

# Structures and Energies of the Lithium, Sodium, and Magnesium Derivatives of the Anions $\text{CH}_2\text{CN}^-$ and $\text{CH}_2\text{NC}^-$ . Solvation and Aggregation of the Lithium Species

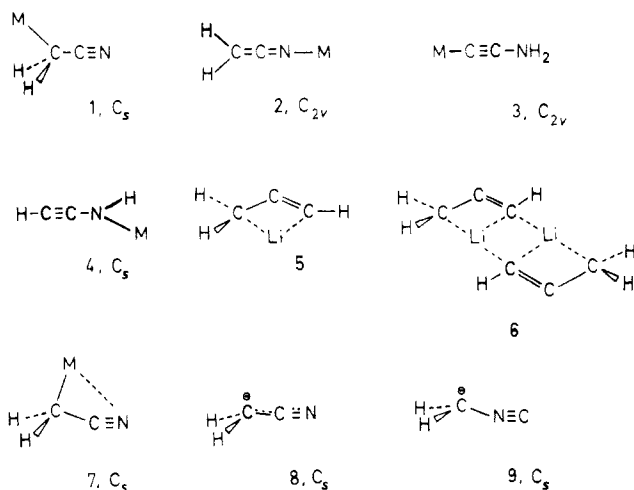
José Kaneti,<sup>†,‡</sup> Paul von Ragué Schleyer,<sup>\*,‡</sup> Timothy Clark,<sup>‡</sup> Alexander J. Kos,<sup>‡</sup> Günther W. Spitznagel,<sup>‡</sup> Juan G. Andrade,<sup>‡</sup> and John B. Moffat<sup>§</sup>

Contribution from the Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany, the Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria, and the Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.  
Received February 5, 1985

**Abstract:** The energetic and structural relationships among various  $\text{C}_2\text{H}_2\text{NM}$  isomers ( $\text{M} = \text{Li}, \text{Na}, \text{MgH}$ , and the anion) are explored by theoretical calculations. The cyanomethyl anion,  $\text{CH}_2\text{CN}^-$ , is predicted to have a pyramidal structure but with a very low inversion barrier of 0.3 kcal/mol ( $\text{MP2}/6\text{-}31\text{+G}^*/6\text{-}31\text{+G}^*$ ). At the same level of ab initio theory, a significantly higher barrier of 2.8 kcal/mol is found for the isocyanomethyl anion,  $\text{CH}_2\text{NC}^-$ .  $\pi$ -Delocalization in  $\text{CH}_2\text{CN}^-$  results in a large stabilization relative to  $\text{CH}_3^-$  (calculated 45.3, experimental 44.4 kcal/mol). In contrast, the  $\text{CH}_2\text{NC}^-$  anion is stabilized (by 36.3 kcal/mol relative to  $\text{CH}_3^-$ ) largely inductively by the sp-hybridized nitrogen. Extensive ab initio examination of the lithium, sodium, and magnesyl ( $\text{MgH}$ ) derivatives of these anions (as well as those of isomeric structures) found lithium-bridged and, to a somewhat lesser extent, sodium-bridged geometries **7** and **12** to be favored. The magnesyl derivatives, **1** and **12**, have more covalent character and nearly classical structures. The metallated ketenimine forms,  $\text{M}-\text{N}=\text{C}=\text{CH}_2$  (**2**,  $\text{M} = \text{Li}, \text{Na}, \text{MgH}$ ), are next lowest in energy. The metallated nitrile ylides,  $\text{M}-\text{C}=\text{N}=\text{CH}_2$ , are substantially higher in energy than the bridged forms but also show the geometrical variations associated with increasing ionic character. Other  $\text{C}_2\text{H}_2\text{NM}$  isomers, including metallated aminoacetylenes and carbene complexes, are energetically unfavorable. The energy orderings of the acyclic  $\text{C}_2\text{H}_2\text{NM}$  isomers also reflect the relative stabilities of the parent systems (in kcal/mol), e.g.,  $\text{CH}_3\text{CN}$  (0.0),  $\text{CH}_3\text{NC}$  (+20.8),  $\text{H}_2\text{C}=\text{C}=\text{NH}$  (+35.3),  $\text{HCC}-\text{NH}_2$  (+51.4),  $\text{HC}=\text{N}=\text{CH}_2$  (+69.0), at the  $6\text{-}31\text{G}^*/6\text{-}31\text{G}^*$  level. More revealing are the stabilization energies relative to  $\text{CH}_3\text{M}$  or to  $\text{NH}_2\text{M}$ , depending on the principal site of metal attachment of the metal derivatives based on the parent  $\text{C}_2\text{H}_3\text{N}$  structures. Thus, the amino (vs.  $\text{NH}_2\text{M}$ ) stabilization energies, 40.9 kcal/mol for  $\text{Na}-\text{N}=\text{C}=\text{CH}_2$  and 32.4 kcal/mol for  $\text{Li}-\text{N}=\text{C}=\text{CH}_2$  ( $3\text{-}21\text{G}/3\text{-}21\text{G}$ ), are 70% and 56% those of the free anion; the value for  $\text{M}=\text{MgH}$  (23.3 kcal/mol) is decreased even further. Likewise, the methyl stabilization energies (vs.  $\text{CH}_3\text{M}$ ) of the  $\text{CH}_2(\text{M})\text{CN}$  forms ( $\text{Li}$ , 21.5;  $\text{Na}$ , 23.2; and  $\text{MgH}$ , 8.7 kcal/mol) are all substantially less than that of the free anion, 45.3 kcal/mol ( $\text{CH}_2\text{CN}^-$  vs.  $\text{CH}_3^-$ ). Similar attenuation is found for the  $\text{CH}_2(\text{M})\text{NC}$  species vs. the  $\text{CH}_2\text{NC}^-$  anion. Aggregation and solvation effects were probed by MNDO calculations. The most stable unsolvated dimers of both  $\text{LiCH}_2\text{CN}$  and  $\text{LiCH}_2\text{NC}$  are indicated to prefer eight-membered-ring structures, but solvation favors the alternative four-membered-ring N-lithiated ketenimine dimer form of the former, which may be the structure in the solid state.

The importance of cyano-stabilized carbanions as synthetic intermediates is underscored by Volume 31 of "Organic Reactions", the latest in a series of reviews devoted to this topic.<sup>1</sup> The sodium salt of propionitrile was first described almost a 100 years ago.<sup>2</sup> Lithium derivatives of aliphatic nitriles were reported by Ziegler in 1932<sup>3</sup> and the corresponding magnesium derivatives by Ivanoff at the same time.<sup>4</sup> Although more recent in origin, isocyano-stabilized anions are even more versatile in their synthetic potential.<sup>5</sup>

The physical organic chemistry of these species is much less well developed. While abundant energetic information on the anion of acetonitrile,  $\text{CH}_2\text{CN}^-$ , and a number of its derivatives are available from  $\text{pK}_a$  measurements in solution<sup>6</sup> and from gas-phase proton affinities from ion cyclotron resonance measurements,<sup>7</sup> there is no similar quantitative experimental data on the  $\text{CH}_2\text{NC}^-$  and its derivatives. The nature of the metallated species in solution has been the subject of some confusing in-



<sup>†</sup> Permanent address: Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

<sup>‡</sup> Universität Erlangen-Nürnberg.

<sup>§</sup> University of Waterloo.

(1) Arseniyadis, S.; Kyler, K. S.; Watt, D. S. *Org. React.* **1984**, *31*, 1-364. For other reviews, see: "Houben-Weyl, Methoden der Organischen Chemie"; G. Thieme Verlag: Stuttgart 1970, Bd. XIII/1, XIII/2a. Ciganek, E.; Linn, W. J.; Webster, O. W. In "The Chemistry of the Cyano Group"; Rappoport, Z., Ed.; Wiley: New York, 1970; p 589. Schoellkopf, U. *Angew. Chem.* **1977**, *89*, 351; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 339. Schoellkopf, U. *Pure Appl. Chem.* **1979**, *51*, 1347. Walborsky, H. M.; Periasamy, M. P. In "The Chemistry of Triple-bonded Functional Groups", Suppl. C.; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; p 835. Charton, M. *Ibid.*, pp 288-292. Stowell, J. C. In "Carbanions in Organic Synthesis"; Wiley: New York, 1979; p 164.

(2) von Meyer, E. *J. Prakt. Chem.* **1888**, *38*, 336.

(3) Ziegler, K.; Ohlinger, H. *Lieb. Ann.* **1932**, *495*, 84. Kaiser, E. M.; Hauser, C. R. *J. Org. Chem.* **1968**, *33*, 3402. Ivanov, D.; Vassilev, G.; Panayotov, I. *Synthesis*, **1975**, 83.

(4) Ivanov, D.; Paounoff, I. *C. R. Hebd. Seances Acad. Sci.* **1933**, *197*, 923. Ivanov, D.; Blagoev, B. *Bull. Soc. Chim. Fr.* **1963**, 1422. For literature and a mechanistic study, see: Toullec, J.; Mladenova, M.; Gaudemar-Bardone, F.; Blagoev, B. *J. Org. Chem.* **1985**, *50*, 2563.

(5) Schoellkopf, U.; Gerhart, F. *Angew. Chem.* **1968**, *80*, 842. Schoellkopf, U.; Gerhart, F.; Schroeder, R. *Ibid.* **1969**, *81*, 701.

(6) Reutov, O. A.; Beletskaya, I. P.; Butin, K. P. "CH-Acids"; Pergamon Press: Oxford, 1978. Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In "Comprehensive Carbanion Chemistry"; Bunzel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1980; p 323. Bordwell, F. G.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 4327.

(7) Bartmess, J. E.; McIver, R. T. In "Gas phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 87-121.

formation. As deduced from reactivity studies,<sup>8</sup> metalated aliphatic nitriles were proposed to exist as equilibrium mixtures of a C-metalated carbanionic form (usually formulated classically) (**1**) and a N-metalated ketenimine (**2**).<sup>1</sup> Infrared and NMR data were also interpreted to indicate isomerization to alkali metal derivatives of amino acetylene (**3** and **4**).<sup>8</sup> Since these species are still mentioned in the current literature,<sup>1,8</sup> they have been included in the present study. However, later, much more detailed reinvestigations excluded such forms and attributed the observed infrared bands to the presence of free carbanions and solvent separated ion pairs.<sup>9</sup> Aggregation is a further possibility. Cryoscopic measurements in dimethyl sulfoxide solution were interpreted as indicating lithiated acetonitrile to be a tetramer and lithiated phenylacetonitrile to be a dimer.<sup>10</sup> However, recent NMR and cryoscopic measurements in tetrahydrofuran solution indicated that  $\text{LiCH}_2\text{CN}$  is dimeric between  $-108^\circ\text{C}$  and room temperature, while  $\text{C}_6\text{H}_5\text{CHLiCN}$  is largely monomeric.<sup>11</sup> Dimers are likely to be present in the solid crystalline state, but no X-ray determinations of carbanions stabilized by a single CN or NC group are yet available.<sup>12</sup> The known X-ray structures of alkali-metal tricyanomethanides indicate preferential association of the cation with several nitrogens, but not with carbon atoms.<sup>12</sup> Because of the aggregation tendency of lithium compounds,<sup>12-17</sup> the study reported in this paper deals not only with metalated monomers but also with some of the possible dimers and tetramers as well as with their solvates.

The structures of the readily formed and extensively studied transition-metal complexes with cyano- and isocyano-substituted ligands,<sup>18</sup> along with the structure deduced calculationally for a large number of organolithium compounds,<sup>15-17,19</sup> serve as a general guide to the possible  $\text{C}_2\text{H}_2\text{NLi}$  isomers. In particular, the isoelectronic allenyllithium favors a bridged geometry (**5**);<sup>20</sup> this is retained in the dimer (**6**), for which X-ray analyses are available.<sup>12,19b</sup> The many other examples of lithium (and of sodium) bridging, e.g., in allyl derivatives<sup>21</sup> and in  $\pi$ -heteroatom systems, suggest that **7** may be lower in energy than **1**, at least for these

metals. On the other hand, the structure of allylmagnesium hydride indicates a much lower bridging tendency of this more covalent metal.<sup>21,22</sup>

This paper reports a comprehensive examination of the structures and energies of lithium, sodium, and magnesyl ( $\text{MgH}$ ) derivatives of the anions derived from methyl cyanide, methyl isocyanide and their tautomers. The corresponding free anions **8** and **9** have also been reexamined for comparison at higher theoretical levels than formerly available. The  $\text{CH}_2\text{CN}^-$  and  $\text{CH}_2\text{NC}^-$  anions and their simple alkyl-substituted derivatives have classical structures, but as we have shown elsewhere,<sup>23,24</sup> earlier investigations in which diffuse functions were not included in the basis sets are inadequate. The electron affinities of typical carbanions are not very large (e.g., the EA of  $\text{CH}_3^-$  is marginal (0.08 eV) and that of  $\text{CH}_2\text{CN}^-$  is  $1.507 \pm 0.018$  eV);<sup>25</sup> hence, the highest occupied molecular orbitals extend rather far from the nuclei. Therefore, diffuse function-augmented basis sets are needed to give theoretical proton affinities in reasonable agreement with experiment. More recent calculations, e.g., on  $\text{CH}_2\text{CN}^-$ , have been carried out in this manner by Chandrasekhar et al.<sup>23</sup> and Hopkinson et al.,<sup>26</sup> but not at high enough levels to provide reliable estimates of inversion barriers at the carbanion center.

One of us reported a pertinent study of a metalated system.<sup>27</sup> Three minima on the  $\text{LiCH}_2\text{CN}$  potential energy surface were located. The most stable form (**7**,  $\text{M} = \text{Li}$ ) involved a bridged lithium arrangement, whereas the other two isomers, **10** ( $\text{M} = \text{Li}$ ) and **11** ( $\text{M} = \text{Li}$ ), were much higher in energy and can be considered as carbene complexes,  $\text{H}_2\text{C} \cdots \text{LiCN}$  and  $\text{LiCN} \cdots \text{CH}_2$ . The minimal basis set employed, STO-3G, has now been superseded by more flexible mathematical representations. These have been used in the present examination and an additional isomer, **2**, an N-lithiated ketenimine, has been included. Both **2** ( $\text{M} = \text{Li}$ ) and **7** ( $\text{M} = \text{Li}$ ) are found to have similar energies, and higher levels of theory are needed to decide which form is the more stable.

Our early STO-3G calculations on lithiated methyl isocyanide resulted in a similar picture. Four local minima, **12-15** ( $\text{M} = \text{Li}$ ), were located, but we now find that **13** does not survive at the next level of approximation (3-21G//3-21G), i.e., rearrangement to **12** on geometry optimization occurs. To make the present examination of acyclic  $\text{C}_2\text{H}_2\text{NLi}$  structures even more comprehensive, we have also calculated the C- and N-lithiated yneamines **3** and **4**, which have been suggested from reactivity, infrared, and NMR studies<sup>8</sup> to be involved in "metallotropic" equilibria with the other forms, and **16**, which is the 2-azaallenyl anion derivative. The ethynylamide and aminoacetylenide anions, **17** and **18**, were also included in the comparison. The possible role of association and solvation on the observable structural and energetic features of lithiated acetonitrile was investigated at the semiempirical MNDO level.<sup>28</sup> MNDO calculations are known to provide reliable structural information on lithiated organic molecules<sup>21,28</sup>

(8) Krueger, C. *J. Organomet. Chem.* **1967**, *9*, 125. Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1971**, *93*, 1714.

(9) Juchnovski, I. N.; Binev, I. G. *J. Organomet. Chem.* **1975**, *99*, 1. Juchnovski, I. N.; Dimitrova, J. S.; Binev, I. G.; Kaneti, J. *Tetrahedron* **1978**, *39*, 779. Kaneti, J.; Nazir, A. F.; Binev, I. G.; Radomirska, V. B.; Juchnovski, I. N. *J. Mol. Struct.* **1980**, *68*, 11.

(10) Das, R.; Wilkie, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 4555.

(11) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972. Bauer, W., private communication. The reported value of association of  $\text{LiCH}_2\text{CN}$  in THF, 1.33, was recently corrected to 1.99–2.07, due to reassessment of the stoichiometry of the crystallosolvate of  $\text{LiCH}_2\text{CN}$  and THF:  $\text{LiCH}_2\text{CN} \cdot \text{THF}$  instead of  $\text{LiCH}_2\text{CN} \cdot 2\text{THF}$ .

(12) For a review of the crystal structures of organolithium compounds, see: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. For a review of the organometallic structures of the heavier alkali metals, see: Schade, C.; Schleyer, P. v. R., *Ibid.*, to be published [ $[\text{LiCH}(\text{CN})_2 \cdot \text{HMPT}]_n$  also is associated through Li–N contacts (Lorenzen, N. P.; Weiss, E., private communication)].

(13) Andersen, P.; Klewe, B.; Thom, E. *Acta Chem. Scand.* **1967**, *21*, 1530. Katagiri, A.; Yoshimura, S.; Yoshizawa, S. *Inorg. Chem.* **1981**, *20*, 4143. Konner, J.; Britton, D. *Inorg. Chem.* **1966**, *5*, 1193. Witt, J. R.; Britton, D. *Acta Crystallogr.* **1971**, *B27*, 1835. Desiderato, R.; Sass, R. *Ibid.* **1965**, *18*, 1. Biondi, C.; Bonamico, M.; Torelli, L.; Vaciago, A. *J. Chem. Soc., Chem. Commun.* **1965**, 191.

(14) (a) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974. (b) Brown, T. L. *Pure Appl. Chem.* **1970**, *23*, 447.

(15) Kaufmann, E., Diplomarbeit, Universität Erlangen-Nürnberg, 1982. Kaufmann, E.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 1856.

(16) Sapse, A.-M.; Kaufmann, E.; Schleyer, P. v. R.; Gleiter, R. *Inorg. Chem.* **1984**, *23*, 1569.

(17) Sapse, A.-M.; Raghavachari, K.; Schleyer, P. v. R.; Kaufmann, E. *J. Am. Chem. Soc.* **1985**, *107*, 6483.

(18) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

(19) For literature summaries, see: (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355. (b) Schleyer, P. v. R. *Ibid.* **1984**, *56*, 151. (c) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. "Ab Initio Molecular Orbital Theory"; Wiley: New York, 1986, Chapter 7.3.3 and the references therein.

(20) (a) Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 2848. (b) Schleyer, P. v. R.; Kaufmann, E.; Spitznagel, G. W.; Janoschek, R.; Winkelhofer, G. *Organometallics* **1986**, *5*, 79.

(21) (a) Rohde, C., Diplomarbeit, Universität Erlangen-Nürnberg, 1982. (b) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344.

(22) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

(23) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609. Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *3*, 294.

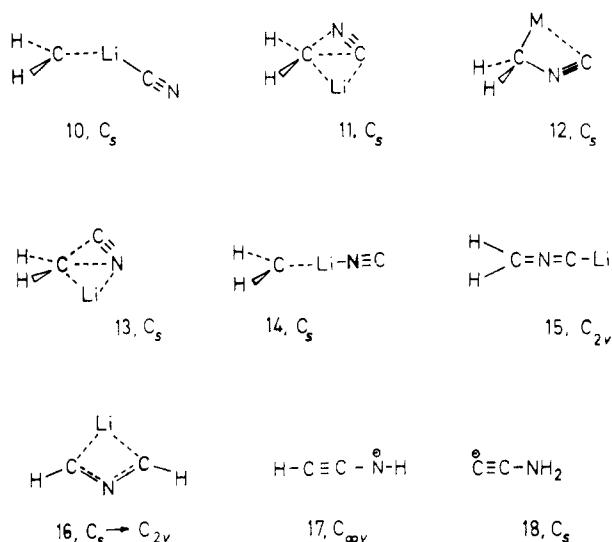
(24) (a) Schleyer, P. v. R.; Chandrasekhar, J.; Kos, A. J.; Clark, T.; Spitznagel, G. W. *J. Chem. Soc., Chem. Commun.* **1981**, 882. (b) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363.

(25) Janousek, B. K.; Brauman, J. I. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 53–87.

(26) Lien, M. H.; Hopkinson, A. C.; McKinney, M. A. *J. Mol. Struct.* **1983**, *103*, 37. Hopkinson, A. C.; McKinney, M. A.; Lien, M. H. *J. Comput. Chem.* **1983**, *4*, 513. Moffat, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 3949. Also see: Delbecq, F. *J. Org. Chem.* **1984**, *49*, 4838. Edgecombe, K. E.; Boyd, R. *J. Can. J. Chem.* **1983**, *61*, 45.

(27) Moffat, J. B. *J. Chem. Soc., Chem. Commun.* **1980**, 1108. Moffat, J. B. *Int. J. Quantum Chem.* **1982**, *22*, 299.

(28) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. (b) Thiel, W.; Clark, T., Lithium parametrization, to be published. (c) Thiel, W. MNDO, Quantum Chemistry Program Exchange Program No. 438 (QCPE Bull. **1982**, *2*, 36) contains MNDO parameters for Li–F and Al–Cl.



and could help to verify or to reject earlier interpretations of spectroscopic and reactivity data.

### Methods

The GAUSSIAN series of ab initio programs<sup>29</sup> was employed. As in all theoretical studies of this type care is needed to ensure the adequacy of the basis sets, the electron correlation corrections which were chosen, and the level(s) at which the geometries were calculated. Analytical gradient geometry optimizations either without any geometry constraints or restricted to a given point symmetry group were carried out first on the neutral species with the split-valence 3-21G<sup>30</sup> and then with the polarized 6-31G\*<sup>31</sup> basis sets. The geometries of the free cyanomethyl carbanion  $\text{CH}_2\text{CN}^-$  and the free isocyanomethyl carbanion  $\text{CH}_2\text{NC}^-$  also were optimized with the 6-31+G\* basis set,<sup>23</sup> which is augmented with diffuse functions on all non-hydrogen atoms. These improve the description of the weakly bonding HOMO's of anionic species dramatically<sup>23,24</sup> and the description of lone pairs on first row atoms in neutral molecules as well.<sup>22</sup> In contrast to the anions, the HOMO's of the neutral organometallics are lower in energy and the extra diffuse basis functions have negligible effect on their structures. Thus, 6-31G\* and 3-21G geometries suffice, and do not differ greatly. In contrast to the geometries, the relative energies of the various organometallic species vary quite appreciably with the theoretical level. This behavior is well understood. When a heteroatom electron pair is involved in bonding interaction with the metal, significant basis set superposition errors (BSSE)<sup>32</sup> occur. That is, especially at the 3-21G level, the basis functions centered on the metal help to describe the rest of the molecule, and the energies are lowered artificially. This is largely corrected by additional polarization functions; hence, more reliable relative energies are obtained with the 6-31G\* basis set. In addition, the key isomers **2**, **7**, **12**, and **15** for  $\text{C}_2\text{H}_2\text{NLi}$  were investigated more extensively. Reoptimization with the 6-31G\* basis improved the absolute energies marginally and the relative energies were little changed (Table I). This indicates the adequacy of 3-21G geometries for the other species. Single-point MP2/6-31G\*//6-31G\* calculations on **2**, **7**, **12**, and **15**, i.e., including Møller-Plesset<sup>33</sup> corrections to

**Table I.** Absolute (au) and Relative (kcal/mol) Energies of  $\text{C}_2\text{H}_2\text{NLi}$ ,  $\text{C}_2\text{H}_2\text{NNa}$ , and  $\text{C}_2\text{H}_2\text{NMgH}$  Isomers

formula	3-21G// 3-21G	6-31G*// 3-21G	6-31G*// 6-31G*	MP2/ 6-31G*// 6-31G*
$\text{CH}_2(\text{Li})\text{CN}$ (7)	-138.00169 0.0	-138.78385 0.0	-138.78426 0.0	-139.20455 0.0
$\text{CH}_2\text{CNLi}$ (2)	-138.00928 -4.8	-138.77463 5.8	-138.77495 5.8	-139.18912 9.7
$\text{CH}_2(\text{Li})\text{NC}$ (12)	-137.96265 14.5	-138.73820 28.6	-138.73964 28.0	-139.15221 32.8
$\text{CH}_2\text{NCLi}$ (15)	-137.92595 37.5	-138.70083 52.0	-138.70103 52.2	-139.12679 48.8
$\text{HC}\equiv\text{CNHLi}$ (4)	-137.96561 22.6	-138.72818 34.9		
$\text{LiC}\equiv\text{CNH}_2$ (3)	-137.95050 32.1	-138.71305 44.4		
$\text{CH}_2\text{LiNC}$ (14)	-137.92314 39.3	-138.69373 56.5		
$\text{CH}_2\text{LiCN}$ (11)	-137.92255 49.0	-138.70184 51.4		
$\text{CH}_2\text{LiCN}$ (10)	-137.90873 58.3	-138.68730 60.5		
$\text{Li}(\text{HCNCH})$ (16)	-137.82161 103.0	-138.60351 113.2		
$\text{CH}_2(\text{Na})\text{CN}$ (7)	-291.45224 0.0	-293.17158 0.0		
$\text{CH}_2\text{CNNa}$ (2)	-291.45092 0.8	-293.15819 8.4		
$\text{CH}_2(\text{Na})\text{NC}$ (12)	-291.40958 26.8	-293.12383 30.0		
$\text{CH}_2\text{NCNa}$ (15)	-291.37466 48.7	-293.08674 53.2		
$\text{HMgCH}_2\text{CN}$ (1)	-329.64247 0.0	-331.50934 0.0		
$\text{CH}_2\text{CNMgH}$ (2)	-329.64710 -2.9	-331.49389 9.7		
$\text{HMgCH}_2\text{NC}$ (12)	-329.60260 25.0	-331.45790 32.3		
$\text{CH}_2\text{NCMgH}$ (15)	-329.56537 48.4	-331.42023 55.9		

**Table II.** Energies of Reference Compounds Used in the Thermochemical Evaluations (au)

formula	3-21G// 3-21G	6-31G*// 6-31G*	6-31+G*// 6-31+G*	MP2/ 6-31+G*// 6-31+G*
$\text{CH}_3^-$	-39.23940 <sup>a</sup>	-39.46684 <sup>a</sup>	-39.50415	-39.65424
$\text{CH}_4$	-39.97688 <sup>a</sup>	-40.19617 <sup>a</sup>	-40.19567	-40.33394
$\text{CH}_3\text{Li}$	-46.75248 <sup>a</sup>	-47.01554 <sup>a</sup>	-47.01760	-47.16669
$\text{NH}_2^-$	-55.13599 <sup>a</sup>	-55.47608 <sup>a</sup>	-55.51808	-55.70805
$\text{NH}_3$	-55.87220 <sup>a</sup>	-56.18436 <sup>a</sup>	-56.18950 <sup>a</sup>	-56.36265
$\text{LiNH}_2$	-62.69519 <sup>a</sup>	-63.04195 <sup>a</sup>	-63.05044	-63.23678
$\text{H}_2\text{C}=\text{NH}$	-93.49478	-94.02846		
$\text{H}_2\text{C}=\text{NLi}$	-100.33404	-100.89589		
$\text{HC}\equiv\text{C}-\text{NH}^-$	-130.48001 <sup>a</sup>		-131.20936	
$\text{H}_2\text{N}-\text{C}\equiv\text{C}^-$			-131.22550	
$\text{CNCH}_2^-$			-131.25892	-131.67890
$\text{NCCH}_2^-$			-131.31184	-131.73326
$\text{H}_2\text{C}=\text{NCH}$			-131.81758	
$\text{HC}\equiv\text{CNH}_2$	-131.12430 <sup>a</sup>		-131.84557	
$\text{H}_2\text{C}=\text{C}=\text{NH}^-$	-131.13467 <sup>a</sup>	-131.87126	-131.87654	-132.28619
$\text{CH}_3\text{NC}$	-131.15916 <sup>a</sup>	-131.89436	-131.90083	-132.30074
$\text{CH}_3\text{CN}$	-131.19180 <sup>a</sup>	-131.92753	-131.93117	-132.34079
$\text{CH}_3\text{Na}$	-200.20030 <sup>a</sup>	-201.39970 <sup>b</sup>		
$(\text{H}_2\text{C}=\text{NLi})_2$	-200.78180			
$\text{H}_2\text{NNa}$	-216.12320 <sup>a</sup>	-217.41482 <sup>a</sup>		
$\text{CH}_3\text{MgH}$	-238.41362 <sup>a</sup>	-239.75438 <sup>b</sup>		
$\text{H}_2\text{NMgH}$	-254.34748 <sup>a</sup>	-255.77709 <sup>a</sup>		

<sup>a</sup>Reference 34. <sup>b</sup>6-31G\*//3-21G(\*) values. <sup>c</sup>For earlier theoretical studies, see: Kaneti, J.; Nguyen, M. T. *J. Mol. Struct.* **1982**, *87*, 205. Ha, T.-K.; Nguyen, M. T. *Ibid.* **1982**, *87*, 355. Nguyen, M.-T.; Hegarty, A. F. *J. Am. Chem. Soc.* **1983**, *105*, 3811.

the second order, indicate electron correlation to have a relatively minor effect (ca.  $\pm 4$  kcal/mol) on the relative energies; there is no change in the qualitative ordering of isomers. This possible source of error should

(29) Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. GAUSSIAN 76, Quantum Chemistry Program Exchange Program No. 368 (*QCPE Newsletter* **1978**, *63*, 48). Schlegel, H. B.; Wolfe, S.; Bernardi, F. *J. Chem. Phys.* **1975**, *63*, 3622. Poppinger, D. *Chem. Phys. Lett.* **1975**, *34*, 322. Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; Schlegel, H. B.; DeFrees, D. J.; Topiol, S.; Kahn, L. R.; Pople, J. A. GAUSSIAN 80, Quantum Chemistry Program Exchange Program No. 406 (*QCPE Newsletter* **1980**, *71*, 36). Binkley, J. S.; Frisch, M. M.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, 1983. We thank Sawaryn, A., University of Erlangen, 1984, for adapting this program to CDC computers.

(30) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797.

(31) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654 and the references therein.

(32) Carsky, P.; Urban, M. "Ab Initio Calculations" (Lecture Notes in Chemistry, Vol. 16); Springer Verlag: Heidelberg, 1980.

(33) Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* **1975**, *9*, 229.

**Table III.** Structural Parameters (Å and deg) of CH<sub>3</sub>CN, CH<sub>2</sub>CN<sup>-</sup>, CH<sub>3</sub>CN, and CH<sub>2</sub>NC<sup>-</sup>, 6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>

parameter	CH <sub>3</sub> CN	H <sub>2</sub> CCN <sup>-</sup>	H <sub>2</sub> CNC <sup>-</sup>	CH <sub>3</sub> NC
r(CN)	1.1355	1.1622	1.1539	1.1521
r(CC)	1.4687	1.3927	1.4308	1.4234
r(CH)	1.0821	1.0768	1.0895	1.0807
∠NCC	180.000	178.265	175.795	180.000
∠HCH		117.496		
∠CCH	109.735		107.417	109.427
∠CCx <sup>a</sup>		154.972		
∠CNCH			58.587	
E(HOMO)	-0.4699	-0.0625	-0.0650	-0.4691
q(N)	-0.457	-0.735		
q(C <sub>1</sub> )			-0.102	+0.111
q(C <sub>2</sub> )	+0.396	+0.372		
q(N)			-0.324	-0.344
q(C <sub>3</sub> )	-0.680	-0.958	-0.786	-0.441
q(H)	+0.247	+0.167	+0.106	+0.225

<sup>a</sup>The angle between the C-C bond and the bisector of the angle ∠HCH.

be noted in cases where MP2 calculations were not carried out. All post-SCF calculations employed the frozen core orbital approximation.

The resulting absolute energies, presented in Table I, are designated by notations like 6-31G<sup>\*</sup>//3-21G and MP2/6-31G<sup>\*</sup>//6-31G<sup>\*</sup> (the “//” means “at the geometry of”). Table II includes the energies of reference compounds<sup>34</sup> needed for thermochemical evaluations.

### Discussion

We first consider the parent anions before proceeding to their organometallic derivatives.

**The CH<sub>2</sub>CN<sup>-</sup> and CH<sub>2</sub>NC<sup>-</sup> Anions.** The present calculations of cyanomethyl and isocyanomethyl anions confirm the significant difference between these two species which have been indicated both by experimental observations and by prior calculations.<sup>26</sup> The principal question left open is the geometry at the CH<sub>2</sub> groups and the barriers to inversion. At our highest theoretical level (MP2/6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>), both anions are indicated to have pyramidal structures, but there is a rather large difference in their inversion barriers. Thus, nonplanar C<sub>s</sub> CH<sub>2</sub>CN<sup>-</sup> is indicated to be only 0.3 kcal/mol lower in energy than the C<sub>2v</sub> planar structure. In contrast, CH<sub>2</sub>NC<sup>-</sup> requires 2.8 kcal/mol to undergo pyramidal inversion. These two inversion barriers, while small, differ by an order of magnitude. At the same level of theory, the inversion barrier of the methyl anion is calculated to be 2.4 kcal/mol.<sup>24c</sup> Thus, the cyano substituent decreases the barrier, whereas the isocyano group increases it slightly. As we will see below, this difference is also reflected in the relative stabilizing effects of these two substituents.

Although our calculations refer to isolated molecules approximating those in the gas phase, there is qualitative agreement with the experimentally observed configurational stability of an isocyanocyclopropyl carbanion derivative in solution.<sup>35</sup> The analogous cyano-substituted anion system racemizes completely under the same experimental conditions.<sup>36</sup> Calculations of Hopkinson et al.<sup>26</sup> on the -CN and -NC substituted cyclopropyl anions, which have much larger barriers, are in convincing agreement. Thus, the experimentally observed inversion barriers, which refer to associated and solvated organometallic species,<sup>35,36</sup> reflect the configurational stabilities indicated in the present and other computational studies of free carbanions.<sup>26</sup>

A comparison of calculated inversion barriers of substituted methyl anions shows increasing configurational stability in the order CH<sub>2</sub>CHO<sup>-</sup> (0) < CH<sub>2</sub>CN<sup>-</sup> (0.3) < CH<sub>3</sub><sup>-</sup> (2.4) < CH<sub>2</sub>NC<sup>-</sup> (2.8) < CH<sub>2</sub>F<sup>-</sup> (13.8 kcal/mol).<sup>23,24</sup> Lowered inversion barriers are attributed to π-delocalization to the substituent. This is favored when the carbanion center is sp<sup>2</sup> rather than sp<sup>3</sup> hybridized (more

**Table IV.** Methyl (eq 1) and Amino (eq 10) Stabilization Energies

species	-ΔE, kcal/mol		
	3-21G//3-21G	6-31G <sup>*</sup> //6-31G <sup>*</sup>	MP2/6-31+G <sup>*</sup> //6-31+G <sup>*</sup>
CH <sub>2</sub> CN <sup>-</sup>	57.7 <sup>a</sup>	43.3 <sup>b</sup>	45.3
	57.9 <sup>b</sup>	67.0 <sup>b,c</sup>	63.8 <sup>c</sup>
CH <sub>2</sub> NC <sup>-</sup>	43.3 <sup>a</sup>	31.1 <sup>b</sup>	36.3
CH <sub>2</sub> CNLi (2)	32.4 <sup>c</sup>	28.9 <sup>c</sup>	
CH <sub>2</sub> (Li)CN (7)	21.5	23.2	
CH <sub>2</sub> (Li)NC (12)	15.6	15.6	
CH <sub>2</sub> CNNa (2)	40.9 <sup>b</sup>		
CH <sub>2</sub> (Na)CN (7)	23.2		
CH <sub>2</sub> (Na)NC (12)	16.8		
CH <sub>2</sub> CNMgH (2)	23.3 <sup>b</sup>		
HMgCH <sub>2</sub> CN (1)	8.7		
HMgCH <sub>2</sub> NC (12)	3.8		

<sup>a</sup>Reference 21. <sup>b</sup>6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup> values. <sup>c</sup>Amino-stabilization energy, eq 10.

p-character in the carbanion orbital). The CHO group is more effective than CN in this respect, as indicated by its greater methyl stabilization energy.<sup>23,24</sup> The isocyano group, although a relatively weak π-acceptor, stabilizes adjacent carbanion centers inductively, due to the rather electronegative sp-hybridized nitrogen atom. This is also shown by comparing the geometries of CH<sub>2</sub>CN<sup>-</sup> and CH<sub>2</sub>NC<sup>-</sup> with those of methyl cyanide and methyl isocyanide, respectively (Table III, also see ref 26). In the cyanomethyl anion, the noticeable shortening of the C—C bond length and the modest extension of the C=N linkage are consistent with π-delocalization. In the isocyanomethyl anion, the H<sub>2</sub>C—N distance is affected much less in comparison with the neutral precursor, and the N=C distance hardly changes at all.

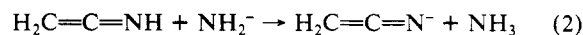
The relative stabilities of cyanomethyl and isocyanomethyl anions can be evaluated by means of isodesmic reaction (1), which indicates the degree to which the substituents stabilize the methyl anion. Both cyano and isocyano groups are quite effective in this respect (Table IV), but the stabilization afforded by the former is some 9 kcal/mol greater (eq 1, MP2/6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>).



6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>: X = CN, 48.3, or X = NC, 31.1 kcal/mol

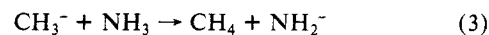
MP2/6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>: X = CN, 45.3, or X = NC, 36.3 kcal/mol

However, there is ambiguity about the CH<sub>2</sub>CN<sup>-</sup> anion, where the negative charge is partially delocalized to nitrogen. In addition, proton removal from the acetonitrile tautomer, ketenimine, also gives the same anion. Hence, the amino anion stabilization energy (based on NH<sub>2</sub><sup>-</sup> instead of CH<sub>3</sub><sup>-</sup> and evaluated by eq 2) also is a useful value. Because of the greater electronegativity of nitrogen, NH<sub>2</sub><sup>-</sup> is 13 kcal/mol (ICR)<sup>7</sup> more stable than CH<sub>3</sub><sup>-</sup>, based on their relative proton affinities. Theoretical results agree (eq 3):



-67.0 kcal/mol (6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>)

-63.8 kcal/mol (MP2/6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>)



-12.6 kcal/mol (6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>)

-15.8 kcal/mol (MP2/6-31+G<sup>\*</sup>//6-31+G<sup>\*</sup>)

However, note (Table II) that the aminoacetylenide anion (H<sub>2</sub>N—C≡C<sup>-</sup>) is calculated to be more stable than its nitrogen-based isomer, ethynylamide (HC≡C—NH<sup>-</sup>), by 10.1 kcal/mol (631+G<sup>\*</sup>//6-31+G<sup>\*</sup>).

The proton affinities (PA) of these anions can also be computed, but zero-point energy corrections are necessary for comparison with experiment. Ab initio calculations refer to motion-free molecules, whereas real systems even at 0 K have residual vi-

(34) Whiteside, R. A.; Frisch, M. J.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 3rd ed., Carnegie-Mellon University: Pittsburgh, Pennsylvania 1983.

(35) Periasamy, M. P.; Walborsky, H. M. *J. Am. Chem. Soc.* **1977**, *99*, 2631.

(36) Walborsky, H. M.; Hornyak, F. M. *J. Am. Chem. Soc.* **1956**, *78*, 872.

**Table V.** Structural Parameters (Å and deg) of the MCH<sub>2</sub>CN Isomers **7** (M = Li, Na, MgH), 3-21G//3-21G

parameter	M = Li	M = Na	M = MgH	M = H
r(C=N)	1.165	1.160	1.144	1.139
r(C—C)	1.398	1.408	1.448	1.457
r(C—M)	2.020	2.435	2.889	1.082
r(C—H)	1.076	1.078	1.086	1.082
∠CCN	161.4	167.6	177.1	180.0
∠CCM	76.8	70.2	106.0	110.1
∠CCH	116.1	115.1	109.9	110.1

**Table VI.** Structural Parameters (Å and deg) of the MCH<sub>2</sub>CN Isomers **12** (M = Li, Na, MgH), 3-21G//3-21G

parameter	M = Li	M = Na	M = MgH	M = H
r(N=C)	1.167	1.163	1.163	1.160
r(C—N)	1.499	1.492	1.469	1.432
r(C—M)	1.991	2.306	2.119	1.081
r(C—H)	1.081	1.084	1.083	1.081
∠CNC	172.5	173.8	178.7	180.0
∠NCM	70.4	76.6	95.9	109.6
∠NCH	107.0	106.7	107.6	109.6

**Table VII.** Structural Parameters (Å and deg) of Keteneimine Derivatives, H<sub>2</sub>C=C=NM (**2**) (M = Na, Li, MgH), 3-21G//3-21G

parameter	M = Na	M = Li	M = MgH	M = H
r(C=C)	1.333	1.325	1.317	1.298
r(C=N)	1.180	1.184	1.187	1.207
r(N—M)	2.051	1.729	1.869	1.010
r(C—H)	1.071	1.071	1.070	1.071
∠CCH	120.1	120.5	120.4	120.6

brations. In general, the zero-point energy (ZPE) difference between a carbanion and its neutral counterpart is about 9 kcal/mol (estimated from the difference in vibrational fundamentals of CH<sub>3</sub> and CH<sub>4</sub>, 8.9 kcal/mol, and of NH<sub>2</sub> or NH<sub>2</sub><sup>-</sup> and NH<sub>3</sub>, 9.3 kcal/mol);<sup>37</sup> and we have used this value to correct our calculational data. Thus, PA = 372.2 kcal/mol for CH<sub>2</sub>CN<sup>-</sup> is calculated from our MP2/6-31+G\*//6-31+G\* data (Table II); the experimental value also is 372 kcal/mol.<sup>7</sup> No experimental PA value for CH<sub>2</sub>NC<sup>-</sup> appears to be available.<sup>48</sup> Our calculated estimate PA = 381 kcal/mol can be expected to have comparable accuracy. The use of the relative energies from eq 1, along with the experimental PA(CH<sub>3</sub><sup>-</sup>) = 416.6 kcal/mol,<sup>7</sup> is essentially the same procedure for obtaining theoretical PA values for anions, as the ZPE corrections tend to cancel. On this basis, the estimated PA's are 380 for CH<sub>2</sub>NC<sup>-</sup> and 371 kcal/mol for CH<sub>2</sub>CN<sup>-</sup>.

**C<sub>2</sub>H<sub>2</sub>NLi Isomers.** Lithium derivatives of acetonitrile and of methyl isocyanide, the simplest organometallic systems of their type, are the most convenient to examine extensively calculationally. We attempted to locate all the stationary points on the 3-21G potential surface which correspond to acyclic C<sub>2</sub>H<sub>2</sub>NLi structures. Ten such species were found, of which only **7** derives formally from acetonitrile and **12** from methyl isocyanide. Two isomers with linear C<sub>2v</sub> structures are based on keteneimine (**2**) and on a "planar nitrile ylide" (**15**). Two less stable isomers are related to ethynylamine (**3**, **4**) and another minimum corresponds to a metallated "bent" nitrile ylide (**16**). The least stable isomers on the 3-21G energy surface (**10**, **11**, and **13**) correspond to carbene complexes of LiNC and of LiCN. The structural parameters of all species are listed in Tables V–IX.

The calculated geometries of lithiated methyl cyanide and methyl isocyanide reveal notable differences from CH<sub>3</sub>CN and CH<sub>3</sub>NC, which prefer linear C<sub>3v</sub> arrangements. In contrast, the C—C≡N and C—N≡C linkages are bent in the metal derivatives

**Table VIII.** Structural Parameters (Å and deg) of "Planar Nitrile Ylide" Derivatives H<sub>2</sub>C=N=C—M (**15**) (M = Na, Li, MgH), 3-21G//3-21G

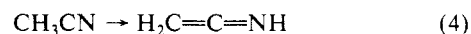
parameter	M = Na	M = Li	M = MgH	M = H <sup>a</sup>
r(C—N)	1.313	1.302	1.289	1.233
r(N=C)	1.181	1.184	1.184	1.252
r(C—M)	2.198	1.901	2.009	1.088
r(C—H)	1.069	1.069	1.069	1.115
∠NCH	119.4	119.6	119.6	120.9

<sup>a</sup>4-31G//4-31G geometry, E.-U. Würthwein, unpublished calculations. The most stable form of H<sub>2</sub>C=N=CH is the "bent nitrile ylide", the energy of which is given in Table II.

and the bridging lithium atom is at bonding distances from all three non-hydrogen atoms. However, such distances do not necessarily imply that bonding actually is present (see the discussion below).<sup>15b,16</sup> Similar bridged lithium structures are well-known from studies of lithiated unsaturated hydrocarbons;<sup>19,21</sup> the structure of the isoelectronic allenyllithium<sup>20</sup> provides the closest comparison. The bridged structure **7**, written as CH<sub>2</sub>-(Li)CN, is the global minimum on the MP2/6-31G\*//6-31G\* C<sub>2</sub>H<sub>2</sub>NLi energy surface. The next most stable species, H<sub>2</sub>C=C=NLi (**2**), corresponds to lithiated keteneimine and is 9.7 kcal/mol higher in energy (Table I).

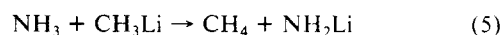
The two lithium derivatives of aminoacetylene, **3** and **4**, are less stable than CH<sub>2</sub>(Li)CN (**7**) by 35–45 kcal/mol at the 6-31G\*//3-21G level and are also indicated to be less favorable than CH<sub>2</sub>(Li)NC (**12**). Thus, **3** and **4** are unlikely to be in the tautomeric equilibrium with **2** and **7** suggested by earlier reactivity and spectroscopic experiments.<sup>8</sup>

Why is lithiated keteneimine H<sub>2</sub>C=C=NLi (**2**) only 5.8 kcal/mol less stable than bridged CH<sub>2</sub>(Li)CN (**7**) at 6-31G\*//6-31G\* (9.7 kcal/mol at MP2/6-31G\*//6-31G\*) (Table I), when the parent (hydrogen) systems differ by 34.3 kcal/mol at the same level (eq 4 and Table II)? Deprotonation of acetonitrile and keteneimine gives the same anion; the lithium salt has largely ionic character and the cation placement is less critical. Moreover, lithium favors nitrogen over carbon attachment. This is shown by eq 5 and by comparing the energy of this equation with that for the corresponding free anions (eq 2). The N–Li bonding energy is further enhanced by the sp-nitrogen hybridization (eq 6) and still further by delocalization (eq 7).



$$+34.3 \text{ kcal/mol, 6-31G*//6-31G*}$$

$$+34.3 \text{ kcal/mol, MP2/6-31+G*//6-31+G*}$$

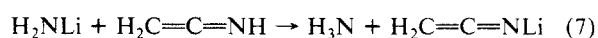


$$-24.0 \text{ kcal/mol, 6-31G*//6-31G*}$$

$$-25.9 \text{ kcal/mol, MP2/6-31+G*//6-31+G*}$$



$$-10.2 \text{ kcal/mol, 6-31G*//6-31G*}$$



$$-34.0 \text{ kcal/mol, 6-31G*//6-31G*}$$

Other factors contribute to the relative stabilization of C<sub>2</sub>H<sub>2</sub>NLi isomers as well, e.g., the partial N–Li bonding character in **7** (stabilizing) and its bending distortion (destabilizing). Metalation, therefore, shifts the tautomeric equilibrium favoring acetonitrile over keteneimine (eq 4) considerably toward metal derivatives of the latter. Another shift in a tautomeric equilibrium is predicted by the calculated greater stability of HC≡C—NHLi compared to Li—C≡C—NH<sub>2</sub>; the relative energies of the corresponding anions are reversed, <sup>-</sup>C≡C—NH<sub>2</sub> is more stable than HC≡C—NH<sup>-</sup>. This demonstrates again the preference of lithium for nitrogen over carbon attachment<sup>37</sup> (compare eq 3 for the CH<sub>3</sub><sup>-</sup> and NH<sub>2</sub><sup>-</sup> anions vs. eq 5 for the lithium derivatives, CH<sub>3</sub>Li and H<sub>2</sub>NLi).

(37) (a) Würthwein, E.-U.; Sen, K. D.; Pople, J. A.; Schleyer, P. v. R. *Inorg. Chem.* **1983**, *22*, 496. The zero-point energy of NH<sub>2</sub><sup>-</sup> is calculated to be 12.4 or 11.2 kcal/mol after scaling. (b) Kollmar, H. *J. Am. Chem. Soc.* **1978**, *100*, 2665.

(38) Schlosser, M. "Struktur und Reaktivität polarer Organometalle"; Springer-Verlag: Berlin-Heidelberg 1973.

**Table IX.** Detailed Structural Parameters (Å and deg) of MC<sub>2</sub>H<sub>2</sub>N (M = Li, Na, MgH), 3-21G//3-21G and 6-31G\*\*/6-31G\*

species	parameter	3-21G// 3-21G	6-31G**/ 6-31G*	species	parameter	3-21G// 3-21G	6-31G**/ 6-31G*		
CH <sub>2</sub> (Li)CN (7)	r(CN)	1.1649	1.1589	Li(HC=N=CH) (16)	r(LiN)	1.9732			
	r(CC)	1.3983	1.4073		r(CN)	1.2304			
	r(CH)	1.0763	1.0785		r(CH)	1.0567			
	r(C <sub>1</sub> Li)	2.0204	1.9942		r(CLi)	2.1303			
	r(C <sub>2</sub> Li)	2.1790	2.1592		∠LiNC	79.687			
	∠NCC	161.395	160.107		∠NCH	138.617			
	∠CCH	116.082	114.615		r(NC)	1.1598			
	∠LiCC	76.798	76.656		r(CC)	1.4077			
	∠NCCH	110.497	113.001		r(CH)	1.0780			
	CH <sub>2</sub> LiCN (10)	r(CN)	1.1528			CH <sub>2</sub> (Na)CN (7)	r(C <sub>2</sub> Na)	2.4348	
r(C <sub>1</sub> Li)		1.9581		r(C <sub>1</sub> Na)	2.3649				
r(C <sub>2</sub> Li)		2.1872		∠NCC	167.644				
r(CH)		1.0887		∠CCH	115.085				
∠NCLI		179.512		∠HC <sub>2</sub> C <sub>1</sub> Na	112.674				
∠CLiC		178.698		r(NaN)	2.0508				
∠LiCH		125.726		r(NC)	1.1800				
∠CLiCH		90.130		r(CC)	1.3333				
CH <sub>2</sub> LiNC (11)		r(CN)	1.1723		CH <sub>2</sub> CNNa (2)		r(CH)	1.0708	
		r(CC)	2.2375				∠CCH	120.5190	
	r(C <sub>1</sub> Li)	2.0504		r(C <sub>1</sub> N)		1.1638			
	r(C <sub>2</sub> Li)	2.0660		r(NC <sub>2</sub> )		1.4916			
	r(CH)	1.0820		r(CH)		1.0835			
	∠NCC	64.636		r(C <sub>2</sub> Na)		2.3058			
	∠C <sub>2</sub> C <sub>1</sub> Li	57.416		r(NNa)		2.4388			
	∠CCH	107.754		∠CNC		173.770			
	∠NCCH	59.112		∠NaC <sub>2</sub> N		76.602			
	CH <sub>2</sub> CNLi (2)	r(LiN)	1.7290	1.7621		CH <sub>2</sub> NCNa (15)	∠NCH	106.675	
r(NC)		1.1839	1.1815	∠CNCH	121.589				
r(CC)		1.3247	1.3320	r(C <sub>1</sub> N)	1.1806				
r(CH)		1.0707	1.0723	r(NC <sub>2</sub> )	1.3130				
∠CCH		120.500	120.075	r(CH)	1.0690				
LiCCNH <sub>2</sub> (3)	r(LiC)	1.8933		HMgCH <sub>2</sub> CN (1)	r(NaC <sub>1</sub> )	2.1976			
	r(CC)	1.2189			∠NCH	119.390			
	r(CN)	1.3384			r(CC)	1.4473			
	r(NH)	0.9957			r(C <sub>1</sub> Mg)	2.8870			
	∠CNH	121.122			r(CN)	1.1442			
HCCNHLi (4)	r(HC)	1.0480		r(C <sub>2</sub> Mg)	2.1287				
	r(CC)	1.1994		r(CH)	1.0863				
	r(CN)	1.3383		r(MgH)	1.7177				
	r(NH)	1.0092		∠C <sub>2</sub> C <sub>1</sub> Mg	45.0810				
	r(NLi)	1.7582		∠CCN	177.0910				
LiCH <sub>2</sub> NC (12)	∠CNH	112.366		CH <sub>2</sub> CNMgH (2)	∠CCH	109.9020			
	∠CNLi	117.556			∠C <sub>1</sub> MgH	207.443			
	r(LiC <sub>1</sub> )	2.6312	2.5025		∠NCCH	120.731			
	r(LiN)	2.0514	2.0400		r(HMg)	1.7129			
	r(LiC <sub>2</sub> )	1.9911	1.9984		r(MgN)	1.8687			
	r(C <sub>1</sub> N)	1.1673	1.1583		r(NC)	1.1866			
	r(NC <sub>2</sub> )	1.4993	1.4563		r(CC)	1.3169			
	r(CH)	1.0814	1.0817		r(CH)	1.0703			
	∠CNC	172.510	166.591		∠CCH	120.375			
	∠NC <sub>2</sub> Li	70.387	70.394		r(CN)	1.4689			
CH <sub>2</sub> LiNC (14)	∠NC <sub>2</sub> H	106.975	107.739	HMgCH <sub>2</sub> NC (12)	r(NMg)	2.7004			
	∠CNCH	120.737	120.925		r(NC)	1.1627			
	r(CN)	1.1671			r(CH)	1.0833			
	r(NLi)	1.7748			r(MgH)	1.7179			
	r(LiC)	2.1968			∠CNMg	51.300			
	r(CH)	1.0899			∠CNC	178.694			
	∠LiCH	125.854			∠NCH	107.630			
	CH <sub>2</sub> NCLi (15)	r(LiC <sub>1</sub> )	1.9009		1.9016	∠MgNCH	121.685		
		r(C <sub>1</sub> N)	1.1839		1.1758	r(C <sub>1</sub> N)	1.1840		
		r(NC <sub>2</sub> )	1.3015		1.2973	r(NC <sub>2</sub> )	1.2894		
r(CH)		1.0691	1.0711	r(CH)	1.0689				
∠NCH		119.565	119.101	r(CMg)	2.0090				
			r(MgH)	1.7113					
			∠NCH	119.574					

**Sodium and Magnesium Derivatives of Methyl Cyanide and of Methyl Isocyanide.** Since lithium is a first-row element with a relatively small ionic radius, organolithium compounds may exhibit unique behavior, or at least not be representative of other organometallic reagents. Hence, comparisons of the calculated structures and relative energies of sodium and of magnesium (MgH) derivatives of methyl cyanide and methyl isocyanide with those of the corresponding lithium compounds should contribute to the understanding of organometallic structures and relative stabilities.

At 6-31G\*\*//3-21G, the same stability order for the various

C<sub>2</sub>H<sub>2</sub>NNa isomers was found as for lithium analogues (Table I). The most stable structures, **7** and **12** (M = Na), are slightly less bent than the corresponding lithium derivatives. As in other cases,<sup>22</sup> sodium bridges less effectively than lithium. Magnesium derivatives, C<sub>2</sub>H<sub>2</sub>NMg, also repeat the energy relationships found for C<sub>2</sub>H<sub>2</sub>NLi isomers; at the 6-31G\*\*//3-21G level the relative stabilities of the structures **2**, **7**, **12**, and **15** (M = MgH) are the same as for lithium and sodium. However, the optimized structures of **7** and **12** (M = MgH) are classical (Figure 1) and the C—C=N angle in HMgCH<sub>2</sub>CN (structure **1**) as well as the

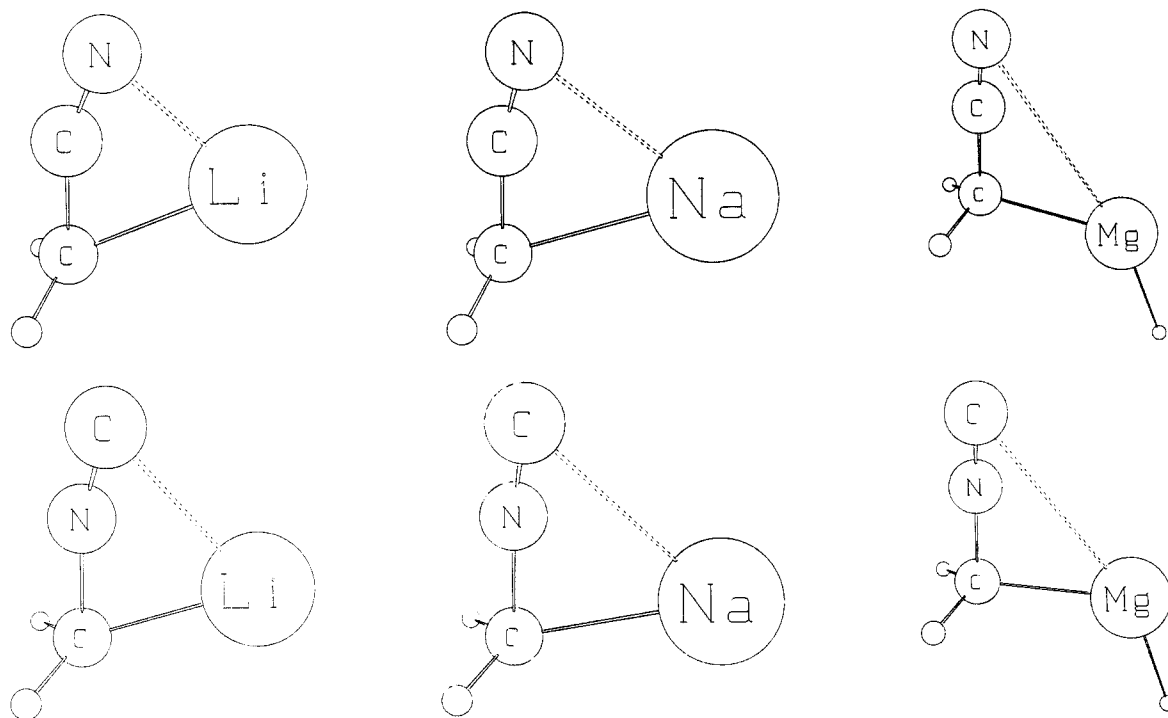


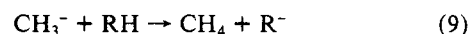
Figure 1. The most stable lithium, sodium, and magnesyl (MgH) derivatives of acetonitrile and methyl isocyanide (6-31G\* geometries with Li, 3-21G geometries with Na and MgH).

C—N=C angle in  $\text{HMgCH}_2\text{NC}$  are only slightly bent. The bridging tendency, reduced with sodium, is of little significance with magnesium. This was shown earlier with allyl derivatives<sup>21</sup> and also is reflected by the Mulliken populations. In **7** these are 0.321, 0.373, and 0.270 between the terminal carbon atom and  $\text{M} = \text{Li}$ ,  $\text{Na}$ , and  $\text{MgH}$ , respectively. While the overlap populations between the metal atom and the nitrile carbon of **7** are close to zero, the values between the metal and the nitrogen are 0.134, 0.078, and 0.006, for  $\text{M} = \text{Li}$ ,  $\text{Na}$ , and  $\text{MgH}$ , respectively. In **12**, the calculated Mulliken overlap populations show the same trends, viz., between the methylene carbon and the metal—0.269, 0.216, and 0.330 for  $\text{M} = \text{Li}$ ,  $\text{Na}$ , and  $\text{MgH}$ —and between the isonitrile carbon and the metal—0.107, 0.069, and 0.023, respectively. The overlap populations between the metal atoms and the isonitrile nitrogen also are close to zero. Hence, in both instances the overlap populations indicate bonding interactions between the metal and terminal atoms of the nitrile and the isonitrile ligands and negligible interactions with the central atoms. The situation in allyllithium and allenyllithium, where the negative charge is delocalized to the terminal atoms, is similar.<sup>20,21</sup> The bond lengths between the heavy atoms of structures **7** and **12** change smoothly along the sequence Li, Na, MgH (Tables V and VI), as do the calculated valence angles. The distances between the heavy atoms in keteneimine metal derivatives **2** also change smoothly but along the sequence Na, Li, MgH (Table VII). This ordering follows the expected ionicity of nitrogen–metal bonds. Regular variations of calculated bond lengths between the heavy atoms are also obtained for the “planar nitrile ylide” derivatives **15**, Table VIII, where the trends are similar to the case of keteneimine derivatives **2**. Following these results, we conclude that these organometallic structures depend both on the character of the metal atom and the (principal) site(s) of attachment.

**Energetic Relationships between the Cyano- and Isocyano-Stabilized Carbanions and Their Lithium, Sodium, and Magnesium Derivatives.** Most of the “carbanions” used synthetically in solution are in reality polar organometallic derivatives with varying amounts of ionic character.<sup>19</sup> The degree to which the counterions influence the energies and the behavior of the carbanion moieties is of critical importance. We have examined this question in detail in several studies.<sup>20–22,24b</sup>

It is first necessary to establish the “normal” behavior for each metal. In order to do this, we compared the methyl stabilization

energies of sets of about 15 organolithium, organosodium, and organomagnesium derivatives (eq 8) with those of the corresponding carbanions (eq 9).<sup>20b,21a,24a</sup> Good correlations were



obtained; the slopes for both lithium and sodium compounds were about 70–75% vs. the “naked” carbanion values. This non-unit slope does not necessarily indicate covalent character, as electrostatic interactions in ion pairs would be expected to give similarly attenuated values. However, the magnesium derivatives correlated less well against their carbanion counterparts and the slope, only about 40% was considerably less than that of their Li and Na counterparts.<sup>21a</sup> This can reasonably be attributed to the greater covalent character of C–Mg bonds.<sup>21,22</sup> Such  $\text{R}^-/\text{RM}$  correlations are successful when the negative charge in  $\text{R}^-$  is either localized on a single atom or delocalized more or less symmetrically, e.g., in the allyl and allenyl anions.<sup>21,23</sup> The presence of  $\text{Li}^+$  and  $\text{Na}^+$  counterions does not change the charge distributions in such anions and therefore  $\text{RLi}$  and  $\text{RNa}$  compounds in this category can be regarded as being equivalent to the corresponding anions,  $\text{R}^-$ .

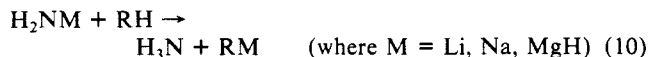
However, there also are numerous exceptions. Our earlier studies revealed two classes of molecules which deviated significantly from regular behavior.<sup>24a</sup> In particular, the lithium derivatives in the first class (the sodium derivatives less so) were more stable than expected on the basis of the relative stabilization energies of the corresponding bare carbanions. This extra stabilization is due to metal bridging to heteroatoms (more effective for lithium than for sodium).<sup>22</sup> The second class of deviations is characterized by lower stabilization energies for the organometallic derivatives than expected from the relative stabilization energies of the corresponding bare carbanions. These instances are characterized by charge localization effects due to the metal counterion or, in addition, to partial covalent bonding to the metal.<sup>22,24a,39</sup> When a delocalized carbanion interacts with a positive counterion unsymmetrically, the negative charge is

(39) Schleyer, P. v. R.; Kos, A. J.; Wilhelm, D.; Clark, T.; Boche, G.; Decker, G.; Etzrodt, H.; Dietrich, H.; Mahdi, W. *J. Chem. Soc., Chem. Commun.* 1984, 1495.



localized and the system becomes relatively less stable as a result. Covalent bonding has the same effect. A composite of all these effects is found in the present study. Table IV provides comparisons among lithium, sodium, and magnesium derivatives.

Consider first the  $\text{H}_2\text{C}=\text{C}=\text{NM}$  (**2**) derivatives, which are properly compared in relative energies to the corresponding metalated amine,  $\text{H}_2\text{NM}$ , by means of eq 10. The amino sta-



bilization energy of  $\text{H}_2\text{C}=\text{C}=\text{NNa}$ , 40.9 kcal/mol (3-21G//3-21G), is 61% of the stabilization energy (67.0 kcal/mol) of the parent anion  $\text{CH}_2\text{CN}^-$  calculated at the 6-31+G\*\*//6-31+G\* level (Table IV). Following the discussion above, this represents the situation expected for ion pairing involving a larger metal counterion. Moreover, the lithium salt shows a significantly reduced relative stabilization energy, 32.4 kcal/mol (48% of the anion stabilization energy) at 3-21G or 28.9 kcal/mol (43%) at 6-31G\*\*//6-31G\*. This reduction is due either to the presence of some covalent N-Li bonding or to the smaller size of the lithium cation which results in greater negative charge localization on the nitrogen and less stabilization due to delocalization. As expected, the stabilization energy of magnesyl keteneimine, 23.3 kcal/mol at 3-21G//3-21G (34% of the anion value), is even less. Since the N-Mg distance is larger than that of N-Li, this decrease indicates the significant covalent character of magnesium bonding.

The stabilization energies (vs.  $\text{CH}_3\text{Li}$ ) for the bridged metalated acetonitrile species **7** ( $\text{M} = \text{Li, Na}$ ) are only about 50% of the stabilization energy of the parent  $\text{CH}_2\text{CN}^-$  anion (vs.  $\text{CH}_3^-$ ). For the bridged isonitrile derivatives  $\text{CH}_2(\text{M})\text{NC}$  (**12**), the methyl stabilization energies ( $\text{M} = \text{Li}$  or  $\text{Na}$ ) are only about 40% of that of the  $\text{CH}_2\text{NC}^-$  anion. The magnesium counterparts, **1** and **12**, show hardly any bridging tendency in their geometries, and their structures are largely covalent. This is also reflected in the very low methyl stabilization energies relative to the free carbanions, 8.7 kcal/mol or only 15% for the nitrile and 3.8 kcal/mol (9%) for the isocyanide derivative. All these values are much less than expected on the basis of the comparisons among simple  $\text{R}^-/\text{RLi}$  or  $\text{R}^-/\text{RNA}$  compounds.<sup>20b,21,24a</sup> The thermodynamic driving force for the reactions of the lithium and sodium derivatives of  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{NC}$  is strongly attenuated relative to that of the bare carbanions; the situation with magnesium is even more extreme since Mg-C and Mg-N bonding has considerable covalent character.

**The Degree of Association of Lithiated Acetonitrile and the Structure of Its Dimer.** The pronounced tendency of lithium compounds to form oligomers in the solid (crystal), in solution, and even in the gas phase has been extensively documented both experimentally and theoretically.<sup>10-17,38,40-43</sup> Lithium derivatives of both carbon and nitrogen compounds exhibit quite variable degrees of aggregation; many X-ray structures of nitrogen compounds have become available recently.<sup>12,40,44</sup> The closest analogies to the possible structures of associated lithiated acetonitriles are afforded by derivatives of the isoelectronic allenyl-lithium **6**, of *N*-lithiated methyleneimines,<sup>15,40</sup> and of lithioacetylene.<sup>41</sup> The two known allenyllithiums are solvated dimers with stacked structures in the solid state.<sup>19b</sup> Most  $\text{R}_2\text{C}=\text{NLi}$  derivatives are solvated tetrahedral tetramers or hexamers, but a sterically crowded example ( $\text{R} = t\text{-Bu}$ ) has been shown recently

**Table X.** MNDO Heats of Formation and Relative Energies of Associated and Solvated  $\text{C}_2\text{H}_2\text{NLi}$  Species (kcal/mol)

species	no.	$\Delta H_f^\circ$	rel energy vs. (no.)	$\Delta E_{\text{solv}}/\text{H}_2\text{O}$
$\text{CH}_3\text{Li}$		-1.4		
$\text{H}_2\text{N}-\text{Li}$		7.9		
$(\text{LiNH}_2)$	$D_{2h}$ (perp)	19	-46.8	
	$D_{2d}$		-36.2	
	$D_{2h}$ (planar)	20	-24.8	
$\text{LiCN}$		5.0		
$(\text{LiCN})_2$	$D_{2h}$		-70.9	
$(\text{H}_2\text{NLi})_4$	" $T_d$ "		-100.0	
	$D_{4h}$	26	-128.4	
$\text{H}_2\text{C}=\text{N}-\text{Li}$		20.9		
$(\text{H}_2\text{C}=\text{NLi})_2$	$D_{2h}$ (planar)		-9.3	
	$D_{2d}$		-7.1	
	$D_{2h}$ (perp)		-3.1	
	" $T_d$ "	25	-60.8	
$(\text{H}_2\text{C}=\text{NLi})_4$		2	35.0	
$\text{H}_2\text{C}=\text{C}=\text{N}-\text{Li}$		7	16.4	-18.6 (2)
$\text{CH}_2(\text{Li})\text{C}=\text{N}$			-11.9	
$\text{CH}_4$			-6.3	
$\text{NH}_3$			-60.9	
$\text{H}_2\text{O}$			-63.0	-18.5 (7) <sup>a</sup>
$\text{LiCH}_2\text{CN}\cdot\text{H}_2\text{O}$	31		-31.4 (7) <sup>a</sup>	-15.7
$\text{LiCH}_2\text{CN}\cdot 2\text{H}_2\text{O}$	32		-39.1 (7) <sup>a</sup>	-13.0
$\text{LiCH}_2\text{CN}\cdot 3\text{H}_2\text{O}$	33		-44.4	+17.1 (31) <sup>a</sup>
$\text{H}_2\text{C}=\text{C}=\text{N}-\text{Li}\cdot\text{H}_2\text{O}$			-18.5 (2)	
$\text{H}_2\text{CCNLi}\cdot 2\text{H}_2\text{O}$			-117.6	+19.1 (32) <sup>a</sup>
				-30.8 (2) <sup>a</sup>
$\text{H}_2\text{CCNLi}\cdot 3\text{H}_2\text{O}$			-187.7	+15.6 (33) <sup>a</sup>
				-40.0 (2) <sup>a</sup>
$(\text{H}_2\text{C}=\text{C}=\text{NLi})_2$	$D_{2h}$ (perp)	23	17.1	-52.9 (2) <sup>b</sup>
	$D_{2d}$		20.7	-49.3 (2) <sup>b</sup>
	$D_{2h}$ (planar)	24	24.6	-45.4 (2) <sup>b</sup>
	" $T_d$ "		11.7	-128.3 (2) <sup>b</sup>
$(\text{H}_2\text{C}=\text{C}=\text{NLi})_4$		27	-27.9	-65.2 (7) <sup>b</sup>
$(\text{CH}_2(\text{Li})\text{CH})_2$	$C_{2h}$			-45.0 (23) <sup>b</sup>
$(\text{CH}_2\text{CNLi})_2\cdot 2\text{H}_2\text{O}$			-135.5	-30.8 (23) <sup>a</sup>
$(\text{CH}_2(\text{Li})\text{CN})_2\cdot 2\text{H}_2\text{O}$			-174.2	-24.6 (27) <sup>a</sup>
$(\text{CH}_2\text{CNLi})_2\cdot 4\text{H}_2\text{O}$			-272.5	-46.0 (23) <sup>a</sup>
$(\text{CH}_2(\text{Li})\text{CN})\cdot 4\text{H}_2\text{O}$			-307.6	-36.1 (27) <sup>a</sup>
$\text{CH}_2(\text{Li})\text{NC}$	12	52.1		
$\text{CH}_2\text{N}=\text{C}-\text{Li}$	15	45.9		
$(\text{CH}_2(\text{Li})\text{NC})_2$	28	-5.6	-109.8 (12) <sup>b</sup>	
$\text{CH}_2(\text{Li})\text{NC}\cdot 3\text{H}_2\text{O}$			-159.7	-29.1 (12) <sup>a</sup>
$(\text{CH}_2(\text{Li})\text{NC})_2\cdot 4\text{H}_2\text{O}$			-285.9	-36.7 (28) <sup>a</sup>
$\text{LiCH}_2\text{NC}\cdot\text{LiCH}_2\text{NC}$	29	66.3		-52.5 (12) <sup>a</sup>
$\text{LiCH}_2\text{CN}\cdot\text{LiCH}_2\text{CN}$	30	26.4		-11.0 (7)

<sup>a</sup>Total solvation energies, i.e., vs. the parent organolithium and the appropriate number of water molecules. <sup>b</sup>Association energies, i.e., vs. the appropriate number of monomers.

to be a solvated dimer in the solid.<sup>40</sup> Lithiated acetylenes are known both as dimers and as tetrahedral tetramers.<sup>41</sup>

An earlier report<sup>10</sup> indicated  $\text{LiCH}_2\text{CN}$  to be a tetramer and  $\text{C}_6\text{H}_5\text{CHLiCN}$  a dimer in dimethyl sulfoxide solution at about room temperatures. A cryoscopic study in tetrahydrofuran (THF) carried out recently at Erlangen<sup>11</sup> gave different results. Crystals of  $\text{LiCH}_2\text{CN}\cdot 2\text{THF}$  dissolved in THF showed a degree of association 1.97-2.09 at -108 °C. <sup>1</sup>H, <sup>13</sup>C, <sup>6</sup>Li, and <sup>7</sup>Li NMR spectra did not change between the freezing point of the THF and room temperature, indicating the dimer as the only associated form of  $\text{LiCH}_2\text{CN}$ .<sup>11</sup> Under the same conditions  $\text{C}_6\text{H}_5\text{CHLiCN}\cdot 2\text{THF}$  had an association degree of only 1.12, i.e., the monomer/dimer ratio was ca. 7:1.<sup>11</sup> Both compounds are presumed to be dimers in the solid, but no X-ray structures are available yet.<sup>45</sup> Lithium NMR studies also indicate dimer-monomer equilibria.<sup>40,44</sup> Hence, we have searched for the best dimeric structures of the parent

(45) X-ray structural studies of lithiated nitriles are being undertaken. The situation in hydrocarbon solvents appears to be different, as higher aggregates are formed at lower temperatures. See: Fraenkel, G.; Henrichs, M.; Hewitt, M.; Su, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 255. Frenkel, G.; Hsu, H.; Su, B. M. in "Lithium: Current Applications in Science, Medicine, and Technology"; Bach, R., Ed., ACS Special Publication, 1985.

(40) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 79. Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R. *Angew. Chem.* **1985**, *97*, 322. Reed, D.; Barr, D.; Mulvey, R. E.; Snaith, R., manuscript in press. Clegg, W.; Snaith, R.; Scheerer, H. M. M.; Wade, K.; Whitehead, G. *Ibid.* **1983**, 1309.

(41) Seebach, D.; Haessig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. Schubert, B.; Weiss, E. *Chem. Ber.* **1983**, *116*, 3212. Schubert, B.; Weiss, E. *Angew. Chem.* **1983**, *95*, 499; *Angew. Chem. Suppl.* **1983**, 703-709; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 496. Fraenkel, G.; Pramanik, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1527.

(42) Haessig, R.; Seebach, D. *Helv. Chim. Acta* **1983**, *66*, 2269. Heinzer, J.; Oth, J. F. M.; Seebach, D. *Ibid.* **1985**, *68*, 1848.

(43) Koester, H.; Weiss, E. *Chem. Ber.* **1982**, *115*, 3422.

(44) Snaith, R., private communication.



Table XI. Association Energies (kcal/mol)

species	no.	aggregate point group	MNDO	3-21G/ 3-21G	best estimate
$(\text{CH}_3\text{Li})_2$		$C_{2h}$	72.2 <sup>a</sup>	46.2 <sup>b</sup>	42.5 <sup>b</sup>
$(\text{H}_2\text{NLi})_2$	19	$D_{2h}$ (perp)	62.6 <sup>c</sup>	83.4 <sup>c,d</sup>	62.6 <sup>c</sup>
		$D_{2d}$	52.0		
$(\text{H}_2\text{C}=\text{NLi})_2$	20	$D_{2h}$ (planar)	40.6		
		$D_{2h}$ (planar)	51.7	71.4 <sup>d</sup>	
		$D_{2d}$	48.9		
		$D_{2h}$ (perp)	44.9		
$(\text{H}_2\text{C}=\text{C}=\text{NLi})_2$	23	$D_{2h}$ (perp)	52.9		
		$D_{2d}$	49.3		
	24	$D_{2h}$ (planar)	45.4		
		$C_{2h}$	97.8		
$(\text{H}_2\text{C}(\text{Li})\text{CN})_2$	27	$C_{2h}$	65.2		
		" $T_d$ "	131.6	199.9 <sup>d,e</sup>	158.4 <sup>e</sup>
$(\text{H}_2\text{NLi})_4$	26	$D_{4h}$	160.0	211.5 <sup>d,e</sup>	167.3 <sup>e</sup>
		" $T_d$ "	144.4		
$(\text{H}_2\text{C}=\text{NLi})_4$	25	" $T_d$ "	128.3		
		" $T_d$ "	128.3		
$(\text{H}_2\text{C}=\text{C}=\text{NLi})_4$	25	" $T_d$ "	128.3		
		" $T_d$ "	128.3		
$(\text{LiCN})_2$		$D_{2h}$	80.9	46.2 <sup>b</sup>	

<sup>a</sup> Value overestimated due to lithium MNDO parametrization. <sup>b</sup> Reference 15. <sup>c</sup> Reference 16. <sup>d</sup> These values<sup>15</sup> are overestimated due to BSSE, see text. <sup>e</sup> Reference 17.

system  $\text{LiCH}_2\text{CN}$  theoretically.

High-level computational studies of molecules of the size of  $(\text{LiCH}_2\text{CN})_2$  are at present beyond our capability. MNDO calculations are quite feasible, however, and have often been demonstrated to predict or to reproduce experimental or higher level theoretical structures quite well.<sup>19a,b,28,39</sup> Nevertheless, the MNDO lithium parametrization<sup>28b</sup> is a compromise, and the known deficiencies need to be appreciated in order to evaluate the results summarized in Tables X and XI. In particular, C-Li bonds are indicated to be too strong.<sup>28b</sup> Thus, eq 5, evaluated by MNDO data, is exothermic by only 3.7 kcal/mol, an error of over 20 kcal/mol. However, N-Li interaction energies are usually given quite well.<sup>15,16</sup> This is shown, e.g., in Table XI, which compares the MNDO and 3-21G association energies and, in some cases, the best available estimates.<sup>17</sup> The MNDO values for  $\text{LiCH}_3$  and  $\text{LiCN}$  dimerization are too large by about 30 kcal/mol, but the association energies of  $\text{LiNH}_2$  and  $\text{LiN}=\text{CH}_2$  are generally satisfactory (Table XI). Furthermore, the MNDO energy difference favoring the bridged  $\text{CH}_2(\text{Li})\text{CN}$  structure (7) over  $\text{H}_2\text{C}=\text{C}=\text{NLi}$  (2) is 18.6 kcal/mol (Table X), not far above the best ab initio (MP2/6-31G\*\*//6-31G\*) value 9.7 kcal/mol (Table I). The MNDO  $\text{CH}_2(\text{Li})\text{CN}$  vs.  $\text{CH}_2(\text{Li})\text{NC}$  energy difference (35.7 kcal/mol) also mirrors the best ab initio value (32.8 kcal/mol) reasonably well. MNDO favors the  $\text{H}_2\text{CN}=\text{C}-\text{Li}$  isomer (15) over the bridged  $\text{CH}_2(\text{Li})\text{NC}$  form (12) by 6.0 kcal/mol; MP2/6-31G\*\*//6-31G\* gives the opposite order, with an energy difference of 16.0 kcal/mol. Again, C-Li binding is overestimated.

We first consider dimers based on the methyleneimine-type structures. Two principle orientations are possible (Figure 2): the substituents on the carbon can lie in or perpendicular to the  $\text{N}(\text{Li})_2\text{N}$  planes. In all cases (Table XI) we find the preferred geometries to be van't Hoff rather than anti-van't Hoff,<sup>46</sup> i.e., "tetrahedral" (perpendicular  $D_{2h}$ ) for  $\text{R}_2\text{N}(\text{Li})_2\text{NR}_2$  (19), planar  $D_{2h}$  for  $\text{R}_2\text{C}=\text{N}(\text{Li})_2\text{N}=\text{CR}_2$  (ethylene-like 21), and perpendicular  $D_{2h}$  for  $\text{R}_2\text{C}=\text{C}=\text{N}(\text{Li})_2\text{N}=\text{C}=\text{CR}_2$  (allene-like 23). These geometries are due more to orbital orientation than to covalent bonding. The energy difference between the two  $D_{2h}$  possibilities is rather large for  $\text{H}_2\text{N}(\text{Li})_2\text{NH}_2$  (22.0 kcal/mol)<sup>15,16</sup> but is relatively small for  $(\text{H}_2\text{C}=\text{NLi})_2$ , 6.8 kcal/mol and  $(\text{H}_2\text{C}=\text{C}=\text{NLi})_2$ , 7.5 kcal/mol, Figure 2. Indeed, the one known derivative in this category, solvated  $[(t\text{-Bu})_2\text{C}=\text{NLi}]_2$ , has a twisted structure (dihedral angle  $58^\circ$ ) in the solid state,<sup>40</sup> i.e., in between the two  $D_{2h}$  extremes. This distortion evidently is due to the bulky *tert*-butyl substituents. The methyleneimine anion lone pairs and  $\pi$ -electrons combine to give a quasicylindrical

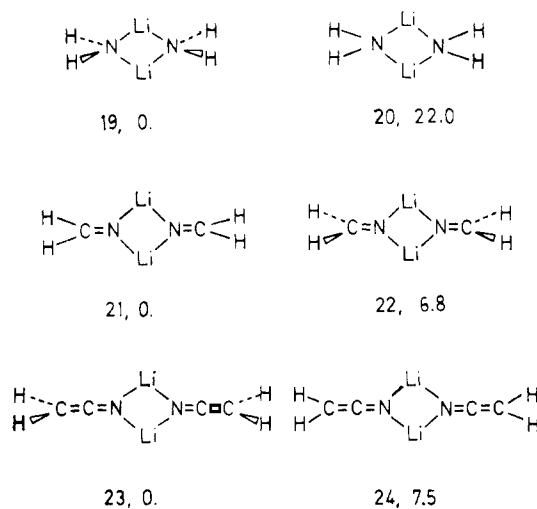
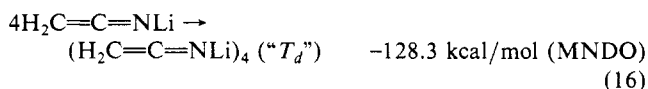
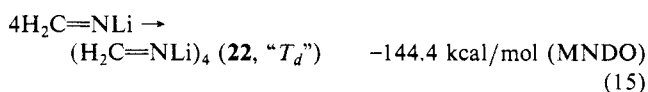
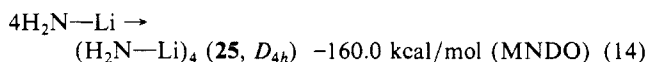
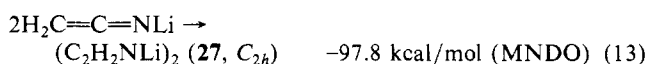
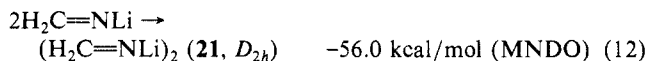
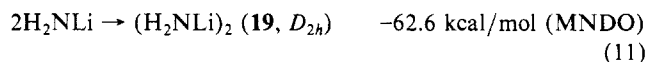


Figure 2. Relative energies (MNDO, kcal/mol) of van't Hoff and anti-van't Hoff structures ( $D_{2h}$  point group) of  $\text{NH}_2\text{Li}$ ,  $\text{H}_2\text{C}=\text{NLi}$ , and  $\text{H}_2\text{C}=\text{C}=\text{NLi}$  dimers.

electronic arrangement at nitrogen. Hence, the lithium cation placements in the dimer  $(\text{H}_2\text{C}=\text{NLi})_2$  are not very critical. The same is true for  $(\text{H}_2\text{C}=\text{C}=\text{N}-\text{Li})_2$ , as the same factors are involved.

The MNDO dimerization energies (in kcal/mol) of the NLi species (eq 11-13 and Table XI) show some attenuation in going from  $\text{H}_2\text{NLi}$  (62.6) to  $\text{H}_2\text{C}=\text{NLi}$  (51.7) or  $\text{H}_2\text{C}=\text{C}=\text{NLi}$  (52.9, to give dimer 19), expected from delocalization of the negative charge in the larger systems. The tetramerization energies (eq 15-17, Table XI) fall off even more. This trend explains why lithiomethyleneimines tetramerize (Figure 3) (or form higher oligomers, see ref 40), but not N-lithiated acetonitrile: the energy gain for the latter is 16.1 kcal/mol lower (-144.4 vs. -128.3 kcal/mol). In addition, as we will see below, solvation of the smaller aggregate is more effective. The quasicylindrical electronic arrangement at nitrogen in the  $\text{H}_2\text{C}=\text{N}^-$  and  $\text{H}_2\text{C}=\text{C}=\text{N}^-$  anionic moieties (like that at  $\text{RC}\equiv\text{C}^-$ ) explains why these lithium derivatives prefer tetrahedral tetramer structures (25), whereas the  $(\text{H}_2\text{NLi})_4$  tetramer, with directed lone pairs at nitrogen, prefers a cyclic eight-membered-ring arrangement (26).<sup>17</sup> For calibration, the best ab initio tetramerization energies of  $\text{LiOH}$  (to 24, X = OH),  $\text{LiNH}_2$  (to 25), and  $\text{LiF}$  (to 24, X = F) are indicated to be in the 167-190 kcal/mol range.<sup>17</sup>



However, the  $D_{2h}$  lithiated acetonitrile dimer (23, Figure 2) is far from being the most stable form according to MNDO. If the

(47) Boche, G.; Decker, G.; Etzrodt, H.; Mahdi, W.; Kos, A. J.; Schleyer, P. v. R.; J. Am. Chem. Soc., Chem. Commun. 1984, 1493.

(48) See: Bierbaum, V. M.; DePuy, C. N. Symposia Preprints, Div. Petrol. Chem., Am. Chem. Soc. 1985, 30, 575.

(46) Krogh-Jespersen, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. J. Am. Chem. Soc. 1979, 101, 4843.

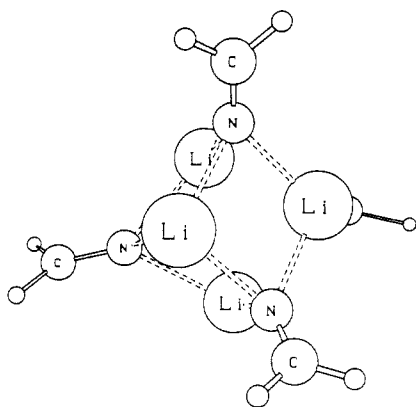
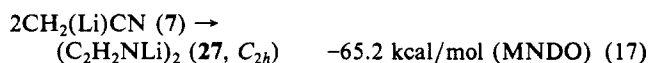


Figure 3. The " $T_d$ " tetramer of  $H_2C=NLi$  (MNDO).

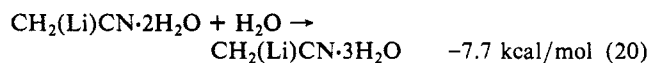
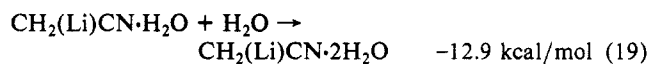
symmetry restriction is reduced to  $C_{2h}$ , the geometry optimization gives a much more stable ring isomer. This ring  $C_{2h}$  dimer (**27**, Figure 4), in reality, is a derivative of neither **7** nor **2**, since each lithium atom resides between the nitrogen atom of one of the ligands and the carbon atom of the other. Although the calculated difference between the two dimerization energies (44.9 kcal/mol, MNDO) probably is overestimated due to the MNDO C-Li binding error (see above), the unsolvated dimer should clearly prefer the ring structure. On the basis of the most stable  $CH_2(Li)CN$  monomer (**7**) the dimerization energy to **27** is



The preferential formation of this dimer provides an alternative to "metallotropic" interconversion of **7** to **2**. However, solvation by donor solvents is also of critical importance.

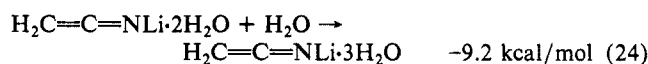
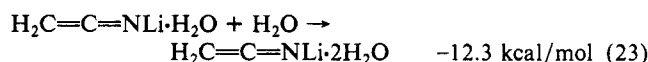
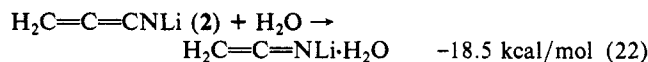
**Effects of Solvation and the Structure of the Solvated Dimer.** MNDO calculations provide particularly valuable estimates of solvation energies of lithium compounds.<sup>15,47</sup> Sterically uncrowded ether solvents like tetrahydrofuran or dimethyl ether can be

modeled most simply with  $H_2O$ . The supermolecule approach, which does not take bulk solvent effects into account, is used. We considered a series of model hydrated species (Table X) with various numbers of water ligands. As expected from our general experience,<sup>15</sup> solvation energies are the largest for the first solvent attachment (eq 18), slightly smaller for the second (eq 19), and smallest for the third (eq 20), e.g., for (**7**):



$$\text{total (MNDO): } -39.1 \text{ kcal/mol (21)}$$

For the less stable ketenimine derivative **2** we obtain similar values for each solvation step (eq 22-24):



$$\text{total (MNDO): } -40.0 \text{ kcal/mol (25)}$$

The relative stabilities of solvated **2** and **7** remain unchanged, as the total solvation energies of the two isomers are nearly the same (eq 21 vs. eq 25).  $C_4H_4N_2Li_2$  dimers are solvated less effectively than  $C_2H_2NLi$  monomers; this effect is expected, since the first solvent molecule attaches to lithium as the third ligand. The  $H_2C=C=N(Li)_2N=C=CH_2$  dimer (**23**) behaves regularly in this respect. The attachment of the first two water molecules (one to each lithium) is exothermic (eq 26) by an average of 15.4

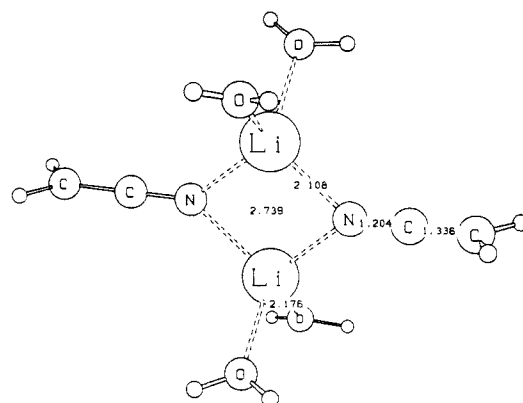
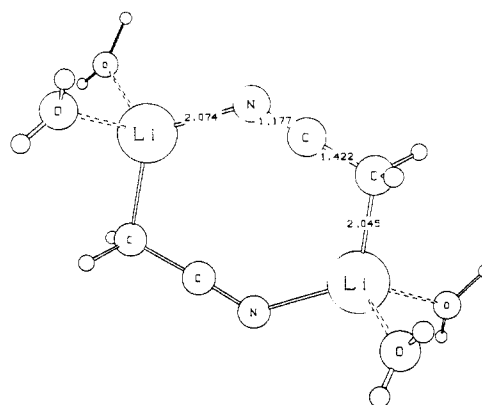
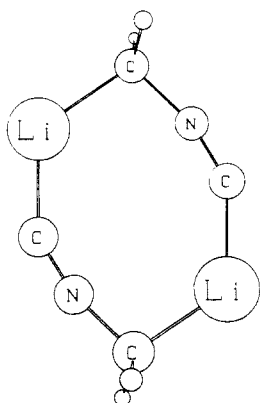
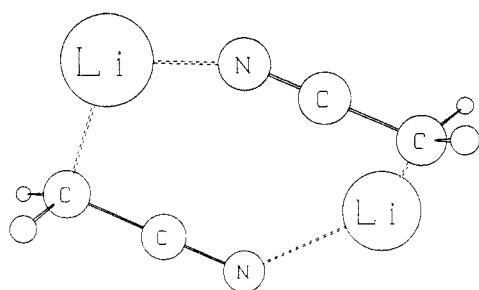
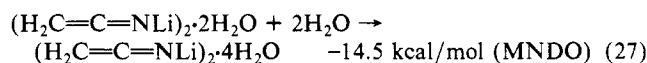
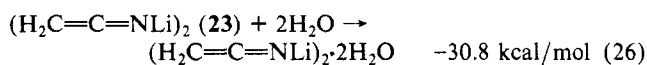
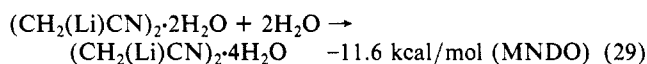
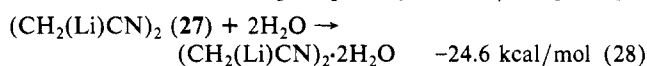


Figure 4. Ring dimer structures of lithiated acetonitrile **27** and methyl isocyanide (**28**) and tetrasolvated dimer structures, **27**· $4H_2O$  and **23**· $4H_2O$ , MNDO.

kcal/mol per molecule (compare with eq 19 and 23). Each water of the second solvation pair (eq 27) attaches with an average energy of 7.2 kcal/mol which is comparable to the values found for eq 20 and 24. The cyclic  $(\text{LiCH}_2\text{CN})_2$  dimer (**27**) is solvated

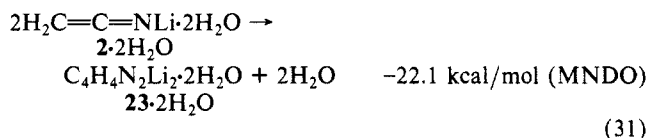
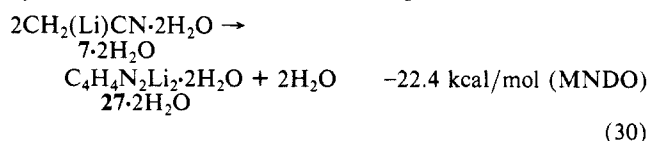


somewhat less effectively. The attachment of the first two solvent molecules (eq 28) is exothermic by 12.3 kcal/mol per water molecule, and the next stage (eq 29) by 5.8 kcal/mol per  $\text{H}_2\text{O}$ .



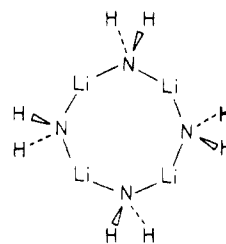
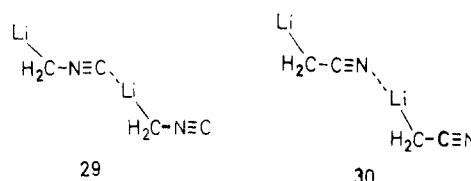
The total effect of solvation is to reduce the energy difference between the competing dimer structures. While the ring dimer **27** is 45.0 kcal/mol (MNDO) more stable than the  $D_{2h}$  form **23** when no solvent is present, this decreases to 38.7 when two and to 35.1 kcal/mol when four solvent molecules are attached (Table X). By taking into account the expected 30 kcal/mol MNDO overestimation of C-Li binding in the cyclic dimers (**27** and its solvated forms), solvated  $(\text{C}_2\text{H}_2\text{NLi})_2$  dimer may well favor the ketenimine structure (**23**, Figure 4) in donor solvents and in the solid when such ligands are present. We conclude that the energy difference between the two solvated dimers, **23** and **27**, probably is small.

The behavior of  $\text{C}_2\text{H}_2\text{NLi}$  associates in ether solvents is best modeled by the disproportionation of two molecules of solvated monomer  $\text{C}_2\text{H}_2\text{NLi} \cdot 2\text{H}_2\text{O}$  ( $7 \cdot 2\text{H}_2\text{O}$  and  $2 \cdot 2\text{H}_2\text{O}$ ) to a dimer dihydrate and two solvent molecules (eq 30 and 31). The di-



merization enthalpy of the solvated monomers is relatively small and explains the somewhat unusual Li coordination 3 (note, however, that Li enolates<sup>11</sup> and lithiated imines<sup>40,44</sup> show the same Li coordination 3). The entropy loss for the coordination of a further solvent molecule most likely cannot be compensated by the corresponding solvation enthalpy which is reduced even further. The calculated MNDO energy difference between  $23 \cdot 2\text{H}_2\text{O}$  and  $27 \cdot 2\text{H}_2\text{O}$  is 38.7 kcal/mol, while the incipient error in the MNDO parametrization is ca. 35 kcal/mol per Li-C contact. We therefore expect dimers of the type of  $23 \cdot 2\text{H}_2\text{O}$  to be more stable and to be observed in ether solvents and in solid state. Preliminary support to this conclusion is given by the recent cryoscopic measurements and NMR results.<sup>11</sup> Since the entropy contribution is less important at lower temperatures, the disproportionation equilibria between solvated oligomers should favor the lesser number of particles (e.g., monomer disolvates) in this case and the larger number of particles (e.g., dimer disolvates and solvent molecules) at higher temperature. There is an increasing number of similar examples in the literature.<sup>11,40,42</sup>

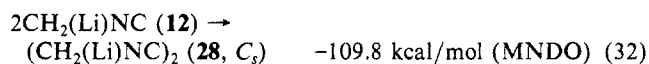
**Association and Solvation of Lithiated Methyl Isocyanide.** On the basis of previous experience, e.g., the allenyllithium and lithioacetonitrile dimer structures,<sup>19,20</sup> several possible dimer geometries of  $\text{CH}_2(\text{Li})\text{NC}$  were examined by means of MNDO calculations. Most of these structures were found to be unfavorable, but a chain head-to-tail dimer, **29**, had an association energy of 52.5 kcal/mol. A cyclic dimer, **28**, with a structure like

26,  $D_{4h}$ 

29

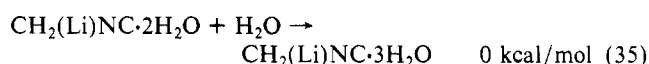
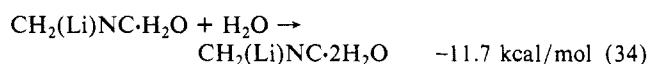
30

that of **27**, was found to be the most stable. The association energy of this dimer (eq 32) is very high:



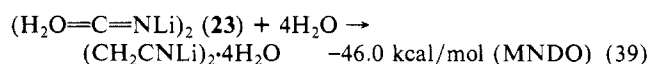
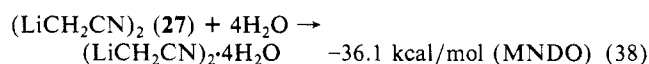
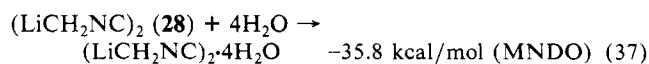
This value for association energy is certainly overestimated, as the MNDO dimerization energy of LiCN to a  $D_{2h}$  dimer with the two lithium atoms bridging between the two carbons is -80.9 kcal/mol; 3-21G//3-21G calculations give<sup>35</sup> -46.2 kcal/mol (Table XI). Even after applying an estimated correction of ca. 35 kcal/mol, the association energy of the lithiated isocyanide (eq 32) is still considerably higher than that of the nitrile derivatives (eq 17).

Model MNDO calculations show that the total solvation energy of the trihydrate of lithiomethyl isocyanide (29.1 kcal/mol, eq 36) is less than that of lithioacetonitrile (eq 21) or lithioketenimine (eq 25). The first two solvation energies (eq 33 and 34) are normal, but the third  $\text{H}_2\text{O}$  breaks the C-Li-C bridge; the resultant energy is zero (eq 35):

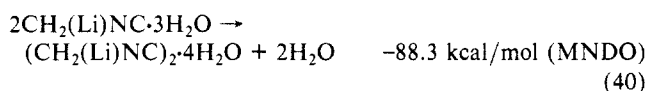


$$\text{total (MNDO): } -29.1 \text{ kcal/mol (36)}$$

The total solvation energy (eq 37) of the lithiated isocyanide dimer (**28**) is about the same as that of the cyclic lithiated acetonitrile dimer (**27**) (eq 38, the sum of eq 28 and 29). However, the total solvation energy of the lithiated ketenimine dimer (**23**) is much higher (eq 39):



The higher dimerization energy of the unsolvated lithiomethyl isocyanide and the high solvation energy of the cyclic dimer result in much more favorable dimerization energy relative to that of the cyclic lithiated acetonitrile dimer (compare eq 40 with the corresponding disproportionation, eq 30):



We thus predict that lithiated isocyanides should prefer to be associated both in solution and in the solid state. We have not explored higher aggregates but do not expect tetramers to be favorable. However, besides the cyclic dimer (**28**), open chain oligomers similar in structure to that found for allyllithium-TMEDA in the solid state<sup>43</sup> also are possible. The association energy for the chain dimer of lithiomethyl isocyanide (**29**), 52.5 kcal/mol, is only slightly less than half of the association energy for **12** (eq 31). In contrast, the MNDO association energy for a head-to-tail chain dimer of lithiated acetonitrile **30** is only 11.0 kcal/mol (Table X).

### Conclusions

The specific metal, M = Li, Na, or MgH, determines the geometries and stabilization energies of the C<sub>2</sub>H<sub>2</sub>NM isomers, **1**, **2**, **7**, **12**, and **15**, but not the order of relative stabilities. The geometry favored by each of these compounds depends on the ionic radii of the Li<sup>+</sup> and Na<sup>+</sup> cations, the partial covalent character of Mg-C and Mg-N bonds, and the capability of especially the alkali metals to bind to more than one ligand site and participate in multicenter bonding. The structures of Li and Na derivatives are similar, but lithium bridges more effectively. The sodium derivatives give relative energies closest to those of the corresponding anions and in this sense can be considered to be more ionic. The Li and Na salts of acetonitrile and of methyl isocyanide may be regarded as being essentially contact ion pairs with the corresponding carbanions. However, the interaction energies are large, and the geometries of the carbanion moieties are strongly influenced as a consequence. Due to their greater covalent character, the magnesium derivatives of acetonitrile and of methyl isocyanide have rather classical unbridged structures and have reduced stabilization energies relative to the free carbanions. C<sub>2</sub>H<sub>2</sub>NMgH are polar organometallic rather than "carbanionic" species.

MNDO calculations, corrected for known and systematic deficiencies of the parametrization, afford an efficient way to examine the effects of aggregation and of solvation. While R<sub>2</sub>NLi and R<sub>2</sub>C=NLi derivatives are known experimentally to be aggregated in ether solvents, LiCH<sub>2</sub>CN is largely monomeric. The solvation energies of the monomeric C<sub>2</sub>H<sub>2</sub>NLi isomers (modeled by three water molecules) are similar and the solvated CH<sub>2</sub>(Li)CN monomer should form a bridged structure (**7**). However, solvation reduces the energy difference between dimers **23** and **27**. While the unsolvated lithioacetonitrile prefers a cyclic, eight-membered-ring structure (**27**), we conclude that the ketenimine dimer,

(H<sub>2</sub>C=C=NLi)<sub>2</sub>·4R<sub>2</sub>O (Figure 4), should be favored by solvation and may be found in the solid state.<sup>45</sup> Aggregation and solvation effectively interconvert lithiated acetonitrile (**7**) into the ketenimine form **2**.

The energy difference between the alternative dimer structures probably is small and examples of both may be expected in substituted cases. The apparent Li coordination 3 in tetrahydrofuran solutions of the dimeric lithiated acetonitrile is due to the relatively low solvation enthalpy and competing entropy contribution. In contrast, the dimerization energy of LiCH<sub>2</sub>CN is unusually large. The cyclic eight-membered-ring dimer (**28**) is also solvated effectively, so that this form should be present in solution or in the solid. Chain oligomers are also possible.

The degree of aggregation of a given organolithium compound is a balance between the aggregation and solvation energies of monomer, dimer, and higher oligomers, and the entropy. The aggregation energies are influenced by the electronegativity and the hybridization of the atom(s) to which lithium is attached, the anion orbital orientation(s), and the degree of negative charge present in these orbitals (delocalization). The solvation energies are determined by the number of available sites at lithium and the energies of each individual solvent-solute interaction. The first solvation is more favorable than the second, and the third contributes relatively little. Steric effects (bulky substituents or solvents) should be important. Entropy favors a smaller degree of solvation, and lithium compounds are known to tend to be more highly associated at higher temperatures and in the solid.<sup>11,40,42</sup>

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Drs. W. Bauer and R. Snaith for information prior to publication and Professor H. Walborsky and Dr. E.-U. Würthwein for their interest. The cooperation of the staff of the Regionales Rechenzentrum Erlangen and the Leibniz Rechenzentrum München, in particular R. Woitok, RRZE, is gratefully acknowledged. J.K. thanks the Institute of Organic Chemistry, Sofia, for an extended academic leave.

**Registry No.** **1** (M = MgH), 99749-06-1; **2** (M = Li), 55440-71-6; **2** (M = Na), 58855-09-7; **2** (M = MgH), 99749-07-2; **2** (M = H), 17619-22-6; **3** (M = Li), 99749-00-5; **4** (M = Li), 99749-01-6; **10** (M = Li), 99748-92-2; **12** (M = Li), 74555-48-9; **12** (M = Na), 99749-03-8; **12** (M = MgH), 99749-08-3; **15** (M = Li), 99749-02-7; **15** (M = Na), 99749-04-9; **15** (M = MgH), 99749-09-4; **15** (M = H), 99749-10-7; **19/20**, 88656-96-6; **21/22**, 99748-93-3; **23/24**, 99748-95-5; **25**, 99748-94-4; **26**, 98331-83-0; **27**, 99748-97-7; **28**, 99766-98-0; **29**, 99748-98-8; LiCN, 2408-36-8; (LiCN)<sub>2</sub>, 99766-99-1; (H<sub>2</sub>C=C=NLi)<sub>4</sub>, 99748-99-9; (CH<sub>3</sub>Li)<sub>2</sub>, 74309-22-1; CH<sub>3</sub>CN, 75-05-8; CH<sub>3</sub>NC, 593-75-9; CH<sub>2</sub>CN<sup>-</sup>, 21438-99-3; CH<sub>2</sub>NC<sup>-</sup>, 81704-80-5; (H<sub>2</sub>NLi)<sub>4</sub>, 99748-96-6; H<sub>2</sub>C=N—Li, 99749-05-0.