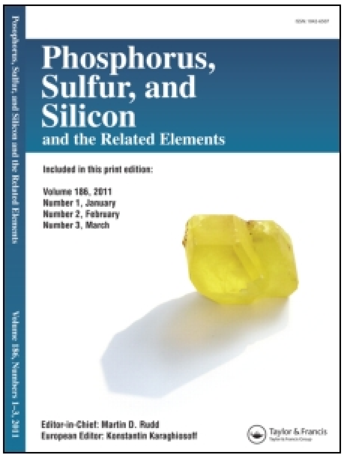

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Frenzel, Christoph and Hey-hawkins, Evamarie(1998) 'BENZOPHENONE OXIDATION OF PRIMARY LITHIUM PHOSPHANIDES TO CYCLOOLIGOPHOSPHANES WITH FORMATION OF LITHIUM DIPHENYLMETHANOLATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 143: 1, 1 — 17

To link to this Article: DOI: 10.1080/10426509808045480

URL: http://dx.doi.org/10.1080/10426509808045480

Phosphorus, Sulfur and Silicon, 1998, Vol. 143, pp. 1-17
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BENZOPHENONE OXIDATION OF PRIMARY LITHIUM PHOSPHANIDES TO CYCLOOLIGOPHOSPHANES WITH FORMATION OF LITHIUM DIPHENYLMETHANOLATE

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(Received 25 May, 1998; Revised 13 July, 1998)

The lithium phosphanides LiPHR (R = Ph, 2,4,6-$Me_3C_6H_2$ (Mes)) are oxidised by benzophenone in THF at room temperature to give the cyclooligophosphanes $(PPh)_n$ (n = 4, 5, 6) and $(PMes)_n$ (n = 3 (**1**), 4 (**2**)). Compounds **1** and **2** have been characterised by X-ray structure determination. In the solid state, the P_4 ring in **2** is puckered (torsion angle P-P-P-P 41.04(3)°). The reduction product, $LiOCHPh_2$ (**3**), was characterised by IR and NMR spectroscopy (^1H, ^{13}C, ^7Li) and X-ray structure determination. $LiOCHPh_2$ is hexameric in the solid state and forms a slightly distorted hexagonal prism composed of alternating Li and O atoms.

Keywords: Lithium phosphanides; cyclooligophosphanes; lithium diphenylmethanolate; crystal structure

INTRODUCTION

P-functionalised zirconocene monophosphanido complexes $[Cp_2Zr\{P(SiMe_3)_2\}(X)]$ (X = Cl, Me) and $[Cp°_2ZrCl(PHCy)]$ (Cp° = C_5Me_4Et, Cy = cyclohexyl) undergo insertion of polar multiply bonded systems into the Zr-P bond[1-4] to form novel P-functionalised phosphino ligands that are not accessible from the corresponding lithium phosphanides.[1c,5,6] It was recently shown that aldehydes and ketones readily react with the *in situ* generated zirconocene monophosphanido complex $[Cp_2ZrMe$

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[*] corresponding author.

{PH(2,4,6-$Bu^t{}_3C_6H_2$)}] to give the zirconocene phosphinoalcoholate insertion products in reasonable yield.[7] We now report the reaction of the lithium phosphanides LiPHR (R = Ph, 2,4,6-$Me_3C_6H_2$ (Mes)) with benzophenone, which yields cyclooligophosphanes as the oxidation product and lithium diphenylmethanolate as the reduction product.

RESULTS AND DISCUSSION

Reaction of LiPHPh and LiPHMes with benzophenone

The lithium phosphanides LiPHR (R = Ph, 2,4,6-$Me_3C_6H_2$ (Mes)) react with benzophenone in THF at room temperature according to eq. 1 to form cyclooligophosphanes and lithium diphenylmethanolate. A different course of reaction was observed in toluene, but no reaction products were characterised. No reaction was observed between LiPH(2,4,6-$Bu^t{}_3C_6H_2$) and Ph_2CO, PhMeCO or cyclohexanone in toluene.[7]

$$\mathrm{LiPHR + Ph_2C{=}O \xrightarrow{THF} 1/n\,(PR)_n + 1/6\,[LiOCHPh_2]_6} \qquad (1)$$

R = Ph, n = 4 - 6
R = 2,4,6-$Me_3C_6H_2$ (Mes), n = 3 (**1**), 4 (**2**)

In contrast, the reaction of alkali metal phosphanides derived from secondary phosphines $MPPh_2$ (M = Li, Na, K) with aldehydes or ketones $R^1R^2C{=}O$ gave the intermediate $MOCR^1R^2PPh_2$, which was not isolated. Workup by oxidative hydrolysis yielded the stable α-hydroxy-tert-phosphine oxides, $HOCR^1R^2P(O)\,Ph_2$.[8,9] For the reaction of $MPPh_2$ (M = Li, Na, K) with benzophenone, it was shown by absorption spectroscopy that in ether solvents the intermediate $MOCPh_2PPh_2$ is in equilibrium with the ketyl (ketyl equilibrium) $Ph_2P\cdots M\cdots OCPh_2$, which in turn is in equilibrium with the diphosphane P_2Ph_4 and the ketyl radical anion {$MOCPh_2$}, which has a deep blue or purple colour.[9–11] Similarly, on reacting LiPHR with benzophenone in THF, we observe the formation of deep purple solutions. The P-containing reaction products $(PR)_n$ were detected by ^{31}P NMR spectroscopy. Simultaneously, an EPR study of the same solution showed the presence of the radical $LiOCPh_2$ as well as to a lesser extent the diradical $\{LiOCPh_2\}_2$, both of which have already been reported.[12] Reduction of benzophenone was also observed for lithium amides[13] and lithium alkoxides[14] (with β-hydrogen atoms) in the so-called Meerwein-Ponndorf-Verley reductions.

In analogy to the reaction of secondary alkali metal phosphanides,[9–11] the first step in the reaction shown in eq. (1) is apparently the formation of the diphosphane $P_2H_2R_2$ and the ketyl radical anion and the diradical dianion $\{LiOCPh_2\}_2$. While $P_2H_2Ph_2$ decomposes to cyclooligophosphanes and primary phosphine,[15] $P_2H_2Mes_2$ is stable in solution.[16] As only cyclooligophosphanes are formed in the reaction, abstraction of a hydrogen atom from the diphosphane to yield the stable cyclooligophosphanes and lithium diphenylmethanolate must be assumed, a course of reaction which is not possible for secondary alkali metal phosphanides.

Cyclooligophosphanes were first prepared as early as 1877,[17] although their cyclic nature was only recognised in 1952[18] and demonstrated by X-ray structure determination in 1964.[19] While a few reports on $(PMes)_n$ ($n = 3, 4$) have appeared in the literature, no detailed information concerning their spectroscopic properties (other than ^{31}P NMR) or molecular structures was given.[20–24] Formation of $(PMes)_n$ ($n = 3, 4$) is observed in the reaction of $(Mes)P(H)GeCl_3$ with DBU, but no spectroscopic data were given for the products.[22] Formation of $(PMes)_n$ ($n = 3, 4$; characterised by ^{31}P NMR spectroscopy) is also observed in the photolysis of *trans*-2,3-dimethyl-1-mesitylphosphirane.[24] On irradiation at 77 K, a triplet phosphinidene was shown to be the intermediate.[25] Generally, on reduction of $RPCl_2$ with $[W(PMe_3)_6]$[20] or Mg,[21] the formation of diphosphenes RP=PR, which are only stable with bulky substituents ($R = 2,4,6\text{-}Bu^t{}_3C_6H_2$ and $2,4,6\text{-}(CF_3)_3C_6H_2$), or $(PR)_3$ (for R = Mes, $2,4,6\text{-}Pr^i{}_3C_6H_2$) is observed. The products were characterised by ^{31}P NMR spectroscopy. For $[W(PMe_3)_6]$, an intermediate with a W=PR group was proposed.[20] Similarly, when $[Re(NBu^t)_3(PHMes)]$ was treated with Bu^tLi, formation of a complex having a Re=PMes group was expected.[23] However, $[Re(NBu^t)_2(\mu\text{-}NBu^t)]_2$ was formed in a redox reaction, and formation of the cyclotriphosphane $(PMes)_3$ was assumed. The supposedly formed $(PMes)_3$ was isolated as a colourless crystalline solid, and the $^{31}P\{^1H\}$ spectrum of this compound exhibited two singlets at −111.2 and −118.35 ppm in a ratio of 2:1, which, according to the authors, "are in close agreement with values reported for similar compounds". This is, however, erroneous since $(PMes)_3$, like all other known cyclotriphosphanes, exhibits a triplet and a doublet (-109 and −143 ppm, $^1J_{PP}$ = 184 Hz).[20,21] Presumably, the product formed in this reaction is the diphosphane $P_2H_2Mes_2$,[16] with which both the NMR data and the analytical data are in agreement. Thus, $P_2H_2Mes_2$ exhibits two singlets in the $^{31}P\{^1H\}$ spectrum (ratio 3:2) at -109.9 (d,l) and −117.1 ppm (meso) due to the presence of two diastereomers.[16]

In the ^{31}P NMR spectra, both cyclooligophosphanes exhibit resonances which are in agreement with those reported previously in the literature [$(PMes)_3$: −109.32 d - 143.84 t, $^1J_{PP}$ 184.7 Hz[20,21,24], $(PMes)_4$: −43.08 ppm [24]].

Molecular structures of $(PMes)_n$ (n = 3 (1), 4 (2))

Both cyclooligophosphanes crystallise in the triclinic space group P $\bar{1}$ with two formula units in the unit cell (Table I). Selected bond lengths and angles are summarised in Tables II and III.

TABLE I Crystal data and structure refinement for $(PMes)_3$ (**1**), $(PMes)_4$ (**2**) and $[LiOCHPh_2]_6$ (**3**)

	1	*2*	*3*
Formula	$C_{27}H_{33}P_3$	$C_{36}H_{44}P_4$	$C_{78}H_{66}Li_6O_6$
Molecular weight	450.44	600.59	1140.96
Temperature (K)	220(2)	223(2)	223(2)
Crystal system	triclinic	triclinic	trigonal
Space group	P $\bar{1}$ (no. 2)	P $\bar{1}$ (no. 2)	R $\bar{3}$ (no. 148)
Cell constants:			
a (Å)	8.464(2)	10.8867(6)	21.978(2)
b (Å)	10.833(2)	11.2424(6)	21.978(2)
c (Å)	14.220(3)	15.8969(8)	11.2653(10)
α (°)	82.45(3)	73.768(1)	90
β (°)	78.81(3)	70.985(1)	90
γ (°)	77.33(3)	66.054(1)	120
V (Å³)	1242.5(5)	1656.6(2)	4712.6(7)
Z	2	2	3
d_{calc} (g/cm³)	1.204	1.204	1.206
2Θ range (°)	3.0–52.5	2.7–56.4	3.7–52.7
h (min., max.)	-9/10	-13/14	-26/23
k (min., max.)	-13/13	-8/14	-19/26

	1	*2*	*3*
l (min., max.)	-17/12	-20/20	-13/11
Total reflections	5669	9510	6946
Independent reflections	4221 [R(int.) 0.0717]	6845 [R(int.) 0.0766]	1912 [R(int.) 0.0494]
Parameters	367	538	180
Absorption coefficient (μ/mm^{-1})	0.251	0.251	0.073
Largest diff. peak/hole (e/Å^3)	0.57/-0.64	0.65/-0.70	0.27/-0.17
Final R indices [I > 2σ(I)]	R1 = 0.0623, wR2 = 0.1847	R1 = 0.0600, wR2 = 0.1812	R1 = 0.0560, wR2 = 0.1122
R indices (all data)	R1 = 0.0874 wR2 = 0.2498	R1 = 0.0702, wR2 = 0.1926	R1 = 0.0797 wR2 = 0.1242
Goodness-of-fit (F^2)	0.939	1.084	1.112

TABLE II Selected bond lengths (Å) and angles (deg) for **1**

P(1)-P(2)	2.2092(16)	P(1)-P(3)	2.2307(16)
P(2)-P(3)	2.2220(15)	P(1)-C(1)	1.853(4)
P(2)-C(10)	1.852(4)	P(3)-C(19)	1.851(4)
C(1)-C(2)	1.403(6)	C(1)-C(6)	1.416(6)
C(2)-C(3)	1.387(7)	C(3)-C(4)	1.381(7)
C(5)-C(4)	1.390(7)	C(6)-C(5)	1.382(6)
C(2)-C(7)	1.511(6)	C(4)-C(8)	1.508(7)
C(6)-C(9)	1.504(6)	C(11)-C(10)	1.420(6)
C(15)-C(10)	1.413(6)	C(11)-C(12)	1.378(7)
C(13)-C(12)	1.387(7)	C(14)-C(13)	1.389(7)
C(15)-C(14)	1.408(6)	C(11)-C(16)	1.522(6)
C(13)-C(17)	1.518(8)	C(15)-C(18)	1.495(7)
C(20)-C(19)	1.407(6)	C(24)-C(19)	1.417(6)
C(20)-C(21)	1.397(7)	C(21)-C(22)	1.385(7)
C(22)-C(23)	1.378(7)	C(24)-C(23)	1.401(7)
C(20)-C(25)	1.511(7)	C(22)-C(27)	1.517(7)
C(24)-C(26)	1.510(7)		
P(2)-P(1)-P(3)	60.06(5)	P(1)-P(2)-P(3)	60.45(5)
P(2)-P(3)-P(1)	59.49(5)	C(1)-P(1)-P(2)	97.69(14)
C(1)-P(1)-P(3)	99.98(14)	C(10)-P(2)-P(1)	112.13(14)
C(10)-P(2)-P(3)	113.32(14)	C(19)-P(3)-P(2)	110.69(14)
C(19)-P(3)-P(1)	108.15(14)	C(2)-C(1)-P(1)	120.5(3)
C(6)-C(1)-P(1)	120.8(3)	C(5)-C(6)-C(1)	119.4(4)
C(2)-C(1)-C(6)	118.6(4)	C(3)-C(2)-C(1)	119.6(4)

C(4)-C(3)-C(2)	122.2(4)	C(6)-C(5)-C(4)	122.2(5)
C(3)-C(4)-C(5)	117.7(4)	C(3)-C(2)-C(7)	118.2(4)
C(1)-C(2)-C(7)	122.1(4)	C(3)-C(4)-C(8)	120.2(5)
C(5)-C(4)-C(8)	122.1(5)	C(5)-C(6)-C(9)	117.9(4)
C(1)-C(6)-C(9)	122.6(4)	C(11)-C(10)-P(2)	111.5(3)
C(15)-C(10)-P(2)	129.6(3)	C(14)-C(15)-C(10)	118.8(4)
C(12)-C(11)-C(10)	120.1(4)	C(11)-C(10)-C(15)	118.7(4)
C(13)-C(14)-C(15)	122.2(5)	C(14)-C(13)-C(12)	118.1(4)
C(11)-C(12)-C(13)	122.1(5)	C(12)-C(11)-C(16)	117.3(4)
C(10)-C(11)-C(16)	122.5(4)	C(14)-C(13)-C(17)	120.5(6)
C(12)-C(13)-C(17)	121.4(6)	C(14)-C(15)-C(18)	116.7(4)
C(10)-C(15)-C(18)	124.6(4)	C(20)-C(19)-P(3)	123.0(3)
C(24)-C(19)-P(3)	116.9(3)	C(21)-C(20)-C(19)	118.9(4)
C(23)-C(24)-C(19)	119.1(4)	C(22)-C(21)-C(20)	122.8(4)
C(23)-C(22)-C(21)	117.8(4)	C(22)-C(23)-C(24)	122.2(5)
C(20)-C(19)-C(24)	119.1(4)	C(21)-C(20)-C(25)	117.9(4)
C(19)-C(20)-C(25)	123.1(4)	C(23)-C(24)-C(26)	118.1(4)
C(19)-C(24)-C(26)	122.7(4)	C(23)-C(22)-C(27)	121.9(5)
C(21)-C(22)-C(27)	120.2(5)		

TABLE III Selected bond distances (Å) and angles (deg) for **2**

P(1)-C(1)	1.860(3)	P(1)-P(2)	2.2153(10)
P(1)-P(4)	2.2460(9)	P(2)-C(10)	1.844(3)
P(2)-P(3)	2.2510(10)	P(3)-C(19)	1.861(3)
P(3)-P(4)	2.2542(9)	P(4)-C(28)	1.852(3)
C(1)-C(2)	1.403(4)	C(1)-C(6)	1.420(4)
C(2)-C(3)	1.391(4)	C(2)-C(7)	1.514(4)
C(3)-C(4)	1.382(4)	C(4)-C(5)	1.389(4)
C(4)-C(8)	1.502(4)	C(5)-C(6)	1.394(4)
C(6)-C(9)	1.508(4)	C(10)-C(11)	1.413(4)
C(10)-C(15)	1.418(4)	C(11)-C(12)	1.398(4)
C(11)-C(16)	1.506(4)	C(12)-C(13)	1.387(4)
C(13)-C(14)	1.384(4)	C(13)-C(17)	1.509(4)
C(14)-C(15)	1.394(4)	C(15)-C(18)	1.508(4)
C(19)-C(24)	1.401(4)	C(19)-C(20)	1.415(4)
C(20)-C(21)	1.395(4)	C(20)-C(25)	1.514(5)
C(21)-C(22)	1.383(5)	C(22)-C(23)	1.387(4)
C(22)-C(26)	1.520(4)	C(23)-C(24)	1.398(4)
C(24)-C(27)	1.508(4)	C(28)-C(29)	1.410(4)
C(28)-C(33)	1.421(4)	C(29)-C(30)	1.394(4)

C(29)-C(34)	1.515(4)	C(30)-C(31)	1.395(4)
C(31)-C(32)	1.387(4)	C(31)-C(35)	1.513(4)
C(32)-C(33)	1.393(4)	C(33)-C(36)	1.512(4)
C(1)-P(1)-P(2)	102.35(8)	C(1)-P(1)-P(4)	113.95(8)
P(2)-P(1)-P(4)	79.89(3)	C(10)-P(2)-P(1)	105.48(9)
C(10)-P(2)-P(3)	114.66(9)	P(1)-P(2)-P(3)	85.02(3)
C(19)-P(3)-P(2)	101.31(9)	C(19)-P(3)-P(4)	105.24(9)
P(2)-P(3)-P(4)	78.96(3)	C(28)-P(4)-P(1)	108.67(8)
C(28)-P(4)-P(3)	108.21(9)	P(1)-P(4)-P(3)	84.24(3)
C(2)-C(1)-C(6)	118.1(2)	C(2)-C(1)-P(1)	129.0(2)
C(6)-C(1)-P(1)	112.9(2)	C(3)-C(2)-C(1)	119.8(3)
C(3)-C(2)-C(7)	117.0(3)	C(1)-C(2)-C(7)	123.2(3)
C(4)-C(3)-C(2)	122.9(3)	C(3)-C(4)-C(5)	117.1(3)
C(3)-C(4)-C(8)	121.3(3)	C(5)-C(4)-C(8)	121.5(3)
C(4)-C(5)-C(6)	122.3(3)	C(5)-C(6)-C(1)	119.6(2)
C(5)-C(6)-C(9)	117.4(3)	C(1)-C(6)-C(9)	123.0(3)
C(11)-C(10)-C(15)	118.6(2)	C(11)-C(10)-P(2)	127.9(2)
C(15)-C(10)-P(2)	113.4(2)	C(12)-C(11)-C(10)	119.3(2)
C(12)-C(11)-C(16)	117.2(3)	C(10)-C(11)-C(16)	123.6(2)
C(13)-C(12)-C(11)	122.5(3)	C(14)-C(13)-C(12)	117.7(3)
C(14)-C(13)-C(17)	120.5(3)	C(12)-C(13)-C(17)	121.8(3)
C(13)-C(14)-C(15)	122.3(3)	C(14)-C(15)-C(10)	119.6(3)
C(14)-C(15)-C(18)	117.5(3)	C(10)-C(15)-C(18)	123.0(3)
C(24)-C(19)-C(20)	119.1(3)	C(24)-C(19)-P(3)	123.5(2)
C(20)-C(19)-P(3)	117.1(2)	C(21)-C(20)-C(19)	119.3(3)
C(21)-C(20)-C(25)	118.3(3)	C(19)-C(20)-C(25)	122.4(3)
C(22)-C(21)-C(20)	121.9(3)	C(21)-C(22)-C(23)	117.8(3)
C(21)-C(22)-C(26)	121.1(3)	C(23)-C(22)-C(26)	121.0(3)
C(22)-C(23)-C(24)	122.4(3)	C(23)-C(24)-C(19)	118.8(3)
C(23)-C(24)-C(27)	117.8(3)	C(19)-C(24)-C(27)	123.4(3)
C(29)-C(28)-C(33)	118.4(2)	C(29)-C(28)-P(4)	128.1(2)
C(33)-C(28)-P(4)	113.3(2)	C(30)-C(29)-C(28)	119.5(2)
C(30)-C(29)-C(34)	116.5(3)	C(28)-C(29)-C(34)	124.0(2)
C(29)-C(30)-C(31)	122.2(3)	C(32)-C(31)-C(30)	118.0(2)
C(32)-C(31)-C(35)	121.2(3)	C(30)-C(31)-C(35)	120.9(3)
C(31)-C(32)-C(33)	121.7(3)	C(32)-C(33)-C(28)	120.0(3)
C(32)-C(33)-C(36)	117.7(2)	C(28)-C(33)-C(36)	122.3(2)

In cyclotriphosphanes $(PR)_3$, two of the R groups are on one side of the P_3 ring, and one is on the other side. In **1** (Fig. 1) and other known cyclotriphosphanes (Table IV), one structural feature is apparent: the P-P-C bond angles at P atoms with *cis*-oriented R groups are always significantly larger than the corresponding values for the *trans*-substituted P atoms, the reason being steric interaction between the R groups or lone pairs, respectively.[26]

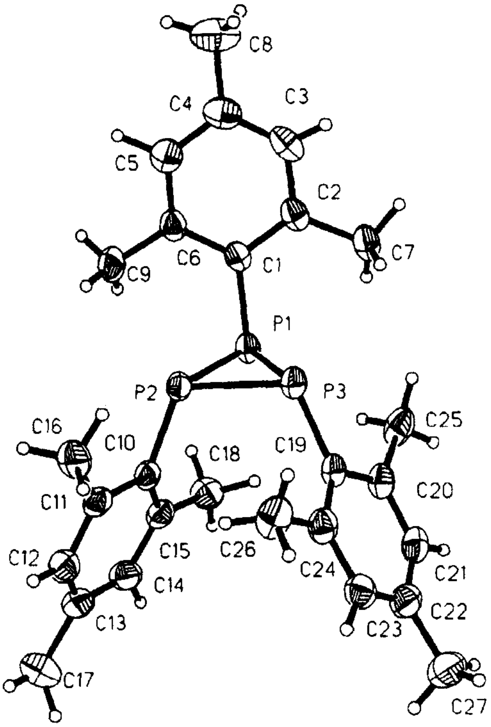

FIGURE 1 Molecular structure of $(PMes)_3$ (**1**) showing the atom numbering scheme employed (ORTEP plot, 50 % probability, SHELXTL PLUS; XP[47])

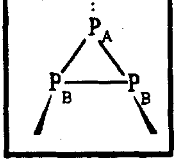

TABLE IV Selected bond lengths and angles of $(PR)_3$

R	*P-P / Å*	*P-P-P / deg*	*P-P_A-C / deg*	*P-P_B-C/ deg*	*Ref.*
Bu^t	2.185(2)- 2.218(2)	59.5(1)- 60.9(1)	105.0- 106.9	105.3- 123.7	27
CH(SiMe$_3$)$_2$	2.201(4)- 2.220(4)	59.5(1)- 60.4(1)	100.0(3)- 100.6(3)	109.4(3)- 111.6(3)	28
Mes	2.208(2)- 2.230(2)	59.46(5)- 60.44(5)	97.7(1)- 100.0(1)	108.1(1)- 113.3(1)	this work

All known cyclotetraphosphanes, including **2**, have a folded P_4 ring (torsional angles of ± 24 – 46°) with the R groups on alternate sides of the ring, and the molecules approach S_4 symmetry. The P-P and P-C bond lengths of **2** are comparable to those of other cyclooligophosphanes.[26] However, while the four endocyclic P-P-P bond angles of all known cyclotetraphosphanes are mainly similar (80 – 87° ; Table V), **2** exhibits alternatingly large (at P(2) and P(4)) and small (at P(1) and P(3)) endocyclic P-P-P bond angles due to steric hindrance between the bulky Mes groups.

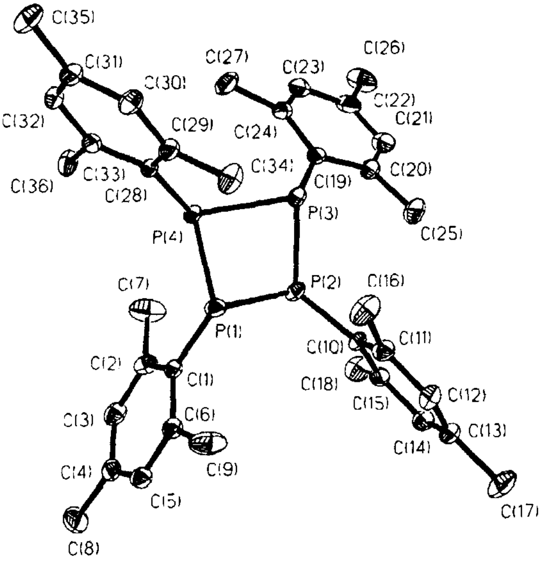

FIGURE 2 Molecular structure of $(PMes)_4$ (**2**) showing the atom numbering scheme employed (ORTEP plot, 50 % probability, SHELXTL PLUS; XP[47]). H atoms omitted for clarity

TABLE V Selected bond lengths and angles of $(PR)_4$

R	*mean P-P / Å*	*P-P-P / deg*	*P-P-P-P torsion angle / deg*	*Reference*
Bu^t	2.212(2)	87.11(5)-87.49(4)	24.5	29
CF_3	2.213	84.7	34.0	30
C_6F_5	2.236(2)	85.09(4)-85.39(4)	32.1	31
Cy	2.224	85.47(6)	31.4	32
$2\text{-}MeOC_6H_4$	2.225(1)	83.9(1)-84.4(1)	-	33
$N(SiMe_3)_2$	2.234(3)	79.6(1)-80.2(1)	45.7	34
tmp$^{1)}$	2.250(2)	81.6(1)-82.6(1)	40.7	34
Mes	2.242(1)	78.96(3)-85.02(3)	41.04(3)	this work

1) tmp - 2,2,6,6-tetramethylpiperidyl

Molecular structure of $[LiOCHPh_2]_6$ (3)

Lithium diphenylmethanolate crystallises in the trigonal space group R $\bar{3}$ with three formula units in the unit cell (Table I). Selected bond lengths and angles are summarised in Table VI.

TABLE VI Selected bond distances (A) and angles (deg) for **3**

O(1)-C(1)	1.403(2)	O(1)-Li(1)	1.864(4)
O(1)-Li(1B)	1.900(4)	O(1)-Li(1A)	1.995(4)
Li(1)-O(1C)	1.900(4)	Li(1)-O(1D)	1.995(4)
C(1)-C(8)	1.519(3)	C(1)-C(2)	1.525(3)
C(2)-C(7)	1.386(3)	C(2)-C(3)	1.388(3)
C(3)-C(4)	1.388(3)	C(4)-C(5)	1.381(4)
C(5)-C(6)	1.367(4)	C(6)-C(7)	1.387(3)
C(8)-C(9)	1.371(3)	C(8)-C(13)	1.399(3)
C(9)-C(10)	1.419(4)	C(12)-C(11)	1.364(5)
C(12)-C(13)	1.375(4)	C(10)-C(11)	1.361(5)
Li(1)···C(1D)	2.787(4)	Li(1)···C(2C)	2.761(4)
Li(1)···C(3C)	2.769(4)	Li(1B)···C(2)	2.761(4)

Li(1B)···C(3)	2.769(4)	Li(1A)···C(1)	2.787(4)
C(1)-O(1)-Li(1)	132.0(2)	C(1)-O(1)-Li(1B)	115.9(2)
C(1)-O(1)-Li(1A)	108.9(2)	Li(1)-O(1)-Li(1B)	112.0(2)
Li(1)-O(1)-Li(1A)	81.6(2)	Li(1A)-O(1)-Li(1B)	80.7(2)
O(1)-C(1)-C(8)	114.2(2)	O(1)-C(1)-C(2)	109.6(2)
C(8)-C(1)-C(2)	111.4(2)	O(1)-C(1)-Li(1A)	42.63(11)
C(7)-C(2)-C(3)	118.2(2)	C(7)-C(2)-C(1)	120.7(2)
C(3)-C(2)-C(1)	120.9(2)	C(4)-C(3)-C(2)	120.7(2)
C(5)-C(4)-C(3)	120.1(2)	C(6)-C(5)-C(4)	119.9(2)
C(5)-C(6)-C(7)	120.1 (2)	C(2)-C(7)-C(6)	121.0(2)
C(9)-C(8)-C(13)	118.4(2)	C(9)-C(8)-C(1)	122.5(2)
C(13)-C(8)-C(1)	119.1(2)	C(8)-C(9)-C(10)	119.9(3)
C(11)-C(12)-C(13)	119.7(3)	C(11)-C(10)-C(9)	119.8(3)
C(10)-C(11)-C(12)	120.8(3)	C(12)-C(13)-C(8)	121.4(3)
O(1)-Li(1)-O(1C)	125.2(2)	O(1)-Li(1)-O(1D)	99.1 (2)
O(1C)-Li(1)-O(1D)	97.9(2)		

The compound is hexameric and forms a slightly distorted hexagonal prism of alternating Li and O atoms (Fig. 3, 4). The cage results from the symmetry involved in the space group R $\bar{3}$. The original two atoms in the asymmetric unit (Li(1), O(1)) generate the rest of the cage (Li(1A-E), O(1A-E)) through a $\bar{3}$ axis.

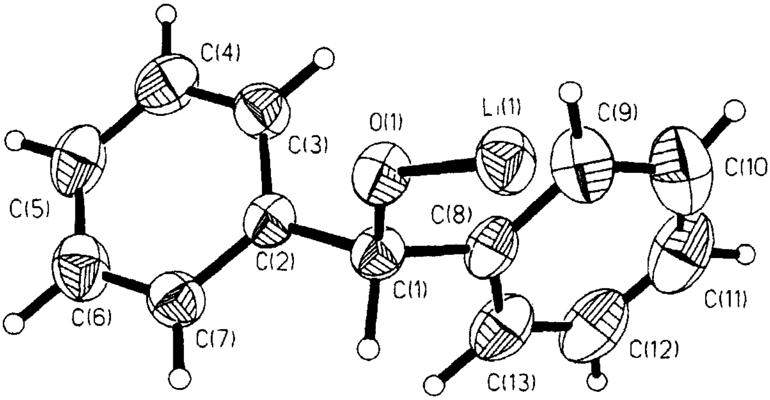

FIGURE 3 Monomeric asymmetric unit of [LiOCHPh$_2$]$_6$ (3) showing the atom numbering scheme employed (ORTEP plot, 50 % probability, SHELXTL PLUS; XP[47])

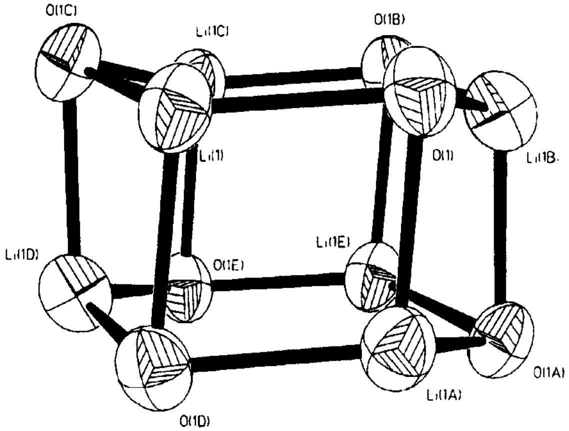

FIGURE 4 Central Li_6O_6 fragment of $[LiOCHPh_2]_6$ (3) showing the atom numbering scheme employed (ORTEP plot, 50 % probability, SHELXTL PLUS; XP[47])

Numerous main group metal compounds with cage structures are known.[35] Comparable structural motifs to hexameric lithium diphenylmethanolate are found in $[LiOCMe_2Ph]_6$,[36] $[LiOSiMe_2(2\text{-}C_4H_3S)]_6$,[37] $[LiOCHPr^i(2\text{-}C_4H_3S)]_6$,[37] $[Li\overline{N(CH_2)_5CH_2}]_6$,[38] as well as in the magnesium imide $[Mg(THF)NPh]_6$[40], iminoalanes $[RAlNPr^i]_6$[41] and the tin compound $[PhSn(O)O_2CC_6H_{11}]_6$,[42] while $[NaOBu^t]_6$[39] forms a very distorted hexagonal prism.

Two different descriptions are possible for these hexameric compounds M6X6: two stacked trimers (short or medium bond lengths within and longer bond lengths between the six-membered rings) or a cyclic ladder with six M-X steps (short or long bond lengths within and medium bond lengths between the six-membered rings). In heMxamethyleneimidolithium $[Li\overline{N(CH_2)_5CH_2}]_6$,[38] [LiOSiMe2(2-C4H3S)]6,[37] and $[LiOCHPr^i(2\text{-}C_4H_3S)]_6$,[37] the observation of Li-X (X = N or O) six-membered rings with alternating short ($[Li\overline{N(CH_2)_5CH_2}]_6$: 1.99(1)-2.00(2) Å[38]; $[LiOCHPr^i(2\text{-}C_4H_3S)]_6$: 1.8747(7) Å[37]) and long ($[Li\overline{N(CH_2)_5CH_2}]_6$ 2.06(1)-2.12(2) Å[38]; $[LiOCHPr^i(2\text{-}C_4H_3S)]_6$: 1.940(8) Å[37]) Li-X distances and medium Li-X distances between the six-membered rings ($[Li\overline{N(CH_2)_5CH_2}]_6$: 2.06–2.09 Å[38]; $[LiOCHPr^i(2\text{-}C_4H_3S)]_6$: 1.923(7)

Å[37]) suggests describing these compounds as cyclic ladders. On the contrary, in $[LiOCMe_2Ph]_6$,[36] the magnesium imide $[Mg(THF)NPh]_6$,[40] the iminoalanes $[RAlNPr^i]_6$,[41] and $[PhSn(O)O_2CC_6H_{11}]_6$,[42] the M-X bonds between the six-membered rings (M = Li, X = O: Li-O 1.9185(16), 1.9795(27) Å,[36] M = Mg, X = N: Mg-N 2.08 Å;[38] M = Al, X = N: R = H:[41a] Al-N 1.948(6) to 1.963(3) Å; R = Cl:[41b] Al-N 1.955(3) Å; M = Sn, X = O: Sn-O 2.069(3) to 2.089(3) Å[42]) are slightly longer than those within the six-membered rings (M = Li, X = O: Li-O 1.8742(1) to 1.9185(16) Å,[36] M = Mg, X = N: Mg-N 2.05 Å;[38] M = Al, X = N: R = H:[41a] Al-N 1.897(2) to 1.898(3) Å; R = Cl:[41b]Al-N 1.898(3) to 1.914(3) Å; M = Sn, X = O: Sn-O 2.096(3) to 2.124(3) Å[42]), this is indicative of two stacked trimers. Accordingly, **3** can also be described as two stacked trimers, as the Li-O bond lengths between the six-membered rings (Li-O 1.995(4) Å) are longer than the bonds within the six-membered rings, which have alternating Li-O distances of 1.864(4) and 1.900(4) Å. The parallel six-membered Li_3O_3 rings have an ideal chair conformation (Fig. 4, deviation from best plane: ±0.105 Å).

Each Li atom is bonded to three O atoms in a T-shaped fashion. The fourth coordination site is blocked by interaction with an aryl ring of the neighbouring alkoxide group in the same six-membered ring and interaction with the C1 atom of the adjacent alkoxide group in the other six-membered ring [Li(1)···C(1D) 2.787(4), Li(1)···C(2C) 2.761(4), Li(1)···C(3C) 2.769(4), Li(1B)···C(2) 2.761(4), Li(1B)···C(3) 2.769(4), Li(1A)···C(1) 2.787(4) Å] (Fig. 5). The Li··· C distances lie at the higher end of the range of distances observed for lithium compounds.[43]

In the six-membered rings, the O-Li-O [O(1)-Li(1)-O(1C) 125.2(2)°] and Li-O-Li bond angles [Li(1)-O(1)-Li(1B) 112.0(2)°] differ from the ideal 120°; the same is observed for the four-membered rings [ideal 90°, O-Li-O: O(1)-Li(1)-O(1D) 99.1(2), O(1C)-Li(1)-O(1D) 97.9(2)°; Li-O-Li: Li(1)-O(1)-Li(1A) 81.6(2), Li(1B)-O(1)-Li(1A) 80.7(2)°].

EXPERIMENTAL

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. The NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker), ^1H NMR: internal standard solvent (e.g., benzene, toluene), external standard TMS; ^{13}C

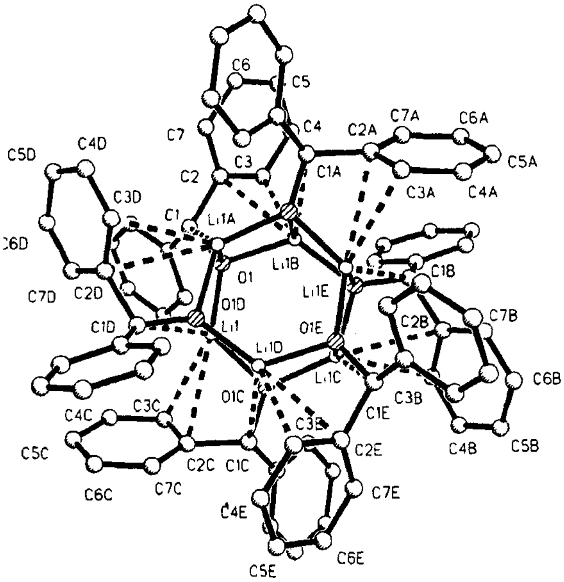

FIGURE 5 Molecular structure of $[LiOCHPh_2]_6$ (3) showing the Li···C interaction (SHELXTL PLUS; XP[47]). H atoms omitted for clarity

NMR: external standard TMS, internal standard solvent; ^{31}P NMR: external standard 85% H_3PO_4; ^{7}Li NMR: external standard 1 M LiCl in H_2O. The IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer in the range 350–4000 cm^{-1}. The melting points were determined in sealed capillaries under argon and are uncorrected. LiPHMes[44] and $PhPH_2$[45] were prepared by literature procedures. Benzophenone is commercially available.

LiPHPh

25 g (0.23 mol) of $PhPH_2$ were dissolved in 400 ml of hexane. A 1.4 M solution of BuLi (156 ml, 0.23 mol) in hexane was added at 0°C. After stirring at r.t. for 2 h, the yellow product was isolated by filtration, washed twice with 50 ml of hexane and dried in vacuum to give 22.04 g (82.6%) of pyrophoric LiPHPh. ^{31}P NMR (162 MHz, C_6D_6/THF, 25°C): -112.1 ppm, d ($^{1}J_{PH}$ 211 Hz). – IR (Nujol): ν(PH) = 2321 cm^{-1}.

Reaction of LiPHMes with benzophenone

2.3 g (12.6 mmol) of benzophenone was dissolved in 20 ml of THF. A solution of 2.0 g (12.65 mmol) of LiPHMes in 20 ml of THF was added with a canula at room temperature. The solution immediately turned blue. After stirring at r.t. for 12 h, the solvent was evaporated, and the resulting purple-blue oily residue was dissolved in 30 ml of ether. The solution was filtered and kept at r.t. for 1 d. The resulting colourless crystals of $[LiOCHPh_2]_6$ (**3**) (1.0 g, 41.7%) were collected by filtration. The mother liquor was reduced to one-quarter of its volume and kept at −22°C. After 7 d, colourless crystals of $(PMes)_3$ and yellow crystals of $(PMes)_4$ (total yield 1.3 g) were obtained. The crystals were separated by hand and characterised by NMR spectroscopy and X-ray crystal structure determination.

$(PMes)_3$:

Yield: 0.5 g, m.p. 143–145°C. – ^1H NMR (400 MHz, C_6D_6, 25°C), δ/ppm: 1.92 (s, 6 H, p-CH_3 of *cis*-oriented 2,4,6-$Me_3C_6H_2$ groups), 2.07 (s, 3 H, p-CH_3 of *trans*-oriented 2,4,6-$Me_3C_6H_2$ group), 2.49 (s, 12 H, o-CH_3 of *cis*-oriented 2,4,6-$Me_3C_6H_2$ groups), 2.79 (s, 6 H, o-CH_3 of *trans*-oriented 2,4,6-$Me_3C_6H_2$ group), 6.5 (s, 4 H, m-H of *cis*-oriented 2,4,6-$Me_3C_6H_2$ groups), 6.69 (s, 2 H, m-H of *trans*-oriented 2,4,6-$Me_3C_6H_2$ group). – ^{31}P NMR (162 MHz, C_6D_6, 25°C), δ/ppm: −109.32 d ($^1J_{PP}$ 184.7 Hz), −143.84 t ($^1J_{PP}$ 184.7 Hz).

$(PMes)_4$:

Yield: 0.6 g, m.p. 195–197°C. – ^1H NMR (400 MHz, C_6D_6, 25°C), δ/ppm: 2.00 (s, 12 H, p-CH_3 in 2,4,6-$Me_3C_6H_2$), 2.80 (s, 24 H, o-CH_3 in 2,4,6-$Me_3C_6H_2$), 6.65 (s, 8 H, m-H in 2,4,6-$Me_3C_6H_2$). – ^{31}P NMR (162 MHz, C_6D_6, 25°C), δ/ppm: −43.08 s.

$[LiOCHPh_2]_6$:

Yield: 1.0 g (41.7%), m.p. 190–198°C dec. – ^1H NMR (400 MHz, THF-d_8, 25°C), δ/ppm: 6.03 (s, 1 H, C-H), 7.04 (m, 1 H, p-H in Ph), 7.18 (m, 2 H, o-H in Ph), 7.41 (m, 2 H, m-H in Ph). – ^{13}C NMR (100.6 MHz, THF-d_8, 25°C), δ/ppm: 80.4 (O-C), 125.8 (Ph), 127.5 (Ph), 128.25 (Ph), 153.7 (ipso-C in Ph). – ^7Li NMR (155.5 MHz, THF-d_8, 22°C), δ/ppm: 0.89 s.

Reaction of LiPHPh with benzophenone

The reaction of LiPHPh with benzophenone was carried out as described for LiPHMes [1.3 g (11.2 mmol) LiPHPh, 2.03 g (11.2 mmol) benzophenone]. After separation of **3**, the ^{31}P NMR spectrum of the remaining solution showed the presence of $(PPh)_5$ (-5.13 ppm, m), $(PPh)_6$ (-21.98 ppm, s), and $(PPh)_4$ (-47.77 ppm, s), (by comparison with ref. 26) only; no attempts were made to isolate the cyclooligophenylphosphanes.

X-ray Crystal Structure Determination of 1 – 3

Data ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) were collected with a Siemens CCD (SMART) diffractometer. All reflections were used for the refinement of the unit cell parameters of **1**, **2** and **3**. Empirical absorption correction with SADABS[46]. The structures were solved by direct methods (SHELXTL PLUS[47]). P, O, Li and C atoms anisotropic, H atoms, other than those of the p-Me groups in **1**, located by difference maps and refined isotropically. H-atoms of p-Me groups in **1** were refined in calculated positions. Table I lists all crystallographic details. Anisotropic atomic parameters and full lists of bond lengths and angles have been deposited as supplementary material with the Cambridge Cristallographic Data Centre (**1**: CCDC-103273, **2**: CCDC-103275, **3**: CCDC-103274).

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie; the company Chemetall GmbH provided a generous donation of lithium alkyls. We thank Prof. Dr. R. Kirmse and Dipl. Chem. A. Voigt for EPR studies and Dr. Fernando B. Somoza, Jr. and Prof. Dr. J. Sieler for crystallographic advice.

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