The Structures of the Carbenoid CH_2FLi: *Ab initio* MO Calculations

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Summary The model carbenoid, CH_2FLi, is indicated by *ab initio* molecular orbital calculations to have a peculiar umbrella shaped ('inverted carbon') structure and CH_2Li^+ F^- ion pair character; metallocarbenium ions may thus be the reactive species in carbenoid reactions.

CARBENOIDS, such as the Simmons-Smith reagent[1] or compounds of the type CR_2XM (X is halogen and M an alkali metal, usually lithium),[2] exhibit distinctly different reactivities than the corresponding free carbenes.[3] The exact nature of such carbenoids has not been established. We have used *ab initio* molecular orbital theory† to investigate the structure of the model carbenoid, CH_2FLi.

To our surprise, complete geometry optimization of a variety of possible structures for CH_2FLi revealed *three* local minima, I, II, and III, at the split valence 4–31G (5–21G for lithium) basis set level[4] (see Figure). The most stable structure I is quite remarkable; all valencies of carbon extend into a single hemisphere. Such umbrella-shaped tetraco-ordinate carbon atoms have only been achieved in the past by means of steric constraints.[5] Our results indicate once again how such unusual geometries

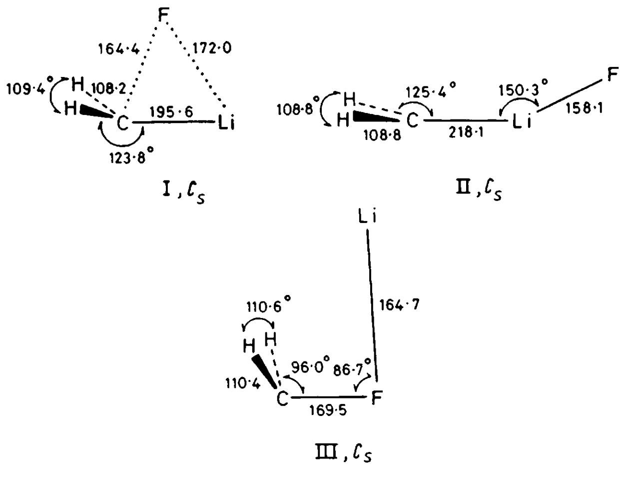

FIGURE. The 4–31G optimised geometries for CH_2FLi. Bond angles are given in degrees, bond lengths in pm. The point groups shown result from optimization from lower symmetry structures and are *not* imposed symmetry constraints.

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† All calculations employed the Gaussian 70 and 76 series of programs (W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE program No. 236; J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, *ibid.*, No. 368). Convergence was ensured by means of an SCF damping routine and geometry optimization was achieved by analytical evaluation of atomic forces.

arise naturally when the substituents are appropriate.[6] The structure of I is best interpreted as being an intimate ion pair between F^- and the very stable lithiomethyl cation, CH_2Li^+.[6b,c] The CF and FLi bonds are long and show little covalent overlap population. The charge distribution, geometry, and overlap populations of the CH_2Li fragment in I correspond closely to those found for CH_2Li^+.[6b,c] The less stable structures, II and III, are singlet methylene–lithium fluoride complexes in which the carbene acts as electron donor or acceptor, respectively. Single point calculations on the 4–31G optimum geometries using the 6–31G* basis set[7] and second order Møller–Plesset correction[8] for electron correlation (MP2/4–31G), confirmed I to be the most stable structure. The total energies for I, II, and III at 4–31G are −145·70879, −145·67896, and −145·65771 Hartrees, respectively, compared with −145·93097, −145·88519, and −145·88053 at MP2/4-31G and −145·87315, −145·84220, and −145·83130 at 6-31G*. I is therefore calculated to be 80—120 kJ/mol more stable than II, and 115—135 kJ/mol more stable than III. 4–31G reaction profiles for the conversion of II and III into I indicate barriers of only 6 and 10·5 kJ/mol, respectively, so that II and III at best are suggested to be metastable species. Triplet CH_2FLi was also investigated, but proved to be significantly higher in energy than I.

At least when isolated in the gas phase, to which conditions our calculations refer, I should be a very stable species, both thermodynamically and towards all possible unimolecular dissociation pathways. The isodesmic bond separation reaction (1)[9] shows an unusually large net

$$CH_3F + CH_3Li \longrightarrow CH_2FLi\ (I) + CH_4 \qquad (1)$$

stabilisation of 79 kJ/mol (4–31 G) owing to interaction of the F and the Li substituents in I. An earlier, standard geometry study on 'classical' CH_2FLi was somewhat misleading in finding this reaction to be practically thermoneutral.[9] I is bound relative to singlet methylene and lithium fluoride by 200 kJ/mol. However, two molecules of I are unstable relative to ethylene plus two lithium fluorides by 391 kJ/mol.

Other than direct reaction of I, the most likely carbene-like reaction of CH_2FLi involves separation of the ion pair to give CH_2Li^+. This ion, which to our knowledge has not been observed directly, is calculated[6] to be highly stabilised, and to have a strong CLi bond. It is therefore better regarded as a metallocarbenium ion than as a methylene–Li^+ complex. The frontier orbitals of CH_2Li^+, however, are very similar to those of singlet CH_2,[10] so that the two species may be expected to exhibit similar reactivity. Both HOMO and LUMO of CH_2Li^+ are, however, stabilised relative to the corresponding orbitals in the free carbene. The carbenoid is therefore expected to be more electrophilic than methylene, and less likely to undergo reactions, such as single bond insertion, in which the carbenoid HOMO must interact with a high-lying σ^* orbital. These predictions are in accord with many of the known reactivity differences between carbenoids and free carbenes.[11]

Interestingly, the reactions of CCl_3Li have been interpreted as involving an equilibrium between at least two forms of this carbenoid.[12] One form was suggested to be $CCl_2Li^+\ Cl^-$.[13] This idea is supported by subsequent matrix isolation studies.[14] Köbrich[15] considered the metallocarbenium ion–halide anion form to be a contributor to the structure of lithium carbenoids. There is a further indication that metallocarbenium ions may be intermediates in carbenoid reactions. Such carbenoids readily undergo nucleophilic substitution.[16] Since calculations indicate that S_N2 displacements should be unfavourable for CH_2FLi,[17] halogen exchange may occur in the ion pairs.

Structures of type I are indicated by our further studies[18] to be quite general for a variety of R_2CXM carbenoids involving different metals, halogens, and organic groups.

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Note added in proof. Since the submission of this manuscript a report of the ^{13}C n.m.r. spectra of three α-bromolithiocyclopropanes has appeared.[19] The results appear to be in accordance with a structure of type I.

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