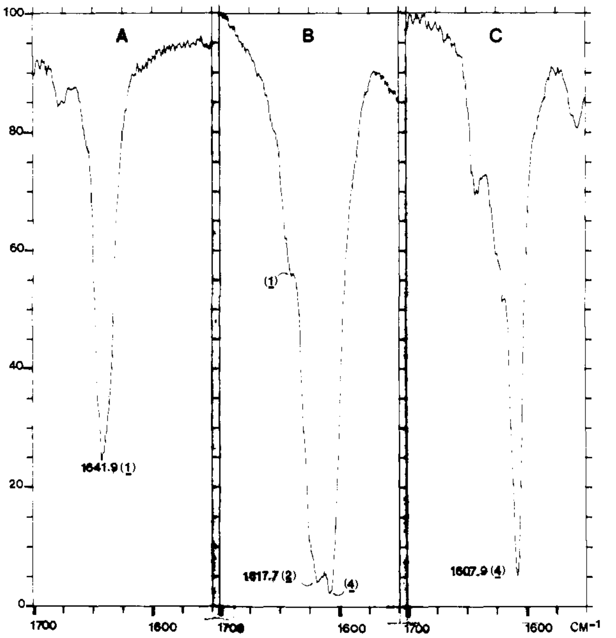

Figure 1. IR spectra (C═N stretch) of *N'-tert*-butylhexahydroazepine formamidine: (A) formamidine in THF; (B) formamidine in THF with *t*-BuLi at room temperature (t = 0 min); (C) formamidine in THF with *t*-BuLi at room temperature (t = 15 min).

α-amino carbanion and benzaldehyde in a 1:1 erythro–threo ratio) was obtained. Thus, in DME, the complex **2** proceeded to give a normal Cannizzaro reaction between benzaldehyde and *t*-BuLi. In fact, the exact same results were obtained in DME, in the absence of the azepine formamidine.[5,6]

The other solvents depicted in Table I furnished clear, lightly colored solutions when the formamidines were treated with *tert*-butyllithium. The formation of the precipitates (in DME) and their lack of D incorporation indicate strongly that these species are complexes (**2**) that involve only formamidine, the base, and solvent. The unique behavior of DME is attributed to its bidentate nature, which forms a very stable complex and does not allow dissociation to **3** which exposes one of the lithium sites of coordination. When the latter occurs, metalation ensues leading to carbanion **4**. This premise is reinforced by the behavior of the other solvents in Table I. Both ether and DMTHF are sterically encumbered ligands that form weaker solvates thus allowing dissociation (**2** to **3**) and ultimately metalation. The lower rates of metalation in THF for the diethyl- and piperidinylformamidines probably reflect entropic factors.[7]

The formation of complex **2** and the resulting carbanion **4**, except in DME, was also observable in the infrared. The salient features are given in Figure 1, which shows the behavior of the formamidine of hexahydroazepine. Thus, the C═N stretch for the formamidine in THF shows a band at 1641.9 cm^{-1} (curve A), and a new band appears at 1617.7 cm^{-1} <1 min after addition of *t*-BuLi (curve B) along with another band at 1607.9 cm^{-1} due to the carbanion. After 15 min, the complex at 1617.7 cm^{-1} is virtually gone, leaving only the carbanion at 1607.9 cm^{-1} (curve C).[8] In DME the addition of *t*-BuLi to the azepine formamidine after removal of solvent gave a viscous oil[6] that exhibited only the *t*-BuLi–formamidine complex **2** as a borad band at 1636 cm^{-1} but no carbanion band at lower wavenumbers. This spectral behavior for formamidines is in good agreement[2] with the absorptions of hindered tertiary amides (1650 cm^{-1}), *sec*-butyllithium-complexed amides (1625 cm^{-1}), and the α-carbanions derived from these amides (1588 cm^{-1}).[2]

Table II. Metalation of Piperidine-TBF in Ether-THF Mixtures[a]

ether, %	10	20	35	50	80	90
THF, %	90	80	65	50	20	10
D, %[b]	32.2	43.4	53.4	85.6	94.4	97.7

[a] Reactions performed at −25 ±5 °C for 20 min using 1.1 equiv of *t*-BuLi and quenching with D_2O. [b] Determined by mass spectroscopy.

Finally, to further support the premise that dissociation of the complex is necessary prior to metalation (**2** to **3**), the piperidine formamidine was treated with *t*-BuLi at −25 °C for 20 min using different ratios of ether and THF (Table II). The dramatic increase in D incorporation on going from 10% ether–THF to 90% ether–THF argues strongly for the poorer ligand properties of ether (thus greater dissociation to **3**) as compared to THF.

The observations reported here coupled with those obtained by Beak are consistent with the notion of a complex prior to metalation; this process may be halted or allowed to proceed depending on the solvents employed. This selectivity will undoubtedly find use in syntheses involving dipole-stabilized anions.

Acknowledgment. We are grateful to the National Science Foundation for support of this work and to the National Institutes of Health for a postdoctoral fellowship (to L.M.F.). Warm thanks are due to Professor J. R. Norton, Jeffrey M. Sullivan, and Bruce D. Martin for their infrared capabilitities and assistance. Finally, we acknowledge helpful discussions with Professor Peter Beak and his kind willingess to delay his paper so that we could publish simultaneously.

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(5) When a 0.5 M *t*-BuLi solution in DME was added (−78 to −25 °C) to benzaldehyde, quenched, and worked up, there was isolated (~50%) a 3:1 ratio of benzyl alcohol and benzyl benzoate.

(6) Additional evidence for complexed *t*-BuLi in **2** was also gathered by titration (*sec*-BuOH, phenanthroline as indicator) and showed roughly 40% *t*-BuLi present after 20 min at −25 °C.

(7) All reactions were run for 20 min. For longer reaction time with *t*-BuLi, much higher deuteration levels were achieved.

(8) The carbanion band in Figure 1 (C) was verified by D_2O quench of the spectrum sample furnishing the α-D azepine formamidine in 70% yield.

Tetralithiotetrahedrane: Is It a Minimum?[†]

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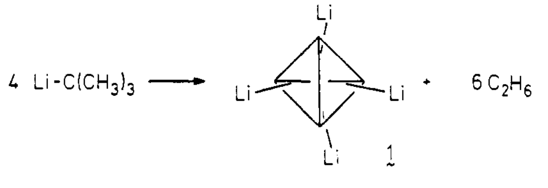
Recent quantum mechanical calculations have suggested that lithiocarbons possess structures having no precedent in hydrocarbon chemistry.[1,2] Probably the most striking of the unusual structures proposed for lithiocarbons are those of the tetralithiotetrahedranes. Schleyer and co-workers have found that calculations favor the face-lithiated tetralithiotetrahedrane, **1**, over the classical corner-lithiated tetralithiotetrahedrane by 65.2 kcal at the STO-3G level.[3] Although **1** is the lowest energy tetralithiotetrahedrane, other C_4Li_4 isomers lie lower in energy.[3] Using eq 1, Schleyer and co-workers suggested that **1** possesses little or



(1)

H_r

STO-3G 1.9 kcal

[†] This work was conducted under the auspices of the U.S. Department of Energy.

(1) A complete list of references would be too long to list here; the papers contained in ref 2, however, provide extensive citations.

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Table I. Optimized Parameters for **1** and **2**[a]

	symmetry	parameters	basis set			
			STO-3G	4-31G/5-21G	6-31G*/6-31G	6-31G*/6-31G (no p)
1	T_d	energy	−178.74371	−180.75555	−181.04382	−180.94938
		R(C-C)	1.592	1.609	1.541	
		R(C-Li)	1.937	2.018	1.990	
2	D_{2d}	energy	−178.80333	−180.81171	−181.05596	−180.91899
		R(C-C)	1.374, 1.972	1.362, 2.065	1.354, 1.876	
		R(C-Li)	1.858, 2.075	1.940, 2.214	1.917, 2.169	

[a] Energies are in au, bond lengths in Å.

Table II. Calculated Vibrational Frequencies

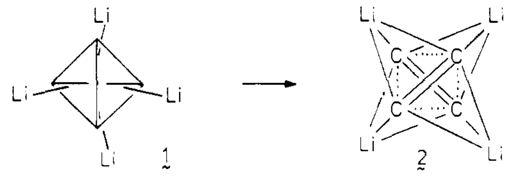
isomer	basis set	calculated frequencies, cm^{-1}			
1 (T_d)	STO-3G	226i (1e)	274 (1t$_1$)	352 (1t$_2$)	658 (2e)
		737 (2t$_2$)	793 (1a$_1$)	976 (3t$_2$)	1290 (2a$_1$)
	4-31G/5-21G	153i (1e)	249 (1t$_1$)	295 (1t$_2$)	612 (2e)
		616 (2t$_2$)	656 (1a$_1$)	846 (3t$_2$)	1076 (2a$_1$)
2 (D_{2d})	STO-3G	235 (1e)	336 (2e)	340 (1a$_1$)	346 (1b$_1$)
		411 (1b$_2$)	535 (1a$_2$)	541 (2a$_1$)	602 (3e)
		641 (2b$_1$)	696 (2b$_2$)	770 (3a$_1$)	801 (4e)
		1367 (3b$_2$)	1631 (4a$_1$)		

no ring strain.[3,4] This is in sharp contrast with a ring strain for tetrahedrane of 195 kcal, calculated in a similar fashion. Additionally, ref 3 offers some preliminary experimental data regarding the possible synthesis of **1**.

Since Schleyer's initial investigation, programming and computer technology have progressed to the point where force-constant calculations for molecules the size of C_4Li_4 are now feasible. Furthermore, calculations for C_4Li_4 isomers using bigger basis sets than before are now easily performed. These advances warrant a closer examination of the C_4Li_4 surface than was previously possible. This communication is a preliminary account of a larger investigation of the C_4Li_4 potential-energy surface, which will be published in full at a later date. The conclusions presented here suggest that tetralithiotetrahedrane is not a minimum in the potential-energy surface and, hence, cannot be synthesized and isolated.

The results of energy optimization and force-constant calculations are summarized in Tables I and II, respectively. These calculations were carried out with the STO-3G[5a] and 4-31G/5-21G[5b,c] basis sets, using the program HONDO5.[6] Additionally, energy-optimization calculations were performed with a 6-31G*/6-31G basis set, which uses the 6-31G*[7] and 6-31G[5c] functions for carbon and lithium, respectively. Finally, lithium p orbitals were deleted from the 6-31G*/6-31G basis set to form the 6-31G*/6-31G (no p) basis set. Calculations with this basis set were performed at the 6-31G*/6-31G optimized geometry.

At the STO-3G and split valence levels, **1** has two negative force constants. These yield the imaginary vibrational frequencies found in Table II. Displacement of **1** along one the eigenvectors associated with the negative force constants, followed by geometry optimization, yielded the structure **2**. Inspection of the other eigenvector indicated that the decomposition of **1** can lead to any one of the three degenerate isomers shown in Figure 1. The force-constant calculations in Table II verify **2** as a minimum at these levels of theory. Examination of the molecular orbitals of **2** reveal that it is separated from two molecules of dilithioacetylene by an MO crossing, as are **1** and dilithioacetylene; **2** and **1**, however, are not separated by an MO crossing.



(2)

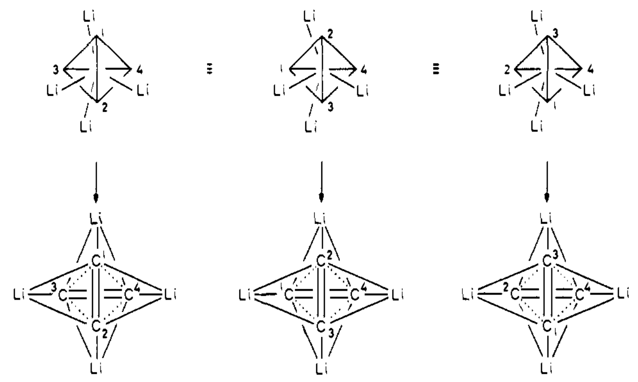


Figure 1. The three degenerate pathways for the conversion of **1** to **2**.

Structure **2**, of D_{2d} symmetry, lies 37.4, 35.2, and 7.6 kcal below **1** at the STO-3G, 4-31G/5-21G, and 6-31G*/6-31G levels, respectively. Although calculations including d orbitals on carbon yield a smaller energy difference between **1** and **2** than basis sets without d orbitals on carbon,[8] the 6-31G*/6-31G (no p) calculations imply that improvement of the lithium basis set will preferentially stabilize **2**. As a result, I expect that the inclusion of d orbitals on lithium would favor **2** more than **1**. It appears, then, that **1** would remain a hilltop with even larger basis sets. The extraordinarily long and, presumably, weak C–C bonds in **2** of 1.876 Å suggest that this structure is artificially stabilized at the SCF level because occupied and unoccupied MO's are not able to cross. Higher levels of theory are not expected to impose this spurious barrier, and it seems likely that, in reality, **2** would decompose to two molecules of dilithioacetylene or a dilithioacetylene dimer.[9]

The findings reported in this communication predict that **1** cannot be isolated as a stable compound; therefore, the thermo-

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(9) At the 6-31G*/6-31G level, **2** lies 34.8 kcal above two molecules of dilithioacetylene; however, a simple dilithioacetylene dimer of D_{2d} symmetry, which is topologically similar to **2**, is the lowest energy C_4Li_4 structure yet found. **2** lies 91.2 kcal above this dimer. I thank a referee for pointing out the relevance of these results.

dynamic stability of **1**, implied by eq 1, is not mirrored by a corresponding increase in kinetic stability. Indeed, because tetrahedrane itself is predicted to be a minimum,[10] substitution of lithium for hydrogen results in a dramatic kinetic destabilization of the tetrahedral framework.

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A Simple One-Step Route to a Transition-Metal Complex Containing a Phosphorus–Phosphorus Double Bond. Synthesis and X-ray Crystal Structure of {*trans*-Bis[bis(trimethylsilyl)methyl]diphosphene}-bis[tetracarbonyliron(0)][‡]

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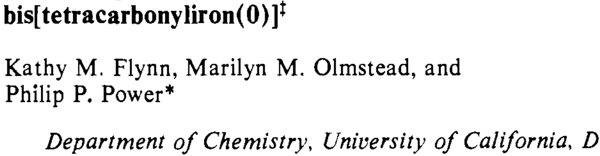
Received December 20, 1982

Multiple bonding between the heavier main-group elements has long been thought unlikely for a variety of reasons, which usually involve orbital overlap and thermodynamic considerations.[1] Recently, a number of publications have shown that, by using suitable ligands, compounds containing Si–Si,[2] P–P,[3,4] As–As,[5,6] and Sb–Sb[7] multiple bonds can be stabilized under ambient conditions. However, structural reports in which the multiple bond is unbridged by other species remain quite rare.[3] Here we report (a) a simple one-step, moderate yield (50%) synthesis of a transition-metal complex of the phosphene $(Me_3Si)_2CHP{=}PCH(SiMe_3)_2$ in which both phosphorus centers behave as simple two electron donors and (b) its spectroscopic (NMR, UV–vis, and IR) and X-ray crystallographic characterization.

The synthesis of the title compound was via the route shown in eq 1. {*trans*-Bis[bis(trimethylsilyl)methyl]diphosphene}bis-



(1)

1, 50%

[tetracarbonyliron(0)], [*trans*-{$[Fe(CO)_4]_2[PCH(SiMe_3)_2]_2$}] (**1**), was isolated by slow addition of $Na_2Fe(CO)_4 \cdot 1.5$-dioxane (1.29 g, 3.8 mmol) to a stirred solution of dichlorobis(trimethylsilyl)methylphosphine (1 g, 3.8 mmol) in diethyl ether (30 mL) at 0 °C. The solution gradually became red and was allowed to warm to room temperature. Stirring was continued for 12 h, and the volatiles were removed in vacuo. The residue was redissolved in *n*-hexane (20 mL) to give a deep red solution. Filtration and subsequent cooling to −20 °C gave the product as dark red-brown crystals (1.4 g, 50%, mp 145–147 °C).

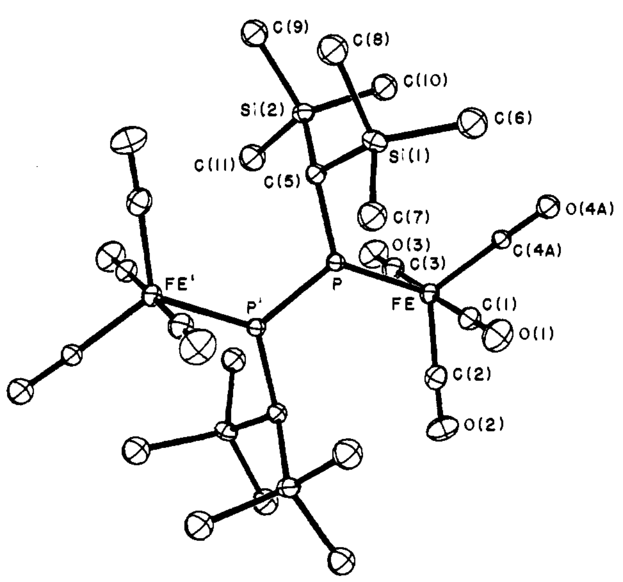


Figure 1. Computer-generated representative diagram of $[Fe(CO)_4]_2[PCH(SiMe_3)_2]_2$. Important bond distances (Å) and angles (deg) are P–P′ = 2.039 (1), P–C(5) = 1.821 (2), Fe–P = 2.226 (1), C(5)PP′ = 107.1 (1), FePC(5) = 125.8 (1), FePP′ = 126.6 (1).

The complex can be handled in air and shows no apparent decomposition after several days exposure to the atmosphere. It is soluble in hydrocarbon solvents, affording solutions that are also air-stable. The complex is thermally stable, melting at 145–147 °C and not decomposing until >200 °C.

The structure of the complex has been solved by single-crystal X-ray diffraction and is illustrated in Figure 1.[8] It consists of isolated neutral molecules with no short intermolecular contacts. The molecule has a center of inversion as crystallographically required. Each iron atom exhibits trigonal-bipyramidal coordination to four carbonyl ligands and one (equatorial) phosphorus atom with Fe–P of 2.226 (1) Å. Compound **1** is the first reported example of a complex in which the group 5b multiple bond is unbridged by a transition-metal atom. The geometry at each phosphorus atom is planar, and this planarity extends to include the two $Fe(CO)_2$(equatorial) moieties. The angles at phosphorus (figure) are distorted from the pure trigonal values with the C(5)PP′ angle = 107.1 (1)°; this is wider than the 102.8 (1)° found in bis(2,4,6-tri-*tert*-butyldiphosphene) (**2**), the only other structurally characterized compound containing an unbridged P–P double bond.[3] The P–P′ distance in **1**, 2.039 (1) Å, is ca. 0.2 Å shorter than single P–P bond lengths and very close to the value of 2.034 (2) Å found in **2**.[10] The phosphorus lone-pair involvement

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[‡] No reprints available.

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(8) A red-brown prism of **1** was cut to the dimensions 0.25 × 0.50 × 0.37 mm and mounted on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. With Mo Kα radiation (λ 0.71069 Å) and crystal cooled to 140 K, crystal data were as follows: triclinic, space group $P\bar{1}$ (No. 2); a = 9.090 (2) Å, b = 9.551 (3) Å, c = 11.830 (4) Å; α = 109.74 (2)°, β = 91.73 (2)°, γ = 115.52 (2)°; Z = 1; μ = 10.45 cm^{-1} (range of absorption correction factors 1.1–1.2). Data were collected to $2\theta_{max}$ of 55° with an ω-scan technique. A total of 3922 unique data were collected, of which 3493 had $I > 3\sigma(I)$. No absorption or extinction corrections were performed. Scattering factors and corrections for anomalous scattering were from Vol. IV of the International Tables. Computer programs were those of SHELXTL, version 3, July 1981 package. The structure was solved by direct methods. The hydrogen bonded to C(5) was located on a difference Fourier map and allowed to refine isotropically. With anisotropic thermal parameters for non-hydrogen atoms and with the methyl hydrogen atoms riding on the bonded carbon, R = 0.035 and R_w = 0.035. One of the equatorial carbonyl groups, C(4)–O(4), had three-fold disorder and was refined with occupancies as least-squares parameters C(4A)–O(4A) 36%, C(4B)–O(4B) 34% and C(4C)–O(4C) 30%. Only one of these carbonyl groups, C(4A)–O(4A), is shown in Figure 1. Atomic coordinates, thermal parameters, and tables of bond lengths and angles are available as supplementary material.

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