Acknowledgment. We are grateful for generous financial support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Note Added in Proof. Professor Strausz has kindly informed us that, subsequent to the appearance of his recent paper,[6] he found strong evidence against the ketocarbene assignment for the carbonyl-containing species observed by IR. In particular, matrix photolysis of perfluoro-4-diazo-3-pentanone gave concentrations of the derived ketocarbene which were too low to detect by ESR, yet IR revealed a carbonyl-bearing species analogous to that from **1**. The Strausz group has made an additional interesting observation, viz. that vapor-phase photolysis of **1** in the presence of perfluoro-2-butyne at λ ≥ 320 nm yields a ketocarbene trapping product, perfluorotetramethylfuran.

Registry No. 1, 2834-21-1; **5**, 87282-23-3; **7**, 87282-24-4.

Isolation and X-ray Structure of $[Li_2(\mu_3\text{-}t\text{-}Bu_2P)(\mu_2\text{-}t\text{-}Bu_2P)(C_4H_8O)]_2$ Containing a Staggered, Planar Li_4 Unit. The First Structurally Characterized Alkali Metal Diorganophosphide

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Alkali metal diorganophoshides (MPR_2, M = Li, Na, K, ...; R = alkyl, aryl) have been used for many years as useful synthetic reagents in both organic and inorganic chemistry.[1] Although they are normally represented simply as "MPR_2", very little is known about their actual constitution in solution or in the solid state. In solution molecular weight measurements have suggested some degree of aggregation,[2] and recent NMR studies by McFarlane and co-workers suggested a dimeric structure for $LiPPh_2$ in diethyl ether.[3]

Structural information on lithium derivatives is available for a number of alkyls,[4] aryls,[5] dialkylamides,[6] and alkoxides.[7] We report here the isolation and X-ray crystal structure of $[Li_2(\mu_3\text{-}t\text{-}Bu_2P)(\mu_2\text{-}t\text{-}Bu_2P)(C_4H_8O)]_2$ (**1**), which to our knowledge is the first structurally characterized alkali metal diorganophosphide to be reported.

As part of a study of the steric effects of bulky phosphide (R_2P^-) groups as ligands for d-block transition metals, we have used the lithium derivative of di-*tert*-butylphosphine "Li^tBu_2P" generated in situ.[8] In order to correlate factors such as the reactivity, the degree of aggregation, and the steric bulk of the alkyl groups, we have isolated and characterized crystals of this useful starting material.

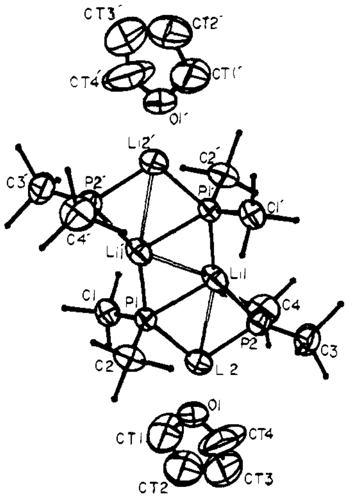

Figure 1. General view of $[Li_2(\mu_3\text{-}t\text{-}Bu_2P)(\mu_2\text{-}t\text{-}Bu_2P)(C_4H_8O)]_2$ (**1**). For clarity methyl groups of the *t*-Bu units are represented as sticks.

Evaporation to dryness of pale yellow "Li-*t*-Bu_2P" solutions, generated in situ in Et_2O or THF, followed by recrystallization of the residue from hexane at −20 °C yields large colorless crystals of **1** in high yield. These crystals rapidly crumble to a white powder under vacuum or in the absence of either hexane or THF vapor. Crystals suitable for X-ray diffraction were therefore mounted in thin-walled glass capillaries under a nitrogen atmosphere saturated with hexane vapor.

A view of the molecular structure of **1** is shown in Figure 1.[9] There are a number of interesting features. The structure consists of an unusual distorted "Z" of four Li atoms, all of which have virtually planar coordination geometries. The Li–Li distances of 3.065 (13) Å (Li(1)–Li(2)) and 3.025 (19) Å (Li(1)–Li(1')) suggest that direct Li–Li bonding is relatively unimportant.[4] There is a crystallographically imposed center of inversion at the midpoint of the two central Li atoms (Li(1) and Li(1')). Two of the phosphide groups (P(1) and P(1')) are triply briding to three Li atoms while the other two (P(2) and P(2')) bridge only two (see Figure 1). The two end Li atoms (Li(2) and Li(2')) each bear a coordinated THF molecule. The overall Li_4P_4 framework is virtually planar.[10] The Li–P distances for the doubly bridging P atoms (P(2) and P(2')) are notably shorter by ca. 0.15 Å than those of the triply bridging phosphorus atoms.[11] These distances

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(9) Mp 113–115 °C; IR (Nujol mull, KBr plates) 1258 (m), 1160 (m), 1100 (m), 1028 (m), 795 (m), 665 (m) cm^{-1}; ^1H NMR (in C_6D_6) at 31 °C, δ 3.69 (m, 8 H THF), 1.67 (s, ($\Delta\omega_{1/2} = 6$ Hz), 36 H, Bu), relative to Me_4Si δ 0.0. The other THF peak is obscured by the *t*-Bu resonance. CAD 4, crystal data: $Li_4O_2P_4C_{40}H_{88}$, monoclinic, space group $P2_1/n$, $a = 11.816$ (1) Å, $b = 20.490$ (2) Å, $c = 12.356$ (5) Å, $\beta = 96.95$ (2)°, $U = 2969.6$ (3) Å^3, $D_c = 0.842$ g cm^{-3}, $Z = 2$ (tetramers), λ(Mo Kα) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 1.5 cm^{-1}. Patterson and difference Fourier techniques were used to solve and refine the structure. Refinement (full matrix, least squares) of 2162 reflections ($I > 2\sigma(I)$). 5562 measured (4° < 2θ < 50°), gives current R and R_w values of 0.0982 and 0.1312, respectively. Data/parameter ratio = 9:1. All non-hydrogen atoms anisotropic, hydrogen atoms not located. We think that the relatively high R values are due to substantial thermal motion, especially in the THF molecules. We plan to collect a low-temperature data set in order to try to resolve this. Details will be published separately.

(10) Deviations (in Å) from the best least-squares planes are as follows. Plane 1 (Li(1)–Li(2)–P(1)–P(2)): Li(1) −0.033 (17), Li(2) 0.034 (19), P(1) 0.032 (3), P(2) 0.035 (3). Plane 2 (Li(1)–Li(1')–P(1)–P(1')): Li(1) 0.006 (17), Li(1') 0.006 (14), P(1) −0.006 (3), P(1') 0.006 (2). Dihedral angle between planes 1 and 2 = 2.5 (2) Å.

are all slightly longer than the sum of the normal covalent radii for Li (1.34 Å) and P (1.10 Å)[12] suggesting electron-deficient bridge bonding between Li and P atoms.

A variety of different structures have so far been found for bulky lithium derivatives. The planar zig-zag geometry found in **1** is quite different from those in other systems. For example, $[Li(N(SiMe_3)_2)(OEt_2)]_2$[6] and $[Li(N(SiMe_3)_2)]_3$[13] contain a planar Li_2N_2 ring and an alternating $(LiN)_3$ planar-trigonal framework. The structures of $[Li(CH(SiMe_3)_2)]$ (pmdeta) and $[Li(CH(SiMe_3)_2)]$[4] (tmeda) contain monomeric Li atoms while that of $[Li(OC_6H_2Me\text{-}4\text{-}t\text{-}Bu_2\text{-}2,6)(OEt_2)]_2$ has a planar Li_2O_2 ring.[7]

Unlike $LiPPh_2$,[3] $^{31}P\{^1H\}$ NMR spectra of **1** redissolved in Et_2O or THF show only a sharp singlet (δ 38.51 relative to H_3PO_4, in THF at 31 °C), which broadens slightly on cooling to −85 °C. The data could mean a rearrangement with the basic tetrameric unit intact or that the tetramer no longer exists. At present we have no data that provide information on the solution structure of this lithium diorganophosphide. Further studies on the structures and reactivities of alkali metal diorganophosphides and related compounds are in progress.

Acknowledgments. We thank the National Science Foundation (Grant CHE82-11883) for support. The X-ray diffractometer was purchased with funds from the National Science Foundation (Grant CHE82-05871) and the University of Texas at Austin.

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond lengths and angles, and structure factors (25 pages). Ordering information is given on any current masthead page.

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(11) A complete listing of bond lengths and angles is provided as supplementary material. For convenience the key bond lengths (Å) and angles (deg) not mentioned in the text are as follows. Lengths: Li(1)–P(1) 2.669 (9), Li(1)–P(2) 2.498 (9), Li(2)–P(1) 2.595 (10), Li(2)–P(2) 2.476 (10), Li(2)–O(1) 1.923 (10), P(1)–Li(1′) 2.586 (9). Angles: P(1)–Li(1)–P(2) 104.9 (3), P(1)–Li(2)–P(2) 107.7 (3), P(1)–Li(2)–O(1) 127.8(5), P(1)–Li(1)–Li(1′) 70.29 (33), P(1)–Li(1)–P(1′) 109.71 (33), P(2)–Li(1)–P(1′) 145.46 (39).

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(14) **Note Added in Proof**: The X-ray structures of $[Li(12\text{-crown-}4)_2][PPh_2]$ and $[Li(12\text{-crown-}4)_2][AsPPh_2]$ have recently been determined [Hope, H.; Olmstead, M. M.; Power, P. P.; Xiaojie, X. *J. Am. Chem. Soc.*, submitted]. We thank Dr. P. Power, University of California, Davis, for a preprint of his work prior to publication.

Interaction of $MCl_2N(SiMe_3)_2$, M = P or As, with Carbonylmetalate Dianions of Iron and Chromium: Syntheses and X-ray Crystal Structures of New Transition-Metal Complexes Involving Phosphorus and Arsenic in Multiple Bonding

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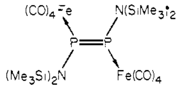
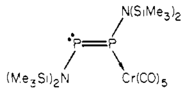
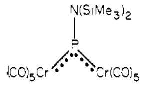
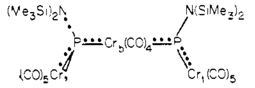
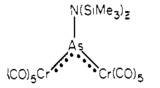
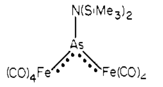
We recently reported that the reaction of $P[CH(SiMe_3)_2]Cl_2$ with $Na_2Fe(CO)_4$ in ether solvent afforded [*trans*-$\{[Fe(CO)_4]_2[PCH(SiMe_3)_2]_2\}$] (**1**), the first example of a transition-metal complex containing an unsupported phosphorus–phosphorus double bond.[1,2] We have since begun to investigate the effect of changing (i) the bulky substituent, (ii) the main group 5 element, (P, As, Sb, or Bi) and (iii) the transition metal on the nature of the product.

Table I. Structural Formulas and Selected Bond Distances (Å) and Angles (deg) for Compounds **2–7**

complex	remarks
 **2**	$\bar{1}$ symmetry; P–P = 2.053 (1), Fe–P = 2.232 (1). P–N = 1.682 (2); PPN = 110.2 (1). PPFe = 128.7 (1). FePN = 120.9 (1)
 **3**	characterized on the basis of IR. ^1H and ^{31}P NMR, and elemental analysis; structure is probably very similar to the alkyl analogue[5]
 **4**	planar phosphorus geometry; Cr–P = 2.286 (1), 2.290 (1), P–N = 1.697 (3); CrPN = 115.8 (1). 116.0 (1). CrPCr = 128.2 (1)
 **5**	both phosphorus atoms are planar; Cr_bP = 2.277 (2), 2.288 (2), Cr_tP = 2.321 (2), 2.319 (2), P–N = 1.708 (5), 1.691 (5); Cr_tPN = 115.5 (2). 116.0 (2), Cr_tPCr_b = 129.5 (1), 128.2 (1). Cr_bPN = 116.3 (2), 116.0 (2), PCr_bP = 169.6 (1)
 **6**	arsenic geometry is planar; twofold rotation axis about As–N bond; Cr–As = 2.381 (1). As–N = 1.864 (4); CrAsN = 113.3 (1), CrAsCr = 133.4 (1)
 **7**	characterized on the basis of IR, ^1H NMR, and elemental analysis

In this paper we report the synthesis of six new products involving the bis(trimethylsilyl)amido substituent on phosphorus and arsenic and the X-ray crystal structures of four of these. These compounds, whose structural formulas are shown in Table I, are [*trans*-$\{[Fe(CO)_4]_2[PN(SiMe_3)_2]_2\}$] (**2**) and $[Cr(CO)_5\{PN(SiMe_3)_2\}_2]$ (**3**), containing P–P double bonds, the mono- and bis(phosphinidine) complexes $[[Cr(CO)_5]_2PN(SiMe_3)_2]$ (**4**) and *trans*-$[Cr(CO)_4[PN(SiMe_3)_2]_2[Cr(CO)_5]_2]$ (**5**), and the arsinidine complexes $[[Cr(CO)_5]_2AsN(SiMe_3)_2]$ (**6**) and $[[Fe(CO)_4]_2AsN(SiMe_3)_2]$ (**7**). The compounds were synthesized by the general reaction of the disodium carbonylmetalate salt with either $PCl_2N(SiMe_3)_2$ (**8**) or $AsCl_2N(SiMe_3)_2$ (**9**) in Et_2O at 25 °C.

The compound **2** was obtained, via a route identical with that of **1**, in 45% yield and crystallized as orange-red needles, mp 134–136 °C. The reaction of $Na_2Cr(CO)_5$ with either **8** or **9** is quite complex. We have monitored the products of the reaction with **8** by ^{31}P NMR and have identified three different complexes, which may be separated by fractional crystallization. These are the compounds **3**, **4**, and **5**. We have determined the structures of **4** and **5**; crystals of **3** have, so far, proved unsuitable for X-ray studies. Due to the number of new species produced, the yields of **3** (orange crystals, mp 95–97 °C), **4** (dark blue-purple crystals, mp 182–184 °C), and **5** (dark blue crystals, mp 195 °C, dec) are about 25% based on the group 5B atom. However, these yields compare favorably to those of the only previously reported complexes; the manganese phosphinidine $[[Mn(\eta^5\text{-}C_5H_5)(CO)_2]_2PPh]_2$ and the chromium arsinidines $[[Cr(CO)_5]_2AsPh]$ and $[[Cr(CO)_5]_2AsCl]$,[3] which are synthesized by somewhat longer routes. The complex **7** was isolated as a deep green oil.

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