A variety of aggregation motifs dominate the structural chemistry of organolithium compounds. At least four distinct modes of dimerization exist: the common 4-center dimers, 6-center dimers as in 2-lithio-2-methylthiolane, solvent-bridged dimers as in (LiBr)\(_2\)\((\text{HMPA})_3\), and triple ions (lithium ate complexes) of type \(\text{R-Li}^-\text{R}^-/\text{Li}^+\). The reactivity of these various dimers compared to monomers or higher aggregates is usually unknown. Triple ions possess an intriguing combination of features of both a dimer and a solvent-separated ion pair. Several lithium amides are also known; however, there is only a single report of a localized carbanion trimethylsilylmethyl lithium. Here, we present NMR evidence for the internal lithium, the middle one belonging to the mixed triple ion. A crystal structure was obtained of the triple ion of tris-trimethylsilylimethyl lithium. Present NMR evidence that triple ions form in THF/HMPA solution for a variety of 6Li NMR (52.98 MHz) spectra of 6Li isotopically enriched aryllithiums (0.16 M in 4:1 THF/ether at \(-125\) °C with 2 equiv of HMPA): (A) 1a; (B and C) 2:1 and 1:2 ratio of 1a and 2a; (D) 2a; (E) phenyllithium with 5 equiv of HMPA.

Support of our assignment comes from NMR studies of mixtures of these two aryllithiums. Thus, 1a and 1b were mixed in a 2:1 and a 1:2 ratio in the presence of 2 equiv of HMPA (Figure 1B,C). The mixed experiments show three distinct signals for the internal lithium, the middle one belonging to the mixed triple ion. The mirror-like appearance of the two spectra is

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strong evidence that triple ions are responsible for the spectral data observed.

Figure 1E shows the parent phennyllithium 1c in the presence of 5 equiv of HMPA. A small signal is observed at δ 3.2 ppm, which is equal in intensity to the small signal at −0.4 ppm, and we assign these signals to a triple ion, by analogy to the above results. Wittig, when considering possible structures of a PhLi dimer, proposed a triple ion structure.16 The species that he was referring to is known today to be a 4-centered dimer, but we now have evidence that a small amount of the triple ion he proposed does form in THF/HMPA solutions of PhLi.

In addition, we have observed that small amounts of triple ion also form in THF/HMPA solutions of 1e, 1g, and 2-lithio-5-methylthiophene, while significant amounts form with 1f and 1d.

The relative amount of triple ion is sensitive to σ-substitution on the aryllithium: monomeric 1a and 1b form 65 to 80% triple ion in the presence of 1–3 equiv of HMPA, whereas 1c and 1e, which are a mixture of monomer and dimer in THP, formed less than 20% at 5 equiv of HMPA.

Pyridylthio-substituted carbanions 4 show a propensity to form triple ions in THF/HMPA solutions. Figure 2 compares the 7Li NMR (139.96 MHz) spectra15 of natural abundance and 13C-enriched 4a (0.16 M in 3:2 THF/ether at −125 °C) with 1.5 equiv of HMPA.

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shifts of the triple ions indicate that they are bis-chelated, as each successive pyridyl coordination causes a 2–2.5 ppm downfield shift (ascribed to lithium’s location coordinated to the edge of an aromatic ring, as amine coordination does not cause such large chemical shift changes).16 The chemical shifts of the HMPA-coordinated monomers demonstrate that chelation is intact for them as well.

Two diastereomeric triple ions are observed due to the stereogenic carbon centers. In principle, there should be a third diastereomer due to the stereochemical arrangement about lithium. The fact that only two are observed indicates one of the following: (1) isomerization about lithium is fast on the NMR time scale (even down to −150 °C), (2) the structure is not chelated, (3) two of the signals are coincident, or (4) one isomer does not form. We doubt the third explanation, since in 4c–e, which have appreciably different chemical shifts for their triple ion signals, we still see only two (4b, lacking a stereocenter, forms only one). A β-ketoaldehyde anion possessing stereogenic centers also showed only two triple ion diastereomers.16

Figure 3. 4Li NMR (52.98 MHz) spectra15 of 4Li isotopically enriched 1:1 mixtures of bis(2-pyridylthio)methylithium (6) and phenylthiomethylithium (7), 0.16 M in total lithium reagent in 3:2 THF/ether at −125 °C, with and without 13C labeling at the carbaneion carbons. The signal for 6-HMPA at 4.8 ppm splits into a doublet (JLi–Li = 2.5 Hz) at lower temperatures.

An electronic effect was observed by comparing 4a–e. The better stabilized carbaneions formed triple ions with less HMPA and to a greater extent, consistent with the greater ease of ion pair separation.

To probe the significance of chelation in promoting triple ion formation, bis(2-pyridylthio)methylithium (6) was investigated, and it was found to form mixed triple ions with a variety of nonchelated organolithium reagents. For instance, phenylthiomethylithium (7) formed a mixed triple ion 8 almost quantitatively when 2 equiv of HMPA (relative to total lithium reagent) were added. The connectivity was proved by 13C labeling of the carbaneion carbon in both components (Figure 3). The coupling across the lithium (JLi–Li) in the doubly 13C-labeled material was not observed. The coupling to HMPA of the monomer signal at δ 4.7 ppm could be resolved at −145 °C (JLi–Li = 9.2 Hz).40

Lithium halide salts are often present in organolithium reactions. A significant result is that LiCl also quantitatively formed triple ions with 6 and, therefore, could affect its chemistry if the triple ion is a reactive species. Lithium phenolate, intended as a model for enolates and alkoxides which are also present in many organolithium reactions, showed no evidence of mixed aggregation with 6.

Triple ion formation is not unique to the chelated and aryl systems. Several nonchelated sulfur-, selenium-, and silicon-stabilized alkylithiums also form significant fractions of triple ions in ether/THF/HMPA solution. This was shown by 13C labeling of the carbaneion carbons of phenylethenemethylithium (9) and bis(trimethylsilyl)methylithium (10), which converted the internal lithium signals into triplets, whereas the labeled carbons showed coupling to only one Li nucleus.

It is noteworthy that the addition of HMPA, which normally deaggregates lithium reagents,17 converts a monomeric lithium reagent into a dimeric triple ion. The presence of triple ions in this range of systems suggests that even in cases where they are not detectable ground-state structures, they should be considered as possible reactive intermediates for all organolithium reactions run in relatively polar media. Triple ions might be expected to have reactivities competitive with contact ion pair monomers. For instance, the downfield shift of the carbanion carbon of 1a from the monomer (193.3 ppm) to the triple ion (197.7 ppm) is indicative of increased electron density at the carbanion carbon. It remains to be shown whether triple ions are reactive species, but for lithium reagents such as 1, 7, 9, and 10 that do not form classical separated ion pairs even with large excesses of HMPA, triple ion involvement in their chemistry seems especially likely.

Acknowledgment. We thank the National Science Foundation for financial support of this research. The spectrometers are funded by the NSF (CHE-8306121) and the National Institute of Health (NIH 1 S10 RR02388).

JA9741382