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Structures and Energetics of Planar and Tetrahedral Dilithiomethane. A Near Degeneracy of Singlet and Triplet Electronic States

Sir:

In a very important recent paper,¹ Collins, Dill, Jemmis, Apeloig, Schleyer, Seeger, and Pople (CDJASSP) have shed new light on the stabilization of planar tetracoordinate carbon. Pople and Schleyer predict¹ that because of their π -acceptor and σ -donor character, electropositive substituents, especially lithium, are particularly effective in stabilizing the planar arrangements selectively. Perhaps the simplest viable candidate for planar carbon is CH_2Li_2 , dilithiomethane, for which the predictions of Pople and Schleyer are summarized in Table I. Although not particularly emphasized by CDJASSP, we were particularly struck by their prediction that both planar and tetrahedral CH_2Li_2 have triplet electronic ground states. CDJASSP explicitly note that the triplet states are artificially favored in their work, since the single determinant Hartree-Fock approximation does not treat singlet and triplet states of this type on an equal footing.² They conclude that "it is difficult to assign the ground state configuration of CH_2Li_2 but the two states should be close in energy". The purpose of the present research is to provide state-of-the-art theoretical predictions, including the effects of electron correlation,^{2,3} of the relative energies of planar and tetrahedral CH_2Li_2 in its lowest singlet and triplet electronic states.

The basis set used in the present research was of double ζ plus polarization (DZ + P) quality⁴ and may be precisely designated C(9s 5p 1d/4s 2p 1d), Li(9s 4p/4s 2p), H(4s 1p/2s 1p). Experience with systems such as methylene⁵ suggest that, in conjunction with large-scale configuration interaction (CI) techniques⁶ and many body theory corrections⁷ for unlinked clusters, predictions of singlet-triplet separations reliable to within 3 kcal may be achieved. With the above specified basis set, self-consistent-field (SCF) theory was used to predict the equilibrium geometrical structures, shown in Figure 1, of the

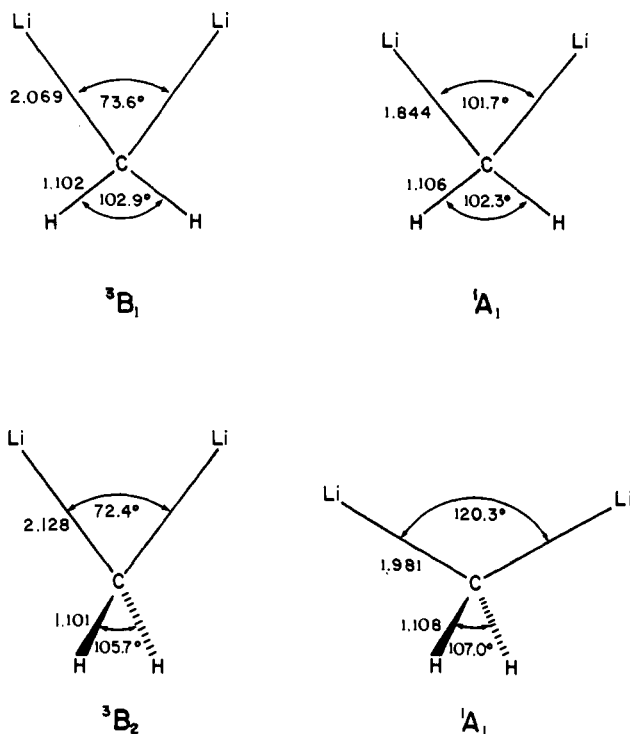


Figure 1. Predicted geometries of planar (upper) and tetrahedral (lower) CH_2Li_2 in its lowest singlet and triplet electronic states. Bond distances are in ångströms.

Table I. Summary of the Self-Consistent-Field Predictions of Collins, Dill, Jemmis, Apeloig, Schleyer, Seeger, and Pople (CDJASSP)¹ Concerning the Relative Energies of CH_2Li_2

species	minimum basis	double ζ basis
tetrahedral singlet	0	0
tetrahedral triplet	-12	-16
planar cis singlet	17	10
planar cis triplet	-2	-13
planar trans singlet	54	48

four species in question. Our structures are in qualitative agreement with the minimum basis predictions of CDJASSP, although a few quantitative differences may be cited. The present C-Li distances are all longer, by from 0.058 to 0.100 Å, and the LiCLi bond angles are from 0.2 to 4.7° (planar triplet) larger than those of CDJASSP. However, the most important conclusion of CDJASSP, that the singlet LiCLi bond angles are much greater than the comparable triplet angles, is given strong support here.

At the predicted SCF equilibrium geometries, CI wave functions including all single and double excitations were determined variationally using the BERKELEY system⁸ of mini-computer-based programs. The numbers of space- and spin-adapted configurations actually included were 7075, 9241, 6724, and 8814. The original Davidson correction⁷ was also applied to these results, which are summarized in Table II. Before going on to the energetic results, we note the remarkable dipole moment predictions also seen in Table II. The planar and tetrahedral singlets have very large dipole moments, with polarity C^-Li^+ , while the triplet μ values are much smaller, and, quite surprisingly, of C^+Li^- polarity.

As suggested by Pople and Schleyer,¹ electron correlation preferentially lowers the singlet states, and in a dramatic fashion. From lying 16.6 kcal above the tetrahedral triplet at the SCF level of theory, the cluster corrected CI eliminates this gap and actually predicts the tetrahedral singlet to lie 2.1 kcal lower. However, the planar triplet lies only 1.8 kcal above the

Table II. Relative Energy Predictions for Dilithiomethane. The Absolute Energies of the Tetrahedral Singlet are -53.8362 hartrees (SCF) and -54.0216 hartrees (CI)

	E (SCF), kcal	μ (SCF), D	E (CI), kcal	E (CI), ^a kcal
planar singlet	3.2	4.85	7.4	8.3
planar triplet	-15.8	-1.22	+0.9	3.9
tetrahedral singlet	0.0	5.42	0.0	0.0
tetrahedral triplet	-16.6	-0.76	-0.8	+2.1

^a Corrected for unlinked clusters.

tetrahedral triplet. The near degeneracy of these four electronic moieties is to our knowledge without precedent and suggests an urgent need for experimental studies of this simple molecule.

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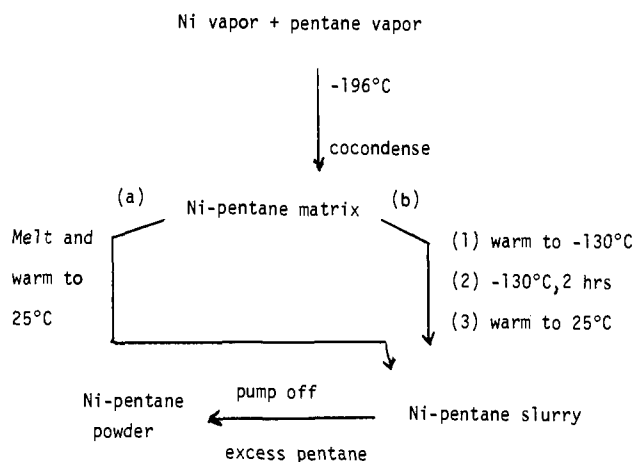
Low Temperature Cleavage of Alkanes by Small Nickel Particles. Clustering of Metal Atoms in Organic Media. 7¹

Sir:

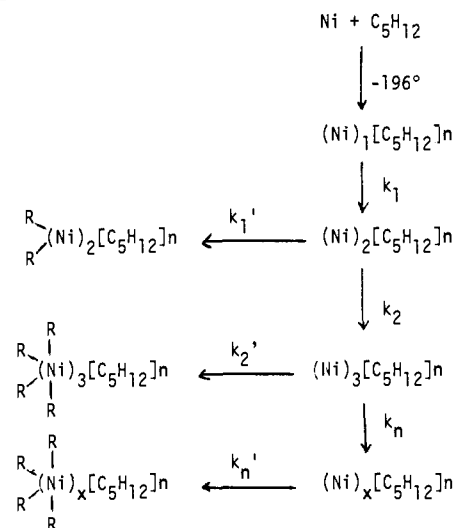
We recently reported chemical and microscopy studies of small metal particles formed by clustering of nickel atoms in organic media.² We have since directed much of our attention to further chemical and catalytic characterization of active metal powders produced by cocondensation of nickel atoms and alkanes, which have been shown to be extremely active and selective hydrogenation catalysts.³ In our previous Ni-alkane work² we had tacitly assumed that the alkanes were simply physis- and chemisorbed on the Ni cluster surfaces, and these intact alkane (hexane) molecules were cleaved upon pyrolysis of the Ni-alkane powders. However, we wish to report here that alkane cleavage (pentane, hexane, or others) occurs at very low temperature, about -130 °C, during formation of Ni clusters from Ni atoms dispersed in the alkane.

When nickel is cocondensed with a high excess of pentane at -196 °C and the resultant matrix allowed to warm to room temperature, a fine black powder is obtained after vacuum removal of excess pentane (Scheme Ia). This stable black powder contains a remarkably large amount of organic material. Elemental analyses, pyrolyses, and exhaustive high

Scheme I



Scheme II



temperature H_2 and O_2 treatments have all independently been in experimental agreement, and have revealed a Ni:C:H mole ratio of 2-5:1:2 depending upon preparative details. When a large excess of pentane is used (>300 -fold) during the cocondensation, the final dry powder is nonferromagnetic with very small nickel crystallites. If a lesser amount of pentane is used (<100 -fold), larger ferromagnetic particles are obtained. It is interesting that the larger ferromagnetic particles contain less organic material than the nonferromagnetic particles (5:1:2 vs. 2:1:2 Ni:C:H ratios, respectively). Furthermore, we have found that by allowing the Ni-pentane matrix to warm to -130 °C (pentane slush) and remain at that temperature for 2 h, followed by normal warm-up to room temperature, nonferromagnetic powder can be obtained with as little as a 40-fold excess of pentane (Scheme Ib). This powder then possesses the Ni:C:H ratio similar to the powder prepared by using a large pentane excess (>300 -fold), and powder X-ray studies yield crystallite size estimates for both of these nonferromagnetic samples as <30 Å, whereas the ferromagnetic samples consistently show >80 -Å crystallite sizes. (These data show, of course, only the larger crystallites present, which are probably a fairly small percent of the total Ni, much of it surely being essentially noncrystalline.) These results strongly suggest the presence of a competition between nickel particle growth in pentane (k) and nickel particle reaction with pentane (k'). Scheme II illustrates this competition in general form. Thus, we believe nickel clusters form at very low temperatures, and these grow larger with temperature increase (-196 to -130 °C). However, also with temperature rise, rates of oxidative