Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for **2** (9 pages); listing of observed and calculated structure factors for **2** (11 pages). Ordering information is given on any current masthead page.

Triple Ion Formation in Ethereal Solutions of Lithium N-Isopropylanilide Induced by Hexamethylphosphoric Triamide

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It is well known that the addition of small quantities (~4 equiv/cation) of certain cosolvents of high Lewis basicity, such as hexamethylphosphoric triamide (HMPT)[1,2] and N,N'-dimethyl-N,N'-propylene urea,[2] to solutions of alkali metal salts of carbon acids in weakly polar solvents (e.g., ethers) can dramatically enhance the nucleophilicity of the anion as well as changing its regiochemistry. In the absence of the cosolvent, lithium salts of very weak organic acids are usually aggregated contact ion pairs, and the role of the cosolvent is presumably concerned with inducing some degree of dissociation of the aggregates. For example, ^{13}C chemical shift data[3,4] for lithium enolates in HMPT/ether solvents strongly indicate such a dissociative process although the nature of the resulting species is unknown. We now show that the addition of 2–4 equiv of HMPT to lithium N-isopropylanilide (a model for lithium enamides) in diethyl ether results in the conversion of a dimer to a mixture of a monomer and a triple ion salt(ate complex[5]).

Lithium N-isopropylanilide in diethyl ether exists as a dimer characterized by its ^{13}C chemical shifts ($\delta_{c(4)}$, 110.4 ppm at –100 °C).[6] The addition of 4.1 equiv of HMPT completely converts the dimer to a mixture of two new species, **1** ($\delta_{c(4)}$, 101.9 ppm) and **2** ($\delta_{c(4)}$, 103.1 ppm) in a 6:1 ratio. The same system, however, exhibits *three* ^6Li and ^7Li resonances (Figure 1). The identities of the two new species are established by the low-temperature ^{15}N and ^6Li spectra (Figures 2 and 3)[7] of the fully labeled $^{15}N,^6Li$ isotopomer. The ^{15}N and ^6Li resonances of **2** are a 1:1:1 triplet and a 1:1 doublet, respectively, proving that it is the monomeric ion pair. $J_{6Li,15N}$ and δ_{15N} are similar to those (7.5 Hz and 152.5 ppm, respectively) observed for the same salt in THF at –100 °C.[5] The ^{15}N resonance of the major species is also a 1:1:1 triplet showing that each nitrogen is attached to only *one* lithium atom. The corresponding ^6Li resonance, however, is a 1:2:1 triplet thus establishing the presence of the structural element, $(-NLiN-)^-$. The remaining peak (δ 2.3 ppm) in the ^6Li spectrum is a singlet with the same area as the triplet and is assigned to the Li-$(HMPT)_4^+$ counterion. The line widths of the corresponding ^7Li resonances (Figure 1) are in accord with these assignments. Thus, that of the δ 2.3 ppm peak is very narrow (~7 Hz) as expected for ^7Li in a tetrahedral environment. The other two peaks are broad (~51 and ~25 Hz for δ 4.6 and 3.7 ppm, respectively).[8]

(1) Normant, H. *Bull. Soc. Chim. Fr.* **1968**, 791.
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(6) Jackman, L. M.; Scarmoutzos, L. M. *Quart. Rev.* **1987**, *109*, 5348.
(7) ^{15}N spectra are referenced to external 0.5 M N-methylaniline (52.8 ppm) in diethyl ether. ^6Li and ^7Li chemical shifts are relative to external 0.1 M LiOH (aqueous) (0.00 ppm).
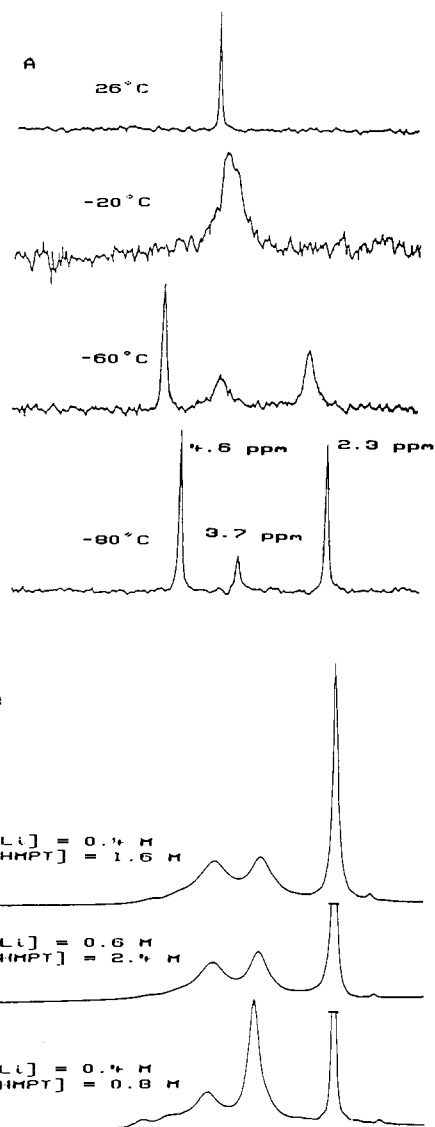

Figure 1. (A) ^6Li spectra (52.99 MHz) of [^6Li]-lithium N-isopropylanilide (0.4 M) with HMPT (1.6 M) in diethyl ether. (B) ^7Li spectra (139.95 MHz) of lithium N-isopropylanilide in diethyl ether at –60 °C.
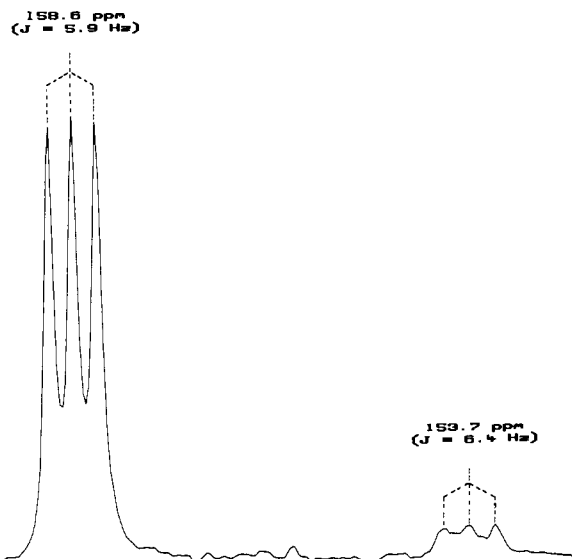

Figure 2. ^{15}N spectrum (20.2 MHz) of [$^6Li,^{15}N$]-lithium N-isopropylanilide (0.5 M) with HMPT (2.0 M) in diethyl ether at –85 °C.

The two species exchange rapidly on the ^6Li NMR time scale at room temperature (Figure 1a). The addition of HMPT causes
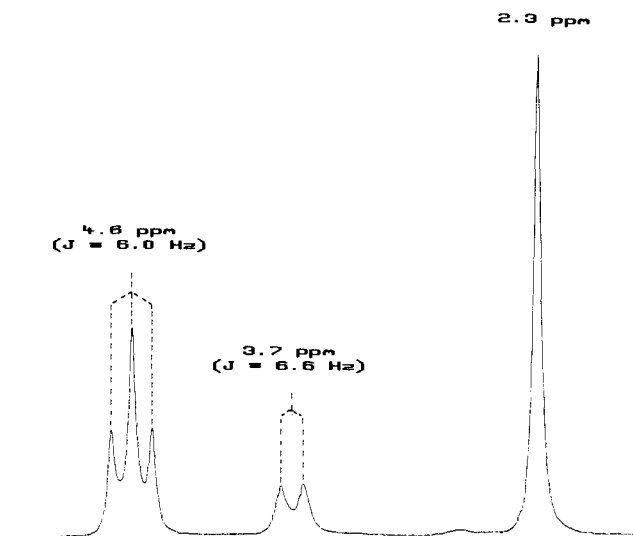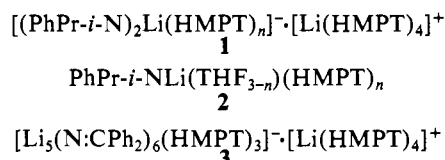
2.3 PPM

4.6 PPM
(J = 6.0 Hz)

3.7 PPM
(J = 6.6 Hz)

Figure 3. ^{6}Li spectrum (52.99 MHz) of [^{6}Li,^{15}N]-lithium N-isopropyl-anilide (0.5 M) with HMPT (2.0 M) in diethyl ether at –90 °C.

conversion of the dimer to the monomer which, in turn is converted to the triple ion salt with increasing HMPT concentrations (Figure 1b). The ^{31}P spectra of all solutions exhibit only single sharp resonances indicating that exchange between free and bound HMPT is rapid on the ^{31}P NMR time scale. The structure of the triple ion salt is formulated as **1**. The degree of solvation of the triple ion is probably $n = 1$ since the line width of its ^{7}Li resonance is twice that of the monomer, suggesting a trigonal arrangement of ligands. The very narrow line width for ^{7}Li in genenion shows that it is in a tetrahedral environment.

$$[(\text{PhPr-}i\text{-N})_2\text{Li}(\text{HMPT})_n]^-\cdot[\text{Li}(\text{HMPT})_4]^+$$
$$\textbf{1}$$

$$\text{PhPr-}i\text{-NLi}(\text{THF}_{3-n})(\text{HMPT})_n$$
$$\textbf{2}$$

$$[\text{Li}_5(\text{N:CPh}_2)_6(\text{HMPT})_3]^-\cdot[\text{Li}(\text{HMPT})_4]^+$$
$$\textbf{3}$$

Fraenkel and co-workers[9] have used ^{7}Li NMR to show that the addition of THF as a cosolvent to solutions of peralkyl-cyclohexadienyllithium in cyclopentane induces triple ion formation. They also observe two resonances for the triple ion salt and one for a monomeric ion pair, although in this case all line widths appear similar presumably because the ion pairs are π- rather than σ-types. ^{7}Li NMR has also been used to show that cryptand complexes of ethyl lithioacetoacetate form triple ions.[10] Barr, Clegg, Mulvey, and Snaith[11] have published a number of X-ray structures of HMPT-solvated lithamides. Although none of these corresponds to the type of structure we have found in solution, they do describe a more highly aggregated, polyhedral ate complex[11b] **3** derived from the much less sterically hindered anion of diphenyl ketimine.

In view of the above findings, it appears likely that, in the reactions of lithium enolates, triple ions or more complex ate ions may be better candidates for the reactive species in the presence of HMPT as cosolvent than are tetramers in which the positions of cosolvent and anion are juxtaposed.[12]

(8) For a discussion of ^{7}Li quadrupole coupling constants in related systems, see: Jackman, L. M.; Scarmoutzos, L. M.; Debrosse, C. W. *J. Am. Chem. Soc.* **1987**, *109*, 5355.

(9) Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657.

(10) Cambillau, C.; Ourevitch, M. *J. Chem. Soc., Chem. Commun.* **1981**, 996.

(11) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. (a) *J. Chem. Soc., Chem. Commun.* **1984**, 79; (b) 226; (c) 285; (d) 469; (e) 700.

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Alkyne Cyclizations at Reduced Tantalum Centers: Synthesis and Molecular Structure of (η^6-C$_6$Me$_6$)Ta(O-2,6-i-Pr$_2$C$_6$H$_3$)$_2$Cl
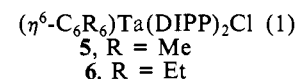
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Many transition metals are known to catalyze the cyclo-trimerization of alkynes[1,2] and thereby provide an elegant strategy for assembling complex organic molecules.[3] The intermediates most often implicated in these cyclizations are metallacyclo-pentadienes[4,5] (**1**, Scheme I). Arene formation by the addition of a third alkyne is proposed to occur either through an intermediate (a) metallacycloheptatriene (**3**), or (b) Diels–Alder adduct "7-metallanorbornadiene" (**4**). Since $d^{n \geq 2}$ metal centers are required for the oxidative coupling of alkynes, and since certain niobium and tantalum complexes polymerize[6] and cyclize[6c,7] alkynes, we have begun to investigate mid-valent tantalum chemistry with a view to understanding the details of these reactions in the early transition metals.

Yellow Ta(DIPP)$_2$Cl$_3$ (DIPP = 2,6-diisopropylphenoxide),[8] upon reduction with 2 equiv of Na/Hg in the presence of RC≡CR (R = Me, Et; 3 equiv in Et$_2$O, –30 °C), provides blue solutions containing the complex (C$_6$R$_6$)Ta(DIPP)$_2$Cl (R = Me (**5**), R = Et (**6**)) (eq 1). The removal of all volatiles from the reaction

$$\text{Ta(DIPP)}_2\text{Cl}_3 + 2\text{Na/Hg} + 3\text{RC}\equiv\text{CR} \rightarrow$$
$$(\eta^6\text{-C}_6\text{R}_6)\text{Ta(DIPP)}_2\text{Cl} \quad (1)$$
$$\textbf{5}, \text{ R = Me}$$
$$\textbf{6}, \text{ R = Et}$$

filtrate provides the blue, thermally sensitive, microcrystalline product in 65% yield. This reaction also produces a quantity of insoluble alkyne polymer and, in the presence of excess alkyne, free hexaalkylbenzene. The ^{1}H NMR spectrum of the C$_6$Me$_6$ compound (**5**, C$_6$D$_6$, 30 °C) displays diisopropylphenoxide resonances[9] in addition to a singlet at δ 2.02 (18 H, C$_6$Me$_6$); in

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(2) See, for example: (a) Krüerke, U.; Hübel W. *Chem. Ber.* **1961**, *94*, 2829. (b) Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 4729. (c) Hoover, F. W.; Webster, O. W.; Handy, C. T. *J. Org. Chem.* **1961**, *26*, 2234. (d) Jhingan, A. K.; Maier, W. F. *Ibid.* **1987**, *52*, 1161.

(3) (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (c) Vollhardt, K. P. C. In *Strategies and Tactics in Organic Synthesis*; Lindberg, T., Ed.; Academic Press: Orlando, 1984; pp 299–324.

(4) (a) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298. (b) Whitesides, G. M.; Ehmann, W. F. *J. Am. Chem. Soc.* **1969**, *91*, 3800. (c) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *Ibid.* **1977**, *99*, 1666. (d) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1975**, *96*, C23. (e) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, *51/52*, 4549.

(5) Other intermediates have been suggested, see: (a) Crocker, M.; Green, M.; Orpen, A. G.; Thomas, D. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1141. (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.

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(7) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094.

(8) (a) Synthesized from the reaction of TaCl$_5$ (10.30 g, 28.8 mmol) and LiDIPP·OEt$_2$ (14.86 g, 57.6 mmol) in benzene/ether (50:1/v:v). The compound crystallizes from pentane (–40 °C) as the etherate Ta(DIPP)$_2$Cl$_3$·OEt$_2$ in 82% yield. The ether-free material has been reported, ref 8b. (b) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575.

(9) Full spectroscopic and analytical details are available as Supplementary Material. Selected ^{13}C NMR data: **5** (C$_6$D$_6$, 30 °C) δ 120.6 (s, C_6Me$_6$), 16.2 (q, C$_6$Me$_6$); **6** (C$_6$D$_6$, 30 °C) δ 126.8 (s, C_6Et$_6$), 23.9 (t, C$_6$(CH$_2$CH$_3$)$_6$), 17.7 (q, C$_6$(CH$_2$CH$_3$)$_6$); **7** (tol-d_8, 50 °C) δ 205.1 (s, C$_\alpha$), 163.1 (s, C$_\beta$), 29.2 (t, C$_\alpha$CH$_2$CH$_3$), 22.0 (t, C$_\beta$CH$_2$CH$_3$), 15.5 (q, C$_\beta$CH$_2$CH$_3$), C$_\alpha$CH$_2$CH$_3$ is coincident with either isopropyl methyls (δ 24.4) or C$_\beta$CH$_2$CH$_3$ (δ 15.5). Typical 2,6-diisopropylphenoxide resonances occur at δ 157 (s, C$_{ipso}$), 137 (s, C$_o$), 124 (d, C$_m$), 123 (d, C$_p$), 26 (d, CHMe$_2$), 25 (q, CHMe$_2$).