding to stationary points on the potential energy surface were located by spin-restricted Hartree–Fock (RHF) calculations by use of the SV 3-21G basis set. Average and maximum gradients of 0.0005 and 0.00075, respectively, were taken as the convergence criteria.

Acknowledgements

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