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 $[Li(12\text{-}crown\text{-}4)_2][PPh_2]$ and $[Li(12\text{-}crown\text{-}4)_2][AsPPh_2]$ 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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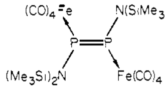
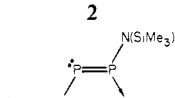
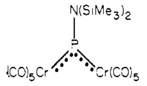
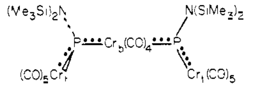
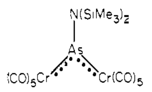
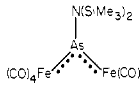
We recently reported that the reaction of $P[CH(SiMe_3)_2]Cl_2$ with $Na_2Fe(CO)_4$ in ether solvent afforded [*trans*-$\{[Fe(CO)_4]_2[PCH(SiMe_3)_2]_2\}$] (**1**), the first example of a transition-metal complex containing an unsupported phosphorus–phosphorus double bond.[1,2] We have since begun to 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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The structures of **2**,[4a] **4**,[4b] **5**,[4c] and **6**[4d] were determined via single-crystal X-ray diffraction; important bond distances and angles are given in the table. The complex **2** has a structure that is almost identical with its alkyl analogue, **1**.[1] The main feature of interest is the P–P distance of 2.053 (1) Å, which is slightly longer than the values 2.039 (1) Å reported for **1** and 2.034 Å recently reported for the free ligand.[5] These slight increases are expected in view of the more electronegative amido substituent reducing the electron density in the bonding orbitals of the P–P link and σ-donation reducing the repulsion between the phosphorus lone pairs. The P–N distance in **2** (1.682 (2) Å) is significantly shorter than in the free ligand (1.769 Å). This is probably due to a substantial reduction in the repulsive interaction between the nonbonding electron pairs on nitrogen and phosphorus. The probable structure of **3** involves a $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ unit in which one of the phosphorus atoms behaves as a two-electron donor to $Cr(CO)_5$. This has been assigned on the basis of ^{31}P NMR and elemental analysis and by analogy to the known structure of its isoelectronic alkyl analogue.[6]

Both **4** and **6** may be thought of a derivatives of the ligand :$\ddot{P}$(or As)$N(SiMe_3)_2$ in which the main group 5 center is in a formally 1+ oxidation state and behaves as a two-electron donor to each chromium (0) atom. The phosphorus and arsenic centers in each molecule are planar and may be regarded as being approximately sp^2 hybridized. The remaining empty p orbital may behave as a π-acceptor via overlap with chromium d orbitals. The Cr–P distances, 2.290 (1) and 2.286 (1) Å, are similar to those found in complexes with π-acceptor phosphines such as $[Cr(CO)_5P(OPh)_3]$ (Cr–P = 2.309 (1) Å) and *trans*-$[Cr(CO)_4(P(OPh)_3)_2]$ (Cr–P = 2.252 (1) Å).[7]

For the arsinidene ligand, available data concern arsine ligands which are unlikely to be good π-acceptors and give Cr–As distances varying between 2.405 (2) and 2.516 (2) Å.[8] It can be argued that the M–As distances for arsenic π-acceptor ligands should, like their phosphorus counterparts, be similarly reduced so that a value somewhat less than 2.4 Å would be predicted. This predicted value is very close to that found in **6**, 2.381 (1) Å. It therefore seems that both phosphinidene and arsinidene ligands behave as four-electron donor and two-electron π-acceptor ligands. In **4** and **6** the P–N and As–N distances are normal, and the shortening expected from π-donation by the nitrogen p orbital is significantly reduced by a corresponding Si–N d–pπ interaction.

Compound **5** is the only known transition-metal complex in which the metal is bonded to two phosphinidene ligands. The bond distances and angles surrounding phosphorus are very similar to those in **4**. The terminal Cr–P distances of 2.323 (2) and 2.318 (2) Å are slightly longer than the central Cr–P distances of 2.279 (2) and 2.287 (2) Å. This is probably due to the fact that on the central chromium two phosphinidenes are trans to each other while at the terminal chromium they are trans to carbonyl. The planes defined by Cr_tPNCr_b and Cr_bPNCr_t are at ~96° with respect to each other so that the core geometry resembles that of allene.

NMR data are as follows: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, relative to external 85% H_3PO_4) **2** δ 403.9, **3** (d of d) δ 534.5, 542.3, 556.5, and 564.3, $J_{PP} = 631$ Hz. ^1H NMR (C_6H_6) **2** δ 0.54, **3** δ 0.52, **4** δ 0.46, **6** δ 0.33, **7** δ 0.35. More complete spectroscopic studies involving IR, UV–vis, and other NMR data will be reported in a full account of this work.

In summary the presence of both phosphene and phosphinidene complexes in the same reaction mixture suggests a close interrelationship. Work is in progress to determine the mechanism of formation of these interesting species.

Acknowledgment. We are grateful to the NSF (CHE-8116355) for generous financial support.

Registry No. 2, 87829-45-6; **3**, 87829-46-7; 4, 87829-47-8; **5**, 87829-48-9; **6**, 87829-49-0; **7**, 87829-50-3; **8**, 54036-90-7; **9**, 76505-23-2; $Na_2Cr(CO)_5$, 51233-19-3.

Supplementary Material Available: Summary of data and structure refinement, listing of atom coordinates, temperature factors, and bond distances and angles, and structure factor tables (75 pages). Ordering information is given on any current masthead page.

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[4] Crystal data with Mo Kα radiation ($\lambda = 0.71069$ Å) $T = 140$ K: (a) **2**, triclinic $P\bar{1}$ (No. 2), $a = 8.598$ (2) Å, $b = 9.983$ (2) Å, $c = 10.964$ (3) Å, $\alpha = 71.38$ (2), $\beta = 85.23$ (2), $\gamma = 68.37$ (2)°; $Z = 1$; $\mu = 11.5$ cm^{-1}; 2166 unique data, 191 parameters; $R = 0.025$. (b) **4**, monoclinic, $P2_1/n$ (No. 14); $a = 8.586$ (4) Å, $b = 18.284$ (10) Å, $c = 15.859$ (7) Å, $\beta = 90.74$ (4); $Z = 4$; $\mu = 10.56$ cm^{-1}; 4387 unique data, 307 parameters, $R = 0.046$. (c) **5**, orthorhombic *Pcab*, $a = 16.751$ (5) Å, $b = 19.542$ (3) Å, $c = 25.546$ (6) Å; $Z = 8$; $\mu = 9.9$ cm^{-1}; 6055 unique data, 287 parameters, $R = 0.055$. (d) **6**, monoclinic $C2/c$, $a = 16.784$ (5) Å, $b = 10.479$ (4) Å, $c = 17.434$ (4) Å, $\beta = 126.45$ (2)°; $Z = 4$; $\mu = 23.3$ cm^{-1}; 2049 unique data; 156 parameters; $R = 0.029$.

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Retention of Chirality during Thermal Automerization of Methyl 1,2-Diphenylcyclopentane-1-carboxylate

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Many observations on single rotational epimerizations in optically active cyclopropanes reveal a preference of one group to rotate over another.[1] The strongest recorded preference involves methyl 1,2-diphenylcyclopropane-1-carboxylate, where the rotational propensity, $R_A = 18$, strongly favors rotation of the phenyl hydrogen carbon.[2] In terms of the well-known hypothesis of diradical qua intermediate protected by a barrier to reclosure of ~9 kcal/mol,[3] this observation is hard to explain.

A single example, 1-cyano-2-vinylcyclobutane ($R_A = 1.48$) reveals the phenomenon in a cyclobutane ring but at a reduced level.[4] No diastereomeric cyclopentanes have been examined, although thermal rearrangements of cyclopentane and two monosubstituted derivatives are reported.[5]

As depicted in Figure 1 for methyl 1,2-diphenylcyclopentane-1-carboxylate (**1**), the situation in cyclopentanes is qualitatively different owing to the accessibility of five conformations of an intermediary diradical, each protected against reclosure by at least one rotational barrier of the *n*-butane type.

Compound **1** commends itself for study for its close relation to the corresponding cyclopropane[2] and the radical-stabilizing effectiveness of its substitutents (estimated $E_a \sim 48$ kcal/mol vs. ~80 kcal/mol for cyclopentane).[6]

We report here its thermal epimerization with a surprisingly high degree of retained optical activity. Work is in progress to refine R_A by extrapolation to zero time and to establish the configurational relation required to identify which group has the higher rotational propensity.

Its synthesis, outlined in Figure 2, was thwarted by the failure of the most drastic conventional methods to effect hydrolysis of

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