

Synthesis and Spectroscopic and X-ray Structural Studies of the Mesitylphosphines PH₂Mes and PHMes₂ (Mes = 2,4,6-Me₃C₆H₂) and Their Lithium Salts [Li(THF)₃PHMes] and [[Li(OEt₂)PMes₂]₂]

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Received December 30, 1986

The synthesis and first structural characterization of crystalline primary and secondary mesitylphosphines PH₂Mes (1) and PHMes₂ (2) are described. Treatment of 1 and 2 with 1 equiv of *n*-BuLi affords the solvated lithium phosphides [Li(THF)₃PHMes] (3) and [[Li(OEt₂)PMes₂]₂] (4), which possess previously uncharacterized structural types. A notable feature in the crystal lattice of 1 is the packing of PMes moieties into parallel layers. However, there are no strong interactions between these layers. In 2, the phosphorus center has a pyramidal geometry with bond angles near tetrahedral values. The X-ray crystal structure of 3 shows that it is the first structure of a lithium phosphide with a terminal phosphido group. The pyramidal geometry at phosphorus is in sharp contrast to the planar geometry found for lithium amides. Unlike that of 3, the structure of 4 is dimeric with solvated lithium atoms bridging two [PMes₂]⁻ moieties. The central Li₂P₂ core is essentially planar with the phosphorus centers having distorted tetrahedral geometries. A ³¹P NMR study on the degree of solvation between ion pairs in various primary and secondary organophosphide complexes is also reported. Crystallographic data with Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$) at 130 K: 1, C₉H₁₃P, $a = 6.959 (2) \text{ \AA}$, $b = 8.191 (3) \text{ \AA}$, $c = 15.481 (6) \text{ \AA}$, $Z = 4$, orthorhombic, space group *Pmcn*; 2, C₁₈H₂₃P, $a = 8.572 (2) \text{ \AA}$, $b = 9.794 (2) \text{ \AA}$, $c = 18.481 (4) \text{ \AA}$, $\beta = 97.90 (2)^\circ$, $Z = 4$, monoclinic, space group *P2₁/c*; 3, C₂₁H₃₆LiO₃P, $a = 9.081 (5) \text{ \AA}$, $b = 18.475 (9) \text{ \AA}$, $c = 13.443 (6) \text{ \AA}$, $\beta = 92.01 (4)^\circ$, $Z = 4$, monoclinic, space group *P2₁/n*; 4, C₄₆H_{68.7}Li₂O₂P₂, $a = 12.432 (8) \text{ \AA}$, $b = 14.126 (8) \text{ \AA}$, $c = 20.580 (15) \text{ \AA}$, $\alpha = 92.97 (5)^\circ$, $\beta = 105.45 (5)^\circ$, $\gamma = 106.46 (5)^\circ$, $Z = 3$, triclinic, space group *P1*. For 1, $R = 0.068$, for 2, $R = 0.083$, for 3, $R = 0.074$, and for 4, $R = 0.067$.

Introduction

Since the early 1960s there has been much interest in the structural characterization of organolithium compounds¹ and their isoelectronic lithium amide² and alkoxide/aryloxide analogues.³ Only in the last few years has there been significant activity in their heavier main-group congeners such as lithium salts of silyls,⁴ phosphides,⁵⁻⁹ or thiolates.¹⁰ In addition, although solution and solid-state investigations of primary and secondary amines and alcohols have shown that hydrogen bonding plays a significant role in structure,¹¹ little is known about the solid-state structures of simple thiols and phosphines. For example, all of the structural studies on primary or secondary phosphines have involved the gas-phase techniques using electron diffraction or microwave spectroscopy.^{12,13} No crystal structures of primary or secondary

phosphines in which weak hydrogen bonding might be apparent have been published. Our interest in this aspect of the structure of these compounds has stemmed from our observation that the structure of [HPN(SiMe₃)₂]₂¹⁴ is dimeric with PHP bridging in its crystalline form.

Interest in the structure of lithium phosphides in this laboratory arose from studies in the use of crown ethers to achieve separation of lithium ions from various organometaloid anions.^{6,15} A series of publications^{5,7-9} has shown that lithium phosphides are either oligomeric or polymeric in ether solution. However, when 12-crown-4 is added to a solution of LiPPh₂, separate [PPh₂]⁻ ions may be obtained.^{6,9} In this work we have studied this interesting phenomenon using ³¹P NMR spectroscopy and show that there is a considerable shift in the δ value when cation-anion separation is achieved. However, the direction of these shifts cannot readily be explained in terms of electronegativity of the phosphorus substituents. In addition, the first X-ray structural characterization of a terminal lithium phosphide [Li(THF)₃PHMes] (3) is reported. This shows the phosphorus center to have a pyramidal configuration, in sharp contrast to most metal amides,^{2,9} which have a planar configuration at nitrogen. The structure of the solvated dimer [[Li(OEt₂)PMes₂]₂] (4) is described also and is contrasted with the tetrameric structure of [[Li₂(μ_3 -P(*t*-Bu)₂)(μ -P(*t*-Bu)₂)-THF]₂]⁵.

Experimental Section

General Procedures. All reactions were performed by using modified Schlenk techniques (under N₂). Solvents were freshly distilled from (Na/K alloy)/benzophenone and degassed twice immediately before use. The compounds PCl₂Mes and PH₂Mes were synthesized by literature procedures.¹⁶ The preparation of PCIMes₂ has been previously described;¹⁷ however, we describe an alternative procedure using LiMes rather than the Grignard reagent.

Physical Methods. Infrared spectra were recorded on an IBM IR/32 spectrometer. All values are given cm⁻¹. ³¹P NMR spectra were obtained on an NT-200 FT NMR instrument operating at 81 MHz. All values

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Table I. Crystal Data and Summary of Data Collection and Refinement

	1	2	3	4
formula	C ₉ H ₁₃ P	C ₁₈ H ₂₃ P	C ₂₁ H ₃₆ O ₃ PLi	C ₄₆ H _{68.7} O ₂ P ₂ Li ₂
fw	152.18	270.36	374.44	729.53
cryst system	orthorhombic	monoclinic	monoclinic	triclinic
space group	<i>Pm</i> <i>cn</i>	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>c</i>	<i>P</i> $\bar{1}$
conditions	<i>hk0</i> , <i>h + k = 2n</i> ; <i>h0l</i> , <i>l = 2n</i>	<i>h0l</i> , <i>l = 2n</i> ; <i>0k0</i> , <i>k = 2n</i>	<i>h0l</i> , <i>h + l = 2n</i> ; <i>0k0</i> , <i>k = 2n</i>	none
cryst dimens, mm	ca. 1 × 1 × 1 (melts at room temp)	0.25 × 0.375 × 0.375	0.5 × 0.5 × 0.75	0.35 × 0.40 × 0.50
cryst color and habit	colorless needles	colorless plates	yellow needles	yellow needles
temp, K	130	130	130	130
<i>a</i> , Å	6.959 (2)	8.572 (2)	9.081 (5)	12.432 (8)
<i>b</i> , Å	8.191 (3)	9.794 (2)	18.475 (9)	14.126 (8)
<i>c</i> , Å	15.481 (6)	18.481 (4)	13.443 (6)	20.580 (15)
α , deg				92.97 (5)
β , deg		97.90 (2)	92.01 (4)	105.45 (5)
γ , deg				106.46 (5)
<i>Z</i>	4	4	4	3
<i>V</i> , Å ³	882.5 (6)	1546.9 (6)	2254 (2)	3309 (4)
<i>d</i> _{calcd} , g/cm ³	1.15	1.17	1.10	1.10
radn	Mo K α ($\lambda = 0.71069$ Å)	Mo K α ($\lambda = 0.71069$ Å)	Mo K α ($\lambda = 0.71069$ Å)	Mo K α ($\lambda = 0.71069$ Å)
linear abs coeff, cm ⁻¹	2.3	1.59	1.3	1.28
scan speed, deg min ⁻¹	60	20	60	20
scan width, deg	1.2	1.0	1.3	0.8
max 2 θ , deg	55	55	55	45
type of scan	ω	ω	ω	ω
offset for bkgd, deg	1.0	1.0	1.0	0.8
range of abs factors	1.22–1.31	1.04–1.08	1.04–1.06	1.08–1.15
octants	+ <i>h</i> , + <i>k</i> , + <i>l</i>	+ <i>h</i> , + <i>k</i> , \pm <i>l</i>	+ <i>h</i> , + <i>k</i> , \pm <i>l</i>	+ <i>h</i> , \pm <i>k</i> , \pm <i>l</i>
no. of variables	61	194	203	433
data/variable ratio	14.1	8.9	10.5	10.7
check refl	(1315), (800); no decay	(214), (023); no decay	(017), (273); no decay	(102), (131); no decay
no. of refl collected	1185	3941	5737	8671
<i>R</i> (merge)	0.008	0.015	0.009	0.005
no. of unique data	1047	3509	5190	8666
no. of data used in refinement	860 (<i>I</i> > 2 σ (<i>I</i>))	1720 (<i>I</i> > 3 σ (<i>I</i>))	2149 (<i>I</i> > 3 σ (<i>I</i>))	4627 (<i>I</i> > 3 σ (<i>I</i>))
<i>R</i> (<i>F</i>)	0.068	0.083	0.074	0.067
<i>R</i> _w (<i>F</i>)	0.076	0.091	0.085	0.068
weighting scheme	[$\sigma^2(F_0) + 0.00119F_0^2$] ⁻¹	[$\sigma^2(F_0)$] ⁻¹	[$\sigma^2(F_0)$] ⁻¹	[$\sigma^2(F_0)$] ⁻¹
largest Δ/σ	0.016	0.003	0.007	0.009
largest feature in final diff map, e Å ⁻³	0.47 between P and C(1)	0.74 near C(18)	0.49	0.66 near O(1) (Et ₂ O)

are reported in ppm relative to an external standard of 85% H₃PO₄.

PH₂Mes (1). Crystals of **1** were obtained by dissolving 2.44 g of **1** in 20 mL of *n*-hexane. Slow cooling over 24 h to -20 °C afforded colorless needlelike crystals for X-ray diffraction studies: ³¹P NMR (C₆D₆/THF solution) -153.9 ppm (*J*_{P-H} = 207.3 Hz).

PHMes₂ (2). Synthesis of PCIMes₂ was accomplished by the addition of LiMes (5.15 g, 40.9 mmol) in THF (100 mL) to a solution of PCl₃ (2.5 g, 1.6 mL, 18.3 mmol) in Et₂O (30 mL) at -78 °C. Overnight stirring gave a yellow solution. The solvent was removed under reduced pressure to yield a viscous yellow oil. Extraction into hexane (60 mL) followed by distillation under reduced pressure (0.1 mm, 165–175 °C) gave a clear oil that solidified: yield 3.54 g, 71%; ³¹P NMR (CDCl₃ solution) 85.8 ppm. A solution of PCIMes₂ (3.25 g, 10.7 mmol) in Et₂O (20 mL) was added dropwise to a slurry of LiAlH₄ (0.4 g, 10.7 mmol) in Et₂O (20 mL) at 0 °C. The solution was stirred overnight, filtered, and washed with degassed H₂O (10 mL). The organic layer was dried over MgSO₄ and then filtered. Removal of ether under reduced pressure gave a white solid, which was redissolved in *n*-hexane (20 mL); the resultant mixture was then filtered. Slow cooling gave clear plates suitable for X-ray diffraction studies: yield 1.60 g, 56%; mp 97–99 °C; ¹H NMR (CDCl₃ solution) 2.28 s (9 H), 5.36 (H) (*J*_{P-H} = 235 Hz), 6.87 ppm (2 H); ³¹P NMR (OEt₂ solution) -92.4 ppm (*J*_{P-H} = 235 Hz); IR (P-H) 2361, 2338 cm⁻¹.

[Li(THF)₃PHMes] (3). Crystals of **3** were obtained by treatment of **1** (1.50 g, 9.8 mmol) in THF (10 mL) with *n*-BuLi (10 mmol; 6.5 mL of a 1.65 M *n*-hexane solution) at 0 °C to give a yellow-orange solution. After overnight stirring at room temperature, 75% of the solvents were removed under reduced pressure. Warm (~40 °C) *n*-hexane (20 mL) was added slowly. Slow cooling to -20 °C gave yellow needles of **3**: yield 0.55 g, 15%; mp 198–200 °C; ³¹P NMR (C₆D₆/THF solution) -155.9 ppm (*J*_{P-H} = 170 Hz); ¹H NMR (C₆D₆ solution) 1.40 m (THF), 3.56 m (THF), 2.36 s (3 H), 2.76 s (6 H), 2.86 d (1 H, *J*_{P-H} = 183 Hz), 7.00 ppm (2 H).

[Li(OEt₂)₂PHMes₂] (4). Crystals of **4** were obtained by treatment of PHMes₂ (0.5 g, 2.0 mmol) in Et₂O (8 mL) with *n*-BuLi (1.29 mL of 1.68 M hexane solution) at 0 °C. After 3 h of stirring, the solution was

warmed slightly (~40 °C) and *n*-hexane (10 mL) was added dropwise. Slow cooling over 20 h to -20 °C afforded yellow crystals of the product: yield 0.32 g, 45%; mp 234 °C; ¹H NMR (C₆D₆ solution) 0.92 t (OEt₂), 2.32 s (6 H), 2.47 s (12 H), 3.2 q (OEt₂), 7.02 ppm (4 H); ³¹P NMR (Et₂O solution) -89.3, (THF solution) -62.7 ppm.

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex P₂ diffractometer equipped with a locally modified LT-1 device, Mo K α radiation, and graphite monochromator. Calculations were carried out on a Data General Eclipse computer using the SHELXTL, version 4, programs. Absorption corrections were made by using the program XABS.^{18a} Scattering factors and corrections for anomalous dispersion were from ref 18b.

Colorless needles of **1** were obtained as described and were protected from air contamination by a cooled hydrocarbon oil. A crystal was selected, attached to a glass fiber on a mounting pin, and immediately placed in the low-temperature N₂ stream. Orthorhombic lattice constants were determined by a least-squares fit of 16 accurately centered reflections with 40 < 2 θ < 55°. The space group was determined to be either *Pm**cn* (*bca* of *Pnma* No. 62) or *P2*₁/*cn* (*cba* of *Pna2*₁ No. 33). Attempts to solve the structure by direct methods in both space groups led to the successful refinement of **1** in *Pm**cn* and not in *P2*₁/*cn*. In *Pm**cn* all atoms except the methyl H and H on phosphorus are constrained to lie in a mirror plane. The methyl H's on C(8) and C(9) were located on a difference map. In each set, one H is in the mirror plane. The methyl H's on C(7) do not appear to follow the same pattern, and only one H was located. All hydrogen atoms were included in the structure factor calculation at the positions found on the difference map with isotropic thermal parameters set at 0.05 Å². They were not refined. The data were not corrected for absorption effects. In the final cycles of refinement, phosphorus and carbon atoms were refined with anisotropic ther-

(18) (a) Program XABS was written by H. Hope and B. Moezzi. The program obtains an absorption tensor from *F*_o - *F*_c differences. (b) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

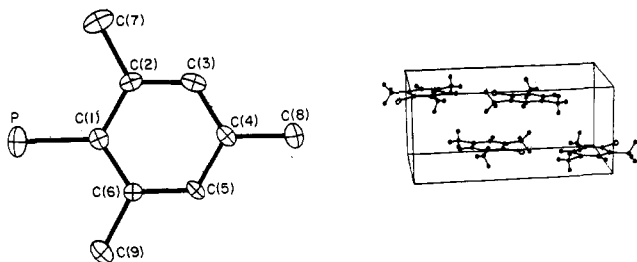


Figure 1. Computer-generated thermal ellipsoid drawing (probability level 50%) of **1** and a diagram illustrating stacking of PMes moieties.

mal parameters. Hydrogen atoms on phosphorus were not located in the final difference map. The largest feature is $0.47 \text{ e } \text{\AA}^{-3}$ between P and C(1). Further details of data collection and refinement are given in Table I.

Colorless plates of PHMes_2 (**2**) were obtained and handled in a fashion similar to that for **1**. The structure was solved by direct methods. An absorption correction was applied. In the final cycles of refinement, all non-hydrogen atoms were refined anisotropically. Similar to the treatment of **1**, hydrogen atoms were included at calculated positions except in this case the H bonded to P was located on a difference map and refined. Further details of data collection and refinement are given in Table I.

Yellow crystals of **3** were obtained as described and handled in a manner similar to that for **1**. The structure was solved by the Patterson technique. All three THF molecules exhibited some disorder, which was modeled by the use of partial occupancies for the disordered sets of atoms. These atoms are labeled C(*na*) and their counterparts C(*nb*). The THF groups and Li atom were assigned isotropic thermal parameters. The phosphorus and carbons of the mesityl group were given anisotropic thermal parameters. The hydrogen bonded to phosphorus was allowed to refine freely while other hydrogens were included at calculated positions. Further details are given in Table I.

Intensity data for **4** were collected in a similar manner. The structure was solved by direct methods. There are one and one-half dimers per asymmetric unit. A *n*-hexane molecule occupies a site near the center of inversion, giving rise to one *n*-hexane molecule per unit cell. In the final cycles of refinement, only P, O, and Li atoms were refined anisotropically. Further details are given in Table I. Atom coordinates for **1**–**4** are given in Table II.

Results and Discussion

Phosphine Structures. The crystal structures of **1** and **2** are the first to be determined of primary and secondary phosphines. Unlike the structure of the unpublished secondary aminophosphine dimer $[\text{HP}(\text{N}(\text{SiMe}_3)_2)_2]_2$, there are no close contacts between the molecules involving P and H in either molecule.¹⁴ Nevertheless, their overall structures do give some degree of information concerning the geometry about phosphorus.

The structure of **1** consists of discrete H_2PMes molecules, as illustrated in Figure 1. Selected bond lengths and bond angles are given in Table III. Since the hydrogens on the phosphorus atom were not located, the HPH bond angles about the phosphorus atom are presumed to be similar to those reported for PH_3 (93.2°) and for H_2PCH_3 (93.3°).¹³ This seems to be a reasonable assumption on the basis of a comparison of the CIPCI angle of 100.4° ¹⁹ in the chloro analogue of **1**, Cl_2PMes , to that of PCl_3 (100.2°).²⁰ The P–C bond distance of $1.807(5) \text{ \AA}$ is quite normal.⁷ An interesting feature of **1** is the crystallization of PMes units into parallel layers. An illustration of this phenomenon is shown in Figure 1. The distance between layers is 3.480 \AA , half the *a* dimension. The closest phosphorus contact (3.077 \AA for P and H(5)) is too long for any significant interactions.

The structure of **2** is shown in Figure 2. Selected bond distances and angles are given in Table III. Complex **2** crystallizes as monomers with no close phosphorus–hydrogen contacts to adjoining molecules. The central phosphorus atom exhibits a

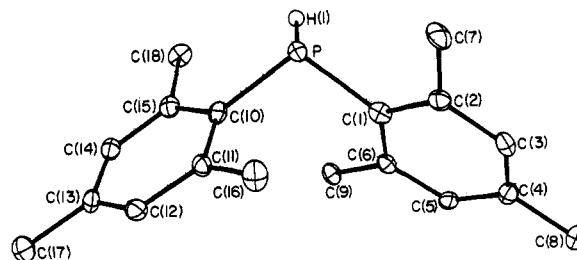


Figure 2. Computer-generated thermal ellipsoid drawing (probability level 35%) of **2**.

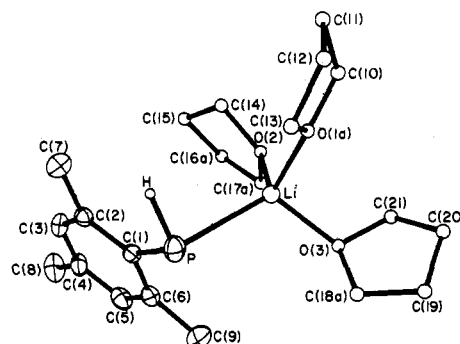


Figure 3. Computer-generated thermal ellipsoid drawing (probability level 50%) of **3**; $n\text{-C}_6\text{H}_{14}$ molecule of crystallization omitted for clarity.

pyramidal geometry. The angles at phosphorus are larger than normally expected, having the values $\text{H}(1)\text{--P--C}(1) = 109(3)^\circ$, $\text{H}(1)\text{--P--C}(10) = 107(3)^\circ$, and $\text{C}(1)\text{--P--C}(10) = 107.0(3)^\circ$. This is probably due to the large steric requirements of the mesityl rings. Even larger angles have been reported in trimesitylphosphine, PMes_3 .²¹ The P–C lengths average 1.854 \AA and, as expected, are slightly longer than that of **1**. The P–H bond distance in **2** is $1.36(7) \text{ \AA}$, somewhat shorter than that reported in the vapor-phase structure of $\text{HP}(\text{CH}_3)_2$ (1.445 \AA).

Lithium Phosphide Structures. The structure of **3** (Figure 3) is the first example of a lithium salt of a primary phosphine and of a monomeric lithium phosphide. Various important bond lengths and angles are given in Table III. The most conspicuous feature of the structure involves the pyramidal geometry surrounding phosphorus. The angles at the phosphorus center total 301° . This is in sharp contrast to the planar geometries that are seen in most metal amides,² including three terminal alkali-metal amido derivatives.^{9,22} However, terminal metal phosphides and arsenides may exhibit planar geometries in some instances. For example, some transition-metal derivatives, where multiple bonding between the phosphide lone pair and the transition metal d orbitals is electronically possible, exhibit planar geometries at phosphorus.²³ Multiple bonding is also evident in the recently reported structures of the boron-substituted phosphides $[\text{Li}(\text{Et}_2\text{O})_2\text{PRBMe}_2]$ ($\text{R} = \text{Ph}, \text{C}_6\text{H}_{11}, \text{Mes}$). Here the involvement of one of the phosphorus lone pairs in bonding to the empty 2p orbital on boron results in a planar configuration at the phosphorus center.²⁴ In **3**, the P–H bond distance is $1.42(6) \text{ \AA}$ and shows no close $\text{H}\cdots\text{Li}$ contacts. The lithium atom is in a distorted tetrahedral environment owing to a compression of the O–Li–O angles for the three THF molecules. It is interesting to note that the closely related (Li–PH and Li–S are isoelectronic) lithium thiolate $[\text{Li}(\text{THF})_3(\text{S}-2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)]$ is also monomeric with a similarly solvated lithium ion. In ether solution a tetrameric structure of formula

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Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^3$)

atom	x	y	z	U	atom	x	y	z	U
Complex 1									
P	2500	1765 (2)	5479 (1)	37 (1) ^a	C(5)	2500	3944 (5)	3094 (3)	18 (1) ^a
C(1)	2500	3263 (6)	4622 (3)	19 (1) ^a	C(6)	2500	2781 (5)	3749 (3)	17 (1) ^a
C(2)	2500	4978 (6)	4816 (3)	19 (1) ^a	C(7)	2500	5599 (8)	5730 (4)	32 (2) ^a
C(3)	2500	6092 (6)	4135 (3)	21 (1) ^a	C(8)	2500	6832 (6)	2549 (3)	27 (2) ^a
C(4)	2500	5610 (6)	3277 (3)	20 (1) ^a	C(9)	2500	1003 (6)	3514 (4)	31 (2) ^a
Complex 2									
P	1026 (2)	2156 (2)	221 (1)	25 (1) ^a	C(9)	-992 (7)	491 (7)	1264 (4)	28 (2) ^a
H	24 (85)	1461 (82)	-279 (38)	40 (21)	C(10)	-148 (7)	3459 (7)	626 (3)	23 (2) ^a
C(1)	1807 (2)	964 (7)	969 (3)	25 (2) ^a	C(11)	569 (8)	4303 (7)	1211 (3)	25 (2) ^a
C(2)	3431 (8)	705 (7)	1091 (3)	27 (2) ^a	C(12)	-358 (8)	5297 (7)	1486 (4)	28 (2) ^a
C(3)	3981 (8)	-276 (7)	1616 (4)	26 (2) ^a	C(13)	-1912 (8)	5516 (7)	1216 (4)	28 (2) ^a
C(4)	3005 (8)	-982 (7)	2016 (4)	26 (2) ^a	C(14)	-2544 (8)	4716 (7)	632 (4)	27 (2) ^a
C(5)	1421 (8)	693 (7)	1894 (3)	24 (2) ^a	C(15)	-1750 (7)	3686 (7)	328 (4)	25 (2) ^a
C(6)	798 (7)	277 (7)	1384 (3)	22 (2) ^a	C(16)	2254 (8)	4147 (8)	1526 (4)	36 (2) ^a
C(7)	4581 (8)	1388 (8)	662 (4)	32 (2) ^a	C(17)	-2890 (10)	6601 (9)	1527 (4)	42 (3) ^a
C(8)	3652 (9)	2006 (8)	2583 (4)	35 (2) ^a	C(18)	-2527 (8)	2901 (8)	-320 (4)	29 (2) ^a
Complex 3									
P	1617 (2)	-856 (1)	3534 (1)	33 (1) ^a	C(12)	-3597 (7)	-1163 (4)	5127 (5)	52 (2)
H	1074 (67)	-1485 (36)	4012 (44)	60 (19) ^a	C(13)	-2153 (7)	-909 (3)	4716 (4)	41 (1)
O(1a)	-2463 (5)	-745 (2)	3681 (3)	32 (1)	C(14)	-1610 (7)	-1722 (4)	1512 (5)	49 (2)
O(1b)	-2327 (19)	-992 (10)	3652 (13)	7 (4)	C(15)	-715 (8)	-1979 (4)	648 (5)	57 (2)
O(2)	-1496 (4)	-961 (2)	1531 (3)	35 (1)	C(16a)	-736 (14)	-1296 (7)	-88 (9)	48 (3)
O(3)	-1178 (4)	499 (2)	2453 (3)	36 (1)	C(16b)	-221 (20)	-1380 (10)	175 (13)	41 (4)
C(1)	2554 (5)	-1183 (3)	2447 (4)	24 (1) ^a	C(17a)	-966 (18)	-671 (7)	608 (9)	29 (3)
C(2)	2807 (5)	-1921 (3)	2217 (4)	25 (2) ^a	C(17b)	-1558 (41)	-706 (19)	511 (25)	39 (10)
C(3)	3544 (6)	-2112 (3)	1352 (4)	30 (2) ^a	C(17c)	-498 (36)	-765 (19)	627 (22)	26 (8)
C(4)	4061 (6)	-1600 (3)	699 (4)	31 (2) ^a	C(18a)	-635 (14)	993 (7)	3205 (10)	30 (3)
C(5)	3848 (6)	-892 (3)	930 (4)	35 (2) ^a	C(18b)	-806 (22)	903 (11)	3514 (15)	41 (5)
C(6)	3105 (6)	-659 (3)	1777 (4)	32 (2) ^a	C(18c)	-469 (24)	1144 (13)	2888 (17)	23 (5)
C(7)	2255 (7)	-2524 (3)	2850 (4)	38 (2) ^a	C(19)	1794 (9)	1481 (5)	3457 (6)	71 (2)
C(8)	4817 (7)	-1845 (4)	-237 (4)	46 (2) ^a	C(20)	-3157 (8)	1208 (4)	2926 (5)	61 (2)
C(9)	2926 (7)	130 (3)	1985 (5)	43 (2) ^a	C(21)	-2619 (6)	730 (3)	2111 (4)	40 (1)
C(10)	-3946 (6)	-967 (3)	3422 (4)	38 (1)	Li	-889 (9)	-513 (5)	2793 (6)	28 (2)
C(11)	-4367 (7)	-1489 (4)	4218 (4)	52 (2)	H	1074 (67)	-1485 (35)	4012 (44)	60 (19)
Complex 4									
P(1)	4956 (1)	2220 (1)	3853 (1)	28 (1) ^a	C(31)	8482 (5)	567 (4)	2064 (3)	31 (2)
P(2)	5092 (1)	1323 (1)	2123 (1)	25 (1) ^a	C(32)	8499 (5)	1355 (4)	2493 (3)	29 (2)
P(3)	219 (2)	4312 (1)	9208 (1)	31 (1) ^a	C(33)	7501 (5)	1627 (4)	2472 (3)	26 (1)
O(1)	3916 (4)	-727 (3)	3291 (2)	44 (2) ^a	C(34)	5270 (5)	-369 (4)	1073 (3)	33 (2)
O(2)	6055 (3)	4292 (3)	2766 (2)	30 (2) ^a	C(35)	9614 (5)	315 (5)	2118 (3)	40 (2)
O(3)	-567 (3)	2841 (3)	10707 (2)	30 (2) ^a	C(36)	7618 (5)	2521 (4)	2943 (3)	31 (2)
Li(1)	4561 (9)	621 (7)	3136 (5)	36 (5) ^a	C(37)	4214 (6)	-1516 (5)	2998 (4)	57 (2)
Li(2)	5402 (9)	2907 (7)	2837 (5)	33 (4) ^a	C(38)	5405 (6)	-1145 (6)	2939 (4)	65 (2)
Li(3)	325 (9)	3989 (7)	10279 (5)	31 (4) ^a	C(39)	2873 (7)	-1089 (6)	3496 (4)	73 (3)
C(1)	3727 (5)	2444 (4)	4090 (3)	26 (1)	C(40)	2464 (7)	-308 (6)	3712 (4)	70 (2)
C(2)	3528 (5)	2320 (4)	4722 (3)	31 (2)	C(41)	6003 (5)	4601 (5)	2109 (3)	42 (2)
C(3)	2556 (5)	2499 (4)	4845 (3)	35 (2)	C(42)	4768 (5)	4181 (5)	1662 (3)	41 (2)
C(4)	1720 (5)	2751 (4)	4367 (3)	33 (2)	C(43)	7116 (5)	4848 (4)	3281 (3)	36 (2)
C(5)	1878 (5)	2824 (4)	3735 (3)	36 (2)	C(44)	7125 (6)	5876 (5)	3498 (4)	49 (2)
C(6)	2850 (5)	2682 (4)	3582 (3)	28 (2)	C(45)	-911 (5)	4337 (4)	8446 (3)	22 (1)
C(7)	4357 (5)	1983 (5)	5275 (3)	40 (2)	C(46)	-2121 (5)	3833 (4)	8370 (3)	28 (2)
C(8)	653 (6)	2933 (5)	4515 (4)	51 (2)	C(47)	-2980 (5)	3937 (4)	7820 (3)	29 (2)
C(9)	2951 (6)	2795 (5)	2875 (3)	39 (2)	C(48)	-2743 (5)	496 (4)	7315 (3)	30 (2)
C(10)	6287 (5)	2705 (4)	4561 (3)	25 (1)	C(49)	-1565 (5)	4976 (4)	7384 (3)	27 (1)
C(11)	7061 (5)	2123 (4)	4740 (3)	28 (1)	C(50)	-670 (5)	4914 (4)	7925 (3)	24 (1)
C(12)	8132 (5)	2527 (5)	5232 (3)	38 (2)	C(51)	-2475 (6)	3147 (5)	8865 (3)	38 (2)
C(13)	8486 (6)	3484 (5)	5570 (3)	39 (2)	C(52)	-3702 (6)	4557 (5)	6713 (3)	47 (2)
C(14)	7726 (5)	4042 (5)	5395 (3)	39 (2)	C(53)	584 (5)	5474 (5)	7958 (3)	33 (2)
C(15)	6658 (5)	3685 (4)	4903 (3)	31 (2)	C(54)	1336 (5)	3918 (4)	8940 (3)	24 (1)
C(16)	6746 (6)	1076 (4)	4413 (3)	39 (2)	C(55)	1075 (5)	3167 (4)	8397 (3)	29 (2)
C(17)	9669 (6)	3896 (6)	6107 (4)	65 (2)	C(56)	1992 (5)	2882 (4)	8267 (3)	33 (2)
C(18)	5889 (5)	4363 (5)	4752 (3)	37 (2)	C(57)	3129 (5)	3260 (4)	8657 (3)	31 (2)
C(19)	3974 (5)	1207 (4)	1316 (3)	24 (1)	C(58)	3390 (5)	3977 (4)	9195 (3)	31 (2)
C(20)	2784 (5)	706 (4)	1256 (3)	22 (1)	C(59)	2518 (5)	4317 (4)	9341 (3)	28 (1)
C(21)	1899 (5)	790 (4)	709 (3)	26 (1)	C(60)	-152 (5)	2615 (5)	7982 (3)	42 (2)
C(22)	2131 (5)	1332 (4)	192 (3)	29 (2)	C(61)	4104 (6)	2915 (5)	8511 (4)	50 (2)
C(23)	3299 (5)	1765 (4)	228 (3)	29 (2)	C(62)	2871 (6)	5127 (5)	9926 (3)	42 (2)
C(24)	4212 (5)	1718 (4)	769 (3)	24 (1)	C(63)	374 (5)	2551 (5)	11123 (3)	37 (2)
C(25)	2428 (5)	75 (4)	1784 (3)	32 (2)	C(64)	1521 (5)	3240 (4)	11086 (3)	35 (2)
C(26)	1146 (5)	1419 (5)	388 (3)	39 (2)	C(65)	-1720 (5)	2208 (4)	10675 (3)	33 (2)
C(27)	5451 (5)	2255 (5)	777 (3)	34 (2)	C(66)	-2076 (6)	1256 (5)	10211 (3)	42 (2)
C(28)	6411 (5)	1065 (4)	2018 (3)	25 (1)	C(67)	165 (8)	374 (6)	5269 (4)	83 (3)
C(29)	6399 (5)	268 (4)	1579 (3)	25 (1)	C(68)	820 (8)	199 (7)	5943 (4)	91 (3)
C(30)	7432 (5)	44 (4)	1615 (3)	30 (2)	C(69)	1240 (9)	1072 (7)	6492 (5)	108 (3)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U* tensor.

Table III. Selected Bond Distances (Å) and Angles (deg)

Complex 1			
P-C(1)	1.807 (5)	P-C(1)-C-(6)	120.9 (3)
P-C(1)-C-(2)	120.7 (3)		
Complex 2			
P-C(1)	1.862 (7)	C(1)-P-C(10)	107.0 (3)
P-C(10)	1.846 (7)	C(1)-P-H(1)	109 (3)
P-H(1)	1.36 (7)	C(10)-P-H(1)	107 (3)
Complex 3			
P-Li	2.533 (9)	Li-P-H	93 (2)
P-C	1.820 (5)	P-Li-O(1a)	111.9 (4)
P-H	1.42 (6)	P-Li-O(1b)	105.1 (6)
Li-O(1a)	1.942 (10)	P-Li-O(2)	117.3 (4)
Li-O(1b)	1.982 (19)	P-Li-O(3)	116.5 (4)
Li-O(2)	1.950 (9)	O(1a)-Li-O(2)	104.4 (4)
Li-O(3)	1.940 (10)	O(1b)-Li-O(2)	98.4 (6)
C(1)-P-Li	101.9 (3)	O(1a)-Li-O(3)	105.2 (4)
C(1)-P-H	106 (2)	O(1b)-Li-O(3)	118.8 (7)
Complex 4			
P(1)-Li(1)	2.483 (1)	Li(1)-P(1)-C(10)	120.6 (3)
P(1)-Li(2)	2.479 (11)	Li(2)-P(1)-C(1)	117.7 (3)
P(1)-C(1)	1.824 (7)	Li(2)-P(1)-C(10)	107.0 (3)
P(1)-C(10)	1.816 (5)	C(1)-P(1)-C(10)	109.7 (3)
P(2)-Li(1)	2.517 (2)	Li(1)-P(2)-C(19)	121.4 (3)
P(2)-Li(2)	2.487 (11)	Li(1)-P(2)-C(28)	111.5 (3)
P(2)-C(19)	1.824 (5)	Li(2)-P(2)-C(19)	109.7 (3)
P(2)-C(28)	1.840 (7)	Li(2)-P(2)-C(28)	116.8 (3)
Li(1)-O(1)	1.926 (11)	C(19)-P(2)-C(28)	113.1 (3)
Li(2)-O(2)	1.924 (11)	P(1)-Li(1)-O(1)	129.8 (6)
P(3)-Li(3)	2.500 (11)	P(2)-Li(1)-O(1)	131.7 (5)
P(3)-Li(3a)	2.526 (11)	P(1)-Li(2)-O(2)	126.2 (5)
P(3)-C(45)	1.815 (5)	P(2)-Li(2)-O(2)	133.8 (6)
P(3)-C(54)	1.831 (7)	Li(3)-P(3)-Li(3a)	76.4 (8)
Li(3)-O(3)	1.873 (11)	P(3)-Li(3)-P(3a)	103.6 (8)
Li(1)-P(1)-Li(2)	81.7 (4)	Li(3)-P(3)-C(45)	118.9 (3)
Li(1)-P(2)-Li(2)	80.9 (4)	Li(3)-P(3)-C(54)	126.0 (3)
P(1)-Li(1)-P(2)	98.2 (4)	P(3)-Li(3)-O(3)	131.1 (6)
P(1)-Li(2)-P(2)	99.2 (4)	P(3a)-Li(3)-O(3)	124.8 (5)
Li(1)-P(1)-C(1)	117.3 (3)		

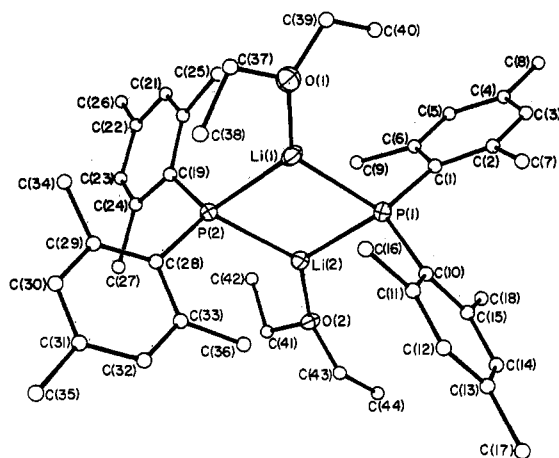
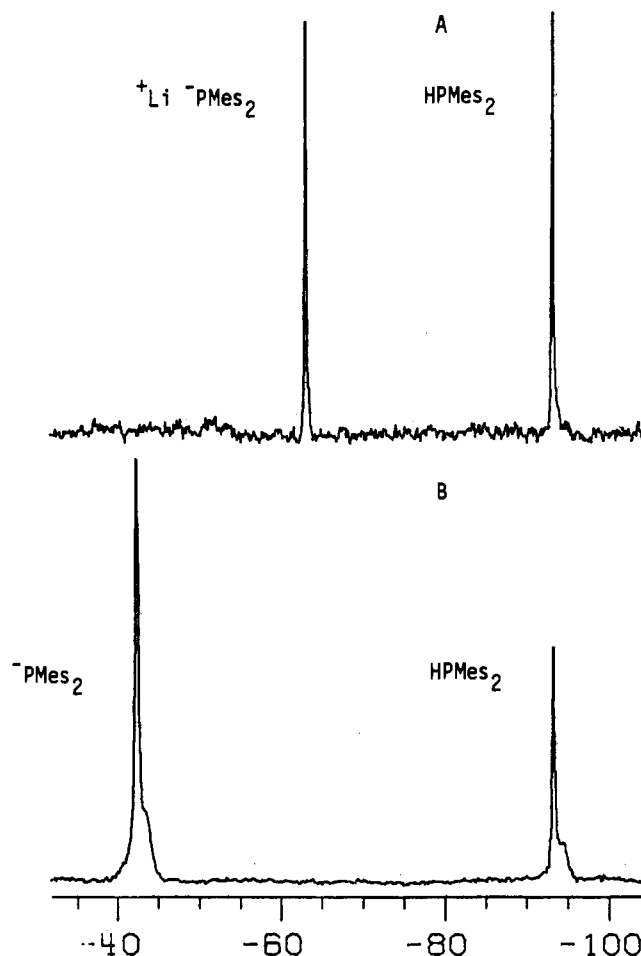


Figure 4. Computer-generated thermal ellipsoid drawing (probability level 35%) of 4.

$[\text{Li}(\text{Et}_2\text{O})\text{PHMes}]_4$ has been assigned on the basis of ^{31}P NMR and ^7Li NMR data.²⁵

The structure of 4 is shown in Figure 4. Selected bond lengths and angles are given in Table III. The molecule is dimeric, and the central P_2Li_2 core is almost planar. The dimeric structure may be compared to the structure of the solvated LiPPh_2 and $\text{LiP}(\text{C}_6\text{H}_{11})_2$ species, which have the polymeric chain structure⁷ and the same coordination number for the Li and P atoms. In fact, the P-C, Li-O, and Li-P distances are almost identical. However, the CPC angles are ca 104° in the case of the LiPPh_2

Figure 5. FT ^{31}P NMR (200-MHz) spectra of PHMes_2 (2) in THF: (a) addition of $1/2$ equiv of $n\text{-BuLi}$; (b) addition of 2 equiv of 12-crown-4/Li.

complex compared to ca. 111° for 4. The wider angle is presumably a consequence of the larger size of the Mes group compared to Ph. The higher steric requirement of the mesityl substituent may also be responsible for the lower degree of association. This view is further supported by the structure of the tetramer $[\text{Li}(\mu_3\text{-P}(t\text{-Bu})_2)(\mu\text{-P}(t\text{-Bu})_2)\text{THF}]_4$, which has CPC angles of ca. 112° .⁵ In this case, although the degree of aggregation is 4 rather than 2, the amount of solvation has been halved, as indicated by the overall stoichiometry of $[\text{Li}(\text{THF})_{0.5}\text{P}(t\text{-Bu})_2]$. This may be due to the fact that $\text{P}(t\text{-Bu})_2$ is a more effective donor than PMes_2 (alkyl vs. aryl substituent) and perhaps is competitive with THF as a solvate for the Li^+ ion.

Evidence from ^{31}P NMR data suggests that 4 also exists as a dimer in THF solutions.²⁶ At -80°C , a poorly resolved septet ($J_{\text{P-Li}} = 55$ Hz (average)) is observed, which implies that each phosphorus nucleus ($I = 1/2$) is coupled to two equivalent lithium nuclei ($I = 3/2$).

^{31}P NMR Studies. The ^{31}P NMR shifts for various primary and secondary phosphines^{27,28} and phosphides are given in Table IV. It can readily be seen that for all the secondary phosphines there is a significant downfield shift upon the addition of $n\text{-BuLi}$ and a further shift downfield when 12-crown-4 is added. These spectral changes are contrary to what is expected on the basis of the electronegativities of lithium and hydrogen. Further, on the basis of the amount of negative charge on phosphorus, the free $[\text{PR}_2]^-$ ion obtained from the addition of 12-crown-4 should be the most shielded but instead is the most electronically deshielded.

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Table IV. ^{31}P NMR Shifts^a of Various Primary and Secondary Phosphines and Phosphides

Primary Phosphines			
R	H ₂ PR	LiHPR	LiHPR + 12-crown-4
Mes	-153.8	-154.1	line broadening
Ph	-124.81	-111.9	line broadening
Secondary Phosphines			
R	HPR ₂	LiPR ₂	LiPR ₂ + 12-crown-4
Mes	-93.6	-62.9	-42.8
Ph	-39.9	-21.4	-7.5
C ₆ H ₁₁	-27.2	-9.5	-7.1
<i>t</i> -Bu	20.7	41.9	

^aAll values are given in ppm relative to H₃PO₄. Plus and minus signs designate downfield and upfield chemical shifts, respectively.

One possible clue for these unusual trends may lie in the difference in coordination number between the starting material (three-coordinate) and the lithium derivative (four-coordinate). The crystal structures of LiPR₂ solvates (R = Ph, C₆H₁₁, Mes) all show the phosphorus to be four-coordinate, and there is a significant ^{31}P chemical shift on lithiation. In contrast, the ^{31}P signal for [(THF)₃LiPHMes], which has three- rather than four-coordinate phosphorus, is only slightly shifted from the parent three-coordinate phosphine H₂PMes.

The addition of 12-crown-4 to LiPR₂ complexes in THF solution results in a further downfield shift to the ^{31}P signal. This is illustrated in Figure 5 for the case of the title compound, HPMe₂.

Addition of *n*-BuLi to HPMe₂ (^{31}P -93.6 ppm), results in the appearance of a new signal 30.7 ppm downfield at -62.9 ppm. Further addition of 12-crown-4 gives a new resonance at -42.8 ppm. The latter downfield shift is difficult to explain since it is expected that the free [PMes₂]⁻ anion having a full negative charge on phosphorus would be more shielded and thus appear upfield. In addition, there is no structural evidence of significant charge delocalization over the mesityl rings of [PMes₂]⁻ to account for the downfield chemical shift. However, a $p\pi-p\pi$ interaction between phosphorus and the aromatic ring has been proposed elsewhere to account for the anomalous ^{31}P shifts.^{27,29} Similar trends are seen in the HPPH₂ system.

Addition of 12-crown-4 to the primary lithium phosphides results in no significant changes in chemical shift, but broadening of the peaks is observed. This might be interpreted as the inability of 12-crown-4 to achieve cation-anion separation in the case of the more nucleophilic primary phosphides. Crystallization and subsequent structural characterization of these species are currently under way.

Acknowledgment. We thank the National Science Foundation (Grant CHE-811-6355) and the Committee of Research at the University of California, Davis, for financial support.

Supplementary Material Available: Full listings (Tables S1a-S4d) of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (10 pages); tables of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

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Osmium Azo Oxime Chemistry. Facial Tris Chelate and Trinuclear OsMOs Species

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Received September 4, 1986

The reaction of ammonium hexabromoosmate(IV) with excess alkaline (NaOH) (phenylazo)acetaldoxime in aqueous methanol affords the facial tris chelate anion Os^{III}A₃⁻ isolated as NaOsA₃·3H₂O (**4**; A⁻ = PhN=NC(=NO⁻)Me). The corresponding tetraphenylarsonium salt, Ph₄AsOsA₃ (**7**), has also been isolated by reacting **4** with Ph₄AsCl. In chloroform solution, the arsenic atom of **7** is covalently bonded to one of the oximate oxygen atoms of facial OsA₃⁻. The conversion **7** → **4** can be achieved with NaPh₄B. Stereochemical identification is made with the help of ¹H NMR spectra. Complex **4** reacts with metal perchlorates, furnishing trinuclear complexes (**5**) of types (OsA₃)₂M^{III} (M = Mg (**5a**), Mn (**5b**), Co (**5d**), Ni (**5e**)) and [(OsA₃)₂M^{III}]ClO₄ (M = Fe (**5c**)). The reconversion **5** → **4** is achieved by selective extrusion of Mⁿ⁺ (n = 2, 3) as the hydroxide with the help of NaOH. The osmometric molecular weights of the (OsA₃)₂M complexes confirm their trinuclear nature. In **5** the six oximate oxygen atoms of the two facial OsA₃⁻ units provide octahedral O₆ coordination for the central metal atom (Mⁿ⁺). In **5b-e** the MO₆ octahedron is high spin. The EPR spectra of the S = 5/2 species, viz. **5b** (g_{||} = 6.28; g_⊥ = 1.99) and **5c** (intense g = 4.2 signal), respectively correspond to primary axial and rhombic distortions of MO₆. In voltammetry characteristic responses due to osmium(III)-osmium(II) (**4**, **7**), M(III)-M(II) (**5b-d**), and the two successive ligand (azo) redox processes (OsA₃)₂M⁻(OsA₂A⁻)(OsA₃)M⁻(OsA₂A⁻)₂M (**5a-e**) are observed. The spectral and electrochemical properties of **4** and **5** are compared with those of the iron(II) complexes, and the strong ligand field and bonding strengths of A⁻ are underscored. It is proposed that the binding of Mⁿ⁺ is significantly stronger in **5** than in the iron(II) congeners. Attempted synthesis of RuA₃⁻ has not succeeded so far.

Introduction

Platinum metal complexes of azo ligands are of current interest to us.¹⁻⁴ Azo-coordinated osmium is rare. The only reports

available to us deal with certain diimine⁵ and azo dicarboxylic ester⁶ species, an azobenzene complex⁷ and certain 2-(aryloxy)pyridine chelates.^{8,9} In contrast, ruthenium has a substantive azo

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