s-Bu₂Zn are stirred with solid MeOK, solutions are produced within a few minutes that have a MeOK to R₂Zn ratio of 0.5, which does not change on longer stirring, with sonication, or with heating.

(3) In some systems, liquids or solids with R'OК to R₂Zn ratios of 0.5 or 1.0 remain from removing R₂Zn at reduced pressure from preparations made from R'OК and R₂Zn. For example, subjecting a benzene solution containing Bu₂OZn and excess Bu₂OK to 0.5 Torr at 30-40 °C for 12 h left a viscous liquid (solidified at 0 °C) that had a s-BuOK to Bu₂Zn ratio of 0.5. Subjecting that oil to 0.01 Torr and 75 °C for 12 h left a solid that had a ratio of 1.0.

(4) More ¹H and ¹³C NMR absorptions for R (Bu and Me₂Si(CH₃)₂) and R'(t-Bu) are seen at R to R'OК ratios in the 0.5-1.0 range when 18-crown-6 is added. A possible explanation of these observations is that coordination of the crown ether with K⁺ slows exchange between the 1:1 species and other species in solution.

We conclude that solutions prepared from R₂Zn and R'OК form zincate species, probably similar to the magnesiate species formed from R₂Mg and R'OК. Equilibration of R and OR' groups between all species in the solutions is more rapid for Zn than for Mg, however, most likely reflecting a lesser tendency of R₂Zn than of R₂Mg to form bonds to oxygens.

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Registry No. [Et₂Zn(t-BuOK)ZnEt₂]₂⁻2K⁺, 131130-36-4; t-BuOK, 865-47-4; Et₂Zn, 557-20-0.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic temperature parameters for [Et₂Zn(BuOEt₂)ZnEt₂]₂⁻2K⁺ (7 pages); table of and calculated structure amplitudes for [Et₂Zn(t-BuOEt₂)ZnEt₂]₂⁻2K⁺ (7 pages). Ordering information is given on any current masthead page.

Lithium-Metalloid Exchange,¹ Dynamics and Equilibrium in the Li/I and Li/Te Exchange in Tetrahydrofuran: Iodide, Tellurium, and Mercury Ate Complexes

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The metal halogen exchange³ and related transmetalations involving selenium,⁴ tellurium,⁵ tin,⁶ and mercury⁷ are powerful methods for the preparation of functionalized and unstable organometallic reagents. The mechanisms of these transformations have been variously described in terms of single electron transfer or four-center processes or ate complex intermediates.⁸ We have previously reported kinetic⁹ and spectroscopic⁴ studies which demonstrated that phenyllithium and iodobenzene combine to form the ate complex Ph₃Li⁺ at low temperatures in THF/HMPA. Described herein are results from spectroscopic studies which implicate ate complex intermediates in the Li/Hg, Li/Te, and Li/I exchanges in THF as well and extend and complement our earlier work. The exchange in pure THF is complicated by the interplay between the monomer-dimer equilibrium of phenyllithium (eq 1), the ate complex equilibrium (eq 2), and the unexpected degenerate process of eq 3. For M = (n = 1), all three processes occur on the DNMR time scale between -76 and -115 °C.

\[
(\text{PhLi})_2 + \text{Ph}_n \text{Li}^+ \rightleftharpoons (\text{Ph}_n \text{TeLi})_2 + \text{PhLi}
\]

\[
(\text{Ph})_n \text{Li}^+ + \text{Ph}_n \text{TeLi}^+ \rightleftharpoons (\text{Ph})_n \text{TeLi} + \text{PhLi}
\]

\[
(\text{Ph}_n \text{Li})_2 + \text{Ph}_n \text{TeLi}^+ \rightleftharpoons (\text{Ph}_n \text{TeLi})_2 + \text{PhLi}
\]
Figure 1. $^7$Li NMR spectra\(^9\) (194.32 MHz) in THF at −105 °C of 0.04 M PhLi solutions with 0.33, 0.67, and 1.0 equiv of (A) Ph$_2$Hg, (B) Ph$_2$Te, and (C) PhI added.

Figure 2. Ortho carbons in the $^{13}$C NMR spectra: 0.08 M PhLi with 0.0, 0.5, and 1.0 equiv and an excess of (A) PhI and (B) Ph$_2$Te. The inset in B is 0.12 M PhLi, 0.04 M Ph$_2$Te.

Figure 3. $^{13}$C NMR spectra in THF at −105 °C. Telluride had been added, its signals could be seen. In contrast, addition of excess iodobenzene produced only a single broad resonance, which is the dynamic average of PhI and Ph$_2$Te$^+$. When more PhI was added, the signal moved as expected for rapid exchange. In this respect, the behavior is similar to that observed in THF/HMPA solution,\(^8\) and for the same reason: there is an exchange process rapid on the NMR time scale in which Ph$_2$Te$^+$ reversibly donates Ph− to PhI (eq 3). Thus Ph$_2$Te$^+$ is more reactive Ph− donor than Ph$_3$Te$^+$. In fact these spectra provide no direct evidence that the tellurium ate complex reacts at all with diphenyl telluride (eq 3).

The spectroscopic results of Figures 1 and 2 demonstrate in a most direct fashion that the monomer-dimer PhLi equilibrium is slow at −105 °C and that the dimer does not participate in the exchange of PhI or Ph$_2$Te on the NMR time scale, but that the monomer does.\(^14\) They also show that the ate complex equilibrium (eq 2) is fastest for PhI, slightly slower for Ph$_2$Te, and much slower.

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\(^1\) No triorganotellurium ate complexes have been observed. Some evidence for lithium pentaphenyltellurate has been reported: Wittig, G.; Fritz, H. Justus Liebigs. Ann. Chem. 1952, 577, 39. We have been able to confirm that Ph$_3$Te$^+Cl^−$ reacts with 2 equiv of PhLi in THF to produce Ph$_3$Te$^+Li^+$.\(^9\)

\(^2\) The $^{13}$C NMR spectrum of Ph$_2$Te$^+Li^+$, on the other hand, shows only a single set of resonances, as expected for a trigonal structure.\(^10\)


for Ph$_2$Hg. $K_2$ is large for all three at -105 °C. 15

We have carried out a quantitative measurement of $K_2$ for PhI.

Between -75 and -20 °C, all species [(PhLi)$_2$], (PhLi), PhI, Ph$_2$[Ph$^-$] are in rapid equilibrium (above coalescence). We have measured values for $\Delta_H^\circ$ and $\Delta_S^\circ$ for the phenyllithium mono-mer-dimer equilibrium, 16 so the population of the other species (PhI, Ph$_2$[Ph$^-$]) can be calculated from the average chemical shift in the 13C NMR spectrum. We obtained $\Delta_H^\circ = -9.9 \pm 0.6$ kcal/mol and $\Delta_S^\circ = -44 \pm 9$ eu for eq 2. Thus $K_2$ is 0.02 M$^{-2}$ at 0 °C (a solution 0.1 M in PhLi and PhI is 0.1% associated), 30 M$^{-2}$ at -78 °C (44% associated), and 1780 M$^{-1}$ at -105 °C (92% associated). The corresponding association constant $K_3$ for Ph$_2$Te is almost the same as for PhI, as shown by a relation in which 1 equiv of PhI was added to a solution of Ph$_2$Te[Li$^-$] in THF at -105 °C. 20 Half of the Ph$_2$Te[Li$^-$] was converted to Ph$_2$[Ph$^-$] + Li$^+$.

Summary. Iodine, tellurium, and mercury ate complexes have been characterized as intermediates in the Ph$^-$/Ph$_2$I (M = I, Te, Hg) exchange reaction in THF solution at low temperatures. Homonuclear phenyllithium is the reactive species in the Li/I and Li/Te exchanges. The formation constant for Ph$_2$[Ph$^-$] is strongly temperature dependent, consistent with the powerful solvent-ordering capacity of a solvent-separated ion pair. 18

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Desulfurization of Thiophene and Thiophenol by a Sulfido-Coalt-Molybdenum Cluster: Toward a Homogeneous Hydrodesulfurization Catalyst

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Conventional hydrodesulfurization (HDS) catalysts are prepared by the coimpregnation of Mo (or W) and Co (or Ni) salts on an alumina support, followed by sulfidation with H$_2$S/H$_2$. The active site is thought to consist of small crystallites of MoS$_2$ with Co atoms coordinated to sulfur at the edges of the basal planes. 3 The mechanism of HDS has been studied through the aid of surface science and organometallic modeling studies, 3 but as yet there is no clear consensus on the detailed structure of the active site or on the mechanistic details of the HDS reaction itself. 4 We have prepared sulfided bimetallic clusters 5 which mimic the metal composition of commercial HDS catalysts and have shown that one such cluster, C$_{18}$M$_{6}$O$_{12}$(CO)$_{18}$S$_4$ (C$_p$' = CH$_2$(C$_H_2$)$_2$) (1), when supported on alumina and sulfided, produces the same active site as found in commercial Mo/Co/S catalysts. 6 We have begun an investigation of the solution chemistry of cluster 1 to see if a homogeneous analogue of the surface-bound HDS catalyst may be constructed.

Cluster 1 reacts under N$_2$ with thiophene 7 at temperatures ranging from 110 to 150 °C to give a >90% isolated yield of C$_{18}$M$_{6}$O$_{12}$(CO)$_{18}$S$_4$ (2), with the production of some black, insoluble material. If 1 is heated to 150 °C in toluene under N$_2$, no conversion to 2 takes place and 1 can be recovered unchanged. This indicates that 2 is not a decomposition product of 1. The high yields (quantitative by NMR) of 2 obtained also indicate that 1 does not decompose to 2. If the reaction is conducted under 200 psi (ca. 15 atm) of H$_2$, cluster 2 is again produced in high yields, the black solid is not formed, and analysis of the gases revealed the presence of ethane, propane, and butanes along with significant amounts of ethene, propene, and butene (eq 1). Compared to the hydrocarbon product slate from heterogeneous HDS catalysis, cracking and hydrogenation are more prevalent in the homogeneous reaction.

Reactions of thiophene with mononuclear organometallics result in the formation of either π-complexes or S-bound thiophene complexes, but the desulfurization of these complexes has not been reported. 11 There is only one other example of the reaction of thiophene with a transition-metal cluster: the reaction of Fe$_2$(CO)$_{12}$ with thiophene gives FeS$_2$ and low yields of the dimetalllic species Fe$_2$(CO)$_{10}$(CH$_2$)$_2$. 12 Thus, eq 1 represents the first desulfurization of thiophene accomplished by a clean, high-yield organometallic conversion. 13


