give rise to selectivities that do not arise from template shape. Although X-ray crystal structures of **3** and **5** exhibit the s-trans and s-cis structures, respectively, solution phase NMR studies and MM2 calculations reveal a very low barrier separating two freely interconverting conformational isomers. These results suggest that the two template molecules (**3** and **5**) should be incorporated into the growing polymer network in a similar manner. The different selectivities that these materials exhibit must be attributed to other factors.

Another possibility recognizes that the rebinding step can result in formation of a bisketal (two-point rebinding) or monoketal (one-point rebinding). FT-IR studies have permitted quantitative evaluation of the residual carbonyl groups remaining after rebinding. Rebinding of **4** with 1,3-diacetylbenzene results in 30 ± 10% sites with one-point rebinding. From a related study, 1,3-diacetylpyrene is found to rebind to **6** with 35 ± 10% one-point rebinding. On the basis of these results, the two materials (**4** and **6**) do not differ with regard to the manner in which the diketone substrates rebind at each site. Furthermore, since a significant fraction of substrate molecules are initially rebound at only one carbonyl, an important component of the selectivity must arise from the *shape* of the site.

The origins of these differences can be traced to the polymerization reactions. Templates of different shape produce sites of different architecture. The application of this finding to the design of shape-selective catalysis is currently under investigation.

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The Lithium-Metalloid Exchange Reaction.[1] NMR Studies of the Phenyllithium-Iodobenzene Exchange

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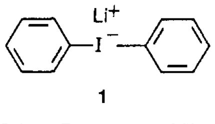
The metal-halogen exchange reaction, independently discovered by Wittig and Gilman,[2] continues to find many applications for the preparation of organolithium reagents. It is a complex reaction for which single electron transfer,[3] four center,[4] S_N2,[4a,b] and ate complex[1a,1b,5] mechanisms have been proposed. Previously we reported kinetic evidence for an intermediate in the degenerate exchange of iodobenzene and phenyllithium,[1a] the hypervalent 10-I-2⁻ diphenyliodinanide species **1**. We report here evidence that **1** can be observed as a discrete solvent-separated ion pair in THF-HMPA solution and that it can function as a phenyl anion donor.



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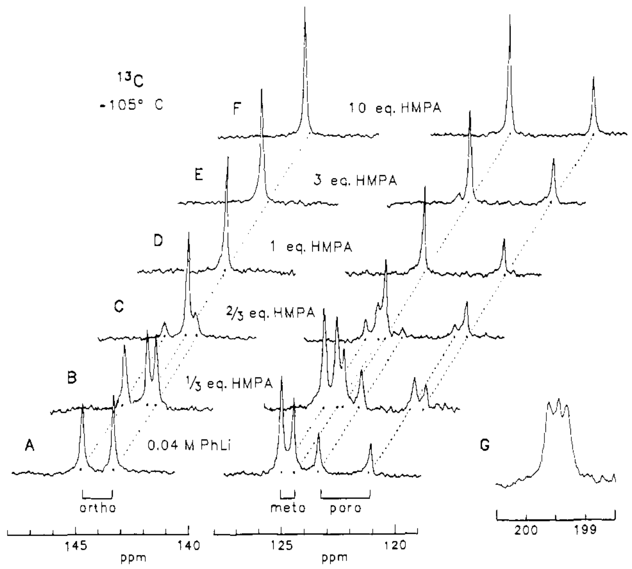

Figure 1. Carbon-13 NMR spectra (90.56 MHz) of THF solutions at −105 °C. A: DEPT-90 spectrum of 0.04 M PhLi. The upfield signal of each pair is $(PhLi)_1$. B–F: DEPT-90 spectra containing 0.013, 0.027, 0.04, 0.12, and 0.4 M HMPA. G: ipso carbon signal of 0.12 M Ph^6Li, 0.08 M HMPA in THF/dimethyl ether (2/1) at −120 °C. The 1:1:1 $^{13}C-^6Li$ splitting is 13 Hz.

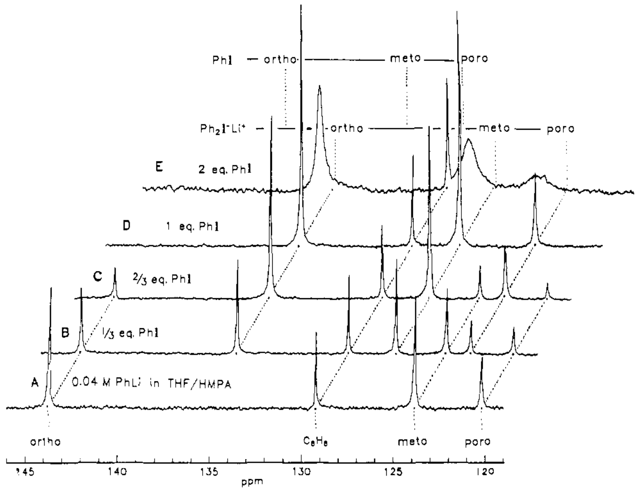

Figure 2. A–E: 90.56 MHz ^{13}C NMR spectra at −105 °C of solutions 0.04 M PhLi, 0.4 M HMPA, containing 0, 0.013, 0.027, 0.04, and 0.08 M PhI. Spectra A–D are DEPT-90 spectra; E is a normal single pulse spectrum.

Table I

δ ^{13}C (−105 °C, THF)	ipso	ortho	meta	para	δ ^7Li
$(PhLi)_1\cdot THF$	196.68	143.24	124.28	120.83	1.05
$(PhLi)_2\cdot THF$	188.48	144.60	124.81	123.18	1.43
$(PhLi)_1\cdot HMPA$	201.90	143.79	123.68	120.0	0.93
$Ph_2I^-Li^+$ (HMPA)	166.51	135.23	126.62	122.51	−0.37
PhI	96.65	138.08	131.36	128.07	

Figure 1 presents ^{13}C NMR spectra of THF solutions containing phenyllithium (0.04 M) and HMPA (0–0.4 M) at −105 °C. In THF, PhLi exists as an equilibrium mixture of monomer and dimer which exchange slowly on the NMR time scale at temperatures below −90 °C (Figure 1A).[1d,6] With one-third and two-thirds of an equivalent of hexamethylphosphoramide (HMPA) present, a new set of signals appeared in direct proportion to the amount added (Figure 1 (parts B and C)). The signals for PhLi·THF were unaffected except for their intensity. After 1 equiv

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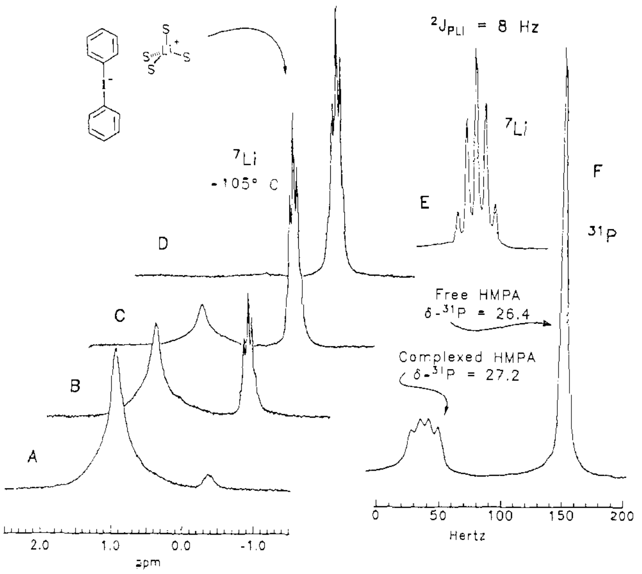

Figure 3. A–D: 139.96 MHz ^{7}Li NMR spectra at −105 °C of solutions 0.04 M PhLi, 0.4 M HMPA, containing 0, 0.013, 0.027, and 0.04 M PhI. Samples with higher concentrations of PhI gave spectra identical with D. E: Horizontal expansion with resolution enhancement of ^{7}Li spectrum D. The splitting is 8 Hz. F: 145.8 MHz ^{31}P spectrum of sample D. The splitting of the signal at 27.2 ppm is 8 Hz. ^{7}Li chemical shifts were referenced to external 0.3 M LiCl in methanol.

of HMPA had been added, only minor changes in the ^{13}C and ^{7}Li spectra occurred. The new PhLi·HMPA has chemical shifts very close to those of monomer PhLi·THF and shows ^{13}C–^{6}Li coupling appropriate for a monomer (Figure 1G).

Kinetic studies of PhLi/PhI solutions[1a] and spectroscopic studies of RLi/R_4Sn[1b,c] have shown that strong donor solvents dramatically increase the equilibrium constant for formation of the respective ate complexes. Low-temperature (−105 °C) ^{13}C NMR spectra of THF/HMPA solutions of PhLi containing one- and two-thirds increments of PhI are presented in Figure 2 (parts B and C). A new set of sharp peaks appeared, which were neither those of PhI nor a weighted average of PhI and PhLi but rather of a new species, $Ph_2I^-Li^+$ (**1**). The two sets of peaks did not coalesce up to −50 °C, above which the PhLi decomposed.

With 1 equiv of PhI present (Figure 2D), the PhLi resonances disappeared leaving only the peaks of **1**. Such solutions do, however, titrate for a full equivalent of PhLi. These results are consistent with our kinetic studies[1a] which showed that in THF/HMPA solution PhLi and PhI quantitatively combine to form a 1:1 complex.

Chemical shift data for the various species is presented below. Compound **1** shows the characteristic strong downfield shift of the ipso carbon which we have observed also for tin ate complexes[1c] and which seems to be characteristic of phenyl carbons in apical hypervalent bonds.[1d]

The ^{7}Li NMR spectra (Figure 3A–D) gave qualitatively the same results and provided some additional information about the ate complex. The ^{7}Li signal was relatively sharp,[7] came in a chemical shift region characteristic for free Li^+,[8] and showed a 1:4:6:4:1 quintet (J = 8 Hz) fine structure (Figure 3E). This can be assigned to ^{7}Li–^{31}P coupling, since *separate* signals were observed for free (singlet) and coordinated HMPA (1:1:1:1 quartet) in the ^{31}P NMR spectrum (Figure 3F).[9] HMPA almost certainly coordinates to lithium on oxygen, so this spectrum represents a rare case of a two-bond coupling between lithium and another nucleus.[10] The ate complex is thus a solvent-separated ion pair, with lithium tetrahedrally coordinated to four HMPA molecules.

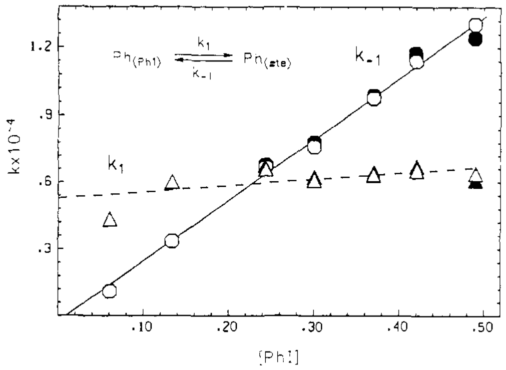

Figure 4. Graph of DNMR rate constant for exchange between PhI and **1** vs excess [PhI] at −105 °C in THF, 1.2 M HMPA measured from ^{13}C spectra such as those in Figure 2D. [**1**] = 0.12 M. Open points are from fitting of the ortho carbon, and closed are for the para carbon.

A PhLi solution containing 2 equiv of PhI (Figure 2E) gave one set of broadened peaks (even at −110 °C, where the solution freezes), the chemical shifts of which corresponded to an average of PhI and **1**. Iodobenzene therefore exchanges with **1** rapidly on the NMR time scale. The observation that excess PhLi·HMPA exchanges slowly and PhI rapidly with the ate complex shows that the simplest mechanism ($PhLi + PhI \rightleftharpoons Ph_2I^-Li^+$) is not the one responsible for the exchange of PhI with the ate complex and that the direct reaction in which **1** transfers Ph^- to PhI is faster than the alternate pathway in which PhI reacts with the microscopic concentration of PhLi·HMPA.[11] This conclusion was confirmed by a DNMR study of a series of solutions containing increasing concentrations of PhI (Figure 4).[12] As expected for a bimolecular reaction between PhI and **1**, but not for reaction between PhLi and PhI, the DNMR rate constant for conversion of **1** to PhI increased linearly with [PhI]. It is astonishing that **1**, which is known to be much less reactive than PhLi toward several electrophiles,[1a] reacts with PhI with a second-order rate constant of 24 000 M^{-1} s^{-1} at −105 °C.

The results reported here, together with the report by Farnham and Calabrese[13] on the isolation and X-ray structure of lithium bis(pentafluorophenyl)iodinanide, provide strong support for the notion that iodine ate complexes are directly involved in the metal–halogen exchange reaction of aryl iodides and lithium reagents. Although other mechanisms may be operative in aliphatic Li/I exchanges, even here recent evidence favors a similar interpretation.[3a,b] Our results also show that in THF/HMPA the ate complex **1** can directly react with PhI. It is thus possible that ate complexes may be the reactive species in other situations in which organolithium reagents are prepared by Li/M exchange in polar solvents.

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Supplementary Material Available: Experimental procedures and preparations, a table of rate constants obtained from the DNMR analysis, a figure showing calculated and experimental spectra for the ortho carbon resonance, and a scheme showing kinetics mechanisms (6 pages). Ordering information is given on any current masthead page.

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