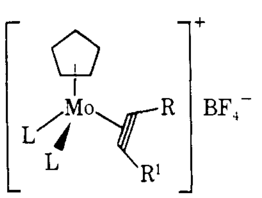
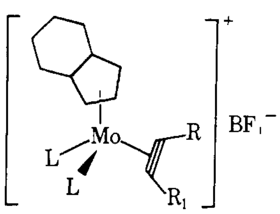
which then undergoes an insertion reaction to give the observed η^3-crotyl species. In agreement with this suggestion reaction



1, L = P(OMe)$_3$



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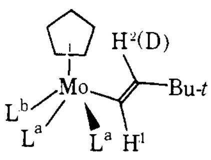

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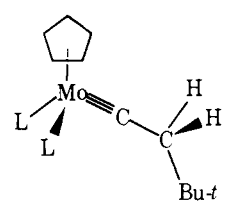

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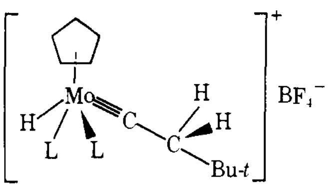
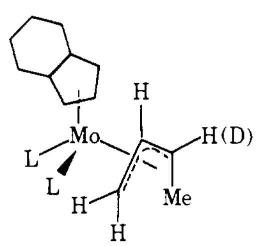


5, L = P(OMe)$_3$



6, L = P(OMe)$_3$

with $NaBD_4$ proceeds regioselectively to give **6** with deuterium incorporated in the illustrated position adjacent to the methyl group. A related β-allylic elimination reaction forming a η^3-crotyl complex has been observed[7] on heating the E isomer of Ir[C(Me)=CHMe]COL_2; however, in contrast to the molybdenum system the Z isomer undergoes a *cis*-β-vinyl H elimination to form the corresponding hydride and but-2-yne.

Acknowledgment. We thank the S.R.C. for support.

References and Notes

(1) Reaction (room temperature, CH_2Cl_2) of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ or $[Mo(CO)_3(\eta^5\text{-}C_9H_7)]_2$ with $AgBF_4$ in the presence of an excess of an acetylene affords a silver mirror, and the cations $[Mo(CO)(\eta^2\text{-}RC_2R^1)_2(\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7)]^+BF_4^-$ ($R = R^1 = H$; $R = R^1 = Me$; $R = Bu\text{-}t$, $R^1 = H$; $R = Me$, $R^1 = H$; $R = Ph$, $R^1 = H$; $R = R^1 = Ph$), which on treatment (room temperature, CH_2Cl_2) with $P(OMe)_3$ (excess) gives the highly colored cations **1** and **2** in good yield. The ^1H NMR spectrum (20 °C, CD_3NO_2) of, for example, $[Mo(\eta^2\text{-}MeC_2Me)[P(OMe)_3]_2(\eta^5\text{-}C_9H_7)]^+BF_4^-$ shows a sharp triplet ($^4J_{HP} = 1.0$ Hz.) at τ 7.7 (MeC≡C) collapsing reversibly (coalescence temperature, in $(CD_3)_2CO$ at −40 °C) to two resonances (τ 7.3 (3 H, brs), 8.4 (3 H, br s)) on cooling, which suggests that acetylene propellor rotation occurs; the observation of ^{31}P coupling excludes acetylene dissociation. The coalescence temperature of the corresponding $\eta^5\text{-}C_5H_5$ substituted cation is even lower (>−90 °C), which is interesting in view of the report[2] that the ^1H NMR spectrum ($(CD_3)_2CO$) of $[Mo(\eta^2\text{-}MeC_2Me)(diphos)(\eta^5\text{-}C_5H_5)]^+PF_6^-$ collapses to a single MeC≡C signal only at 110 °C.
(2) One example of this type of cation has been recently reported (J. A. Segal, M. L. H. Green, J. C. Daren, and K. Prout, *J. Chem. Soc. Chem. Commun.*, 766 (1976)) the synthesis following a less accessible route via bis(arene)molybdenum chemistry.
(3) Satisfactory elemental analyses, NMR spectra, and mass spectra have been obtained for all the complexes described.
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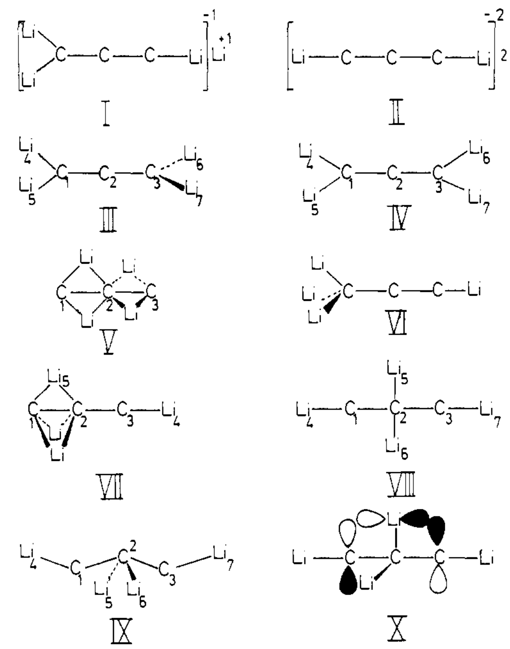
The Curious Structure of the Lithiocarbon[1] C_3Li_4

Sir:

C_3Li_4, prepared by lithiation of propyne by *n*-butyllithium,[2d,3] is a readily available lithiocarbon.[1] Only the most general information is available concerning the structure of this species. C_3Li_4 reacts to give either allene- or propyne-type products depending on the reagents and the conditions.[2d] This suggests an open rather than a cyclic arrangement of the carbon atoms. The IR absorption band of C_3Li_4 in the 1700-cm^{-1} region has been interpreted in terms of formulation I or II.[2d,3]



We have used ab initio molecular orbital calculations[4] to investigate possible C_3Li_4 structures. Complete geometry optimizations within each assumed symmetry were carried out using the minimal STO-3G basis set.[4b] Single point calculations using these optimized geometries followed, employing the split valence 4-31G (for carbon)[4c] and 5-21G (for lithium)[4d] bases. Our earlier work has shown that polylithio derivatives adopt highly unconventional geometries;[5] the same trend was expected in the present search. Nevertheless, we began with the lithiated analogue of allene, III. Although III proved to be a local minimum when optimized within the constraint of D_{2d} symmetry, the energy compared unfavorably with that of other structures. The *planar* D_{2h} allene (IV) (with four π electrons), which had nearly the same bond lengths and angles, was more stable by 0.5 kcal/mol at the 4-31G/5-21G level (Table I). The theoretical estimates for the rotational barrier in allene are between 27 and 92 kcal/mol;[6] experimental values of ~46 kcal/mol have been reported for 1,3-dialkylallenes.[7] Lithiation is thus able not only to reduce the D_{2d}-D_{2h} energy differences dramatically, but also to reverse the normal order of stability. Similarly, 1,1-dilithioethylene has been found to prefer the perpendicular, rather than the normal planar conformation.[5a]

Encouraged by the tendency of lithium to bridge,[5c] we examined the *tetrabridged* D_{2d}-constrained structure, V, which proved to be more stable than III by 19.5 kcal/mol at STO-3G but 13.3 kcal/mol less stable at 4-31G/5-21G. Since both III and V are D_{2d} it is evident that a barrier (within this symmetry) exists between them. On the other hand, the conventional acetylenic structure, VI, is not a local minimum, but collapses to a triply bridged form, VII, upon optimization under C_{3v} symmetry. VII is more stable than III-V at both basis set levels. The effect of the three bridging lithiums is seen in the

Table I. Structure and Relative Energies of Various C_3Li_4 Isomers

				Relative energy, kcal/mol	
Molecule	Point group	Parameter	Values[a]	STO-3G opt.	4-31G/5-21G
III	D_{2d}	$r(C_1-C_2)$	1.323	35.6	19.0
		$r(Li_4-C_1)$	1.791		
		$\angle Li_4C_1C_2$	122.3		
IV	D_{2h}	$r(C_1-C_2)$	1.322	34.2	18.5
		$r(Li_4-C_1)$	1.807		
		$\angle Li_4C_1C_2$	122.6		
V	D_{2d}	$r(C_1-C_2)$	1.371	16.1	32.3
		$r(C_1-Li_4)$	1.902		
		$r(C_2-Li_4)$	1.928		
VII	C_{3v}	$r(C_1-C_2)$	1.409	14.3	12.4
		$r(C_2-C_3)$	1.279		
		$r(C_3-Li_4)$	1.774		
		$r(C_1-Li_5)$	1.913		
		$\angle Li_5C_1C_2$	69.6		
VIII	D_{2h}	$r(C_1-C_2)$	1.316	22.6	
		$r(Li_4-C_1)$	1.741		
		$r(C_2-Li_5)$	1.830		
IX[d]	C_{2v}	$r(C_1-C_2)$	1.326	0.0[b]	0.0[c]
		$r(C_1-Li_4)$	1.794		
		$r(C_2-Li_5)$	1.869		
		$\angle Li_4C_1C_2$	149.3		
		$\angle C_1C_2C_3$	155.7		
		$\angle Li_5C_2Li_6$	93.2		

[a] STO-3G optimized geometries, bond lengths in Ångströms and bond angles in degrees. [b] Corresponding total energy, −141.44166 au. [c] Corresponding total energy, −143.08011 au. [d] See IX for specification of chain structure.

C–C bond distances of VII; the C–C triple bond is lengthened to 1.279 Å while the single bond is shortened to 1.409 Å (in propyne C_1-C_2 = 1.170 Å).[8] Lithium substitution also lengthens the multiple bonds in III, IV, and V, where the C–C lengths are considerably longer than the calculated RHF/STO-3G value for allene (1.288 Å).[8]

Although having no precedent in normal hydrocarbon structures, VIII (D_{2h}) with a planar tetracoordinate carbon[5b] is found to be remarkably low in energy. Distortion of VIII to C_{2v} symmetry by decreasing the $Li_5C_2Li_6$ angle destabilizes the system if the atoms around C_2 are moved in opposite directions toward a *tetrahedral* arrangement. (Such distortion ultimately would lead to a tetralithiocyclopropene structure. We also examined a face lithiated C_{3v} tetralithiocyclopropene which was similarly quite uncompetitive energetically.) On the other hand movement of the atoms around C_2 in the *same direction* (also C_{2v}) so that C_1, C_3, Li_5, and Li_6 lie in the same hemisphere (IX) gives the lowest energy C_3Li_4 structure that we have been able to find (both at STO-3G and at 4-31G/5-21G—see Table I). A further reduction of symmetry to C_2 by moving the central lithiums toward opposite carbons resulted in destabilization. IX possesses a zig-zag Li-C-C-C-Li chain, but one not deviating far from linearity. However, the two additional lithium atoms, Li_5 and Li_6, lie in mutually perpendicular positions ($\angle Li_5C_2Li_6$, 93.2°). The stability of this arrangement can be understood by considering it in a formal way as a C_3^{4-} ion stabilized by four surrounding Li^+ cations. The linear C_3^{4-} fragment is isoelectronic with carbon dioxide and will have allylic type stabilization in both mutually perpendicular π systems. The terminal Li ions, Li_4 and Li_7, form partially covalent σ bonds with C_1 and C_3 and also act as π acceptors. The central *Li* ions, Li_5 and Li_6, interact favorably with highest occupied nonbonding π orbitals of the linear C_3 chain primarily as π acceptors (X).[9] Clearly, the nearly perpendicular angle for $Li_5C_2Li_6$ allows such interactions for both allylic nonbonding π orbitals and thus gives a lower energy than VIII in which only one such orbital can be stabilized. The Mulliken population analysis supports this interpretation. All lithium atoms have substantial valence orbital populations, but, for Li_5 and Li_6, these are primarily associated with the p functions with axes parallel to the C_1C_3 axis. The ion-pair structure II, suggested by West,[3] is analogous to IX, but we have stressed in earlier papers[5] and we reiterate here that it is more satisfactory to emphasize the multicenter, covalent bonding of such polylithium compounds rather than their presumed "ion-pair" character.

The electropositive nature of lithium, and the availability of low lying p orbitals, results in lithiocarbon structures which are quite different from those of the corresponding hydrocarbons. The "bare" carbon[10] (C_2) of IX is remarkable; all four valencies extend in one direction in roughly C_{4v} fashion. Bare carbons are also possessed by V (C_1 and C_3 are tricoordinate, each with local C_{2v} symmetry) and by VII (C_1, tetracoordinate, has C_{3v} symmetry), but these structures, less stable than IX, may not be capable of existence.

In theoretical structural searches of this type where conventional experience is no guide, it is difficult to establish with certainty that the absolute minimum has been found. The large number of geometrical possibilities, and the time required for these calculations (~45 min for each STO-3G C_3Li_4 point on the Telefunken TR 440), precludes a global search. We did not, for example, examine any structures with C_s or with C_1 point groups. Results at the Hartree–Fock level with the minimal STO-3G or with the split valence 4-31G/5-21G bases cannot be considered to be definitive, although (with the exception of V) the same relative energy orderings are found (Table I). Nevertheless, our previous experience with calculations on polylithio derivatives at higher levels including correlation effects indicates that the procedure used here may give reasonable energy orderings.[5] In particular, the relative energies of linear and bridged dilithioacetylene were not greatly changed by allowance of electron correlation.[5c] As always, such calculations refer to isolated species in a vibrationless state. However, C_3Li_4 can be prepared in a hydrocarbon solvent, and may not be highly associated.[2d,3] The ^7Li and ^{13}C NMR spectra should be of interest, to say nothing of more refined experimental structural information. We will report the unusual structures of other lithiocarbons in due course.[12]

Acknowledgments. Part of this work was carried out at Princeton University under support by NSF Grant GP-29078X. NSF Grant CHE75-09808 funded the research at Carnegie-Mellon University. The Fonds der Chemischen Industrie provided support at Erlangen. We thank the Rechenzentrum der Universität Erlangen for computational assistance.

References and Notes

(1) A number of lithiocarbons (binary compounds of carbon and lithium) have been reported, inter alia, CLi_4,[2a] C_2Li_2,[2b] C_2Li_4,[2a,c] C_2Li_6,[2a] C_4Li_6,[2e,f] C_4Li_6,[2c] C_5Li_4,[2i] C_6Li_6.[3]

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(12) In this context, it seems appropriate to quote R. N. Grimes (*Science*, **104**, 709 (1976)) on the 1976 Nobel Award to W. N. Lipscomb, "With carbon frequently assuming a coordination number of five or six, the carboranes constitute an extension of carbon chemistry which has profound (but not yet fully recognized) implications for the future directions of organic synthesis. Thus, the pyramidal molecules, $C_4B_2H_6$ and $C_3B_3H_7$ are in fact new kinds of organic heterocycles, albeit ones that have not yet penetrated the sanctums of standard organic textbooks. Sooner or later, it seems clear that organic chemists will have to come to grips with the revolution in our concept of the covalent bond that has been brought about through the medium of boron chemistry, so strongly influenced and guided by Lipscomb."

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A Four-Center, Concerted, Bimolecular Reaction: $ICl^*(A^3\Pi_1) + H_2 \rightarrow HCl + HI$

Sir:

The rate of the laser-induced chemical reaction

$$ICl^*(A^3\Pi_1) + H_2 \rightarrow HCl + HI \qquad (1)$$

has been measured as a function of ICl* vibrational energy. There is no dark reaction, but the reaction is promoted by water vapor, stopcock grease, metal surfaces, and stray light.[1] The kinetics appears similar to $I_2^* + H_2$,[2-4] and other reactions have been reported which involve electronic excitation of I_2.[5] The problem of four-center reactions has received considerable attention.[6]

ICl is prepared under vacuum from I_2 and Cl_2[7,8] and is never exposed to air. Mixtures of ICl (~5 or 9 Torr) and H_2 (10-600 Torr) are photolyzed for about 90 min in a 1-m-long, 5-cm-diameter quartz cell by a Chromatix CMX-4 flashlamp-pumped dye laser ($\Delta\nu$ = 0.3 cm^{-1}) run at 30 pps. A calibrated thermopile monitors the laser power, which is 1.5 to 6 mJ per pulse in a 1-cm^2 beam. Approximately 60% absorption of the laser light is measured at $I^{35}Cl$ v'' = 0 bandheads.

After photolysis all of the HCl, together with some residual Cl_2,[7] is distilled into a bulb with I_2 crystals. The Cl_2 reacts completely with the I_2, and the HCl is then redistilled. Its pressure is measured with a capacitance manometer, and mass spectra confirm that the product is HCl. HI and ICl react to form HCl and I_2; thus two molecules of HCl are formed in each reaction.

ICl* is removed by reaction 1 and by quenching:

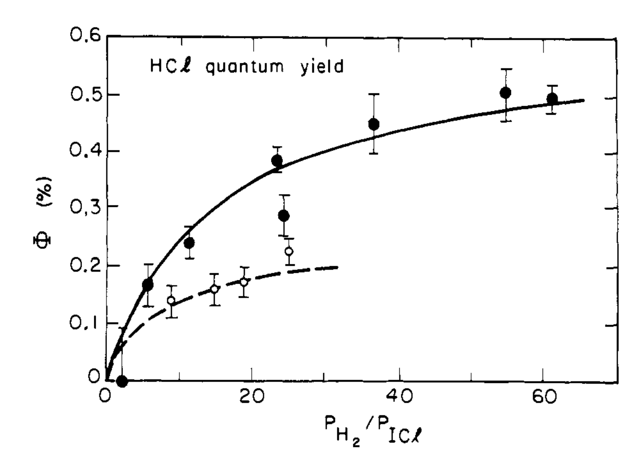

Figure 1. Solid points are data without Ar, P_{ICl} = 8.9 Torr; the solid line is a fit to these points. The dashed line is the *predicted* yield with P_{Ar}/P_{H_2} = 4.75; open circles are corresponding data. Here, P_{ICl} = 4.9 Torr except for lowest P_{H_2}/P_{ICl} point, where P_{ICl} = 8.9 Torr (λ 616.8 nm, exciting 1200 cm^{-1} below dissociation).

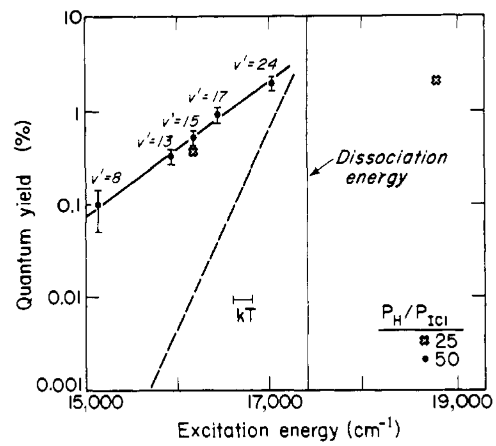

Figure 2. Quantum yield vs. excitation energy. P_{ICl} = 8.9 Torr. The solid line is a fit to the data; the dashed line is a rough estimate of the effect of collisional dissociation. The point at 18 800 cm^{-1} was taken using a doubled YAG laser with 60-mJ, 20-ns pulses.

$$ICl^* + ICl \rightarrow ICl + ICl \qquad (2)$$

$$ICl^* + H_2 \rightarrow ICl + H_2 \qquad (3)$$

Fluorescence is much too slow to complete with reactions 1-3. The quantum yield for reaction is

$$\Phi = \frac{(\text{HCl produced})/2}{\text{photons absorbed}} = \frac{k_1[H_2]}{k_2[ICl] + (k_1 + k_3)[H_2]} \qquad (4)$$

A Stern-Volmer plot of ICl* fluorescence lifetime vs. H_2 pressure gives $(k_1 + k_3) = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; similarly, Steinfeld[9] has measured $k_2 = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; both are nearly independent of wavelength. k_1 is determined from the quantum yield, Figure 1. The solid curve is a least-square fit to the data using eq 4. Note that a two-parameter curve is fit with a single free parameter. The result, $k_1 = (9.0 \pm 0.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (90% confidence limits), corresponds to 9000 gas kinetic collisions. Assuming that the preexponential factor does not exceed the gas kinetic collision frequency, the activation energy is less than 5.5 kcal/mol. The reaction rate is quite large; the quantum yield is low because the quenching rate is even larger.

A single vibrational level of ICl* is excited initially, but vibrationally inelastic collisions spread the population distribution so that reaction may occur from other levels. The extent of this spread, which is limited by quenching, can be estimated