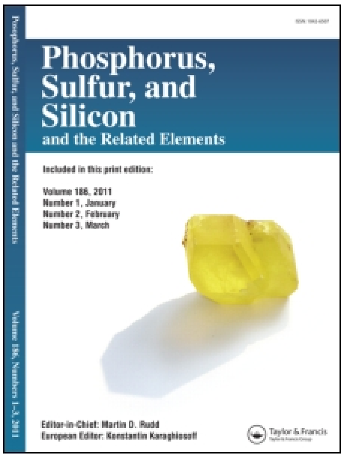

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MECHANISM OF THE LITHIUM-TELLURIUM, LITHIUM-IODINE AND LITHIUM-MERCURY EXCHANGE REACTIONS: HYPERVALENT TELLURIUM AND IODINE ATE COMPLEXES[1]

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Abstract. The lithium-tellurium exchange is among the fastest of the lithium-metalloid exchange reactions; only the lithium-iodine exchange is slightly faster. Tellurium, iodine and mercury ate complexes are formed when diphenyl telluride, iodobenzene or diphenylmercury are treated with phenyllithium in THF. The mechanism of the lithium-tellurium exchange, (as well as the Li/I and Li/Hg) proceeds through such ate complex intermediates. Monomeric phenyllithium is the reactive form of phenyllithium (the dimer does not participate detectably). Tetraphenyltellurium and triphenyliodine also form hypervalent ate complexes under suitable conditions.

INTRODUCTION

The lithium-metalloid exchange reaction is used to prepare organolithium reagents which are not readily available by the reduction of halides or the Li/H exchange reaction (metalation). The most common elements used are bromine, iodine and tin, but selenium, tellurium and mercury have also seen much use. The advantages of the Li/M exchange reactions over other procedures are that they almost always proceed with retention of configuration at carbon, that they are well suited for small scale preparations involving valuable precursors or substrates and that the reactions are extremely fast and allow the preparation of unstable or very reactive functionalized lithium reagents.

There is some anecdotal data in the literature pertaining to the rates of the various Li/M exchanges. Wittig had examined the relative rates of exchange of Ph_3M with *p*-tolyllithium in ether (M = N, P, As, Sb, Bi) and found no detectable exchange for M = N, and the sequence Sb ≈ Bi > P > As for the remaining pnictogens.[2] A similar study by Schlosser et al. showed that $Ph_3P > Ph_2S > PhCl$.[3] There have been kinetic studies of the Li/Br,[4] Li/Sn,[5b] and Li/I[5c] and Li/Pb[5d] exchanges. Kauffmann and coworkers[6] and others[7,8,9,10] have examined the intramolecular competition between M and M' during the reaction of phenyllithium or *n*-butyllithium with compounds of the type $M\text{-}CH_2\text{-}M'$, with the following results:

$Ph_3Pb\text{-}CH_2\text{-}I$	PhLi/THF	$Ph_3Pb\text{-}CH_2\text{-}Li$[6d, 6e, 6f]
$Ph_3Sn\text{-}CH_2\text{-}I$	*n*-BuLi/ether	$Ph_3Sn\text{-}CH_2\text{-}Li$[6c]
$Ph_3Ge\text{-}CH_2\text{-}PbPh_3$	PhLi/ether	$Ph_3Ge\text{-}CH_2\text{-}Li$[6d]
$Me_3Si\text{-}CH_2\text{-}PbPh_3$	PhLi/ether	$Me_3Si\text{-}CH_2\text{-}Li$[6d, 6f]
$Ph_2As\text{-}CH_2\text{-}I$	PhLi/THF	$Ph_2As\text{-}CH_2\text{-}Li$[6a, 6d]
$Ph_2As\text{-}CH_2\text{-}SnBu_3$	*n*-BuLi/THF	$Ph_2As\text{-}CH_2\text{-}Li$[6a, 6d]
$PhSe\text{-}CH_2\text{-}TePh$	*n*-BuLi/THF	$PhSe\text{-}CH_2\text{-}Li$[8]
$PhSe\text{-}CH_2\text{-}Br$	*n*-BuLi/THF	$PhSe\text{-}CH_2\text{-}Li$[9e]
$PhS\text{-}CH_2\text{-}SePh$	*n*-BuLi/THF	$PhS\text{-}CH_2\text{-}Li$[9b, 10c]
$Cl\text{-}CH_2\text{-}Br$	*s*-BuLi/THF	$Cl\text{-}CH_2\text{-}Li$[7]

Experiments of this type are not definitive for two reasons: it is in general not known whether the reactions were run under conditions of kinetic or thermodynamic control, and the comparison is complicated by the different pKa's of the product carbanions (MCH_2Li and $M'CH_2Li$). Nevertheless, taken at face value, and combined with other data they serve to define the following order of reactivities in the Li/M exchange: I > Te, Sn > Pb, Br > Se, As, P, Ge > S, Cl, Si.

The lithium-selenium exchange provides a very flexible route to α-lithio selenides,[1c, 9a, 10a] and has in addition been used to prepare α-lithiosulfides,[1i, 9b, 10c] α-lithiosilanes,[9c] benzyllithium,[9f] and allyllithium reagents.[9f] More general application is limited because the Li/Se exchange is the slowest of the commonly used lithium-metalloid exchange reactions, slower than Li/Br, Li/Sn, Li/I, and Li/Hg (see Figure 1).[1d] This is unfortunate, since selenides are unquestionably easier to prepare than bromides, iodides, stannanes and mercury compounds. The lithium-tellurium exchange, first reported by Seebach[10b] and later studied by Kauffmann,[6b] Hellwinkel,[11] Petragnani,[8] and Sonoda,[12] promises to have some of the advantages of the Li/Se exchange in that the starting materials may be easy to prepare, but will be much faster, so that some side reactions which prevent widespread use of the Li/Se exchange (such as α- and β-metalation) will be minimized. We have examined the various lithium-metalloid exchange reactions in detail, and report here some of the results of our work, with emphasis on the lithium-tellurium exchange.

RESULTS

Comparison of Lithium-Metalloid Exchanges. We began our study by a survey of the rates of the various Li/M exchanges. Figure 1 presents in graphical form the results of our rate study, which was carried out in THF at -78° to 0°, using the exchange between *p*-tolyllithium and phenyl-M. The second row elements Si, P, S and Cl reacted at rates that were too slow to measure (Si) or barely measurable (P, S, Cl) even at room temperature (the rates were comparable to reaction of PhLi with solvent). The third row elements steadily increase from Ge, As, to Se and Br, with Ge again too slow to measure. Of the fourth row elements, Sn is the slowest, the remainder (Sb, Te, and I) were too fast to measure under our conditions. We will report below NMR studies that show that Te and I have closely comparable rates, with I slightly faster. Interestingly, the fifth row element Pb was slower than any of the fourth row elements. The exchange rate of Ph_3Bi is not known, but we have some indirect evidence that it, too, is relatively slow (compared to Te and I).

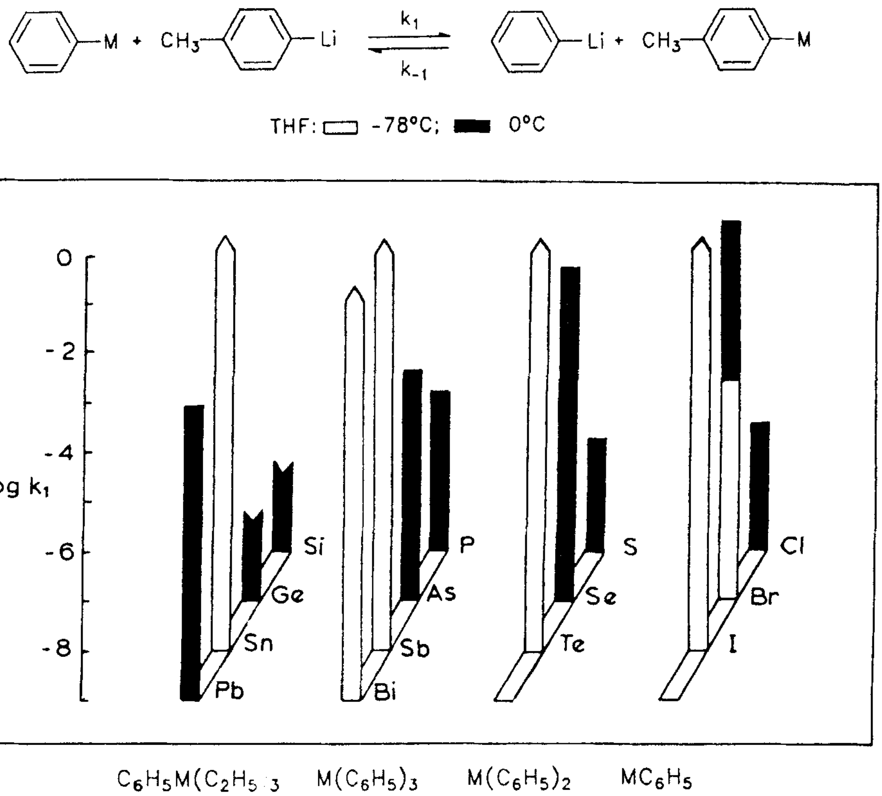
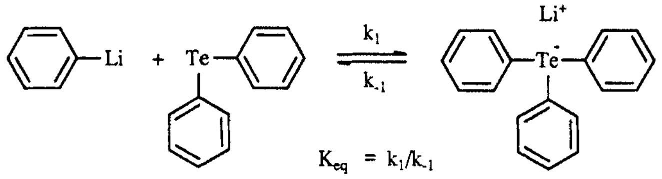
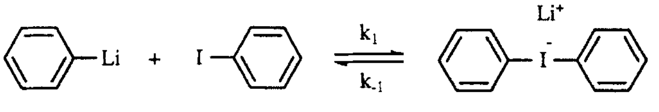


FIGURE 1. Li/M Exchange Rates of the Main Group Elements in THF (k_1 L $mol^{-1}sec^{-1}$). Ge and Si were too slow to measure at 0°; Sn, Sb, Te, I and Bi were too fast at -78° (reaction complete in <5 min).

Kinetic Tests for ate Complex Intermediates. We next performed a series of experiments designed to test for intermediates in the Li/M exchanges. The mechanism of the metal halogen exchange has been intensively investigated over the past two decades, with evidence both for and against SET reactions being reported.[5a,13,14] The other exchanges have been much less studied. We decided to test for the intermediacy of ate complexes in these reactions by comparing the reactivity (both rate and regioselectivity) of PhLi solutions towards a series of substrates, in comparison to reactions of PhLi/PhM mixtures. If significant concentrations of ate complexes were present, one might expect either the regioselectivity (e.g., ratio of 1,2- to 1,4-addition to chalcone) or the rate of reaction (with some electrophilic species) to be different between the PhLi and PhLi/PhM solutions. In fact, we found barely detectable differences when a 1:1 ratio of PhLi/PhM was used for M = Br, SePh, I, TePh, $SbPh_2$, or $SnBu_3$; but a real effect was observed for M = HgPh.[1e] However, when the ratio of metalloid species to lithium reagent was increased, a definite effect was observed for M = I and TePh, which we attribute to equilibria such as those of Eq. 1 and Eq. 2. Figure 2 presents the kinetic results in graphic form. The curves for iodine and tellurium were superimposed, implying that the formation constants K_{eq} for $Ph_2I^-Li^+$ and $Ph_3Te^-Li^+$ were almost identical. We also obtained our first estimates of K_{eq} for these ate complexes by simulation of the kinetic data, assuming simple second order kinetics for the reaction, and obtained values of $K_{eq} \approx 4$ L/mol at -78°. This value is substantially in error because the simulations ignored the monomer-dimer equilibria of PhLi as well as the perturbing effect of the ate complexes on the rates. From NMR studies we now know that the true equilibrium constant is close to 25 L/mol for both Te and I at -78°.[1f, 15]



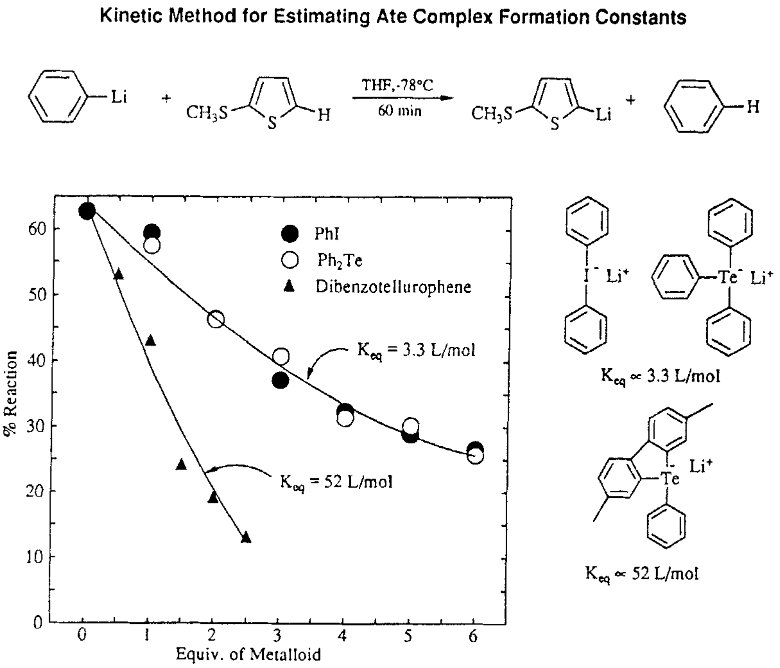
(Eq. 1)



(Eq. 2)

Similar experiments using dibenzotellurophene instead of diphenyl telluride showed that it formed a substantially more stable ate complex (formation constant ≈15 times as large). This is as expected; the natural bond angles are likely to be smaller in the hypervalent ate complex than in the telluride, and thus some relief of strain results on formation of the ate complex. The "small ring effect" has been identified in hypervalent iodine,[1g, 2a] tellurium,[11a] and other metalloids.[11b]

The fact that diphenylmercury formed some ate complex in THF, as judged by our kinetic



Kinetic Method for Estimating Ate Complex Formation Constants

Figure 2. Effect of iodobenzene, diphenyl telluride, and dimethyldibenzotellurophene on the rate of reaction of PhLi with 5-methylthiothiophene. The lines are computer simulations.

tests, but did not in ether, as reported by Wittig[2b] based on vapor pressure studies, provided an important insight into the solution behavior of these systems. Consider the right and left hand side of an ate complex equilibrium such as the one in Eq. 1 or 2. The left side has lithium strongly coordinated to the phenyl anion, so its demand for solvation is relatively low. On the other hand the anion on the right side has a diffuse negative charge which can provide little coordinative stabilization for the lithium. In fact, all ate complexes we have examined so far are present as *solvent separated ion pairs*,[1k, 16] in which the lithium is coordinated only to solvent molecules (in this case THF). This analysis predicts that better coordinating solvents would stabilize both phenyllithium and the ate complex, *but that the ate complex would be stabilized more* (larger association constant K_{eq}), as illustrated schematically in Figure 3.

We have tested this hypothesis with several polar cosolvents, of which HMPA gave the most dramatic results (Figure 4). The addition of HMPA to phenyllithium in THF resulted in very steep rate increases (between third and fourth order in HMPA), and the rate of reaction with our test electrophile, *n*-butyl iodide, rapidly became too fast to measure at -78°. However, when one equivalent of diphenyl telluride or iodobenzene was present, the rate actually *decreased* when

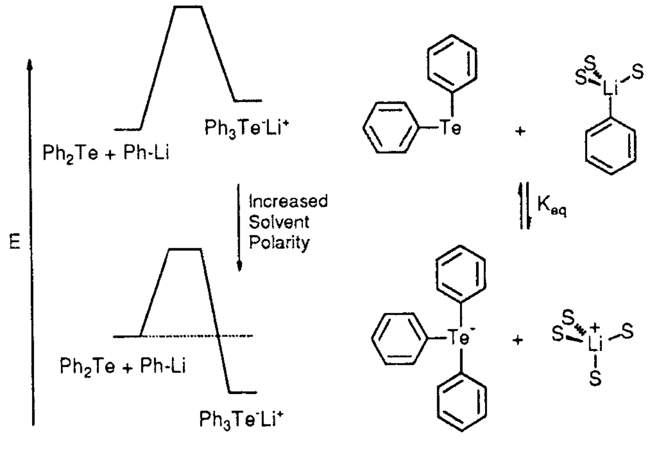


Figure 3. Effect of solvent polarity on ate complex formation constants.

HMPA was added. This can only be attributed to a dramatic displacement of the ate complex equilibria Eq. 1 and Eq. 2 to the right, so that the concentration of free PhLi approaches zero. In fact, solutions of PhLi/Ph_2Te or PhLi/PhI with more than 3 equivalents of HMPA no longer had any detectable reactivity toward *n*-butyl iodide at -78°. No such effect was seen for diphenyl selenide, and at best a very weak effect could be detected for triphenylbismuth, suggesting that it forms little or no ate complex.

We conclude from our kinetic data that ate complexes of iodine and tellurium form with a small association constant in THF, and with very large association constants in THF/HMPA. Tetraorganotin compounds similarly form ate complexes in strongly coordinating solvents.[1h]

NMR Studies of the Lithium-Tellurium Exchange Reaction. NMR spectra of solutions of PhLi and Ph_2Te are complicated by several dynamic processes that occur in the temperature ranges of interest. First of all, phenyllithium is a mixture of monomer and dimer in THF, and the two signals undergo coalescence at -85°. Secondly, the lithium triphenyltellurate has nonequivalent aryl groups (the molecule is T-shaped), which can equilibrate by a dynamic process. Finally, the phenyl groups on Ph_3TeLi, Ph_2Te and phenyllithium monomer/dimer undergo dynamic exchange with each other. The temperature dependence of ^{13}C NMR spectra is thus rather complicated, and has been analyzed only qualitatively. It is important to work at the lowest possible temperatures such that at least some of the processes are slow on the NMR time scale. We were not able to arrive at even a qualitative analysis that was satisfactory until

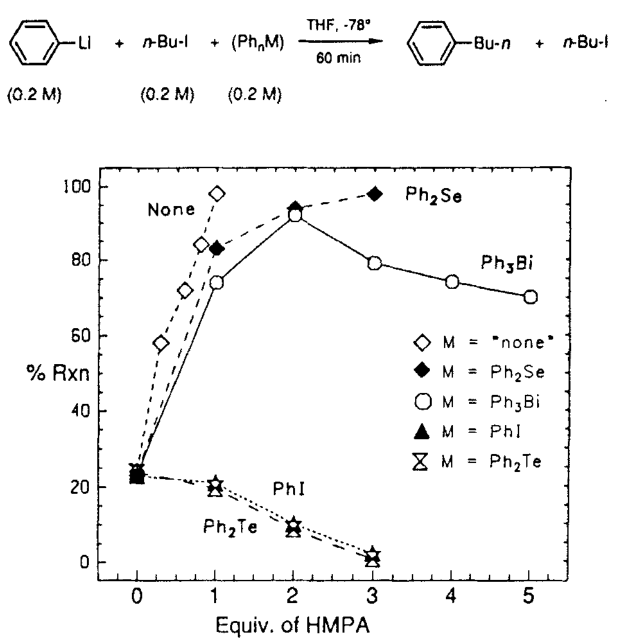


FIGURE 4. Effect of HMPA on the rate of reaction of PhLi with n-BuI in the presence of various metalloids.

we had carefully examined and compared ^{7}Li, ^{6}Li, and ^{13}C spectra (as well as ^{125}Te and ^{31}P when appropriate) of PhLi by itself, with those of PhLi/PhI, Ph$_3$I, PhLi/Ph$_2$Hg and PhLi/Ph$_2$Te.

The first surprise we encountered was that the ate complex formation constants in THF (K_{eq} of Eq. 1 and 2) were very large (>500 L/mol) at the low temperatures (<-105°) used for the spectroscopy, although they were small (<30 L/Mol) at the temperature (-78°) used for the kinetic tests. Figure 5 shows a comparison of ^{13}C spectra in THF at <-100° of the related structures Ph$_3$I, Ph$_2$I$^-$Li$^+$ and Ph$_3$Te$^-$Li$^+$,[17] each formed *in situ* by the addition of a single equivalent of phenyllithium to Ph$_2$I$^+$Cl$^-$, PhI, and Ph$_2$Te, respectively. In each case only a single species can be detected. Each compound has the *ipso* carbons of the apical phenyl group strongly downfield shifted, an effect characteristic of all hypervalent phenyl groups we have encountered. Especially noteworthy is the 2:1 ratio present for each signal of Ph$_3$I and Ph$_3$Te$^-$Li$^+$, which requires a T-shaped geometry (rather than trigonal) for these compounds, and the near identity of the signals for Ph$_2$I$^-$Li$^+$ and the apical resonances of Ph$_3$Te$^-$Li$^+$

With the above in mind, we can now examine spectra having various ratios of PhLi with Ph$_2$Te.[1j] The lowest spectrum in Figure 6 shows the ^{13}C NMR spectrum of phenyllithium (dimer 145 ppm, monomer 143 ppm), the second from the bottom a 1:1 ratio of PhLi and Ph$_3$Te$^-$Li$^+$. Note the broadening of the $(PhLi)_1$ signal at 143 ppm due to the beginning of

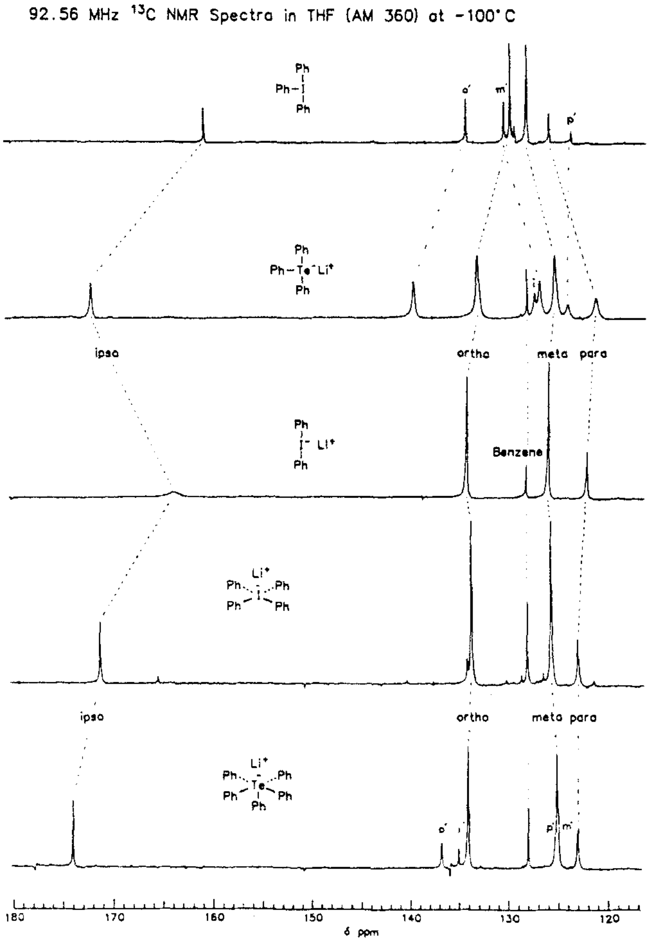


FIGURE 5. ^{13}C NMR spectra of Ph_3I, $PhTe_3^-Li^+$, $PhI_2^-Li^+$, $PhI_4^-Li^+$ and $PhTe_5^-Li^+$ in THF at -100°C.

dynamic exchange between it and the ate complex. The third spectrum shows the pure ate complex, and the top one the effect of excess Ph_2Te (138 ppm). Again the signals of Ph_2Te are broadened because of some residual exchange between it and the ate complex. Iodobenzene and phenyllithium behave in a more complicated manner. At 0.5 equiv. of phenyllithium the monomer is undergoing dynamic exchange with the iodine ate complex, and so only a single broad peak is observed. Similarly, when there is excess iodobenzene, only a single broadened peak is observed as a result of dynamic exchange between it and the ate complex (the ate complex is behaving as phenyl anion donor).[1f]

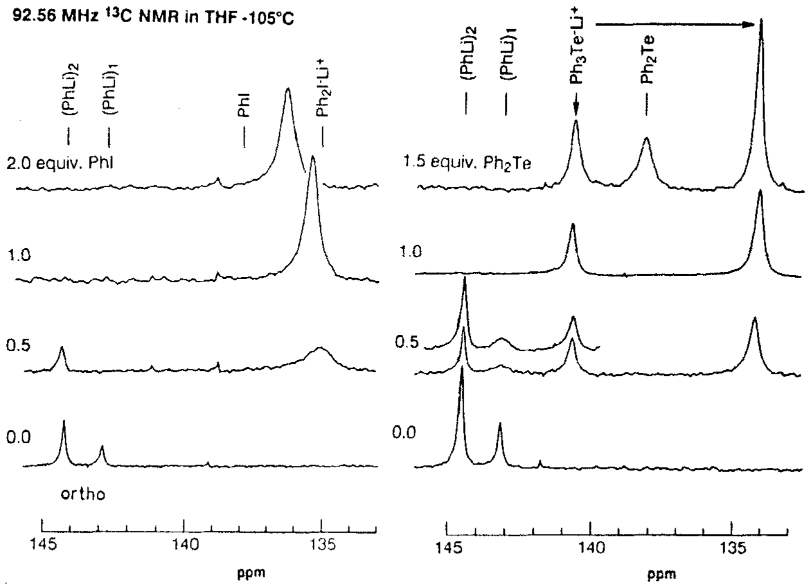


FIGURE 6. Ortho carbon ^{13}C NMR signals of 0.08M PhLi at -105°C with various amounts of iodobenzene and diphenyl telluride.

The kinetic tests (Figure 2) showed that PhI and Ph_2Te had identical association constants at -78°. These two species also have identical association constants at -105°. When one equiv. of PhI and one equiv. of Ph_2Te are allowed to compete for one equiv. of PhLi, close to a 1:1 ratio of $Ph_3Te^-Li^+$ and Ph_2Te results (Figure 7). The PhI/$Ph_2I^-Li^+$ signals are averaged under

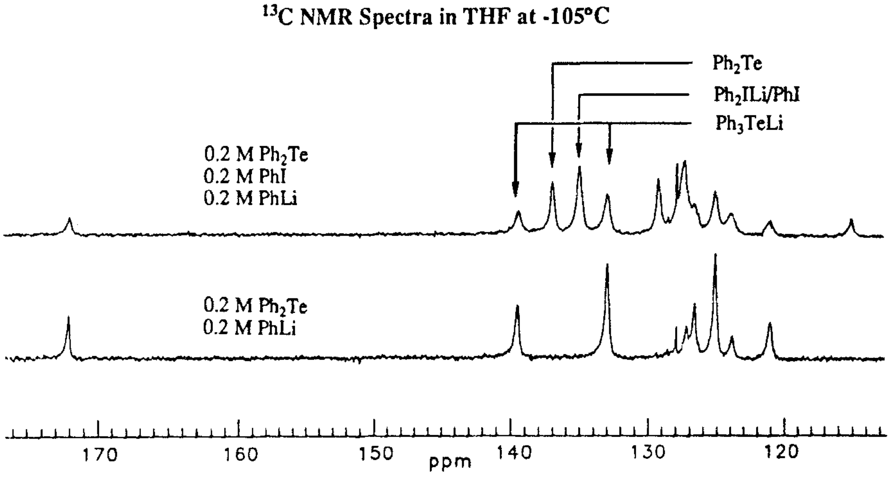


FIGURE 7. ^{13}C NMR signals of 0.2 M $Ph_3Te^-Li^+$ in THF at -105°C, with and without the addition of iodobenzene.

these conditions (135 ppm). This spectrum also demonstrates that the Li/I exchange is considerably faster than the Li/Te, since the telluride signals are not averaged under the identical conditions. It has been shown that the averaging of the iodide signals is due to transfer of phenyls between PhI and the ate complex, with the ate complex acting as an anionic phenyl donor. Evidently the tellurium ate complex is less reactive as a phenyl donor.

We complete our discussion of NMR studies of the Li/Te exchange by examining the lithium NMR spectra shown in Figure 8.[1j] We compare here the behavior of mercury, tellurium and iodine. The addition of diphenylmercury to phenyllithium (Figure 8A) produces a new sharp signal in the ^{7}Li NMR at δ -0.9[18] which has been assigned to tetrahedrally coordinated $Li^+(THF)_4$[1k,19] of $Ph_3Hg^-Li^+$.[20] Since only this signal was present when exactly one equiv. of diphenylmercury had been added, the formation constant of $Ph_3Hg^-Li^+$ (K_{eq}) is large. With less than one equiv., the remaining $(PhLi)_n$ signals were identical to those of phenyllithium itself at

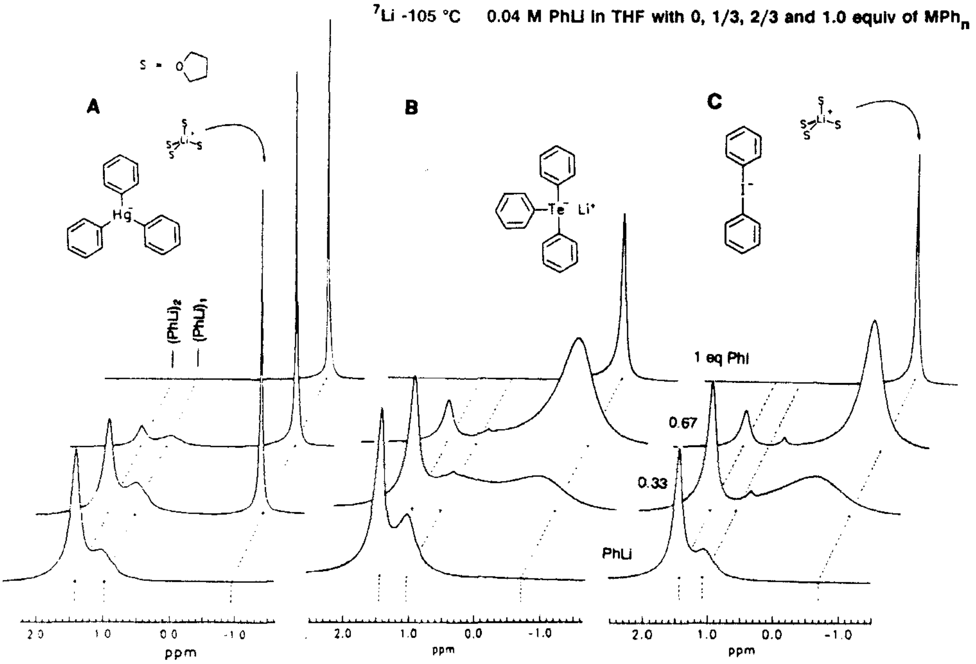


FIGURE 8. ^{7}Li NMR spectra of 0.04M PhLi at -105°C with one third molar increments of diphenyl mercury, diphenyl telluride and iodobenzene.

the appropriate concentration. Hence the Li/Hg exchange process is slow on the NMR time scale at -105°C. The addition of one equiv. of diphenyl telluride (Figure 8B) or iodobenzene (Figure 8C) produced a similar signal at δ -0.8, which we have assiged to the lithium of

$Ph_3Te^-Li^+$ and $Ph_2I^-Li^+$. As with $Ph_3Hg^-Li^+$, the formation constant (K_{eq}, Eq. 1 and 2) for each is large, since no phenyllithium signals were visible. At intermediate points in the titrations, the spectra contain broad signals indicative of rapid exchange. Whereas the $(PhLi)_2$ signal at 1.5 δ was unaffected, as it was in the mercury spectra, $(PhLi)_1$ and ate complex signals had become part of the broad signal between δ -1 and 1. We assign this averaged signal to $(PhLi)_1$ and $Ph_3Te^-Li^+$ (or $Ph_2I^-Li^+$[21]) in dynamic equilibrium, with the tellurium being slightly below coalescence, and the iodine slightly above it. Thus we conclude that although the formation constant of $Ph_3Hg^-Li^+$ is larger than those of I and Te, the Li/M exchange is slowest for mercury, faster for tellurium, and fastest for iodine. The Li/I exchange is therefore probably the fastest of all of the metalloids (only antimony has not been directly or indirectly measured, and one would predict that it would be slower than iodine).

We propose that the mechanism of the Li/Te exchange involves a three-center interaction of the telluride with lithium reagent (Figure 9). As C-Te bond-formation proceeds, the lithium either coordinates to the tellurium (in non-polar solvents) or is released as a separated ion (in THF and more polar solvents) to form the ate complex. The exchange is completed by coordination of lithium to the other carbon accompanied by Te-C bond cleavage.

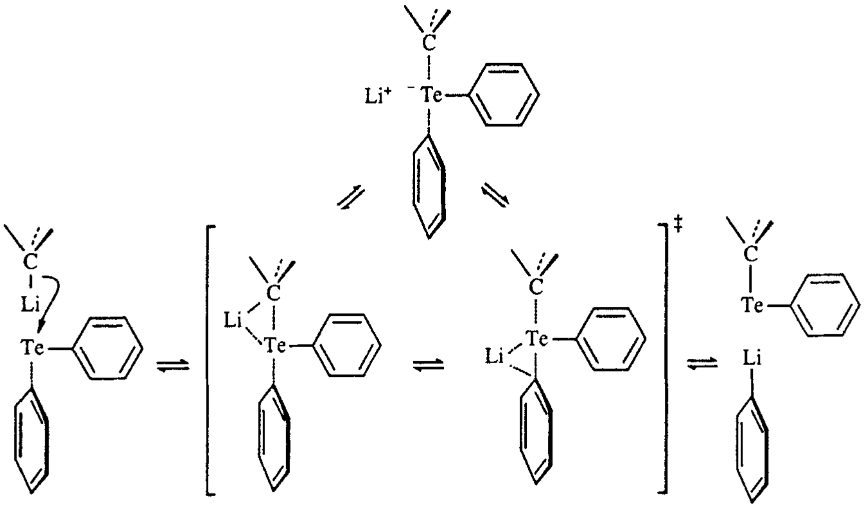


FIGURE 9. Proposed mechanism for the lithium-tellurium exchange.

A Pentacoordinate Tellurium Ate Complex. Daniel and Paetsch have obtained evidence that pentaphenylphosphorus, -arsenic, -antimony and -bismuth will undergo ligand exchange with phenyllithium, and that hexacoordinate ate complexes are formed with antimony and bismuth.[22] Wittig examined the reaction of tetraphenyltellurium with phenyllithium and found some indications of adduct formation, but no definite evidence could be obtained.[2c] We have examined the reaction of triphenyltelluronium chloride with phenyllithium, and can now report that first tetraphenyltellurium[2c] and then lithium pentaphenyltellurium are formed quantitatively. The addition of one equiv. of PhLi to $Ph_3Te^+Cl^-$ at -78° produces a mixture of Ph_4Te and $Ph_5Te^-Li^+$ and unreacted (insoluble) telluronium salt, but at 0° the formation of Ph_4Te is quantitative. Addition of a second equiv. produces $Ph_5Te^-Li^+$ stoichiometrically. Addition of excess PhLi produces the signals of PhLi monomer and dimer. Figure 5 shows ^{13}C NMR spectra which serve to characterize these species. The NMR spectrum of $Ph_5Te^-Li^+$ has a 4:1 ratio of apical and basal signals, as expected for a square pyramidal structure. As found for $Ph_3Te^-Li^+$ (Figure 5), the hypervalent phenyls have strongly downfield shifted *ipso* carbon signals. Addition of methanol to $Ph_5Te^-Li^+$ produces Ph_4Te cleanly. The new ate complex has high kinetic, stereochemical and thermodynamic stability. The apical and basal phenyl signals coalesce near -20°, compared to a coalescence temperature of approximately -90° for $Ph_3Te^-Li^+$. Solutions of $Ph_5Te^-Li^+$ are stable up to room temperature, and they do not decompose to give biphenyl. Hexacoordinate ate complexes of phosphorus,[11b] antimony,[22] and bismuth[22,23] have been detected.

We have also examined the formation of tellurium ate complexes by ^{125}Te NMR spectroscopy (Figure 10). It is interesting that conversion of Ph_2Te to the 10-Te-3 ate complex caused an upfield shift ^{125}Te shift, whereas conversion of Ph_4Te to the 12-Te-5 ate complex caused a downfield shift.

It was of interest to examine the corresponding iodine complex. Reaction of two equiv. of PhLi with $Ph_2I^+Cl^-$ in THF produced only Ph_3I,[2a] PhLi in excess of one equiv. remained in solution. This is in contrast to Ph_4Te and PhLi, which formed ate complex quantitatively under these conditions. However, when several equivalents of HMPA were added to the Ph_3I/PhLi solution the ^{13}C NMR spectra, which initially showed four sets of phenyl signals corresponding to monomer and dimer PhLi, and apical and equatorial phenyls of Ph_3I, simplified to a single set of *ipso*, *ortho*, *meta* and *para* signals. The chemical shifts and high symmetry clearly indicate the formation of square planar $Ph_4I^-Li^+$ (Figure 5). In contrast to the 12-Te-5 complex $Ph_5Te^-Li^+$, the 12-I-4 complex was very unstable, and decomposed cleanly at temperatures above -60° to $Ph_2I^-Li^+$ and biphenyl. This is the only reductive elimination which we have detected in any of the ate complexes so far examined. Reductive eliminations are commonly seen in neutral hypervalent compounds: sulfuranes,[24] selenuranes,[25] and telluranes.[11a,2c,26]

Summary. Phenyllithium reacts with diphenylmercury, diphenyl telluride, tetraphenyltellurium, iodobenzene and triphenyliodine in THF at temperatures below -78° to form ate

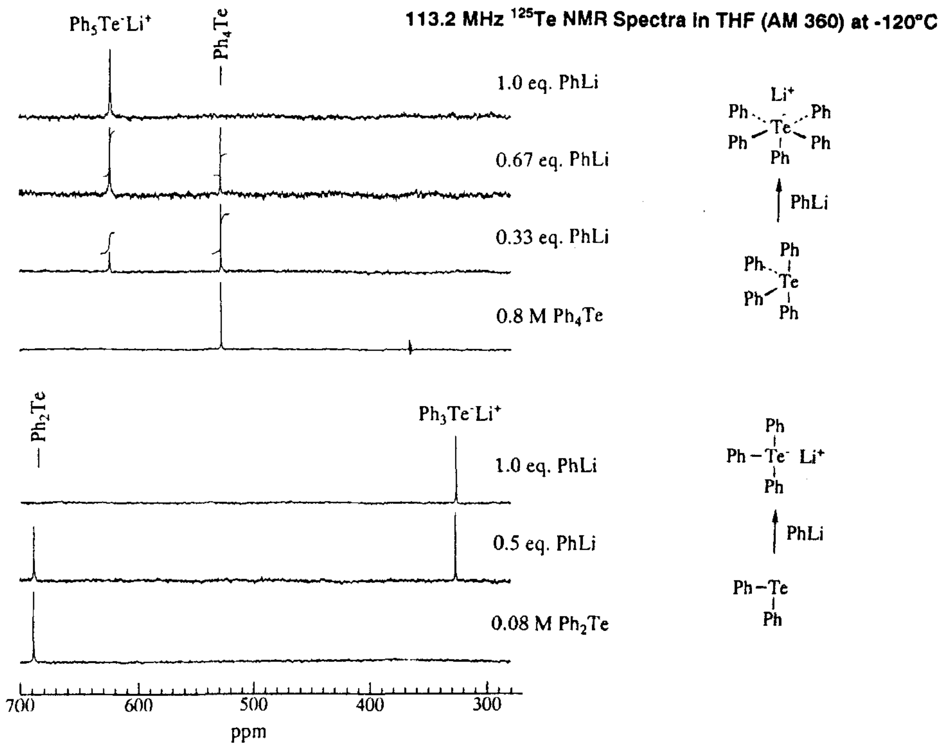


FIGURE 10. ^{125}Te NMR spectra of titration of Ph_2Te and Ph_4Te with phenyllithium at -120°C.

complexes. In THF/HMPA the ate complex formation constants are dramatically higher, and even triphenyliodine and triphenylbismuth appear to form ate complexes under these conditions. These results support the intermediacy of ate complexes in the Li/I, Li/Te and Li/Hg exchange reactions. The main group ate complexes show very characteristic ^{13}C chemical shifts of the hypervalent phenyl groups (apical for $Ph_2I^-Li^+$ and $Ph_3Te^-Li^+$) and basal for $Ph_4I^-Li^+$ and $Ph_5Te^-Li^+$), with *ipso* carbons strongly downfield shifted and *para* carbons upfield from their normal positions.

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