of these and other mononuclear nitrido metalloporphyrins with metallomacrocyclic substrates to evaluate the generality of this reaction.

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Methylamine-Assisted Solubilization of Lithium and Sodium Metals in Various Amine and Ether Solvents

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We wish to report a simple new technique for dissolving lithium metal alone or lithium plus sodium (up to equimolar sodium) in several amine and ether solvents in which the metals alone are either insoluble or only slightly soluble. These methods could provide convenient and inexpensive one-electron or two-electron reducing agents in various solvents without leaving behind nonvolatile organic compounds.

In 1970, we reported the solubilization of alkali metals in tetrahydrofuran (THF) and diethyl ether (DEE) by using dicyclohexano-18-crown-6 to complex the cation.[1] This was later extended to other solvents, metals, and crown ether and cryptand complexants[2-4] and ultimately led to the synthesis of crystalline alkalide[5,6] and electride[7,8] salts. Although solutions that contain metals and cation complexants have been extensively used in organic synthesis,[9-13] the cost of the complexants and their presence at the end of the reduction can limit their usefulness. The use of $Li^+(CH_3NH_2)_4$ instead of a cation that is complexed by a crown ether or cryptand not only enhances metal solubility but also provides an easily removed complexant.

Lithium is soluble in methylamine up to 20 mol %, which represents the metallic liquid compound $Li(CH_3NH_2)_4$,[14,15] freezing at 155 K. The vapor pressure of lithium–methylamine solutions drops suddenly at the composition corresponding to this compound,[16] which provides a convenient monitor of its formation. By controlling the temperature of the solution and of an external trap for methylamine (at a suitable lower temperature), the excess methylamine can be removed by distillation, leaving behind the pure compound. The solubility of sodium in pure methylamine has not been measured, but it is very low, probably less than 10^{-3} M. Conductivity measurements[17] and optical spectra[18] indicate the formation of primarily the solvated sodium cation and the sodium anion, Na^-. The sodium anion has unusual thermodynamic stability, so that reactions such as

$$2e^-_{solv} + Na^+ \rightarrow Na^- \qquad (1)$$

and

$$e^-_{solv} + Na(s) \rightarrow Na^- \qquad (2)$$

are favorable.[4,19] Thus, we anticipated that solutions of lithium in methylamine, which form $Li^+(CH_3NH_2)_4$ and e^-_{solv} upon dilution, should be able to dissolve sodium metal by reaction 2.

The first indication that $Li(CH_3NH_2)_4$ can be dissolved in solvents that do not dissolve lithium alone was the observation[19-21] that lithium enhances the stability of solutions of Cs(18C6) in 2-aminopropane and that lithium metal does not precipitate until the solution is concentrated.

Solvent and metal purification and vacuum-line synthesis methods have been previously described.[6,22] Weighed amounts of lithium and sodium if desired (or a measured length of sodium in calibrated tubing) were introduced into separate arms of a glass vessel in a helium-filled glovebox. After evacuation to ca. 10^{-5} Torr, enough methylamine was condensed in the vessel to dissolve the lithium and form an unsaturated solution (about 10 mol % lithium). If a mirror of sodium in equimolar amounts to lithium was present, agitation at ca. −40 °C over a period of several hours resulted in the complete dissolution of sodium. The ^{7}Li NMR spectrum showed a single peak at 2.5 ± 0.2 ppm relative to Li^+(aq), while the ^{23}Na spectrum consisted of peak at −60.4 ± 0.2 ppm characteristic of Na^- in solution. When no sodium was present, thin liquid films of $Li(CH_3NH_2)_4$ showed a broad plasmon type of optical absorption spectrum similar to that of concentrated metal–ammonia solutions.[23] However, when sodium and lithium were present in equimolar amounts, thin liquid films showed only the optical peak of Na^- at 660 nm.

By distilling another solvent into the vessel that contained $Li(CH_3NH_2)_4$, either alone or with sodium, it was possible to form deep blue solutions even though neither lithium nor sodium would dissolve to an appreciable extent in the solvent used. Thus, $Li(CH_3NH_2)_4$ dissolves readily in dimethylamine and in 2-aminopropane to give concentrated deep blue solutions. When sodium was also present, the latter solvent contained Na^-, which was identified by its ^{23}Na NMR peak at −61 ± 1 ppm and its optical absorption peak at 660 nm. The addition of dimethyl ether to $Li(CH_3NH_2)_4$ resulted in liquid–liquid phase separation, a blue phase, and a less dense bronze phase. The ^{7}Li NMR peak at +20.4 ± 0.2 ppm at −50 °C for the bronze phase was identical with that observed for pure $Li(CH_3NH_2)_4$, while the more dilute blue phase had a peak at 23.0 ± 0.2 ppm at −50 °C.

Upon adding tetrahydrofuran (THF), diethyl ether (DEE), trimethylamine (TMA), or dimethoxyethane (DME) to $Li(CH_3NH_2)_4$, dark blue solutions were initially formed which, however, over a period of minutes became either light blue (DEE, TMA, DME) or colorless (THF) as lithium metal precipitated from the solution. The precipitation of lithium rather than decomposition, at least in DEE, TMA and DME, was indicated by the stability of the light blue solutions and the fact that they became darker blue at lower temperatures. Thus, the initial

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metastable solutions precipitate lithium metal to yield dilute stable solutions in the mixed solvent systems. Similarly, a solution of $Li(CH_3NH_2)_4$ and sodium was initially soluble in DEE but yielded a light blue solution together with precipitated metal(s) upon standing or upon the addition of excess DEE. In addition to sodium metal, rubidium metal also dissolved in a solution of $Li(CH_3NH_2)_4$ to produce a dark blue solution. By analogy with the corresponding solutions of lithium and sodium, it is presumed that the solution contains the species $Li^+(CH_3NH_2)_4$ and Rb^-.

The results described in this paper suggest that lithium, without or with sodium, plus a simple amine such as methylamine or ethylenediamine[24] might provide useful homogeneous reducing agents in various solvents, but such applications have not yet been explored. There is, of course, a vast literature that deals with reductions by active metals such as metal–ammonia and metal–amine solutions,[25,26] solvated metal atoms,[27] and aromatic radical anions.[28] The present work would add to this list relatively concentrated solutions that contain either electrons (solvated or metallic) or the sodide anion, Na^-. This could prove to be useful in reduction reactions in which either one-electron or two-electron reducing agents are needed. It also provides the opportunity to study concentrated alkali metal solutions in other solvents than methylamine and ammonia. Preliminary results show that the other alkali metals can also be solubilized by using $Li(CH_3NH_2)_4$.

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^{13}C NMR Spectroscopy of α,ω-Diphenylpolyenyl Anions. Confirmation of Charge Localization in Soliton Model Compounds

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The notion that delocalization in ostensibly "infinite" polyacetylene chains treated with π-donors or acceptors only extends over a limited domain has been one of the more controversial aspects of the soliton theory. According to this theory,[1] electrical conductivity in such systems is due to the presence of mobile charged defects ("solitons") which are described in terms appropriate for a resonance-delocalized carbanion with a conjugation length of approximately 31 CH units or, more precisely, a full width at half height of 15 CH units. Inasmuch as charge density in short polyenyl anions, e.g., pentadienyl anions, is known to be higher at the central carbon,[2] the extent to which charge accumulates in longer polyenyl anions provides an important reference point between the solid-state physics of one-dimensional conductors and the organic chemistry of resonance-stabilized anions.

Our reference molecules were the linear odd-alternant α,ω-diphenylpolyenyl anions $(Ph(CH)_nPh^-$, $n = 1, 3, 5, 7, 9, 11, 13)$, to which we refer in shorthand notation as DP1, DP3, DP5, etc. Phenyl-terminated anions were chosen for their stability and ease of preparation as well as for their utility for estimating delocalization; that is, at what point does negative charge cease to delocalize into the aromatic rings? The Dewar nonbonded molecular orbital (NBMO) formalism[3] predicts, at the Hückel level, even distribution of negative charge at the odd-numbered carbon atoms and zero charge (nodes) at the even carbons. In contrast, the SSH theory,[1] a modified Hückel treatment reminiscent of the "ω" bond-order approach,[4] predicts accumulation of charge at the central carbon atoms, again with nodes at even carbons. Less intuitively, the Boudreaux, Chance, Brēdas, Silbey (BCBS) modification of the soliton theory,[5] based upon an MNDO method, predicts charge alternation, with even atoms possessing positive charge as a result of charge polarization by the negatively charged odd centers. We have been able to resolve this issue by an appeal to the Spiesecke–Schneider correlation[6] of charge density with ^{13}C chemical shift.

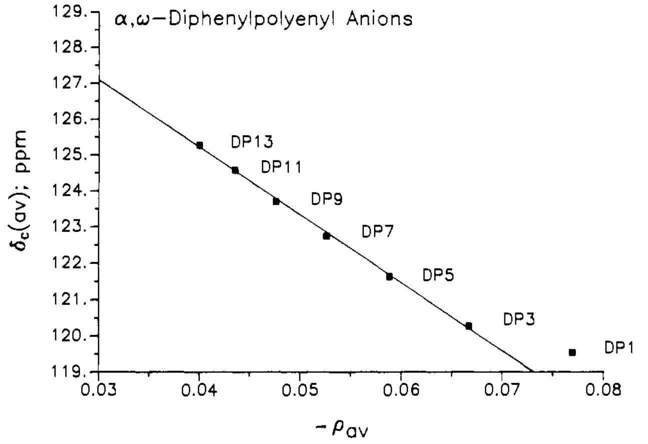

Figure 1. Average ^{13}C chemical shift vs average charge density for diphenylpolyenyl anions.

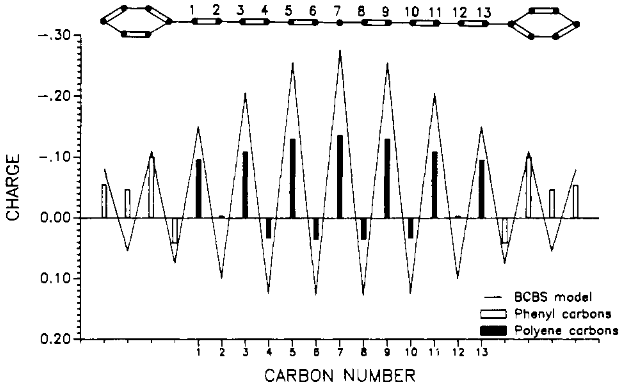

Figure 2. Histogram of charge density vs carbon number for DP13.

The required diphenylpolyenyl anions were generated in dimethyl sulfoxide solution by deprotonation of the corresponding carbon acids with potassium methylsulfinylmethide in dimethyl sulfoxide, a solvent which avoids ion pairing and other spectroscopic complications. The hydrocarbons themselves were generated by straightforward Wittig methodology[7] and presented no special complications apart from an increasing insolubility with chain length, which prevented ^{13}C NMR spectral assignments for

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