tions. Using the calculated force field for $Ni(CO)_3(H_2)$ and this ratio, the angle between the carbonyl ligands was found to be 115.6 ± 1.0°.[23] To further check, intensities were calculated for isotopically labeled $Ni(CO)_3(H_2)$ in two instances and compared with observed spectra. The extent of isotopic substitution was determined from a fit of the spectrum of $Ni(CO)_4$ before photolysis. The agreement was very good, particularly among those modes that were not totally symmetric. In doing this calculation we acknowledge that calculating bond angles for $M(CO)_n$ fragments can especially be in error if there are other π-bonding ligands attached to the metal.[24] The π bonding of hydrogen may not seriously affect the carbonyl intensities because we do not note any coupling of the modes as judged by isotope effects. Thus, the structure of the carbonyl fragment must be viewed as intermediate between trigonal and tetrahedral. To summarize discussions that have already occurred, the hydrogen probably bonds to this fragment in a η^2 fashion, making the observation of the the hydrogen-containing vibrational features difficult.

Experimental Section

Matrices were formed either by depositing a gas mixture which already contained $Ni(CO)_4$ or by subliming $Ni(CO)_4$ into a stream of matrix gas just prior to deposition at liquid-helium temperatures. One liter of a gas mixture containing $Ni(CO)_4$ was made by using Ar and hydrogen as diluent gases. These mixtures were made in a vacuum line which was pumped to 0.02 mmHg. To avoid contamination by residual atmospheres in the apparatus, the apparatus was flushed several times with argon. Typically, mixtures were made with 0.1 mol % of $Ni(CO)_4$ and concentrations of hydrogen between 10 and 20 mol %. Over the course of several hours, a dark deposit forms on the flask walls that is undoubtedly nickel metal formed by $Ni(CO)_4$ decomposition. Other than a band due to free CO, no peaks are noted in the carbonyl region of the infrared spectrum that can be attributed to other decomposition products of $Ni(CO)_4$.

Matrices were also formed by subliming $Ni(CO)_4$ into a matrix gas stream just prior to deposition. The temperature of the $Ni(CO)_4$ was maintained at close to -110 °C in order to assure a low doping level. When the rate of growth of peaks due to $Ni(CO)_4$ deposited in this manner are compared to those formed from gas mixtures, it is clear that the doping level is on the order of 0.1%. The infrared band due to $Ni(CO)_4$ was always symmetric and on the order of 4 cm^{-1} at half-height, also indicating that the sample was adequately isolated. Spectra were recorded by either a Beckman 4260 infrared spectrometer which is coupled to a Zenith Z-100 microcomputer or on a Perkin-Elmer 1760 Fourier Transform infrared spectrometer. Experimental details have been previously published.[5]

The methods used to obtain a energy-factored force field have been described elsewhere.[3] The ratio of intensities of the A_1 and E mode of the carbonyl stretches was measured after first fitting the band envelopes with a product function of Lorentzian and Gaussian line shapes. The areas of the fitted bands were calculated by a trapezoidal method.[5] The ratio of intensities at ν_{max} of the two absorptions observed for $Ni(CO)_3$ which was formed from $Ni(CO)_4$ varied considerably as a function of the matrix identity.[8] In order to guard against similar matrix effects in the spectrum of I, areas were measured of unresolved FTIR spectra in Ar and Kr matrices. The intensity ratio observed in Kr was within experimental error of those observed in Ar. Also, areas were obtained by similar procedures of unresolved FTIR spectra from matrices that ranged from 0.02% to 0.3% $Ni(CO)_4$ which were in good agreement with each other.

Acknowledgment. We gratefully acknowledge the helpful suggestions made by Dr. M. Poliakoff. Support for this work was provided by the donors of the Petroleum Research Fund, administrated by the American Chemical Society, and by the Research Council of the University of New Orleans. We wish to further acknowledge the Louisiana Quality Education Trust Fund, administered by the Louisiana Board of Regents, for funds for the purchase of the FTIR spectrometer.

Registry No. $Ni(^{12}CO)_3(H_2)$, 122382-64-3; $Ni(^{12}CO)_2{}^{13}CO(H_2)$, 122382-65-4; $Ni(^{13}CO)_3(H_2)$, 122382-66-5; $Ni(CO)_4$, 13463-39-3; H_2, 1333-74-0.

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(23) M. Poliakoff, in evaluating this paper, has pointed out that there is a simple equation which allows the calculation of a bond angle from intensity data for a tricarbonyl fragment. The acute angle between the 3-fold axis and the carbonyl groups, T, is given by $\tan(T) = \{I_e/I_a\}^{0.5}$ where I_e and I_a are the intensities of the E and A_1 modes, respectively. Application of this equation is in good agreement with the more empirically derived angle that we have calculated.

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Lithio(diphenylphosphino)methane–Tetramethylethylenediamine: Crystal Structure and NMR Studies of a Coordinatively Unsaturated, Monomeric Organolithium

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A crystal structure determination on the tetramethylethylenediamine (TMEDA) adduct of lithio(diphenylphosphino)methane has shown it to be a *monomeric* species, with tricoordinate lithium *terminally* bonded to the methylene group. The results of ^{13}C NMR studies are consistent with this; only one species is observed at all temperatures, presumably the monomer. ^1H NMR studies reveal that the α-methylene protons are nonequivalent at the lowest temperatures, consistent with the observed crystal structure and indicating slow inversion at carbon.

Organolithium compounds are important reagents in both organic and inorganic synthesis whose structures and aggregation states continue to surprise and confound researchers.[1] Initial studies revealed that organolithiums

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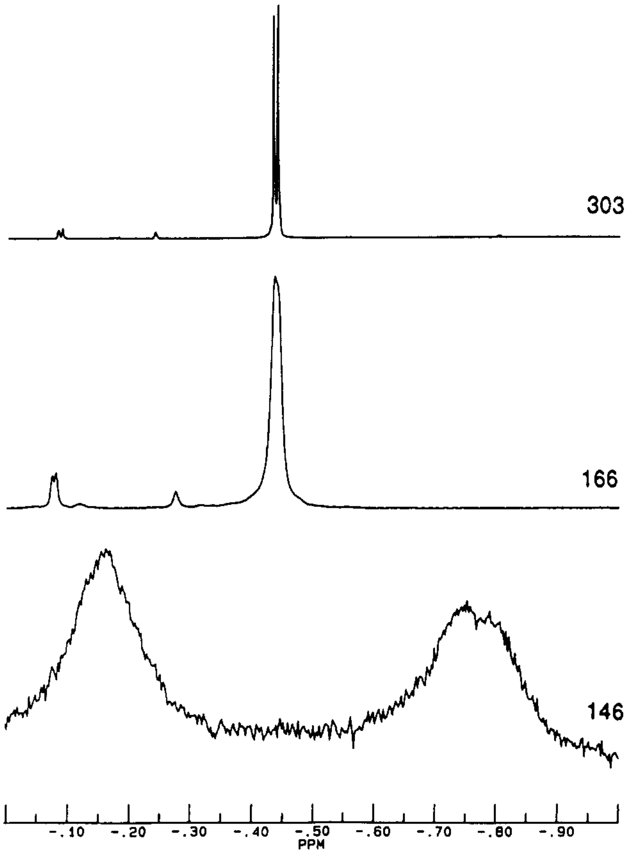

Figure 1. Proton NMR (300 MHz) of *CH_2Li* in 1·TMEDA dissolved in THF-d_8, at 146, 166, and 303 K.

are aggregated in solution with higher aggregates ($(RLi)_9$–$(RLi)_4$) observed in hydrocarbon solvents and lower aggregates ($(RLi)_4$–$(RLi)_2$) in ethereal or chelating solvents.[2] Monomeric organolithiums were rare and generally involved multihapto bonding or delocalized systems. More recently, several monomeric alkyllithium reagents have been characterized: *tert*-butyllithium in THF,[3] neopentyllithium in THF,[4] and a number of lithium reagents with pentamethyldiethylenetriamine (PMDTA).[5] In general, coordination of lithium in these species is four. Herein, we report the synthesis, NMR studies, MNDO calculations, and X-ray structure determination for lithio(diphenylphosphino)methane–tetramethylethylenediamine (TMEDA), a monomeric organolithium compound.

Reaction of methyldiphenylphosphine with (*n*-butyllithium-^{6}*Li*)–tetramethylethylenediamine dissolved in ether, overnight, yielded yellow crystals of 1·TMEDA that were isolated by filtration[6,7] (eq 1). These crystals decompose in air but are stable indefinitely when stored under argon. They are insoluble in pentane and ether but dissolve in THF.

Table I. Important Bond Distances (Å) and Bond Angles (deg) in 1•TMEDA

C(1)Li	2.155 (7)	LiC(1)P(1)	113.8 (2)
C(1)P(1)	1.752 (5)	C(1)P(1)C(2)	110.9 (2)
C(2)P(2)	1.867 (3)	C(1)P(1)C(8)	104.2 (2)
C(8)P(1)	1.835 (2)	C(2)P(1)C(8)	98.3 (1)
LiN(1)	2.110 (6)	N(1)LiN(2)	86.1 (3)
LiN(2)	2.167 (8)		

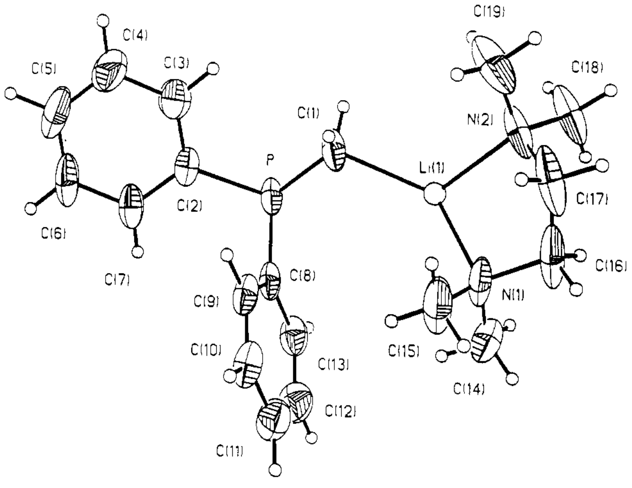

Figure 2. Molecular structure of 1·TMEDA.

$$Ph_2PCH_3 + n\text{-}BuLi{\cdot}TMEDA \rightarrow \underset{1{\cdot}TMEDA}{Ph_2PCH_2Li{\cdot}TMEDA} \quad (1)$$

Variable-temperature NMR spectroscopy was used to characterize the molecule in solution. While ^{31}P–^6Li coupling has been reported for lithiobis(diphenylphosphino)methane[8] the ^{31}P NMR spectrum (101.23 MHz, broad band decoupled, THF-d_8) of 1·TMEDA consisted of a singlet at δ −1.94 ppm and the ^6Li NMR spectrum also was a narrow singlet (line width < 5 Hz) between 200 and 303 K. The observation of coupling between ^6Li and ^{13}C in ^{13}C NMR of organolithium compounds, developed in these laboratories, has been a useful tool in the assignment of aggregation.[9] Study of the ^{13}C NMR of 1·TMEDA using THF-d_8 solutions (0.1 M) between 200 and 303 K showed little variation of the ^{13}C shifts, implying that the composition of the sample did not change with tempera-

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(7) Preparation of lithio(diphenylphosphino)methane: methyldiphenylphosphine (1.0 g, 5 mmol) was added to diethyl ether (20 mL, freshly distilled from sodium/potassium ketyl) followed by TMEDA (1 mL). Then, *n*-butyllithium in hexanes (2.5 mL, 2.4 M, 6 mmol) was added with stirring. After storing undisturbed overnight, crystals had formed and the mixture was filtered under argon and washed with pentane, yielding 0.78 g of yellow crystals. ^1H NMR (250 MHz, 303 K, THF-d_8); δ −0.37 (d, $^2J_{PH}$ = 3.36 Hz, CH_2Li), 2.16 (s, NMe_2), 2.31 (s, NCH_2), 6.89 (t, $^3J_{HH}$ = 7.3 Hz, PhP, para), 7.02 (t, $^3J_{HH}$ = 7.6 Hz, PhP, meta), 7.46 (m, PhP, ortho). ^{13}C NMR (75.46 MHz, 303 K, Waltz decoupled, THF-d_8); δ 2.19 (d, $^1J_{PC}$ = 46.2 Hz, PCH_2Li), 46.2 (s, NMe), 58.8 (s, $N(CH_2)_2$), 125.0 (s, PhP, meta), 127.1 (s, PhP, para), 132.3 (d, $^2J_{PC}$ = 16.5 Hz, PhP, ortho), 155.2 (d, $^1J_{PC}$ = 24.3 Hz, PhP, ipso). ^{31}P NMR (101.3 MHz, 200 K, BB decoupled, THF-d_8); δ −1.9.

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ture. Further, there was no evidence for coupling between directly bonded ^{13}C and ^{6}Li. Yet, at the lowest temperatures used both the $^{13}C_\alpha$ and TMEDA ^{13}C resonances underwent selective broadening compared to the other resonances. It is likely that this reflects the operation of a fast-exchange process that intercoverts different solvates of 1 (eq 2). Consistent with this hypothesis, the $^{13}C_\alpha$ NMR

$$Ph_2PCH_2Li{\cdot}TMEDA \xrightleftharpoons{THF} Ph_2PCH_2Li{\cdot}TMEDA/THF \quad (2)$$

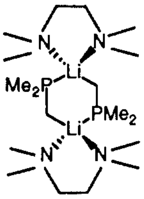
signal of 1 prepared with an excess of THF and no TMEDA was no longer exchange-broadened. In the ^1H NMR spectra of 1·TMEDA in THF-d_8 at the lowest temperatures the α-methylene protons are nonequivalent (cf. Figure 1), indicating an unsymmetrical structure. On warming the sample, these two broad signals coalesce and give rise to a sharp doublet by room temperature. A spectrum unperturbed by dynamic effects could not be obtained because the sample precipitated; hence a complete dynamic analysis was not possible. However, from the coalescence temperature of 160 K and the chemical shift difference of 180 Hz observed at the lowest temperature we compute $\Delta G^{\ddagger}_{160K}$ = 7 kcal/mol.

The results of a crystal structure determination for 1·TMEDA are presented in Figure 2 and Table I.[10] The complex is monomeric, and the lithium atom is tricoordinate. A possible fourth coordination from a phenyl group as observed for $[Li(C(SiMe_2Ph)_3)(THF)]$[11] was considered. However, in the crystal the closest phenyl carbon–lithium distance is 3.6 Å, too far for any significant interaction. The methylene hydrogens are nonequivalent, consistent with the proton NMR results. The Li–C distance, 2.155_7 Å, and the Li–N distances, 2.110_6 and 2.167_8 Å, are comparable to those observed in 2, 3, and similar P-substituted compounds.[12,13] The P–CH_2 distance, 1.752_2 Å, is significantly shorter than the P–C_{Ph} distances, 1.867_3 and 1.835_2 Å. Most likely this difference is due to delocalization of the carbanion lone pair on to the phosphorus. Note that the longer P–C_{Ph} bond distance is antiperiplanar to lithium (dihedral angle = 170.1°).

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

atom	*x*	*y*	*z*	U^a
P	3388 (1)	1490 (1)	5988 (1)	39 (1)
C(1)	2569 (3)	375 (3)	5906 (4)	48 (2)
C(2)	2124 (3)	2253 (3)	7335 (3)	46 (2)
C(3)	1119 (4)	1515 (4)	8481 (4)	94 (2)
C(4)	220 (5)	1998 (4)	9549 (4)	113 (3)
C(5)	323 (4)	3239 (4)	9480 (4)	83 (2)
C(6)	1299 (4)	3994 (4)	8364 (3)	64 (2)
C(7)	2209 (3)	3514 (3)	7291 (3)	47 (2)
C(8)	3257 (3)	3133 (3)	4398 (3)	39 (1)
C(9)	1909 (3)	4050 (3)	4207 (3)	43 (2)
C(10)	1833 (3)	5239 (3)	2973 (3)	51 (2)
C(11)	3109 (3)	5557 (3)	1895 (3)	59 (2)
C(12)	4456 (3)	4682 (3)	2053 (3)	60 (2)
C(13)	4525 (3)	3481 (3)	3290 (3)	46 (2)
Li(1)	3769 (5)	−270 (5)	4150 (5)	46 (3)
C(14)	5023 (5)	1470 (4)	1061 (3)	87 (3)
C(15)	2436 (4)	2255 (4)	2012 (4)	83 (3)
N(1)	3660 (3)	983 (3)	2059 (3)	64 (2)
C(16)	3354 (4)	12 (4)	1693 (4)	85 (3)
C(17)	2234 (4)	−827 (4)	2885 (4)	85 (3)
N(2)	2747 (2)	−1711 (3)	4152 (3)	60 (2)
C(18)	3806 (3)	−3031 (3)	4022 (4)	75 (3)
C(19)	1515 (3)	−2116 (4)	5392 (5)	87 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.



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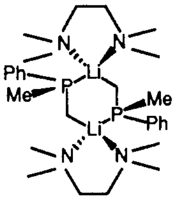

3

Our results complete the series dimethylphosphino-[12a] (2), methylphenylphosphino-[12a] (3), and diphenylphosphino-substituted methyllithium. Compounds 2 and 3 are phosphorus-bridged dimers when crystallized with TMEDA. Molecular weight measurements in benzene solution, however, indicate 1–3 are monomeric and coordinatively unsaturated.[12a] We observe no evidence for dimers in THF, consistent with expectations for the more strongly coordinating solvent, but the structure we have determined is most likely that of the TMEDA-solvated monomer observed in benzene. While the authors ascribe the equatorial positioning of the phenyl groups in 3 to steric effects, this also is electronically favorable, placing the more electronegative phenyl group antiperiplanar to the lithium atom. Finally, the monomeric nature of 1·TMEDA and the increased reactivity of organolithiums in lower aggregation states[15] may rationalize the unusual basicity in the reaction of 1·TMEDA with dimethylfulvene observed by Schore.[14]

The monomeric nature of 1·TMEDA is surprising. It is not a steric effect, since experiments with $Ph_2PCH(Ph)Li{\cdot}TMEDA$ show an equilibrium between monomers and dimers in THF solution. It is also unlikely that just lower donor capacity of the Ph_2Pt groups can rationalize this; note that with sulfur 4 is a heteroatom-bridged dimer and 5 is CH–Li–CH-bridged.[16] Clearly, more work is

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(10) Lithio(diphenylphosphino)methane crystallizes in the centrosymmetric, triclinic space group *P*<<bar1. The unit cell parameters were determined to be *a* = 10.118 (4) Å, *b* = 10.879 (4) Å, *c* = 11.293 (5) Å, α = 61.24 (3)°, β = 65.74 (4)°, and γ = 68.74 (3)° by least-squares fitting to the positions of 25 independent reflections in the range 24° ≤ 2θ ≤ 26°. This unit cell contains two asymmetric units of molecular formula $C_{19}H_{28}N_2Li$ in a volume of 972.05 (0.77) Å^3, which produces a calculated density of 1.10 g/cm^3. A total of 2989 reflections were recorded in the range 3.5° ≤ 2θ ≤ 47° at −100 °C under a stream of dry nitrogen with a Nicolet R3m/E crystallographic system using the θ:2θ scan routine and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). A total of 2543 unique reflections were observed by using the criterion $F_o \geq 2.5\sigma(F_o)$. After Lorentz and polarization corrections, the structure was solved by the SHELXTL 5.1 programs. All non-hydrogen atoms were refined anisotropically. The approximate location of all hydrogen atoms was determined by Fourier difference syntheses. In the final stages of refinement all of the hydrogen atoms except those attached to C(1) were placed in calculated positions and allowed to ride with the atom to which they are attached. The hydrogens attached to C(1) were refined as normal atoms, but the distance to C(1) was constrained to be within 0.97 ± 0.03 Å. The final agreement factors are *R* = 0.059 and weighted *R* = 0.070 for 216 independent parameters where weighted $R = |\sum(w\Delta^2)/\sum(wF_o^2)|^{1/2}$, where $\Delta = |F_o - F_c|$, and the weighting scheme is $w = 1/|\sigma^2(F_o) + 0.0002(F_o^2)|$. Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters along with a computer-generated plot of the crystallographic asymmetric unit with atom labels are given in the supplementary material.

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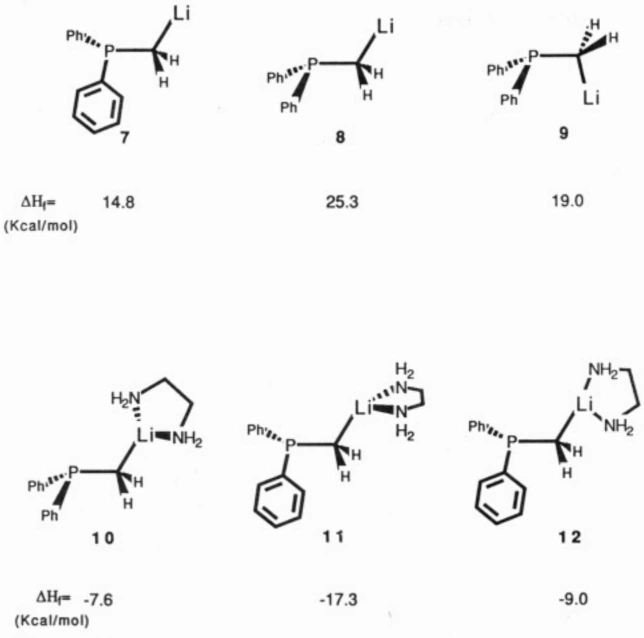
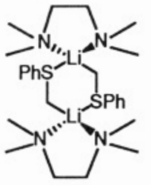


Figure 3.

necessary before one may a priori predict aggregation states of organolithiums.



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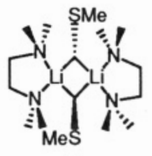
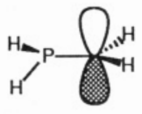


5

Ab initio calculations have been reported for $CH_2PH_2^-$ (**6**).[17] In the most stable conformer for **6**, the P–H bond, arranged for hyperconjugation, is stretched 0.04 Å relative to the hydrocarbon and the P–C bond is 0.09 Å shorter than in methylphosphine (P–C = 1.73 Å in **6** and 1.82 Å in PH_2CH_3). Like **6**, **1**·TMEDA is unsymmetrical: one phenyl group bonded to phosphorus is antiperiplanar to lithium. This bond is 0.03 Å longer (1.867_3 vs 1.835_2 in **6**). The phosphorus–methylene bond (1.752_5 Å) is significantly shorter than the P–phenyl bonds (average 1.85 Å). In order to investigate these effects further we have calculated the energies for a number of geometries of **1** with and without TMEDA using the MNDO approximation.[18] The lowest energy MNDO structures have lithium antiperiplanar from one of the phenyl groups as in the crystal structure (Figure 3). Indeed, without TMEDA the MNDO structure closely resembles that of the crystal. When the TMEDA is included in the calculation, the structure does not change too significantly. However, the TMEDA is rotated approximately 90° relative to the crystal structure, and this new structure is predicted to be 8.3 kcal/mol lower in energy. There is one significant shortcoming of the MNDO calculations: the calculated P–Ph bond distances are 0.1 Å too short (calculated = 1.74 Å, experimental = 1.85 Å).



6

In summary, **1**·TMEDA crystallizes as a monomer, with a shortened P–CH_2 bond reflecting the stabilization by phosphorus of the carbanion. In THF solution **1**·TMEDA likely is monomeric, and in toluene there exists an equilibrium between dimer and monomer.[12a] Studies are in progress to further delineate the aggregation states of organolithium compounds and the nature of the forces that determine these.

Acknowledgment. This research was supported by the National Science Foundation Grant No. 8304636 and in part by the Goodyear Tire and Rubber Co. Purchase of high-field NMR equipment was also financed in part by grants from the National Science Foundation. The work at Brown University was supported by the NIH through Grants GM-35982 and CA-01330. We thank Dr. Charles Cottrell, Central Campus Instrumentation Center, for technical consulting and Dr. Marc McDougal for some of the starting materials.

Registry No. 1·TMEDA, 72400-82-9; 1-^{6}*Li*·TMEDA, 122519-54-4; *n*-butyllithium-^{6}*Li*, 20535-67-5; methyldiphenylphosphine, 1486-28-8.

Supplementary Material Available: Tables atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates and temperature factors and MNDO calculations (19 pages); a listing of structure factors (17 pages). Ordering information is given on any current masthead page.

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