

**Figure 1.** Molecular structure of **1** viewed obliquely (left) and along the V-B(7) axis (right). In the right view the  $C_8$  and  $C_2B_3$  rings are projected onto the same plane so that the ring sizes are directly comparable. Hydrogen atoms are omitted for clarity. Bond lengths ( $\text{\AA}$ ) involving the  $C_8H_8^{2-}$  ligand are as follows: C(R1)-C(R2), 1.460 (17); C(R2)-C(R3), 1.405 (16); C(R3)-C(R4), 1.360 (17); C(R4)-C(R5), 1.336 (15); C(R5)-C(R6), 1.497 (13); C(R6)-C(R7), 1.389 (15); C(R7)-C(R8), 1.377 (17); C(R8)-C(R1), 1.327 (19); V-C(R1), 2.264 (4); V-C(R2), 2.295 (11); V-C(R3), 2.288 (8); V-C(R4), 2.365 (10); V-C(R5), 2.286 (4); V-C(R6), 2.230 (9); V-C(R7), 2.254 (9); V-C(R8), 2.276 (11). Bond distances in the  $(C_2H_5)_2C_2B_4H_4^{2-}$  carborane ligand are normal.

contains formal  $V^{4+}$  sandwiched between  $(C_2H_5)_2C_2B_4H_4^{2-}$  and  $C_8H_8^{2-}$  ligands with vanadium completing a seven-vertex  $VC_2B_4$  pentagonal-bipyramidal (closo) cage that is isostructural with other  $MC_2B_4$  systems;<sup>8</sup> however, the metal is electron deficient with only 17 electrons in its valence shell.<sup>9</sup> The  $C_8$  ring is planar within normal limits of experimental error (largest deviation from the calculated least-squares plane is 0.02  $\text{\AA}$ , comparable to that observed in uranocene,  $U(C_8H_8)_2^{2b}$ ). The mean ring C-C bond length is 1.394  $\text{\AA}$ , with variations in the eight values (Figure 1) that may reflect, to a degree, large thermal motions of the ring carbons. The V-C<sub>ring</sub> distances are nearly equal (mean value 2.282  $\text{\AA}$ ), the longest and shortest differing by only 6%.

The vanadium atom is located 1.375  $\text{\AA}$  from the  $C_8$  plane and 1.830  $\text{\AA}$  from the  $C_2B_3$  ring of the carborane ligand; the latter value is unexpectedly high and may reflect weaker metal-carborane bonding than has been observed previously in complexes of first-row transition-metal ions with  $R_2C_2B_4H_4^{2-}$  ligands.<sup>8</sup> The  $C_8$  and  $C_2B_3$  ring planes are nearly parallel, with a dihedral angle of 3.3°.

The paramagnetism of **1** was investigated via ESR and magnetic susceptibility measurements. The magnetic moment exhibits a slight temperature dependence with a maximum near 6 K, which indicates a much smaller orbital effect than would be expected for pure octahedral ( $^2T_2$ ) symmetry with a  $d^1$  configuration and is consistent with the observed molecular structure. The room-temperature ESR spectrum of a solid sample gives  $g = 1.94$ , which compares with the value of 1.91 estimated by extrapolation of the higher temperature magnetic moment data. The room-temperature spectrum of **1** in toluene/ $CH_2Cl_2$  solution exhibits vanadium

hyperfine coupling ( $A = 155$  G), but no clear evidence of ligand hyperfine arising from interaction with boron can be seen. At low temperatures, extreme broadening of the signal indicates formation of a rigid glass at about  $-80$  °C; at  $-160$  °C, the appearance of a sharp eight-line spectrum confirms  $A_{\text{vanadium}}$ , but no boron hyperfine is observed.

The stable existence of **1**, which has exhibited no signs of decomposition on standing in air for months or on repeated chromatography in organic solvents, seems to reflect the ability of  $R_2C_2B_4H_4^{2-}$  carborane ligands to stabilize unusual organometallic structures and metal-hydrocarbon bonding modes.<sup>1,10</sup> Investigations in this area are continuing.

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**Supplementary Material Available:** Tables of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

(10) Abstracts of Papers, 182nd National Meeting of the American Chemical Society, New York, Aug 1981; INOR-10, INOR-11.

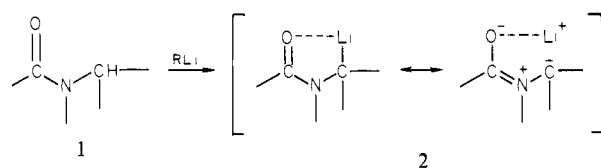
### Dipole-Stabilized Carbanions: Evidence for a Complex in the $\alpha'$ -Lithiation of *N,N*-Dimethyl-2,4,6-triisopropylbenzamide

Munther Al-Aseer, Peter Beak,\* David Hay, Dale J. Kempf, Sander Mills, and Stanley G. Smith\*

Roger Adams Laboratory, Department of Chemistry  
University of Illinois, Urbana, Illinois 61801

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Although interaction of the metal of an organolithium base with a directing group in a complex formed prior to metalation often is postulated to be an important factor in determining the regiochemistry of the reaction, direct experimental evidence that relates the complex to the lithiation has been lacking.<sup>1</sup> For example, in the formation of dipole-stabilized carbanions from amides, the difference between the experimental observation of syn  $\alpha'$  lithiation, shown for the conversion of **1** to **2**, and ab initio



SCF calculations, which predict the anti isomer should be favored as the free carbanion, is attributed to association of the lithium with the carbonyl oxygen, a postulate consistent with strong lithium ion-amide binding.<sup>2-5</sup>

(7) Crystal data: space group  $Pna2_1$ ,  $a = 14.264$  (5)  $\text{\AA}$ ,  $b = 12.595$  (4)  $\text{\AA}$ ,  $c = 8.449$  (2)  $\text{\AA}$ ,  $V = 1518$   $\text{\AA}^3$ ;  $Z = 4$ ;  $2\theta_{\text{max}} = 52^\circ$  (Mo  $K\alpha$  radiation); 1506 reflections were collected, of which 1271 had  $F_0^2 > 3\sigma(F_0^2)$  and were used in refinement, which gave final  $R$  and  $R_w$  values of 0.047 and 0.053. An absorption correction was applied (absorption coefficient = 6.7; maximum and minimum transmission coefficients = 0.90 and 0.88). Full details on this structure determination will be reported later.

(8) (a) Grimes, R. N. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1. (b) Grimes, R. N. *Acc. Chem. Res.* **1983**, *16*, 22 and references therein.

(9) Based on formal assignments of six- and ten-electron bonding interactions between  $V^{4+}$  (one electron) and the  $(C_2H_5)_2C_2B_4H_4^{2-}$  and  $C_8H_8^{2-}$  ligands, respectively. Our assumption that the electron deficiency resides on the metal, rather than in the metallacarborane framework bonding MOs, is consistent with the observation of regular closo geometry in **1** and in several earlier examples; see: Maynard, R. B.; Wang, Z.-T.; Sinn, E. *Inorg. Chem.*, in press, and papers cited therein.

(1) Suggestions of lithium complexes in metalations generally are reasonable interpretations based on established donor-acceptor interactions. (a) For cases involving ortho lithiations see: Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490. Ellison, R. A.; Kotsonis, F. N. *Tetrahedron* **1973**, *29*, 805. Finnegan, R. A.; Altschemd, J. W. *J. Organomet. Chem.* **1967**, *9*, 193. For an excellent review see: Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (b) For cases involving formally dipole-stabilized carbanions see: Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275.

(2) Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandrasekhar, J.; Schleyer, P. V. R. *J. Org. Chem.* **1981**, *46*, 4316.

(3) Lithiation of primarily the syn-methyl group has been established for **3** under similar reaction conditions: Schlecker, R.; Seebach, D.; Lubosh, W. *Helv. Chim. Acta* **1978**, *61*, 3100.

(4) The syn- and anti-methyl groups of **3** are nonequivalent on the laboratory time scale. For a related case see: Staab, H. A.; Lauer, D. *Chem. Ber.* **1968**, *101*, 864.



lithium and a single amide, an equilibrium constant for formation of the complex of  $300 \pm 50$  can be obtained from the data. The most straightforward possibility is that **4** is converted directly to **5**; however, it is also possible that **5** could be formed by reaction of **3** with a small amount of *sec*-butyllithium monomer in equilibrium with the tetramer.<sup>10</sup> Over a range of 0.03–0.24 M *sec*-butyllithium at 0.0048 M **3**, the observed rate constant decreases exponentially, a result that suggests that neither of these processes by themselves provides a complete description of the reaction.<sup>11</sup>

The present results provide the first direct observation of, and quantitative information about, an initially formed complex in the  $\alpha'$  metalation of amides. To the best of our knowledge, this is the first such study of a directed lithiation, and the approach should be applicable to a number of systems. A reasonable inference is that similar complexes may be observed in other directed lithiations, including  $\alpha'$  metalations of other amides,<sup>12</sup> ortho metalations of aromatic amides,<sup>13</sup>  $\beta'$  metalations of  $\alpha,\beta$ -unsaturated amides,<sup>14</sup> and  $\alpha'$  metalations of amidines.<sup>15,16</sup>

**Acknowledgment.** We are grateful to the National Science Foundation and the National Institute of Health for support of this work. We also thank Professor A. I. Meyers for informing us of his related work, which appears in the following communication.

(10) For example, the addition of methyllithium to a ketone is 0.25 order in methyl lithium. Smith, S. G.; Charbonneau, L. F.; Novak, D. P.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *44*, 1059. See: Schlosser, M. "Struktur und Reaktivität Polarer Organometalle"; Springer Verlag: Berlin, 1973; pp 129–38, for other cases.

(11) While such a result might be explained by some combination of the two pathways, among other possibilities, we prefer not to speculate until more information is available.

(12) Reitz, D. B.; Beak, P.; Tse, A. *J. Org. Chem.* **1981**, *46*, 4316 and references cited therein.

(13) Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34. Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.

(14) Kempf, D. J.; Wilson, K. D.; Beak, P. *J. Org. Chem.* **1982**, *47*, 1610.

(15) Meyers, A. I.; TenHoeve, W. *J. Am. Chem. Soc.* **1980**, *102*, 7125. Meyers, A. I.; Rieker, W. F.; Fuentes, L. M. *Ibid.*, following paper in this issue.

(16) A recent study of deuterium isotope effects by Miller and Saunders suggests such species are important in enolate formation from ketones. Miller, D. J.; Saunders, W. H., Jr. *J. Org. Chem.* **1982**, *47*, 5041.

## Initial Complex and the Role of Solvent in Metalations Leading to Dipole-Stabilized Anions

A. I. Meyers,\* William F. Rieker, and Lelia M. Fuentes

Department of Chemistry, Colorado State University  
Fort Collins, Colorado 80523

Received December 16, 1982

The use of dipole-stabilized anions as a synthetic tool for forming C–C bonds is now well documented<sup>1</sup> although there is no experimental evidence to support the postulated pathway. The proposal that there is coordination between the lithium base and the heteroatom necessary for carbanion formation has now been verified by infrared spectroscopy using a stopped-flow technique.<sup>2</sup> In this fashion the equilibrium constant for the complex and the rate constant leading to metalation have been measured. Furthermore, a recent report describes, via X-ray and NMR data, the intramolecular chelation of the heteroatoms with the lithium

(1) Deprotonation leading to carbanions adjacent to nitrogen have been generated via (a) amides: Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275. Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34. (b) Nitrosamines: Seebach, D.; Enders, D. *Angew. Chem., Int. Ed Engl.* **1975**, *14*, 1101. (c) Formamidines: Meyers, A. I.; Hellring, S. *J. Org. Chem.* **1982**, *47*, 2229 and earlier references cited.

(2) Al-Aseer, M.; Beak, P.; Hay, D.; Kempf, D. J.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.*, preceding paper in this issue.

Scheme I

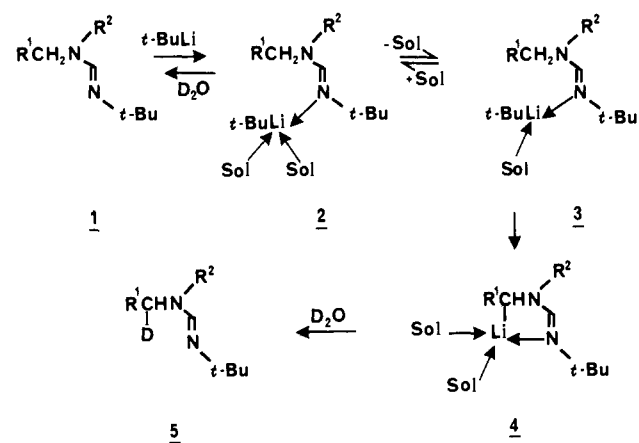


Table I. Metalation–Deuteration of *tert*-Butylformamidines (TBF) in Various Solvents<sup>a</sup>

TBF	TBF	TBF	TBF
solvent	D, %	D, %	D, %
DME	0.05 <sup>b</sup>	12.8 <sup>b</sup>	0.05 <sup>b</sup>
THF	14.5	98.6	25.8
DMTHF	54.1	94.6	91.0
ether	64.2	95.6	92.2

<sup>a</sup> Isolated yields of *tert*-butylformamidines (TBF) were 60–99%. Reactions performed in 0.5 M solutions at  $-25 \pm 5$  °C for 20 min and then quenched with D<sub>2</sub>O. Percent deuteration was determined by mass spectroscopy (ratio of M<sup>+</sup> and M + 1). <sup>b</sup> A white to light yellow solid appeared at  $-25$  °C, prior to D<sub>2</sub>O addition. <sup>c</sup> A clear viscous oil separated at  $-25$  °C prior to addition of D<sub>2</sub>O.

as well as the intermolecular chelation with solvent molecules.<sup>3</sup> However, this study does not address processes *prior* to formation of the carbanion.

We now report the direct observation of complex **2** (Scheme I), which precipitates from solution, and infrared data that corroborate the structure of the complex. We also describe the critical role of various solvents necessary for metalation to **4**. The formamidines **1** (0.5 M in solvent) when treated with an equimolar amount of *t*-BuLi at  $-25$  °C are known to give carbanions that alkylate or deuterate smoothly to **5**.<sup>1c</sup> A series of formamidines derived from secondary amines (Table I) were subjected to treatment with *tert*-butyllithium in various solvents and gave widely variable yields of deuterium incorporation on quenching with D<sub>2</sub>O. As seen from the table, ether and 2,5-dimethyltetrahydrofuran (DMTHF)<sup>4</sup> gave good to excellent yields of the  $\alpha$ -D compounds, whereas THF allowed efficient deuteration for the pyrrolidine and the hexahydroazepine derivatives. Conversely, dimethoxyethane (DME) gave poor to virtually no deuterium incorporation on D<sub>2</sub>O quench. Thus addition of *tert*-butyllithium to DME solutions of all the amine formamidines in Table I resulted in a light-colored powdery precipitates (a viscous oil in the case of the azepine), which when quenched with D<sub>2</sub>O, provided very low levels of D incorporation.

Verification of the lack of formamide metalation was further found when benzaldehyde was added to the viscous oil designated as complex **2**. Isolation of the reaction products provided benzyl alcohol and benzyl benzoate (~50%) along with starting azepine formamide. Furthermore, when this reaction was performed in THF, an 83% yield of the expected carbinol amine (from the

(3) Jastrzebski, T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490.

(4) Aldrich Chemical Co.