The Role of Ate Complexes in the Lithium-Sulfur, Lithium-Selenium and Lithium-Tellurium Exchange Reactions

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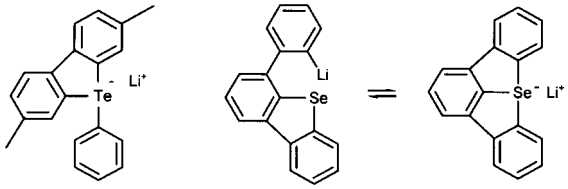
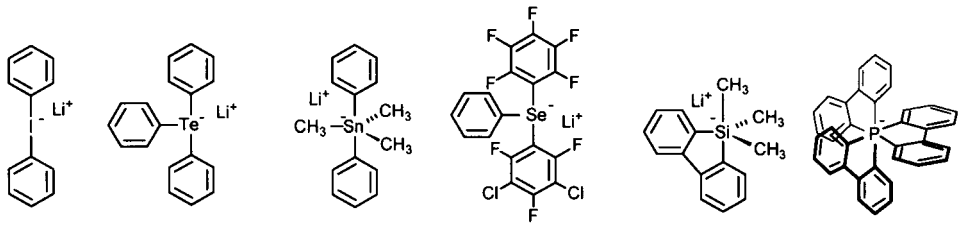
This paper is dedicated to Professor *Dieter Seebach* in honor of his 65th birthday

Hypervalent ate complexes are presumptive intermediates in the metal-halogen, metal-tellurium, and related exchange reactions. The effect of *o*,*o*′-biphenyldiyl *vs.* diphenyl substitution on formation of tellurium ate complexes was studied by a kinetic technique and by NMR spectroscopy. Only a modest increase in the association constant (K_{ate}) was measured. When Li/M exchanges of *o*,*o*′-biphenyldiyl sulfides and selenides were made intramolecular by means of a *m*-terphenyl framework (**12-S**, **12-Se**, **21**), enormous increases ($> 10^9$) in the rate of Li/S and Li/Se exchange were observed compared to acyclic models. Apparently, these systems are ideally preorganized to favor the T-shaped geometry of the hypervalent intermediates. For the selenium systems, ate complex intermediates (**20-Se**, **26**) were detected spectroscopically in THF- or THF/HMPA-containing solutions. A DNMR study showed that Li/Se exchange was substantially faster than exchange of the lithium reagents with the ate complex. Therefore, these ate complexes are not on the actual Li/Se exchange pathway.



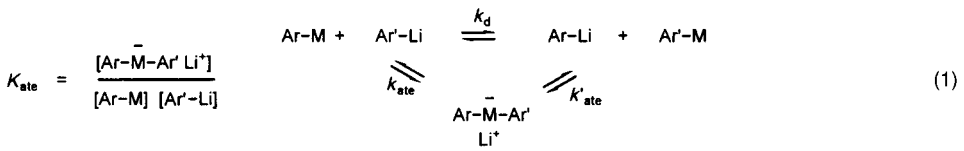
Introduction. – The lithium-metalloid exchange reaction is the mildest and most general procedure for the preparation of organolithium reagents. The lithium-bromine [1][2a] and lithium-iodine exchanges have been the most popular, but the reaction applies to many of the main-group third-, fourth-, and fifth-row elements. Tin [3a][4], selenium (first studied by *Seebach* and *Peleties* [3b], and tellurium [3c] have been used extensively. The reaction fails with second-row C–M bonds like those of chlorides, sulfides, and phosphines, except in exceptional circumstances, *e.g.*, when there are no protons that can be metallated, when an unusually stable carbanion is being prepared, or when a strained ring is being cleaved [5][6].

Hypervalent ate complexes such as **1**–**3** have been spectroscopically characterized and are likely intermediates in the degenerate phenyl-phenyl Li/I [7a][7b][8][9], Li/Te [7b][7c][10a], and Li/Sn [7d][11][12] exchange reactions. Ate complexes of third- and even second-row metalloids Se, P, and Si can be detected in favorable structures, *e.g.*, when the aryl groups are heavily substituted with electronegative halogen atoms (**4**, see [10b]) or when *o*,*o*′-biphenyldiyl ligands are present (**5**, see [13] and **6**, see [14a]).



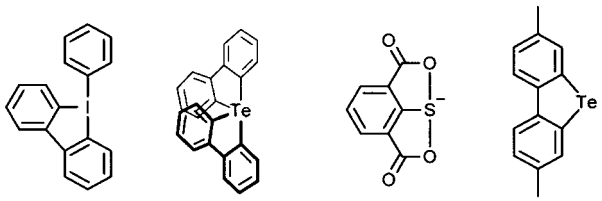
1 **2** **3** **4** **5** **6**

Although the identification of ate complexes such as **1**–**4** suggests strongly that they are intermediates in the various Li/M exchanges, this has not been unambiguously demonstrated. There could, for example, be a direct exchange process k_d (*Eqn. 1*) faster than the path through the ate complex (k_{ate}). We address this question here in the context of studies of the Li/Te, Li/Se, and Li/S exchanges.



$$K_{ate} = \frac{[Ar\text{–}\bar{M}\text{–}Ar'\ Li^+]}{[Ar\text{–}M]\ [Ar'\text{–}Li]} \qquad Ar\text{–}M + Ar'\text{–}Li \underset{k_{ate}}{\overset{k_d}{\rightleftharpoons}} Ar\text{–}Li + Ar'\text{–}M \quad (k'_{ate}:\ Ar\text{–}\bar{M}\text{–}Ar'\ Li^+) \qquad (1)$$

The Li/S exchange is rarely observed, and the Li/Se exchange is relatively slow. To remedy this, and to stabilize potential ate-complex intermediates in the hope that they could be directly observed, we undertook to prepare sulfur- and selenium-containing aryllithium reagents [7e] incorporating the *o*,*o*′-biphenyldiyl ligand, identified by *Hellwinkel* and co-workers [14] and others as providing increased kinetic and thermodynamic stability to hypervalent structures. This motif has allowed the study of mono-, bis-, and even tris-biphenyldiyl substituted hypervalent compounds of I, Te, Se, P, Si, and S, among them **5** [13], **6** [14a], **7** [7f][15], **8** [14b][14c][10c], and their S [10d] and Se [14d][10c] analogs. All of these showed dramatically higher stability than analogous polyphenyl compounds Ph_3I [1b], Ph_4Te [1c][10f], Ph_4Se [10e][10f], and Ph_4S [10g][10f]. For example, Ph_4Te decomposes rapidly at 80° [10f], whereas **8** is stable to 208° [14c].



7 **8** **9** **10**

In the course of studying these systems, we identified structures that allowed us to address the subtle mechanistic question outlined in *Eqn. 1*. Specifically, a system that fulfills the following requirements is needed: *1*) the three species in the triangular equilibrium of *Eqn. 1* must all be present in detectable concentrations under conditions

where the rates k_d, k_{ate}, and k'_{ate} can each be measured (this can be problematic because the rates and the ate complex equilibrium constant are very temperature- and solvent-dependent, and both must be in the measurable range), *2*) the lithium reagent should be monomeric to simplify the rate measurements (this plagues the PhLi/PhI and PhLi/Ph_2Te, and related thiophene systems, since significant concentrations of kinetically inactive PhLi dimer are present), and *3*) there must be minimal interference from the direct exchange between the metalloid and the ate complex, in which the ate complex acts as an anion donor (this process complicates kinetic analysis of Li/I exchanges [7a]).

Results and Discussion. – *Effect of Biphenyldiyl Ligand on Tellurium Ate Complex Stability.* We began our study by investigating a system where the effect of biphenyldiyl *vs.* diphenyl substitution on chalcogen ate-complex stability could be measured. There was some reason to be concerned, since, in contrast to most selenides, which undergo Li/Se exchange on treatment with alkyllithium reagents, selenophene [16] and benzoselenophene [17] are instead metallated by BuLi. Even dibenzoselenophene [18a] and benzotellurophene [12] can be metallated cleanly under appropriate conditions. Thus, these systems, rather than being activated toward Li/M exchange, show an unusual resistance to nucleophilic attack at the heteroatom, perhaps as a result of aromatic stabilization of the heterocyclic ring. To test the '5-ring effect' on ate-complex formation, we compared the propensities of Ph_2Te and the dibenzotellurophene **10** [14c] to form ate complexes with PhLi.

The presence of the ate complexes **1** and **2** was first detected kinetically by measuring the rate of reaction of PhLi with electrophiles in the presence and absence of PhI or Ph_2Te [7g]. Rate reductions were observed when the metalloids were added. This was attributed to the formation of ate complexes that are less reactive than the PhLi in equilibrium with them. When the rate of metallation of 2-(methylthio)thiophene by PhLi was measured with increasing amounts of Ph_2Te, PhI, or **10** present, it decreased progressively, indicating the formation of the unreactive ate complexes (*Fig. 1*). The larger decrease in rate for **10** *vs.* Ph_2Te can be interpreted in terms of a 15-fold larger association constant K_{ate} for **10**.

We also performed a variable-temperature ^{13}C-NMR study on the PhLi/**10** system (*Fig. 2*). At room temperature, the spectrum is the superposition of the spectrum of **10** and PhLi. On lowering the temperature, the chemical shifts of all signals change as **10** is converted to the ate complex **11**. At $-70°$ (*Fig. 2,f*), ate-complex formation is essentially complete ($K_{ate} = 2300$ M^{-1}, $> 94\%$ **11**). Exchange between PhLi, **10**, and **11** is still fast on the NMR timescale, although several of the peaks, notably the C_o(Ph) signal and C(2), are already quite broad due to beginning of decoalescence. Between $-70°$ and $-90°$, the PhLi monomer-dimer exchange goes through decoalescence, and the peaks for $(PhLi)_2$ appear at their final shift positions. PhLi monomer is still in fast exchange with **11** at $-90°$ (note the absence of the PhLi monomer signal at δ 143). Between $-90°$ and $-112°$, the ate-complex exchange of $(PhLi)_1$, **10**, and **11** becomes slow on the NMR time scale, and at $-112°$, all but one of the expected 24 aromatic C-signals are at least partially resolved: 4 for PhLi dimer, 4 for PhLi monomer, and 16 for **11** (the *ipso* signal for PhLi monomer at δ 196.5 was not resolved). We were able to assign all C-atoms except for distinguishing C(x), C(x') for C(2) to C(6). The C-atom of the apical dibenzotellurophene ring was assigned to the upfield signal in each case

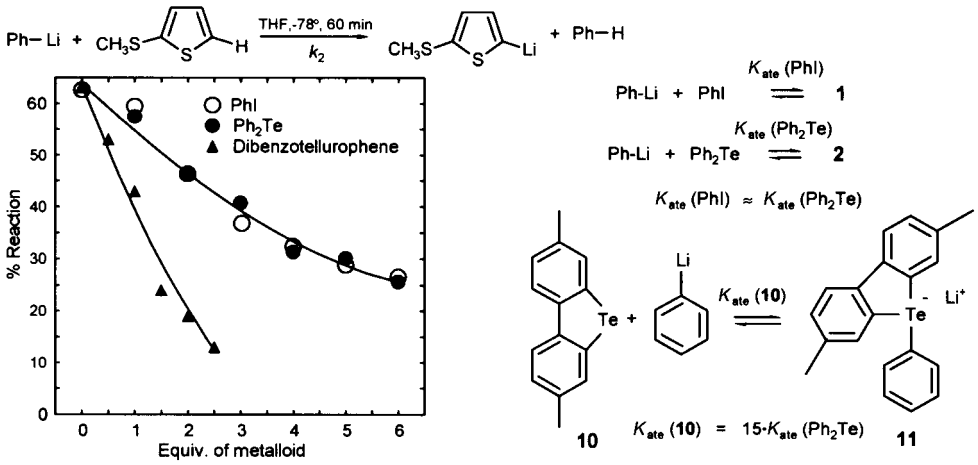


Fig. 1. *Inhibition of the rate of reaction of PhLi with 2-(methylthio)thiophene by the addition of PhI, Ph_2Te, and* **10**

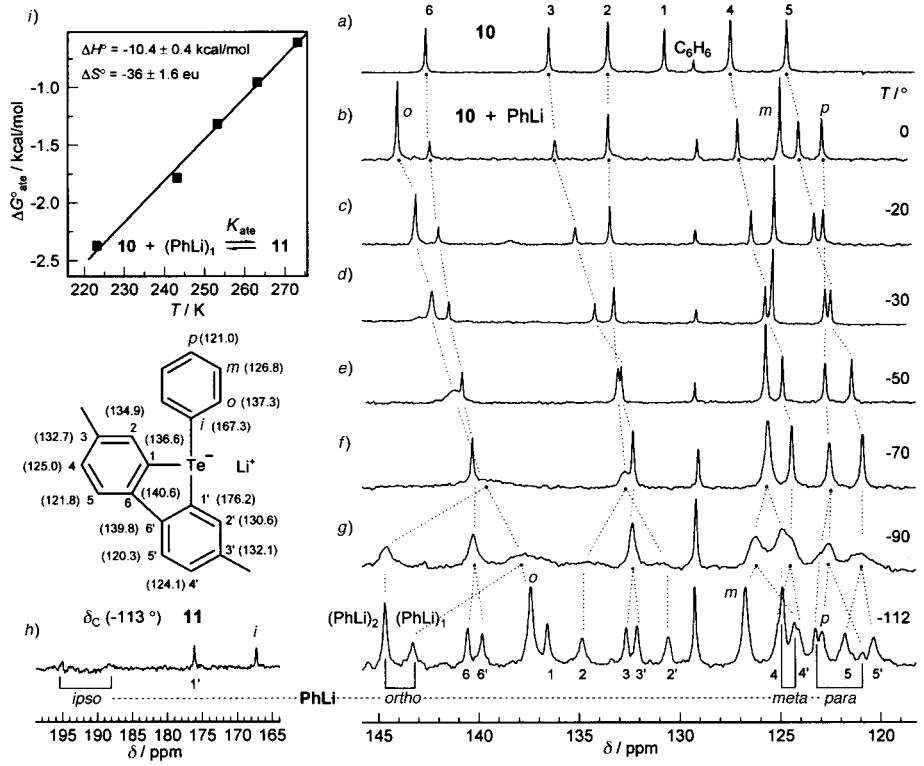


Fig. 2. a) *^{13}C-NMR of* **10** *in THF at* $-110°$. b–h) *variable-temperature ^{13}C-NMR study of PhLi* (0.16M) *and* **10** (0.08M) *in THF* (dotted lines mark the chemical-shift changes due to formation of **11**, decoalescences of monomer and dimer PhLi, and decoalescence of ate complex and PhLi; the graphics gives the ^{13}C-NMR chemical shifts of **11**); i) *temperature dependence and thermodynamic parameters for formation of* **11**

without direct evidence, but consistent with the behavior of other tellurium and iodine ate complexes.

The strong downfield shift of the two apical signals of C(1′) and C_{ipso}(Ph), at δ 176 and 167 provide support for the structural assignment of **11**. A variety of hypervalent metalloid ate complexes with apical aryl groups have such downfield ^{13}C-NMR signals for the C–M C-atom: Ph_3TeLi (δ 174.1) [7b][10a], Ph_5TeLi (175.4) [7c], Ph_2ILi (166.5) [7a], Ph_4ILi (172.4) [7c], Ph_2SnMe_3Li (180.0) [7d]. Neutral hypervalent molecules also show this effect (*e.g.*, in Ph_3I the 'apical' C-I signal is at δ 161.9, the 'equatorial' at δ 125.2 [7c]).

Experiments with excess telluride (0.08M **10**, 0.04M PhLi) showed that **10** and **11** were still in fast exchange at $-110°$, a process that can be assigned to bimolecular transfer of phenyl between **10** and **11** (ate complex as phenyl-anion donor), a process also identified for the Li/I exchange of PhLi/PhI [7a]. With excess PhLi present, the concentration of **10** is very low, and bimolecular exchange becomes very slow, allowing the static NMR spectrum of *Fig. 2,h* to be observed.

Analysis of the chemical shifts of the averaged ^{13}C-NMR signals C(2) to C(6) allows determination of the fraction of **11** at each temperature from 0 to $-50°$. The amount of uncomplexed phenyllithium remaining could then be determined at each temperature, which, in turn, allowed calculation of the concentration of $(PhLi)_1$ and $(PhLi)_2$, by means of the thermodynamic parameters for the monomer-dimer association constant reported ($\Delta H = -0.38$ kcal/mol, $\Delta S^\circ = -9.3$ eu) [7h]. From this data, association constants and thermodynamic parameters for the ate-complex equilibrium of $(PhLi)_1$ and **10** to form **11** could be calculated. The negative entropy seen for this equilibrium is precedented. Substantial negative entropies are generally seen for ArLi/ate complex equilibria (ate complexes are favored at low temperature)[1]), as well as other contact ion pair/separated ion pair equilibria[2]), a consequence of the additional solvent molecules frozen by the free lithium cation. For similar reasons, Li/M exchanges also show negative entropies of activation[3]).

The NMR study, like the kinetic study of *Fig. 1*, showed that **10** formed an ate complex in THF, but not with the expected much larger association constant (*e.g.*, **10** is half-associated with PhLi in THF at $-30°$, Ph_2Te is half-associated at *ca.* $-70°$). Since the increase in K_{ate} for incorporation of the biphenyldiyl moiety in **10** was relatively modest, we did not examine the Se and S analogs. Instead, we chose a *m*-terphenyl framework to provide further pre-organization to maximize the stability of the Se and S ate complexes. This mimics the expected T-shaped geometry and provides additional entropic advantages since the anion addition to S or Se is intramolecular. Although the *m*-terphenyl framework had not been previously used to stabilize hypervalent metalloids, similar structures with 'apical' O- and N-atoms, for example the (2,6-dicarboxyphenyl)sulfuranide(1–) anion **9** [19a], have been used to stabilize ate

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[1]) For equilibration of PhLi/PhI with Ph_2ILi, $\Delta H^\circ = -9.9$ kcal/mol and $\Delta S^\circ = -44$ eu [1c]; for equilibration of biphenyldiyldimethylsilane/MeLi with biphenyldiyltrimethylsilicate, $\Delta H^\circ = -13.1$ kcal/mol and $\Delta S^\circ = -53.8$ eu [13].

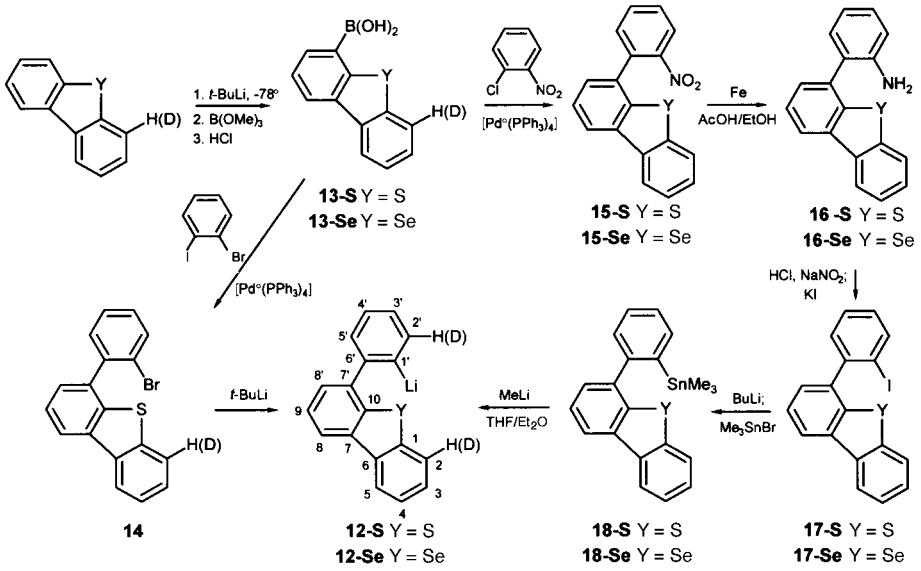
[2]) For the equilibration of lithium fluorenide contact and separated ion pairs in THF, $\Delta H^\circ = -7.5$ kcal/mol and $\Delta S^\circ = -22$ eu [25].

[3]) Negative entropies of activation have been found for the rates of intermolecular PhLi/ArBr exchange in Et_2O ($\Delta H^\ddagger = 14$ kcal/mol, $\Delta S^\ddagger = -24$ eu) [26a] and THF (223 K, $\Delta H^\ddagger = 9.5$ kcal/mol, $\Delta S^\ddagger = -30$ eu).

complexes and neutral hypervalent sulfur [19b][20], phosphorus [14e][21], and tin [22] compounds, among others.

Several precursors to the desired lithium reagents **12-S** and **12-Se** were prepared as shown in *Scheme 1*. *Ortho* metallation of dibenzothiophene [2b] and dibenzoselenophene [18a] allowed introduction of a D-atom (if needed) and a boronic acid moiety. The H/D isotope effect was large enough that >90% of the second metallation of (4-^{2}H)dibenzothiophene occurred at the *ortho′* position. Boronic acids **13-S** and **13-S-d** were coupled with *o*-iodobromobenzene (*o*-dibromobenzene gave substantial amounts of bis-coupling product). Although this synthesis is short and provided a route to the D-substituted compound **14-d**, it was plagued by low yields and difficult purifications. A more effective (albeit longer) route involved *Suzuki* coupling [23] of **13-S** with *o*-nitrochlorobenzene, reduction of the nitro group, and iododediazoniation to form the iodide **17-S**. To permit generation of halide-free lithium reagent **12-S**, the iodide was exchanged with BuLi, and coupled with bromotrimethylstannane to give **18-S**. This synthesis was not useful for preparing isotopically substituted deuterated analogs, since D-scrambling occurred during the reaction of the diazonium compound with iodide. Presumably, radical intermediates in this reaction [24] undergo rapid scrambling through a sulfuranyl radical [19c].

Scheme 1. *Synthesis of* **12-S** *and* **12-Se**



Lithium-Sulfur Exchange. A first estimate of the rate of Li/S exchange was obtained by preparing the deuterated lithium reagent **12-S-d** by treatment of **14-d** with ^{t}BuLi in THF at $-78°$ and quenching the reaction with dimethyl disulfide. The deuterium was completely scrambled within 30 s, as shown by the 0.5 integration of the proton at δ 7.8 in the produced methylthio derivative **19** (=**12-S** with MeS instead of Li, assigned to H–C(2) (H–C(2′) was obscured by other signals) and by the ^{2}H-NMR spectrum,

which showed two signals at δ 7.5 and 7.8 in a 1:1 ratio. A similar reaction in Et_2O as solvent showed less than 3% scrambling at $-78°$ for 10 min ($k_{THF} > 1500 \cdot k_{Et2O}$).

More definitive evidence for a rapid degenerate Li/S exchange was provided by a ^{13}C-NMR spectroscopic study of **12-S** prepared in THF/Et_2O 80:20 (*Fig. 3*). To avoid interference by lithium halides, solutions of lithium reagents for spectroscopic studies were prepared by Li/Sn exchange with low halide methyllithium. At $-78°$ and lower, the structure was static on the NMR timescale as evidenced by 18 signals in the ^{13}C-NMR spectrum corresponding to the 18 C-atoms of **12-S**, including the C-Li signal at 197.4 ppm, a chemical shift strongly suggestive of a monomeric structure [27][7h]. All of the C-signals were assigned. Atoms C(2) and C(2′) were directly identified by the characteristic effect of deuteration (in **12-S-d**), and the C(1), C(1′), C(3), and C(3′) were distinguished by the observation of a D-isotope shift. The quaternary atoms C(1), C(6), C(6′) C(7), C(7′), and C(10) were identified in a fully coupled spectrum; of these, C(6) could be distinguished from C(7) since C(6) was a *t* due to two ^3J(C,H) couplings (^2J(C,H) is < 2 Hz) , whereas C(7) was a *d* (similarly for C(6′) and C(7′)). C(10) was the only quaternary C-atom not broadened in the spectrum at higher temperature (*Fig. 3*). The signals of C(1) to C(6) were assignable and distinguished from those of C(2′) to C(6′) based on their close similarity to model compounds such as the trimethylstannyl derivative **18-S**. A ^{13}C,^{1}H COSY experiment together with homonuclear ^{1}H-NMR decoupling experiments removed any remaining ambiguities in assignment of all ^{1}H- and ^{13}C-signals in the NMR spectra. These assignments were also consistent with those made for the Se analog **12-Se**.

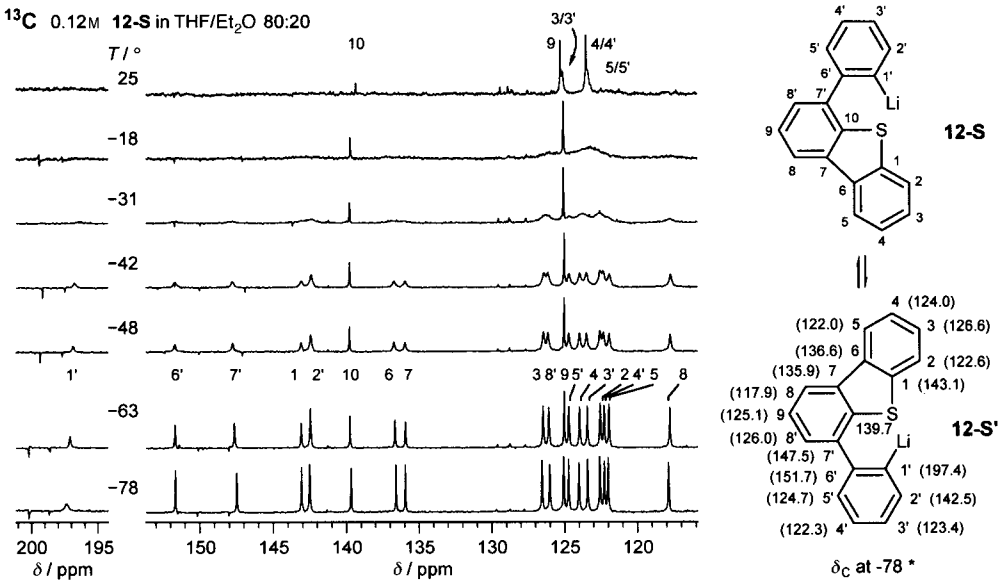


Fig. 3. *^{13}C-NMR Spectra of a variable-temperature study of a THF/Et_2O 80:20 solution of* **12-S** (0.12M)

When the temperature was raised, spectral changes characteristic of a dynamic NMR process occurred. These changes are uniquely consistent with a degenerate Li/S

exchange of **12-S** and **12-S′**. Two of the signals in the ^{13}C-NMR spectrum remained sharp throughout, and these can be assigned to C(9) and C(10), whose environment is unaffected by the process. At room temperature, three pairs of the more closely spaced signals (C(3) and C(3′), C(4) and C(4′), and C(5) and C(5′)) have largely coalesced (see *Fig. 4* for an analysis of the chemical shifts). Of these, the sharpest one (δ 123.5) is at the temperature extrapolated average of signals assigned to C(4) and C(4′) which have the smallest $\Delta\delta$ (1.6 ppm) of all exchanging pairs (the excess broadening of signals above coalescence is roughly proportional to the square of the chemical shift). The other two (δ 123.5, 125.0) have the next smallest $\Delta\delta$ values (C(5) and C(5′), 2.8 ppm; C(3) and C(3′), 3.0 ppm). All other signals have $\Delta\delta > 7.5$ ppm and are still too broad to be seen at 25°. The signal averaging is illustrated in *Fig. 4,b*, which shows the calculated positions of the fully averaged spectrum.

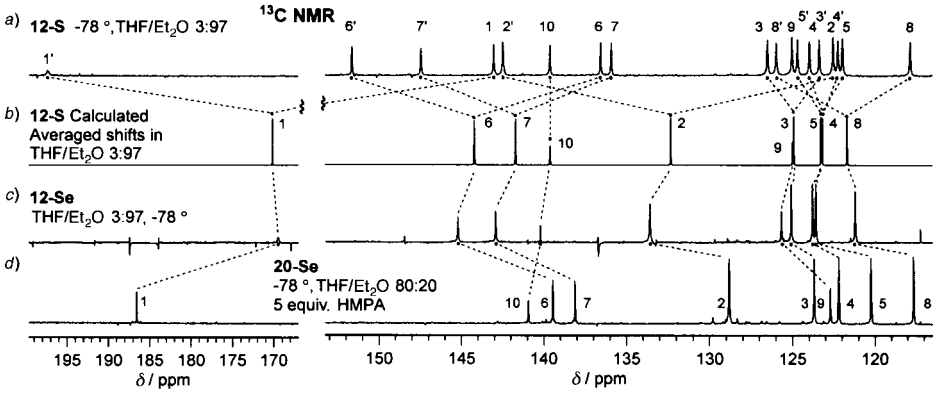


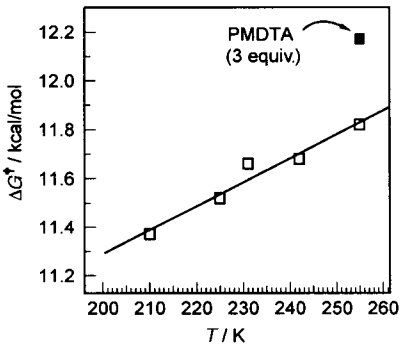
Fig. 4. a) *^{13}C-NMR Chemical shifts of* **12-S** *in THF/Et$_2$O 3:97*; b) *calculated positions of the ^{13}C-NMR chemical shifts of* **12-S** *under conditions of rapid exchange* (**12-S** $\rightleftharpoons$ **12-S′**); c) *^{13}C-NMR chemical shifts of fully coalesced* **12-Se** *in THF/Et$_2$O 3:97*; d) *^{13}C-NMR chemical shifts of* **20-Se** *in THF/Et$_2$O 80:20, 5 equiv. of HMPA (hexamethylphosphoric triamide) at* $-78°$

The signals for C(1), C(6), C(7), C(7′), and C(8) in the spectra of *Fig. 3* were subjected to line-shape analysis[4]) to determine the rate of Li/S exchange. The unaffected signals for C(9) and C(10) were used to establish the line width in the absence of exchange. The rate data and an *Eyring* plot are shown in *Fig. 5*.

Attempts to force conversion of **12-S** to the ate complex by addition of hexamethylphosphoric triamide (HMPA), a technique that has been effective with other metalloids [7a][7d][7g][13], were unsuccessful. Only decomposition products were detected even when the sample temperature never exceeded $-78°$. Similar solutions of **12-Se** formed the ate complex **20-Se** quantitatively (see below) and were stable for weeks at $-78°$.

Lithium-Selenium Exchange. The large stabilization of the transition state for the exchange of **12-S** compared to acyclic models encouraged us to synthesize the analogous selenium compound **12-Se** (*Scheme 1*) and study its behavior by NMR spectroscopy. *Fig. 6* shows variable-temperature ^{13}C-NMR spectra of **12-Se** in THF/Et$_2$O 80:20. At temperatures between 6° and $-126°$ in this solvent mixture, as well as

[4]) Simulations were performed with a version of the computer program WINDNMR [7i].



Temp. / °	k / s^{-1}	$\Delta G^{\ddagger}$ /kcal/mol
-18	400	11.82
-31	145	11.68
-42	45	11.66
-48	31	11.52
-63	6.5	11.37

$\Delta H^{\ddagger} = 9.3 \pm 0.4$ kcal/mol
$\Delta S^{\ddagger} = -9.8 \pm 2$ eu

Fig. 5. *Rates and activation parameters for equilibration of* **12-S**/**12-S′** *in THF/Et$_2$O 80:20.* Also shown is the effect on the rate of adding 3 equiv. of PMDTA (pentamethyldiethylenetriamine).

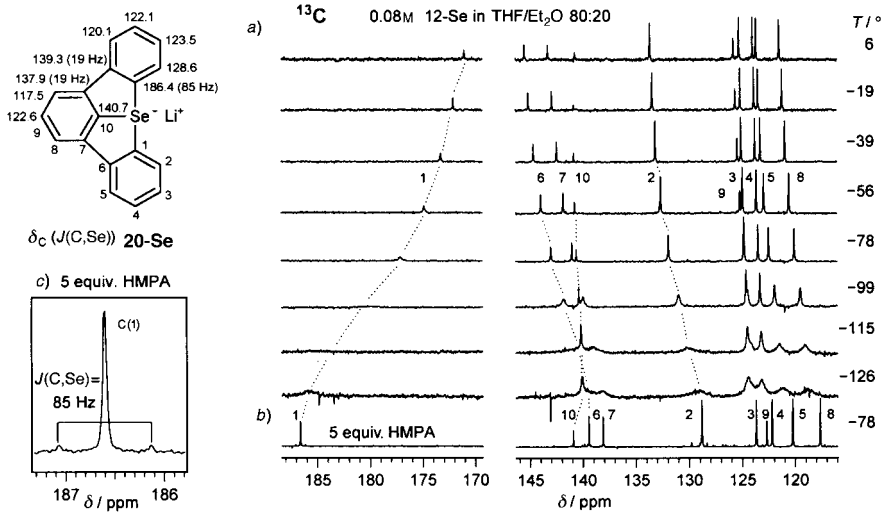


Fig. 6. a) *^{13}C-NMR Spectra of a variable-temperature study of a THF/Et$_2$O 80:20 solution* (0.12M) of **12-Se**; b) *same sample with 5 equiv. of HMPA added at* $-78°$; c) *expansion of the C(1) signal of* **20-Se** *showing the ^{77}Se satellites*

between $-79°$ and $-141°$ in THF/Me$_2$O/Et$_2$O 8:67:25 and at $-78°$ in THF/Et$_2$O 3:97, at most ten signals, two of them with half-intensity, were visible in the ^{13}C-NMR spectrum. This is consistent only with the presence of a rapidly equilibrating mixture of isomeric lithium reagents **12-Se** and **12-Se′** and/or the static selenium ate(1−) complex **20-Se**. Several lines of evidence show that the isomers are in rapid equilibrium, and the ate complex **20-Se** is also present in significant concentrations in solutions containing >10% THF. Thus, in contrast to the behavior of **12-S**, the chemical shifts of **12-Se** in THF/Et$_2$O 80:20 are significantly temperature-dependent (especially C(1), which goes from δ 171 at 6° to δ 186 at $-126°$). The signals also show increased broadening at low temperature as if a decoalescence was occurring. Although the central atoms C(9) and C(10) are sharper than the others, they also broaden at the lowest temperature; so

slowing of the exchange between **12-Se** and **12-Se′** cannot be the only process responsible for the broadening observed.

A ^{77}Se-NMR (7.5% natural abundance, spin «) study clarified the situation (*Fig. 7*). Between 6° and −113°, the Se-signal progressively moved upfield, and broadened substantially below −78°. Between −113° and −128°, the signal decoalesced into two peaks, a small one at 450 ppm very close to the original signal at 6°, assignable to **12-Se**, and a second one at 405 ppm, which we have assigned to the ate complex **20-Se**. We were unable to achieve decoalescence in the ^{13}C-NMR spectra because of a combination of insufficient solubility, the resultant problems with sensitivity, and the smaller chemical-shift changes (in Hz) for most of the ^{13}C- *vs.* the ^{77}Se-NMR signals.

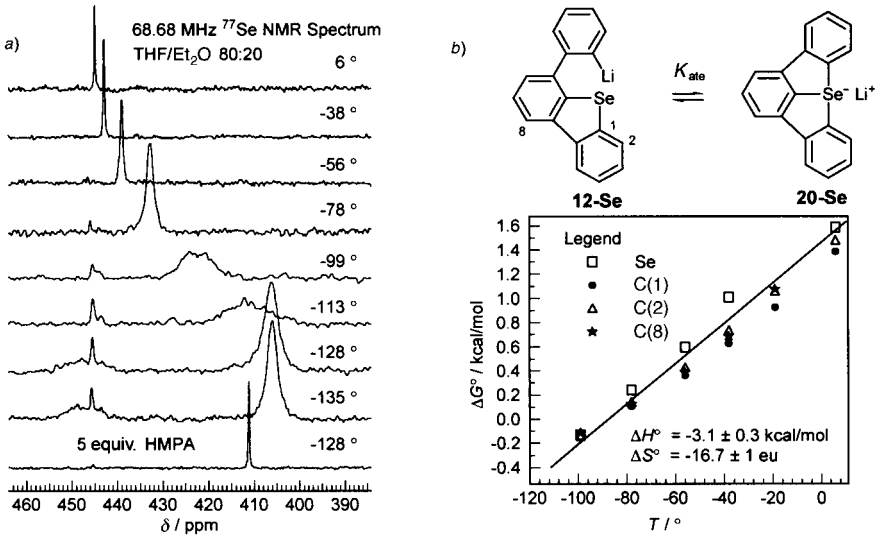


Fig. 7. a) *Variable-temperature 68.68-MHz ^{77}Se-NMR spectra of* **12-Se** *in THF/Et$_2$O 80:20;* b) *thermodynamics of the* **12-Se** ⇌ **20-Se** *equilibrium, determined by measuring the ratio of the two components from the averaged chemical shifts of the ^{77}S-NMR signal and the ^{13}C-NMR signals for C(1), C(2), and C(8)* ($\Delta H^\circ = -3.1 \pm 0.3$ kcal/mol, $\Delta S^\circ = -16.7 \pm 1$ eu)

Several experiments with different solvents and cosolvents supported the assignments made above. In solvents containing only a few percent of THF (THF/Me_2O/Et_2O 8:67:25 and THF/Et_2O 3:97), the ^{13}C-NMR spectra showed ten C-signals, and the ^{13}C- and ^{77}Se-NMR chemical shifts were essentially temperature-independent, consistent with the absence of significant concentrations of **20-Se**. The **12-Se** and **12-Se′** exchange should have no effect on the ^{77}Se-NMR signal, and none was detected. The ^{13}C-NMR signals broadened below −100° as a result of incipient decoalescence between **12-Se** and **12-Se′** although the spectrum was still above coalescence at −141°, the lowest temperature that could be reached.

One consequence of the strong C-Li coordination in ArLi and the weak interaction between lithium and the counter-ion in the ate-complex intermediates is that ate-complex formation for the PhI/PhLi [7a], Ph_2Te/PhLi [7c], and R_3PhSn/PhLi [7d] systems is strongly solvent dependent, with no detectable complex in Et_2O solution but

a significant amount in THF [5]). HMPA is especially effective at stabilizing these ate-complex structures, and that is the case for **12-Se** as well. When 5 equiv. of HMPA was added to a solution of **12-Se**/**20-Se** in THF/Et_2O 80:20, sharp signals were observed in both the ^{13}C- and ^{77}Se-NMR spectra. The NMR spectra are inconsistent with an assignment of these signals to rapidly equilibrating **12-Se**/**12-Se**′. This solution contains only **20-Se**, based on the following considerations.

A comparative analysis of the ^{13}C-NMR chemical shifts of **12-S**, **12-Se**, and **20-Se** is shown in *Fig. 4*. Comparison of the calculated average signals of **12-S** in THF/Et_2O 3:97 (*Fig. 4,a* and *b*) with the coalesced signals of **12-Se** (*Fig. 4,c*) showed a close similarity, with no signal differing by more than 1.3 ppm. On the other hand, the comparison of the signals of **12-Se** with those of a solution containing HMPA (**20-Se**, *Fig. 4,d*) reveals large changes in chemical shifts (*e.g.*, 17 ppm for C(1), 5 ppm for C(6)), confirming that a major change in structure had occurred. The C(1) signal in **20-Se** at δ 187 is similar to that for the tellurium ate(1−) complex **11**, and far from the δ 167 predicted for a rapidly equilibrating structure (average of C(1), *ca.* 140 ppm, and C(1′), *ca.* 195 ppm). In addition, a C,Se coupling (^1J(C,Se) = 85 Hz) was resolved for C(1). An equilibrating structure should have a coupling of *ca.* 50 Hz, the average of ^1J(C,Se) for C(1) (*ca.* 100 Hz[6]) and C(1′) (0 Hz). The ^{77}Se-NMR chemical shift of δ 411 is close to the upfield signal at δ 406 observed in the decoalesced spectrum *Fig. 7* (−135°)[7]).

The ^7Li-NMR is also fully consistent with conversion to **20-Se**. At −115°, the broad *s* at −0.6 ppm for **12-Se** is converted to the characteristic *quint.* of $Li(HMPA)_4^+$ on addition of HMPA, as expected for a separated ion **20-Se** with lithium coupled to four P-nuclei [7j].

Thermodynamics of the Li-Se Exchange Process. The ^{77}Se-MR spectra in *Fig. 7* and ^{13}C-NMR spectra in *Fig. 6* were used to determine the temperature dependance of the equilibrium of **12-Se** and **20-Se**. The shifts for the averaged signal of the exchanging species were used to calculate the equilibrium composition of each component and thus ΔG°. Only the five spectra, from +6° to −99°, could be used because below −99°, decoalescence took place. A ^{77}Se-NMR chemical shift of 406 ppm was used for **20-Se** and 447 ppm for **12-Se**. The ^{13}C-NMR signals for C(1), C(2), and C(8) were chosen for this analysis because they showed the largest chemical-shift change. The signals from *Fig. 4* for pure **12-Se** (C(1) 169.4, C(2) 133.5, C(8) 121.1) and *Fig. 6* for pure **20-Se** (C(1) 186.4, C(2) 128.6, C(8) 117.5) were used as reference signals for the calculations, and were assumed to be temperature-independent. A plot of ΔG° *vs.* T for K_{ate} is presented in *Fig. 7*.

Effect of PMDTA (pentamethyldiethylenetriamine = *N*-[2-(dimethylamino)ethyl]-*N*,*N*′,*N*′-trimethylethane-1,2-diamine). An intriguing and unexpected effect was observed when PMDTA was added to a solution of either **12-S** or **12-Se** in THF/Et_2O 80:20. For both systems, the presence of 3 equiv. of PMDTA slowed the exchange

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[5]) This effect seems also to be present in the transition state leading to the lithium-metalloid exchange since large solvent effects on rates are typically seen (*e.g.*, from the rate data in Et_2O for the PhLi/TolBr exchange reported by *Winkler* and *Winkler* [26] in Et_2O and our data in THF [7c], we calculate k_{THF} / k_{Et_2O} = 13600 at 0°).

[6]) The ^1J(C,Se) in dibenzoselenophene is 99.8 Hz, for compound **18-Se** it is 100.2 Hz for C(2) and 98.2 Hz for C(11) (numbering as shown for **12**).

[7]) Small changes in δ(Te) for the tellurium ate(1−) complex **2** in THF and THF/HMPA have been reported [10a].

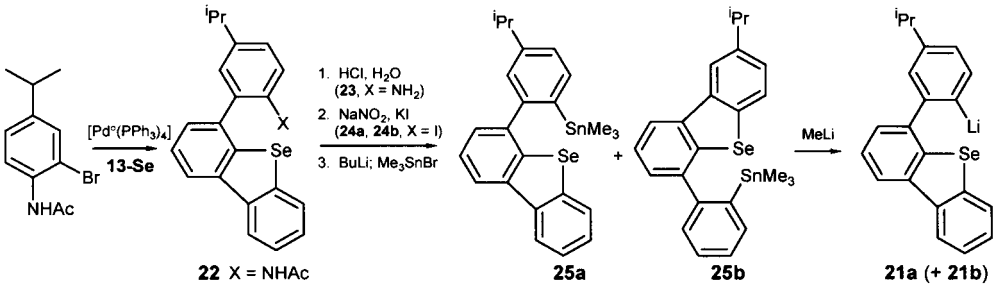
process by at least a factor of 200. For **12-Se**, the rate reduction was large enough that decoalescence could be achieved below $-70°$, so that, at $-111°$, 16 of the 18 possible signals were resolved. This rate reduction must have its origins in a relative destabilization of the ate complex, since the ^{13}C-NMR signals were essentially temperature-independent down to $-141°$, and no signal for **20-Se** was detectable in the ^{77}Se-NMR spectra down to $-123°$, conditions under which $>80\%$ of the material was ate complex in the absence of PMDTA (*Fig. 7*). Evidently, complexation of PMDTA stabilizes the lithium reagent **12-Se** more than it does the ate complex **20-Se** and the transition state leading to it.

Kinetics of the Li-Se Exchange Process. The rate of the **12-Se**/**20-Se** interchange could be estimated from the ^{77}Se-NMR spectra of *Fig. 7* (-78 to $-128°$) by means of line-shape analysis by two-site exchange. Activation parameters in THF/Me_2O 80:20 were $\Delta H^{\ddagger} = 5.7 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -5 \pm 2$ eu for the **12-Se**/**20-Se** equilibrium. Unfortunately, ^{77}Se-NMR cannot be used to measure the key **12-Se**/**12-Se**′ interconversion since the degenerate exchange does not affect the selenium signals.

In principle, the rate of the **12-Se**/**20-Se** exchange as well as the Li/Se exchange (the **12-Se**/**12-Se**′ interconversion), k_d and k_{ate} in *Eqn. 1*, can be simultaneously determined from analysis of the low-temperature ^{13}C-NMR spectra, *e.g.*, by the coalescence of the C(2) and C(2′) ^{13}C-NMR signals. In spite of substantial efforts, this was unsuccessful, partly because of signal-to-noise problems, but more importantly because that rate is probably faster than can be detected by the dynamic NMR (DNMR) method. This will be clearer when we discuss the unsymmetrical system **21** below. Thus, we were not able to establish unambiguously that the ate complex **20-Se** was an obligatory intermediate in the exchange.

Since the ^{77}Se-NMR studies were more effective than ^{13}C-NMR work, we synthesized the unsymmetrical derivative **21**. In this compound, the two isomeric lithium reagents **21a** and **21b** are no longer identical, and both the Li/Se exchange and the exchange with the ate complex are measurable by ^{77}Se DNMR studies. The precursor trimethylstannyl derivatives **25a** and **25b** were prepared by a procedure similar to that used for **12-Se** starting with a *Suzuki* coupling [23] of 2-bromo-4-isopropylacetanilide with the boronic acid **13-Se** (*Scheme 2*). As was observed in the preparation of ^{2}H-labeled **17-S**, iododediazoniation of the diazonium salt prepared from **23** gave a 1:1 mixture of the two iodides **24a** and **24b**. Interestingly, one of the isomers has a diastereotopic isopropyl group in the ^{1}H- and ^{13}C-NMR spectra,

Scheme 2. *Synthesis of* **21a**/**21b**



presumably the result of restricted rotation around the Ar–Ar bond. Although the presence of two isomers in the precursor iodide **24** and stannane **25** was a nuisance synthetically, it was not of concern for the proposed study since the results with **12-Se** show that the lithium reagents **21a** and **21b** would scramble immediately on formation.

The NMR behavior of **21a**/**21b** was analogous to that of **12-Se**. In solvent mixtures rich in THF at low temperature, the ate complex **26** formed in significant concentrations. The defining variable-temperature NMR experiments for this system are displayed in *Fig. 8*. In Me_2O/Et_2O 54:46, no ate complex forms (signal expected at 404 ppm), but the two isomeric lithium reagents **21a** and **21b** can be decoalesced, with ^{77}Se-NMR signals at δ 447 and 453 ppm. They are present in a 26:74 ratio (*p*-tolyllithium and phenyllithium at equilibrium with their bromides are present in a 38:62 ratio [26b]). A line-shape analysis[4]) between $-125°$ and $-146°$ (*Fig. 8,a*) gave $\Delta G^{\ddagger}_{-136} = 6.22$ kcal/mol, $\Delta H^{\ddagger} = 6.3 \pm 0.6$ kcal/mol, and $\Delta S^{\ddagger} = -2.5 \pm 4.5$ eu for the **21a** to **21b** equilibrium.

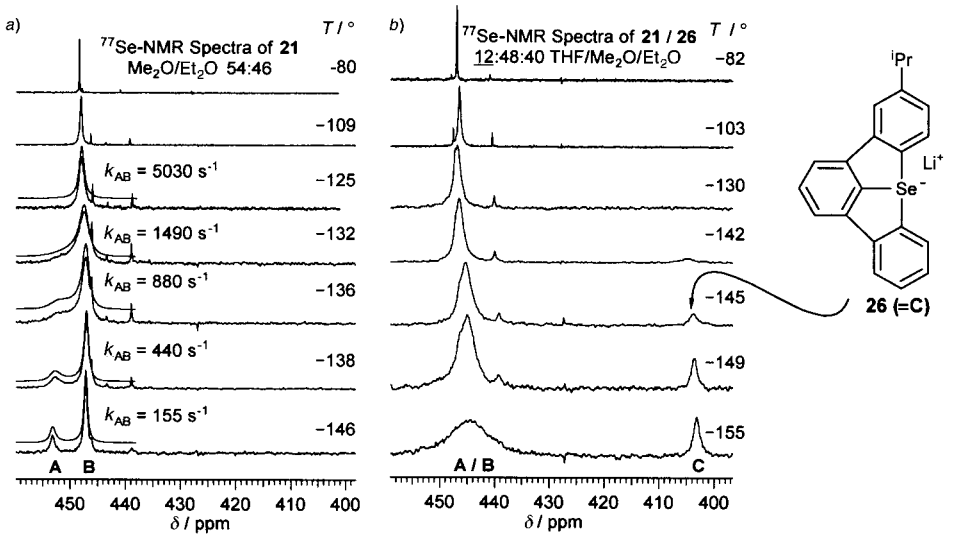


Fig. 8. *Variable-temperature 68.68-MHz ^{77}Se-NMR spectra of* **21a**/**21b** *in* a) *Me_2O/Et_2O 54:46 and* b) *THF/Me_2O/Et_2O 12:48:40*. Signal **A** and **B** correspond to **21a** and **21b**, signal **C** to the ate complex **26**

A similar variable-temperature experiment for the sample in *Fig. 8,a* to which 12% THF had been added is shown in *Fig. 8,b*. Below $-130°$, a new signal at δ 404 decoalesced, which we have assigned to the ate complex **26**. As for **12-Se** (*Fig. 7*), addition of more THF increased the fraction of the signal at δ 404, and addition of HMPA gave complete conversion to the ate complex (signal at δ 411). Like the other ate complexes, **26** showed characteristic downfield ^{13}C-NMR shifts for the apical C-atoms at δ 181.9 and 187.2. Quenching of this solution with bromotrimethylstannane gave 82% yield recovery of the stannyl precursors **25a** and **25b** (3:2 ratio), showing that the structure remained intact despite complete disappearance of the signals for **21a**/**21b** in the ^{77}Se-, ^{13}C-, and ^{7}Li-NMR spectra.

What is remarkable is that, even though the ate-complex ^{77}Se-NMR signal is relatively sharp below $-145°$, the lithium reagents **21a** and **21b** are still in rapid exchange. Although the lithium-reagent signals did show substantial broadening below $-149°$[8]), no sign of decoalescence was detected[9]). Thus, qualitatively, *the Li/Se exchange* (interconversion of **21a** and **21b**, k_d in *Eqn. 1*) *is faster than the exchange of the ate complex with the lithium reagents* (k_{ate}).

We have attempted to quantitate this observation by performing a series of three-site line-shape simulations on the spectrum at $-145°$. We make the assumption that neither the ^{77}Se-NMR chemical shifts of **21a** and **21b** nor their ratio at equilibrium was changed when 12% of THF was added to the Me_2O/Et_2O mixture. To simplify discussion, we assign symbols **A**, **B**, and **C** to **21a**, **21b**, and **26**, respectively. Selecting the inherent line width for the line-shape simulations is problematic since there is clearly some broadening process at very low temperatures (see $-155°$ spectrum) that selectively broadens the **A**/**B** signal compared with the **C** signal. We have used the line width of the small amounts of protonated material for this purpose.

Fig. 9 shows simulations which demonstrate that the spectrum at $-145°$ cannot be explained if exchange through the ate complex **C** is the only path (*i.e.*, if k_{AB} and k_{BA} are zero). If we fit the ate complex peak **C**, then **A** and **B** are well below coalescence (simulation 2). If we increase k_{AC} and k_{BC}, then the ate complex peak **C** broadens

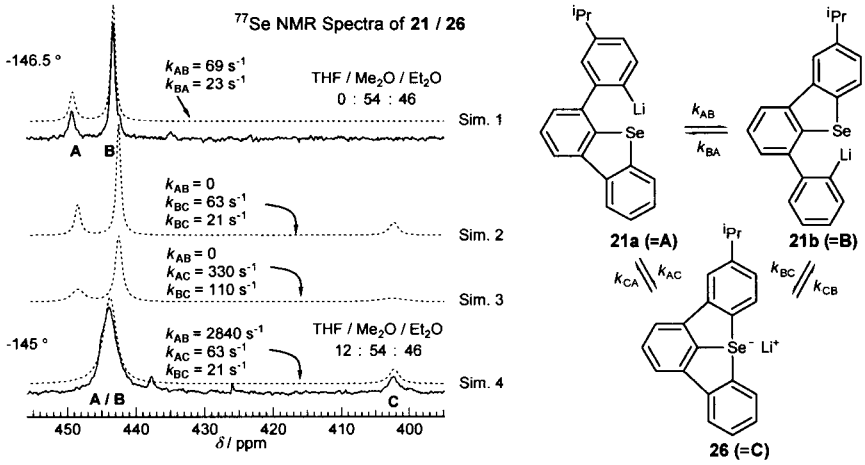


Fig. 9. *^{77}Se-NMR Spectra and computer simulations of* **21**. The top spectrum is in a solution containing no THF, the bottom one has 12% THF in the Me_2O/Et_2O mixture. Simulation 1 is a 2-spin simulation of the **21a**/**21b** exchange at $-146°$ in Me_2O/Et_2O (no ate complex present). Simulation 4 is the optimal 3-spin simulation of the exchange **21a**/**21b**/**26**, including a large rate for the **A**/**B** exchange. In simulations 2 and 3, only processes through the ate complex **C** are allowed ($k_{AB} = k_{BA} = 0$)

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8) The broadening of the peak at $-155°$ is possibly a viscosity effect at these very low temperatures. It cannot be the result of the **21a**/**21b** decoalescence since that requires an unsymmetrical peak shape (see the $-136°$ spectrum in *Fig. 8,a*).

9) The small shoulder on the side of the peak at 445 ppm in the spectra at $-130°$ to $-149°$ is the protonated compound.

(simulation 3). If k_{AC} and k_{BC} are increased sufficiently to coalesce **A** and **B** as in the actual spectrum, then **C** is also coalesced with **A** and **B** (not shown). Only if we include both a k_{AB} term and the k_{AC} and k_{BC} terms, we can simulate the observed spectra (simulation 4). Our best estimate is that k_{AB} is at least 50 times as fast as k_{AC}. To a first approximation, **26** is not an intermediate in the exchange reaction, which must principally occur by some sort of direct exchange (k_d in *Eqn. 1*).

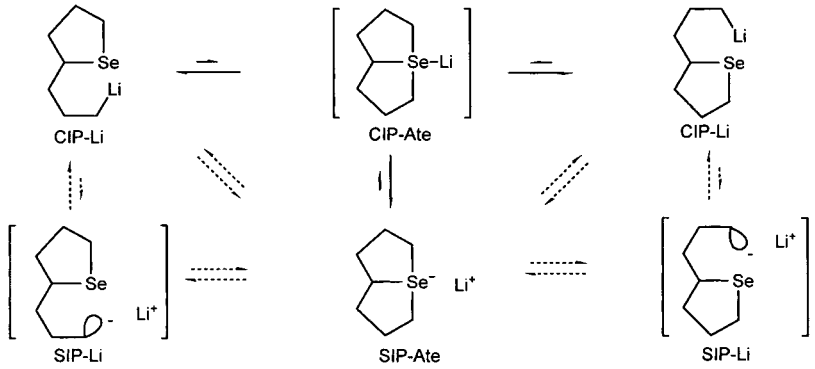
We can consider several possibilities for an exchange process that does not involve the ate complex. Single-electron transfer (SET) reactions have been detected for the metal-halogen exchange of alkyl bromides [28], but not for alkyl iodides or aryl halides [8][29]. We can rule out SET mechanisms in the present system because the solutions of **12-Se** and **21** we have studied have undergone well in excess of 10^{10} Li/Se exchanges in the course of the NMR experiment. There would have to be a cage effect of unprecedented magnitude to avoid quenching if even a minuscule fraction of the exchanges produced radical intermediates. Even the much slower Li/S exchange occurred >24000000 times without mishap during just the approximately 1 h it took to measure the single ^{13}C-NMR spectrum at 25° in *Fig. 3* ($k = 6800\,s^{-1}$).

A better alternative would be a direct S_N2 substitution, or an associative substitution that avoids the spectroscopically detected form of **26**. This behavior can be formulated as follows. Aryllithium reagents like **21a** and **21b** are strong contact ion pairs (CIP). The ate complex **26** is a separated ion pair (SIP). At some point in any exchange process that involves **26**, ion separation must occur. We can identify two limiting processes. Either C–Li first forms the SIP $C^-//Li^+$ and then C^- adds to the C–Se σ^* orbital to give $C-Se-C^-//Li^+$, or C–Li adds to C–Se bond to form the CIP ate complex C–Se–CLi, which can then undergo ion-pair separation to the more stable SIP $C-Se-C^-//Li^+$ (*Scheme 3*). A very satisfactory explanation for our NMR experiment is that the rate of dissociation of the CIP-Ate to CIP-Li is faster than its rate of ion-pair separation to form SIP-Ate, so the reaction effectively bypasses the observed SIP-Ate complex. Another way of looking at this is in terms of the detailed mechanism of the conversion of ate complex to lithium reagents. This is an electrophilic attack of Li^+ on the weak hypervalent C–Se bond of the ate complex. Since the Li^+ of the ate complex will be coordinated to four solvent molecules, it is not a very effective electrophile. If Li^+ loses a solvent molecule and becomes CIP-Ate, the electrophilic substitution then becomes facile. The SIP-Ate complex is thus a parasitic equilibrium on the optimum exchange mechanism which proceeds almost entirely through CIP intermediates (top row in *Scheme 3*).

It is interesting to note that the free energy of activation ($\Delta G^{\ddagger}_{-151} = 5.3$ kcal/mol) we reported for the interconversion of the CIP and SIP of the lithium reagent $(ArS)_2CHLi$ (Ar = 3,5-bis(trifluoromethyl)phenyl) [7k] is very close to those measured here for the **A**/**B** to **C** interconversion at −146° ($\Delta G^{\ddagger}_{AB} < 5.3$ kcal/mol, $\Delta G^{\ddagger}_{AC} \approx 6.2$ kcal/mol) suggesting that the principal barrier for the Li/Se exchange in the very favorable geometry of compounds **12-Se** and **21** might be association and dissociation of coordinated THF solvent.

Intermolecular Li/S, Li/Se, and Other Li/M Exchanges. Fig. 10 shows a comparison of the intramolecular Li/S and Li/Se exchange rates (either k_{ate} or k_d) reported in this paper with intermolecular analogs. The Li/I and Li/Te rates were determined from published spectra [7a][7b], the others were measured by means of the reaction of *p*-

Scheme 3. *Possible pathways for Li/Se exchange.* CIP = contact ion pair, SIP = separated ion pair.



TolLi with PhCl, PhBr, Ph_2S, and Ph_2Se in THF (*Eqn. 2*) [7c][6a]. The temperature dependence was measured only for the Li/Br exchange ($\Delta G^{\ddagger}_{-150} = 16.1$ kcal/mol, $\Delta H^{\ddagger} = 9.5$ kcal/mol, $\Delta S^{\ddagger} = -29.6$ eu). The rate for the very slow exchanges Li/S and Li/Cl could be an upper limit, since there was substantial decomposition of the *p*-TolLi even at very low conversions. The comparisons can only be semiquantitative because some of the rates are for exchanges of RLi with the ate complex that, as we have seen, can be slower processes than the Li/M exchange itself. In addition, different solvent mixtures were employed. The intramolecular exchanges had to be run in weaker solvents such as mixtures of THF, Me_2O, and Et_2O, which would lower the rates significantly compared to the intermolecular exchanges, which were run in pure THF.

$$\mathrm{Ph{-}S{-}Ph} + p\text{-TolLi} \overset{k_2}{\rightleftharpoons} \mathrm{Ph{-}S{-}}p\text{-Tol} + \mathrm{PhLi} \qquad (2)$$

It can be seen that there are very large periodic effects on the rates, with the PhCl/PhBr/PhI series *ca.* $1:10^8:10^{13}$ in k_1. Similarly, the $Ph_2S/Ph_2Se/Ph_2Te$ series is $1:10^4:10^{14}$ (the PhI and Ph_2Te rates are rather inexact extrapolations from DNMR work at temperatures below $-100°$). There has been substantial computational effort at determining energies and structures of ate complexes of the main-group elements [30], and the calculated energies are consistent with our experimental data.

One measure of the acceleration of an intramolecular process is the 'effective molarity', defined as the concentration of a bimolecular reactant needed to give the same rate as an intramolecular process. The extrapolated rate constant for the degenerate exchange of **12-S** at 0° is $1100\ s^{-1}$. The second-order rate constant for approach to equilibrium of Ph_2S and *p*-TolLi at 0° (*Eqn. 3*, see below) is $\leq 2 \cdot 10^{-7}$ $l\ M^{-1}\ s^{-1}$ ($\Delta G^{\ddagger} = 24.3$ kcal/mol). Thus the effective molarity is $> 5 \cdot 10^9$ for **12-S**. It is qualitatively similar for the *p*-TolLi/Ph_2Se-**21** comparison.

The origin of these enormous rate effects is not clear. Five-membered rings in tetracoordinate Si- and P-compounds, with natural bond angles close to tetrahedral, are strained, whereas in pentacoordinate hypervalent structures, the apical-equatorial (or basal) angles are close to 90° and small rings are less strained, resulting, for example, in enhanced rates of cyclic phosphate ester hydrolysis. However, this 'small-ring effect' is

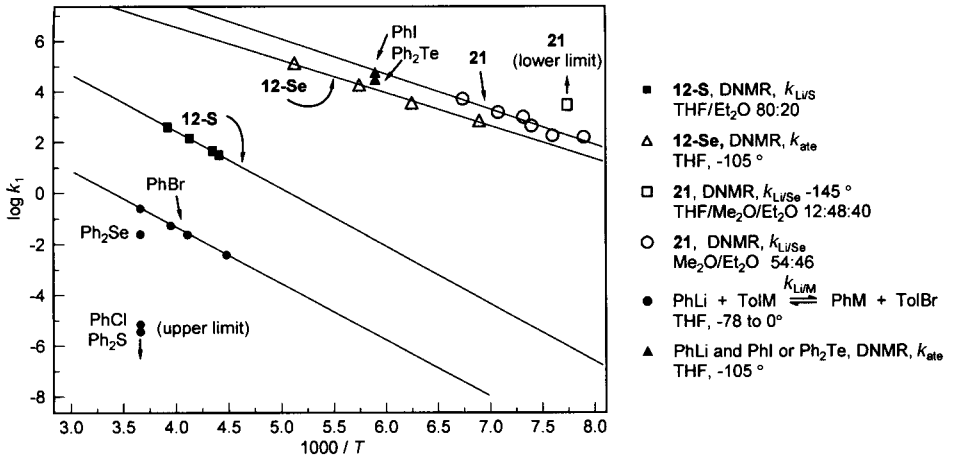


Fig. 10. *Summary of ArLi-halogen and ArLi-chalcogen exchange rates, measured by several different techniques.* The $\Delta G^{\ddagger}$ values are not strictly comparable since they were measured in different ethereal solvents, as indicated. Two of them (open and filled triangles) correspond to k_{ate} (exchange of ArLi with the ate complex), others to an authentic Li/M exchange (k_d). The points ○ were measured by means of the Ph_nM/TolLi exchange in THF (*Eqn. 2*). Second-order rates were converted to pseudo-first-order rates by dividing k_2 by the concentration of ArLi. The lines are least-squares fit.

likely to be only a small fraction of the rate acceleration seen here, since **10** showed only about one order of magnitude increase in K_{ate} (*Fig. 1*) compared to acyclic analogs. A rationale is that the natural bond angle in the heavy chalcogens is close to 90° (H_2S 92.1°, H_2Se 90.6° H_2Te 90.3°). The C-Y-C bond angles in selenides and tellurides are thus below the tetrahedral angle (*e.g.*, in Ph_2Se, the angle is 106°, in Ph_2Te it is 101° [31]), so there is less release of strain in cyclic hypervalent structures. The major portion of the increase in Li/S and Li/Se exchange rates in **12-S**, **12-Se**, and **21** must be a consequence of almost ideal preorganization for 3-center nucleophilic attack of the C–Li bond on the C–Y antibonding orbital [7c].

Conclusions. – The *m*-terphenyl framework in structures **12-S**, **12-Se**, and **21** provides an ideal geometry for the Li/M exchange, to the extent that the Li/S exchange, which is barely detectable at room temperature in acyclic systems, becomes fast on the NMR timescale, a rate acceleration in excess of 10^9. The Li/Se exchange is similarly accelerated, and the selenium ate complexes **20-Se** and **26** become spectroscopically detectable at low temperature in THF-containing mixed solvents. A DNMR experiment showed that a direct exchange not involving the ate complexes was *ca.* 50 times as fast as exchange of the lithium reagent with the ate complexes, an observation that could be rationalized in terms of the contact-ion-pair and separated-ion-pair intermediates. These effects are unlikely to have their principal origins in ring-strain effects, since the ate complex association of PhLi with the dibenzotellurophene **10** was only slightly increased as compared to Ph_2Te.

Experimental Part

General. All reactions involving lithium reagents were run in oven- or flame-dried flasks under dry N_2. Tetrahydrofuran (THF) and Et_2O were freshly distilled from benzophenone ketyl (=oxidodiphenylmethyl). Me_2O was obtained from *Aldrich* and dried with MeLi prior to use. Hexamethylphosphoric triamide (HMPA) was obtained from *Aldrich*, distilled from CaH_2 at reduced pressure (0.5 mm), and stored under N_2 over molecular sieves. Starting materials were commercially available or a literature citation for their preparation is given. FC = flash column chromatography. GC: *SE-30* capillary columns, flame-ionization detector; measurements corrected for response factors. Multinuclear NMR spectra: *Bruker AM-360* spectrometer operating at 90.56 MHz (^{13}C), 139.962 MHz (^{7}Li), and 68.68 MHz (^{77}Se); ^{13}C-NMR, *ca.* 800 transients and exponential multiplication of 2–5 Hz; δ(C) in ppm rel. to internal C_6H_6 (δ 129.18), THF (C(2), δ 67.96), Me_2O (δ 60.08), or Et_2O (C(2), δ 60.51), *J* in Hz; ^{77}Se-NMR, exponential multiplication of 2–20 Hz depending on broadening of signals, spectra referenced externally to Me_2Se in $CDCl_3$ at r.t.; temps. of the experiments measured with an external carbon-13 thermometer (CCl_4/D_6 acetone 1:1 [32]), a resistance temp. device (RTD), or the tris(trimethylsilyl)methane internal δ(C) thermometer [7l]; 20 min were allowed between acquisitions for the temp. to equilibrate; temps. were generally measured regularly during the experiment and after each measurement when accurate variable temp. studies were being performed.

Caution: HMPA is carcinogenic, and organotin and organoselenium compounds are toxic and should be handled in a hood with due care.

Note. The systematic numbering used for the compound names below is *not* the conceptually convenient *ad hoc* numbering used in *Figs. 2–4, 6* and *7.*

2,2′-Diiodo-4,4′-dimethyl-1,1′-biphenyl. Into a 2-l beaker was added 4,4′-dimethyl[1,1′-biphenyl]-2,2′-diamine [33] (38.7 g, 0.182 mol) dissolved in conc. HCl soln. (184 ml) and ice (184 g). The soln. was stirred and kept below 2° while $NaNO_2$ (27.6 g, 0.40 mol, 2.2 equiv.) in H_2O (90 ml) was added dropwise over 30 min. After 15 min, the diazonium-salt soln. was filtered through glass wool/ice into a 4-l beaker containing a cold soln. of KI (90.6 in 175 ml H_2O). During the addition, the KI soln. was kept below 5° and vigorously stirred. Stirring was continued for 2 h at r.t., excess sodium hydrogensulfite was added, and the mixture was left overnight. The mixture was filtered, and the brown precipitate was washed with H_2O and placed in a 1-l beaker containing MeOH (800 ml). After boiling for 10 min, the soln. was filtered leaving crude 2-iodonio-4,4′-dimethyl-1,1′-biphenyl iodide, which was recrystallized from DMF to yield 7.1 g (9%). M.p. 241–243°.

The MeOH filtrate was evaporated and the brown precipitate dissolved in Et_2O (500 ml) and extracted with 3 × 200 ml portions of 6N HCl. The org. layer was washed with 7% $NaHCO_3$ and NaCl soln. and dried (Na_2SO_4). Evaporation gave 14 g of crude 2,2′-diiodo-4,4′-dimethyl-1,1′-biphenyl, which was recrystallized from Et_2O to yield 10.5 g (13.3%). M.p. 108–113° [14f]. ^1H-NMR ($CDCl_3$, 200 MHz): 7.8 (*s*, 2 H); 7.25 (*d*, *J* = 8, 2 H); 7.1 (*d*, *J* = 8, 2 H); 2.3 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$, 50.1 MHz): 146; 139; 130; 128; 99; 20.6.

The acid washings were made basic with 20% NaOH soln., yielding 26 g of crude 3,8-dimethylbenzo[*c*]-cinnoline. Recrystallization from AcOEt gave 22.6 g (59.6%). M.p. 186–188°. ^1H-NMR ($CDCl_3$, 200 MHz): 8.95 (*s*, 2 H); 8.38 (*d*, *J* = 9, 2 H); 7.68 (*d*, *J* = 9, 2 H); 2.6 (*s*, 6 H).

3,7-Dimethyldibenzotellurophene (**10**). Into a dried round-bottom flask (500 ml, 3-necked) was placed 2,2′-diiodo-4,4′-dimethyl-1,1′-biphenyl [14f] (15,75 g, 36.3 mmol). The apparatus was purged with N_2 for 2 h, THF (100 ml) added, the soln. cooled to −78°, and 1.85M ^{t}BuLi (86.5 ml, 160 mmol, 4.4 equiv.) added dropwise. The soln. was warmed to 0° for 20 min, and 2,5-dihydro-3-methyltellurophene 1,1-dichloride (prepared from isoprene and $TeCl_4$ [34]) (40 mmol, 10.64 g, 1.1 equiv.) in THF (100 ml) was added. After 3 h, solvents were evaporated, and the solid was dissolved in H_2O (200 ml) and CH_2Cl_2 (200 ml). The org. layer was washed with sat. brine, filtered through Na_2SO_4, and evaporated to give 11 g of crude **10**. Recrystallization from hexane (decolorized with charcoal) yielded 9.4 g (84%) of **10**. M.p. 156–157° [14c]. ^1H-NMR ($CDCl_3$, 200 MHz): 7.9 (*d*, *J* = 8); 7.7 (*s*, 2 H); 7.24 (*d*, *J* = 8, 2 H); 2.33 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 141.6; 136.4; 132.7; 123.8; 127; 21.2.

Typical Preparation and Standardization of PhLi Solution for Kinetic Studies. An *Erlenmeyer* flask (50 ml, 24/40) was dried, fitted with septum, and purged with N_2. Stock 1.5M PhLi/THF (prepared from halide-free PhLi crystallized at least twice from Et_2O [7h]; 20 ml, 30 mmol) was added and diluted with THF (10 ml). To the soln. was added undecane (0.634 ml, 3.0 mmol) as a GC standard. A 1.0-ml aliquot of the soln. was syringed into each of three dry, purged 5-ml round-bottom flasks equipped with septa and stirring bars. Each was quenched with 100 µl (1.1 mmol) of MeSSMe; sat. NH_4Cl soln. (*ca.* 0.10 ml) was added (white precipitate), and the solns. were dried (Na_2SO_4). PhI was accurately weighed into each soln. (*ca.* 40 µl) as GC standard. Analysis of the solns. by GC gave the concentrations of PhLi and undecane to be 0.90M and 0.11M, resp.

Effect of **10** *on the Reaction of PhLi with 2-(Methylthio)thiophene.* Six round-bottom flasks (5 ml, long-necked) were dried, and **10** was weighed into each in the following amounts: 0 g, 0.0723 g (0.2349 mmol, 0.5 equiv.), 0.0279 g (0.09063 mmol, 1 equiv.), 0.1353 g (0.4395 mmol, 1.5 equiv.), 0.0825 g (0.268 mmol, 2.0 equiv.), and 0.2089 g (0.6786 mmol, 2.5 equiv.). The flasks were equipped with stirring bars and septa, and purged with N_2 for 25 min. THF was added to each in the following amounts: 1.25 ml, 1.95 ml, 0.4 ml, 1.22 ml, 0.56 ml, and 1.13 ml. The solns. were cooled to $-78°$, and 1 equiv. of PhLi (1.20M) was added in the following amounts: 0.25 ml (0.30 mmol), 0.40 ml (0.47 mmol), 0.076 ml (0.0906 mmol), 0.22 ml (0.293 mmol), 0.112 ml (0.134 mmol), and 0.244 ml (0.2714 mmol). After 10 min, 1 equiv. of 2-(methylthio)thiophene was added in the following amounts: 32 µl (0.30 mmol), 50 µl (0.47 mmol), 9.7 µl (0.0906 mmol), 31.3 µl (0.293 mmol), 14.3 µl (0.134 mmol), and 29 µl (0.2714 mmol). After 60 min, the reactions were quenched with MeSSMe (75 µl) and the mixtures allowed to warm to r.t. NH_4Cl (50 µl) was added, and the solns. were dried (Na_2SO_4). GC Analysis gave the results shown in the *Table.*

Table 1. *Reaction of PhLi with 2-(Methylthio)thiophene in the Presence of* **10**

PhLi [mmol/equiv.]	**10** [equiv.]	PhSMe [mmol]	Product [mmol][a])	% Reaction	% Recovery
0.30	0	0.087	0.189	63	92
0.47	0.5	0.2021	0.249	53	96
0.0906	1.0	0.0462	0.039	43	94
0.293	1.5	0.190	0.0703	24	89
0.134	2.0	0.105	0.0255	19	97
0.271	2.5	0.220	0.0352	13	94

[a]) Product = 2,5-bis(methylthio)thiophene.

Similar experiments were performed with Ph_2Te [35] and PhI. Results are summarized in *Fig. 1.*

NMR Spectroscopy of PhLi and **10** *in THF.* Into a dry 10-mm NMR tube was accurately weighed 0.098 g (0.317 mmol) of **10**, and the tube was fitted with a septum and purged with N_2. THF (3.5 ml) was added and the sample cooled to $-78°$, keeping positive N_2 pressure in the tube. Stock 1.2M PhLi soln. (0.516 ml, 0.64 mmol) was added, and the ^{13}C-NMR spectra were obtained at a series of temps. Spectra and δ(C) data are reported in *Fig. 2.* Similar experiments at several other PhLi/**10** ratios confirmed the assignments made.

(4-^{2}H)Dibenzothiophene. To a dry 50-ml flask fitted with a septum was added dibenzothiophene (0.5 g, 2.71 mmol). The flask was cooled to $-78°$ under N_2 and 1.06M *s*-BuLi (3.8 ml, 4.03 mmol) was added over a few minutes. The yellow-orange soln. was stirred at $-78°$ for 2 h, quenched with D_2O (100 µl), and allowed to warm to r.t. The mixture was partitioned between Et_2O/hexane and H_2O and the org. layer dried (Na_2SO_4) and evaporated: 0.483 g (95%) of a white solid. The product was used without further purification. A small amount was recrystallized from hexane for analysis. White needles. M.p. 97.0–98.5°. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.12 (*m*, 2 H); 7.82 (*m*, 1 H); 7.42 (*m*, 4 H). ^{13}C-NMR (75.403 MHz, $CDCl_3$): 139.35 (*s*); 139.23 (*s*, D-isotope shift); 135.6 (*s*); 126.61 (*d*); 126.49 (*d*, D-isotope shift); 124.3 (*d*); 122.7 (*d*); 122.5 (1:1:1 *t*, CD); 121.5 (*d*). HR-MS: 185.0398 (M^+, $C_{12}H_7DS^+$; calc. 185.0409).

Dibenzothiophene-4-boronic Acid (**13-S**). Dibenzothiophene (0.4 g, 2.17 mmol) was metallated as described above. Trimethyl borate (0.62 ml, 5.4 mmol) was added at $-78°$, the soln. warmed to r.t., and then cooled in an ice bath, and 1N HCl (10 ml) added. The mixture was diluted with Et_2O and extracted twice with 1N NaOH. The alkaline extract was washed with Et_2O and acidified with 3N HCl. The white precipitate was filtered and washed with H_2O and Et_2O to afford 0.403 g (81%) of **13-S**. White solid. The crude product, which did not melt or decompose under 300°, was used in the next step. ^{1}H-NMR (200 MHz, (D_6)acetone/(D_6)DMSO): 8.37 (*dd*, *J* = 7.8, 1.3, 1 H); 8.27 (*m*, 1 H); 8.03 (*dd*, *J* = 7.0, 1.3, 1 H); 7.93 (*m*, 1 H); 7.65 (br. *s*, 2 H); 7.50 (*m*, 3 H). ^{13}C-NMR (75.403 MHz, $CDCl_3$): 146.1 (*s*); 141.4 (*s*); 135.7 (*s*); 135.7 (*s*); 134.4 (*d*); 127.1 (*d*); 124.1 (*d*); 124.3 (*d*); 124.2 (*d*); 123.0 (*d*); 122.0 (*d*). HR-MS: 228.0419 (M^+, $C_{12}H_9BO_2S^+$; calc. 228.0416).

4-(2-Bromophenyl)dibenzothiophene (**14-S**). A mixture of benzene (15 ml), **13-S** (0.296 g, 1.3 mmol), 1-bromo-2-iodobenzene (0.44 g, 1.1 mmol), [$Pd(PPh_3)_4$] (0.50 g, 3 mol-%), 2M Na_2CO_3 (1.3 ml), and MeOH (5 ml) was heated to 50–60° under N_2 (TLC monitoring, 1% AcOEt/hexane). After 5 h, the product spot was predominant. The mixture was allowed to stir overnight at r.t. and worked up by partitioning between Et_2O/hexane and H_2O. The org. layer was extracted with H_2O, 10% NH_4OH soln., H_2O, and brine, dried (Na_2SO_4),

and evaporated. The product was passed through a plug of silica gel (2% AcOEt/hexane), excess 1-bromo-2-iodobenzene was removed by distillation, and the residue was submitted to FC. The eluate (0.25 g) was recrystallized from CH_2Cl_2/MeOH: 0.19 g (43%) of **14-S**. White crystals. M.p. 85–95° (small amount of Ph_3P contamination). The reaction was not easily reproducible, yields varied from 20–50%. ^{1}H-NMR (270 MHz, $CDCl_3$): 8.17 (*m*, 2 H); 7.77 (*m*, 1 H); 7.74 (*dd*, *J* = 7.4, 1.5, 1 H); 7.55 (*t*, *J* = 7.5, 1 H); 7.40 (*m*, 4 H); 7.35 (*dd*, *J* = 7.0, 1.4, 1 H); 7.30 (*ddd*, *J* = 8.2, 7.0, 2.1, 1 H).

The (6-^{2}H) compound **14-S-d** was prepared similarly, the ^{1}H-NMR signal at δ 7.77 was missing.

4-[2-(Methylthio)phenyl]dibenzothiophene (**19**). To an oven-dried and N_2-purged 10-ml conical flask, 4-(2-iodophenyl)dibenzothiophene (**17-S**; 20.4 mg, 0.0528 mmol) was added. The flask was repurged with N_2 for 10 min. Freshly distilled Et_2O (3 ml) was added, the soln. cooled to −78°, and 2.57M BuLi (0.08 ml, 0.2056 mmol) added. The reaction was quenched with Me_2S_2 (0.034 ml, 0.3774 mmol) and the mixture allowed to warm to r.t., diluted with hexanes/Et_2O 1:1, washed with H_2O (3×) and brine, and dried ($MgSO_4$). TLC purification gave 9.8 mg (61% of **19**). ^{1}H-NMR (499.89 MHz, $CDCl_3$): 8.20 (*dt*, 2 H); 7.77 (*m*, 1 H); 7.56 (*t*, *J* = 7.5, 1 H); 7.46 (*m*, 4 H); 7.40 (*m*, 1 H); 7.29 (*td*, *J* = 7, 1, 1 H); 2.35 (*s*, 3 H). ^{13}C-NMR (125.70 MHz, $CDCl_3$): 140.0 (*s*); 139.7 (*s*); 138.9 (*s*); 137.9 (*s*); 135.9 (*s*, 2C); 135.3 (*s*); 129.6; 128.9; 127.7; 126.7; 125.7; 124.9; 124.5; 124.3; 122.7; 121.7; 120.9; 16.0. HR-EI-MS: 306.0528 (M^+, $C_{19}H_{14}S_2^+$; calc. 306.0537).

The deuterated compound **19-d** was prepared similarly, the ^{1}H-NMR signal at δ 7.77 was missing. Experiments performed in THF with **19-d** showed a 0.5-H integration for the signal at δ 7.77. ^{2}H-NMR showed two peaks at δ 7.8 and 7.5 in a 1:1 ratio.

4-(2-Nitrophenyl)dibenzothiophene (**15-S**). A soln. of dibenzothiophene-4-boronic acid (2.334 g, 10.2 mmol), 1-chloro-2-nitrobenzene (1.50 g, 9.52 mmol), benzene (100 ml), MeOH (10 ml), and 2M Na_2CO_3 (10 ml, 2 equiv) was sparged with N_2 for 20 min before adding [$Pd(PPh_3)_4$] (0.37 g, 0.32 mmol). The mixture was stirred at 70° for 7 h, allowed to cool to r.t., and partitioned between Et_2O/hexane (200 ml) and H_2O. The org. layer was washed with H_2O, 10% NH_4OH soln., H_2O, and brine, dried (Na_2SO_4), and evaporated. Purification by a short silica-gel column (30% CH_2Cl_2/hexane), collecting the yellow band, gave 3.13 g (100%) of **15-S**. Yellow solid which was used in the next step. A small amount was recrystallized from CH_2Cl_2/MeOH for analysis. M.p. 137–139°. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.15 (*m*, 2 H); 8.07 (*m*, 1 H); 7.60 (*m*, 7 H); 7.30 (*dd*, *J* = 7.0, 1.3, 1 H). ^{13}C-NMR (90.56 MHz, $CDCl_3$): 148.7 (*s*); 139.2 (*s*); 139.0 (*s*); 136.0 (*s*); 135.6 (*s*); 134.8 (*s*); 133.0 (*d*); 132.6 (*s*); 131.9 (*d*); 129.2 (*d*); 126.9 (*d*); 126.2 (*d*); 124.9 (*d*); 124.7 (*d*); 124.6 (*d*); 122.7 (*d*); 121.9 (*d*); 121.3 (*d*). HR-EI-MS: 305.0495 (M^+, $C_{18}H_{11}NO_2S^+$; calc. 305.0510).

2-(Dibenzothiophen-4-yl)benzenamine (**16-S**). A mixture of 4-(2-nitrophenyl)dibenzothiophene (2.83 g, 9.26 mmol), AcOH (26 ml), EtOH (60 ml) and Fe-powder (2.13 g, 38 mmol) was refluxed for 5 h (TLC monitoring, 10% AcOEt/hexane), cooled to r.t., and added to H_2O (100 ml). Solid Na_2CO_3 was added carefully to the mixture until CO_2 bubbling had stopped. The greenish slurry was diluted with H_2O and extracted with Et_2O (3×). The org. layer was washed with H_2O, dried (Na_2SO_4) and concentrated to 50–100 ml. The Et_2O soln. was cooled in an ice bath, and conc. HCl soln. was added dropwise until no more of the solid amine hydrochloride formed. The solid was filtered, washed with cold H_2O and cold Et_2O and allowed to air dry to give 2.263 g (78%) of the HCl salt as a slightly off-white solid, which was used without further purification. A small amount of amine **16-S** was liberated from the HCl salt for analysis. **16-S**: ^{1}H-NMR (200 MHz, $CDCl_3$): 8.16 (*m*, 2 H); 7.78 (*m*, 1 H); 7.55 (*t*, *J* = 7.5, 1 H); 7.46 (*m*, 3 H); 7.25 (*m*, 2 H); 6.86 (*m*, 2 H); 3.46 (br. *s*, 2 H). ^{13}C-NMR (90.56 MHz, $CDCl_3$): 143.5 (*s*); 139.9 (*s*); 139.5 (*s*); 135.9 (*s*); 135.6 (*s*); 133.9 (*s*); 129.9 (*d*); 129.2 (*d*); 127.5 (*d*); 126.6 (*d*); 125.4 (*s*); 124.9 (*d*); 124.2 (*d*); 122.6 (*d*); 121.6 (*d*); 120.5 (*d*); 118.3 (*d*); 115.7 (*d*). HR-EI-MS: 275.0765 (M^+, $C_{18}H_{13}NS^+$; calc. 275.0768).

4-(2-Iodophenyl)dibenzothiophene (**17-S**). A mixture of **16-S**·HCl (1.955 g, 6.27 mmol), conc. HCl soln. (2.5 ml), ice (100 g), and H_2O (10 ml) was cooled in an ice bath, and an aq. $NaNO_2$ soln. (0.455 g, 6.60 mmol) was carefully added with stirring. After 2 h, an aq. KI soln. (5.2 g, 31 mmol) was added to the bright yellow soln. with vigorous stirring (brownish color). After stirring for 2 h at 0° and 2 h at r.t., the mixture was extracted with Et_2O/hexane (3×) and the org. layer washed with H_2O and dried (Na_2SO_4). The dark viscous liquid was passed through a short silica-gel plug (5% AcOEt/hexane) to remove most of the dark impurities, and the eluate was purified by FC (15% CH_2Cl_2/hexane). Recrystallization from CH_2Cl_2/MeOH gave 1.573 g (65%) of **17-S**. White crystals. M.p. 89.0–91.0°. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.20 (*m*, 2 H); 8.03 (*m*, 1 H); 7.79 (*m*, 1 H); 7.55 (*t*, *J* = 7.5, 1 H); 7.45 (*m*, 4 H); 7.33 (*dd*, *J* = 7.5, 1.2, 1 H); 7.15 (*ddd*, *J* = 8.0, 6.0, 3.0, 1 H). ^{13}C-NMR (90.56 MHz, $CDCl_3$): 145.0 (*s*); 139.7 (*s*); 139.5 (*s*); 139.5 (*d*); 139.2 (*s*); 135.7 (*s*); 135.7 (*s*); 129.9 (*d*); 129.7 (*d*); 128.3 (*d*); 127.4 (*d*); 126.8 (*d*); 124.5 (*d*); 124.4 (*d*); 122.7 (*d*); 121.8 (*d*); 120.9 (*d*); 98.9 (*s*). HR-EI-MS: 385.9611 (M^+, $C_{18}H_{11}IS^+$; calc. 385.9622).

4-[2-(Trimethylstannyl)phenyl]dibenzothiophene (**18-S**). To dry Et_2O (20 ml) at $-78°$ under N_2 was added 2.07M BuLi (0.80 ml, 1.66 mmol) and, by cannula, an Et_2O/THF (3.0 ml/0.5 ml) soln. of **17-S** (0.496 g, 1.28 mmol). After 5 min, an Et_2O (3.0 ml) soln. of Me_3SnBr (300 µl, 1.5 equiv.) was added and the soln. stirred for 5 min, allowed to warm to r.t., and quenched with H_2O. The mixture was partitioned between Et_2O/hexane and H_2O and the org. layer washed 3 × with H_2O, dried (Na_2SO_4), and evaporated. The product was passed through a silica-gel plug (5% AcOEt/hexane), and then purified by prep. HPLC (reversed phase MeCN, flow rate 10 ml/min; t_R (protonated compound) 13 s, t_R (product) 18.5 s): 0.40 g (74%) of **18-S**, which crystallized upon standing. M.p. 75.0–76.0°. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.19 (*m*, 1 H); 8.15 (*dd*, *J* = 7.5, 1.0, 1 H); 7.79 (*m*, 1 H); 7.66 (*m*, 1 H); 7.53 (*t*, *J* = 7.5, 1 H); 7.53 (*m*, 1 H); 7.44 (*m*, 4 H); 7.30 (*dd*, *J* = 7.2, 1.1, 1 H); −0.14 (*s*, *J*(Sn,H) = 54.9, 52.6, 9 H). ^{13}C-NMR (90.56 MHz, THF): 148.9 (*s*, *J*(Sn,C) = 29.3); 143.2 (*s*); 140.8 (*s*); 140.6 (*s*, *J*(Sn,C) = 19.0); 140.5 (*s*); 137.3 (*d*, *J*(Sn,C) = 35); 136.6 (*s*); 136.5 (*s*); 129.0 (*d*); 128.9 (*d*, *J*(Sn,C) = 9.5); 127.9 (*d*, *J*(Sn,C) = 45); 127.9 (*d*); 127.4 (*d*); 125.3 (*d*); 125.0 (*d*); 123.2 (*d*); 122.5 (*d*); 121.2 (*d*); −8.6 (*q*, ^{1}*J*(Sn,C) = 352.8, 337.5, 3C). HR-EI-MS: 409.0078 ($[M - CH_3]^+$, $C_{20}H_{17}SSn^+$; calc. 409.0073).

Dibenzoselenophene-4-boronic Acid (**13-Se**). A soln. of dibenzoselenophene [18b] (2.00 g, 8.65 mmol) in THF (50 ml) under N_2 was cooled to −78°, and 1.5M ^{t}BuLi (11 ml, 16.5 mmol) was added. After 5 h at −78°, trimethyl borate (4 ml, 35 mmol) was added. The soln., which turned colorless immediately upon the addition, was allowed to warm to r.t., and worked up as described for **13-S**: 1.93 g (81%) of **13-Se**. White solid. The crude product, which did not melt or decompose below 300°, was used without further purification: ^{1}H-NMR (200 MHz, (D_6)acetone/(D_6)DMSO): 8.34 (*dd*, *J* = 7.9, 1.3, 1 H); 8.26 (*m*, 1 H); 8.19 (br. *s*, 2 H); 8.01(*m*, 2 H); 7.50 (*t*, *J* = 7.6, 1 H); 7.41 (*m*, 2 H). ^{13}C-NMR (75.403 MHz, $CDCl_3$): 146.8 (*s*); 141.5 (*s*); 138.5 (*s*); 138.4 (*s*); 134.2 (*d*); 127.1 (*d*); 126.2 (*d*); 125.4 (*d*); 125.0 (*d*); 124.8 (*d*); 123.1 (*d*); 109.6 (*s*).

4-(2-Nitrophenyl)dibenzoselenophene (**15-Se**). As described for **15-S**, with **13-Se** (2.12 g, 7.73 mmol), 1-chloro-2-nitrobenzene (1.16 g, 7.34 mmol), [$Pd(PPh_3)_4$] (0.31 g, 3.5 mol-%), MeOH (10 ml), 2M Na_2CO_3 (8 ml, 2 equiv), and benzene (100 ml). The product was purified by passing it through a short silica-gel plug: 2.76 g (100%) of **15-Se**. Yellow solid that was pure enough for use in the next step. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.15 (*m*, 2 H); 8.07 (*m*, 1 H); 7.78 (*m*, 1 H); 7.51 (*m*, 6 H); 7.25 (*dd*, *J* = 7.4, 1.1, 1 H).

2-(Dibenzoselenophene-4-yl)benzenamine (**16-Se**). As described for **16-S**, with **15-Se** (2.76 g, 7.83 mmol), AcOH (22 ml), Fe-powder (1.8 g, 32 mmol) and EtOH (50 ml): 2.17 g (82%) of **16-Se** · HCC. A small amount of **16-Se** was liberated from the HCl salt for analysis. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.12 (*m*, 2 H); 7.80 (*m*, 1 H); 7.57 (*t*, *J* = 7.4, 1 H); 7.36 (*m*, 5 H); 6.86 (*m*, 2 H); 3.65 (br. *s*, 2 H). ^{13}C-NMR (90.56 MHz, $CDCl_3$): 143.3 (*s*); 141.3 (*s*); 139.6 (*s*); 138.9 (*s*); 138.7 (*s*); 136.8 (*s*); 129.6 (*d*); 129.4 (*d*); 127.5 (*d*); 127.1 (*s*); 126.9 (*d*); 125.9 (*d*); 125.7 (*d*); 124.8 (*d*); 123.0 (*d*); 121.8 (*d*); 118.6 (*d*); 115.9 (*d*).

4-(2-Iodophenyl)dibenzoselenophene (**17-Se**). As described for **17-S**, with **16-Se** (2.17 g, 6.1 mmol), $NaNO_2$ (0.42 g, 6.1 mmol), and KI (5.03 g, 5 equiv.). After FC and recrystallization from CH_2Cl_2/MeOH, **17-Se** (1.61 g, 62%) was obtained. White crystals. M.p. 118–119°. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.14 (*m*, 2 H); 8.00 (*m*, 1 H); 7.81 (*m*, 1 H); 7.55 (*t*, *J* = 7.6, 1 H); 7.42 (*m*, 4 H); 7.30 (*dd*, *J* = 7.4, 1.1, 1 H); 7.11 (*m*, 1 H). ^{13}C-NMR (90.56 MHz, $CDCl_3$): 146.2 (*s*); 141,9 (*s*); 140.6 (*s*); 139.7 (*s*); 139.5 (*d*); 138.5 (*s*); 138.3 (*s*); 129.6 (*d*); 129.4 (*d*); 128.4 (*d*); 127.3 (*d*); 126.8 (*d*); 125.9 (*d*); 125.1 (*d*); 124.8 (*d*); 123.1 (*d*); 121.9 (*d*); 98.6 (*s*). HR-EI-MS: 433.9088 (M^+, $C_{18}H_{11}ISe^+$; calc. 433.9069).

4-[2-(Trimethylstannyl)phenyl]dibenzoselenophene (**18-Se**). As described for **18-S**, with **17-Se** (0.37 g, 0.85 mmol), 2.07M BuLi (0.47 ml, 1.15 equiv.), and Me_3SnBr (180 µl, 1.8 equiv.). Purification with prep. HPLC gave 0.57 g (86%) of **18-Se**. Colorless thick liquid, which crystallized upon standing. M.p. 92.0–93.0°. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.16 (*m*, 1 H); 8.11(*dd*, *J* = 7.9, 1.1, 1 H); 7.83 (*m*, 1 H); 7.65 (*m*, 1 H); 7.53 (*t*, *J* = 7.6, 1 H); 7.53 (*m*, 1 H); 7.42 (*m*, 4 H); 7.25 (*dd*, *J* = 7.3, 1.1, 1 H); −0.11 (*s*, *J*(Sn,H) = 54.9, 52.6, 9 H). ^{13}C-NMR (90.56 MHz, THF): 150.4 (*s*, *J*(Sn,C) = 29.9); 143.3 (*s*, *J*(Sn,C) = 19.2); 142.9 (*s*, ^{1}*J*(Sn,C) = 469.7, 448.5); 142.1 (*s*, *J*(Se,C) = 98.2); 140.6 (*s*, *J*(Se,C) = 100.2); 139.4 (*s*); 139.1 (*s*); 137.3 (*d*, *J*(Sn,C) = 35.8); 129.0 (*d*, *J*(Sn,C) = 9.9); 128.5 (*d*, *J*(Sn,C) = 35.2); 127.9 (*d*); 127.7 (*d*); 127.4 (*d*, *J*(Se,C) = 7.3); 126.5 (*d*, *J*(Se,C) = 16.6); 125.8 (*d*); 125.4 (*d*); 123.8 (*d*); 122.3 (*d*); −8.3 (*q*, ^{1}*J*(Sn,C) = 352.3, 336.8, 3C). EI-MS: isotopic pattern matched, no exact mass found.

N-[*4-Isopropyl-2-(dibenzoselenophene-4-yl)phenyl]acetamide* (**22**). As described for **15-S**, with dibenzoselenophene-4-boronic acid (**13-Se**; 1.48 g, 5.4 mmol), *N*-(2-bromo-4-isopropylphenyl)acetamide [36] (1.26 g, 4.9 mmol), [$Pd(PPh_3)_4$] (0.17 g, 3 mol-%), MeOH (10 ml), benzene (80 ml), and 2M Na_2CO_3 (2 equiv.). TLC monitoring (Et_2O/hexane 60:40) indicated formation of dibenzoselenophene as a by-product. Therefore, more **13-Se** (0.2 g, 0.7 mmol) and [$Pd(PPh_3)_4$] (0.1 g, 2 mol-%) were added. After a total reaction time of 4.5 h at 60–70°, the crude product was prepurified by filtration through a short silica-gel plug followed by FC (3% Et_2O/CH_2Cl_2): 1.35 g (68%) of **22**. Colorless solid. M.p. 82–85°; ^{1}H-NMR (300 MHz, $CDCl_3$): 8.20 (*m*, 3 H); 7.85 (*m*,

1 H); 7.65–7.30 (*m*, 6 H); 6.96 (br. *s*, 1 H); 2.94 (*sept.*, $J = 6.9$, 1 H); 1.89 (s, 3 H); 1.27 (*d*, $J = 6.9$, 6 H). ^{13}C-NMR (75.403 MHz, $CDCl_3$): 168.3 (*s*); 145.2 (*s*); 141.4 (*s*); 139.7 (*s*); 139.1 (*s*); 138.5 (*s*); 135.9 (*s*); 132.4 (*s*); 131.7 (*s*); 127.5 (*d*); 127.4 (*d*); 127.2 (*d*); 127.2 (*d*); 126.0 (*d*); 125.7 (*d*); 125.0 (*d*); 123.2 (*d*); 122.3 (*d*); 122.2 (*d*); 24.5 (*d*); 24.0 (*q*); 23.9 (*q*). HR-EI-MS: 407.0779 (M^+, $C_{23}H_{21}NOSe^+$; calc. 407.0791).

4-Isopropyl-2-(dibenzoselenophene-4-yl)benzenamine (**23**). A mixture of **22** (1.30 g, 3.2 mmol), conc. HCl soln. (20 ml), and H_2O (10 ml) was refluxed for 20 h. The mixture was cooled in ice and made basic with aq. KOH soln. The mixture was extracted with CH_2Cl_2 , the org. layer washed with H_2O, dried (Na_2SO_4), and evaporated: 1.10 g (95%) of **23**. Yellow oil that was used without further purification. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.15 (*m*, 2 H); 7.85 (*m*, 1 H); 7.60–7.10 (*m*, 6 H); 6.80 (*d*, $J = 7.9$, 1 H); 2.87 (*sept.*, $J = 6.9$, 1 H); 1.25 (*d*, $J = 6.9$, 6 H). ^{13}C-NMR (75.403 MHz, $CDCl_3$): 141.5 (*s*); 141.1 (*s*); 139.8 (*s*); 139.3 (*s*); 139.0 (*s*); 138.8 (*s*); 137.2 (*s*); 127.4 (*d*); 127.4 (*d*); 127.4 (*d*); 127.2 (*s*); 126.9 (*d*); 125.9 (*d*); 125.6 (*d*); 124.8 (*d*); 123.0 (*d*); 121.7 (*d*); 116.1 (*d*); 33.3 (*d*); 24.2 (*q*). HR-EI-MS 365.0704 (M^+, $C_{21}H_{19}NSe^+$; calc. 365.0685).

Isomer Mixture of 4-(2-Iodophenyl)-8-isopropyldibenzoselenophene and 4-(2-Iodo-5-isopropylphenyl)dibenzoselenophene (**24a**/**24b**). As described for **17-S**, with **23** (1.10 g, 3.01 mmol), $NaNO_2$ (0.22 g, 3.2 mmol), conc. HCl soln. (1.5 ml), and KI (2.5 g, 5 equiv.). The crude product was purified by FC: 0.82 g (57%) of **24a**/**24b**. Colorless material. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.20–7.00 (*m*, 20 H); 3.12 (*sept.*, $J = 7.0$, 1 H); 2.96 (*sept.*, $J = 7.0$, 1 H); 1.40 (*d*, $J = 7.0$, 6 H); 1.31 (*d*, $J = 7.0$, 3 H); 1.30 (*d*, $J = 7.0$, 3 H). ^{13}C-NMR (75.403 MHz, $CDCl_3$): 149.5 (*s*); 146.5 (*s*); 146.1 (*s*); 145.9 (*s*); 142.1 (*s*); 142.1 (*s*); 141.0 (*s*); 140.9 (*s*); 139.8 (*s*); 139.6 (*d*); 139.5 (*d*); 138.7 (*s*); 138.5 (*s*); 138.4 (*s*); 136.9 (*s*); 129.7 (*d*); 129.5 (*d*); 128.4 (*d*); 128.2 (*d*); 127.8 (*d*); 127.5 (*d*); 127.2 (*d*); 126.9 (*d*); 126.0 (*d*); 125.9 (*d*); 125.7 (*d*); 125.1 (*d*); 125.0 (*d*); 124.8 (*d*); 123.1 (*d*); 121.9 (*d*); 121.9 (*d*); 120.8 (*d*); 98.7 (*s*); 94.7 (*s*); 34.2 (*d*); 33.7 (*d*); 24.3 (*q*); 23.9 (*q*); 23.7 (*q*). HR-EI-MS: 475.9553 (M^+, $C_{21}H_{17}ISe^+$; calc. 475.9538).

Isomer Mixture of 8-Isopropyl-4-[2-(trimethylstannyl)phenyl]dibenzoselenophene and 4-[5-Isopropyl-2-(trimethylstannyl)phenyl]dibenzoselenophene (**25a**/**25b**). As described for **18-S**, with **25a**/**25b** (0.80 g, 1.68 mmol), BuLi (0.81 ml, 2.5 mmol), and Me_3SnBr (400 µl, 3.4 mmol). The product was purified by FC (hexane): 0.70 g (82%) of **24a**/**24b**. Colorless material. Spectral data for the major isomer after FC purification of a Me_3SnBr-quenched NMR sample: ^{1}H-NMR (75.403 MHz, $CDCl_3$): 8.25–7.30 (*m*, 10 H); 3.13 (*sept.*, $J = 7.0$, 1 H); 1.41 (*d*, $J = 7.0$, 6 H); –0.05 (*s*, J(H,Sn) = 55.1, 52.6, 9 H). ^{13}C-NMR (75.403 MHz, $CDCl_3$): 149.7 (*s*); 145.7 (*s*); 142.6 (*s*); 142.5 (*s*); 141.8 (*s*); 138.8 (*s*); 138.3 (*s*); 137.1 (*s*); 136.8 (*d*); 128.4 (*d*); 128.0 (*d*); 127.4 (*d*); 127.0 (*d*); 125.9 (*d*); 125.7 (*d*); 125.1 (*d*); 121.5 (*d*); 120.8 (*d*); 34.2 (*d*); 24.3 (*q*); –8.2 (*q*, J(C,Sn) = 352.9, 336.9).

Preparation of NMR Samples for the Intramolecular Li/S and Li/Se Exchange Studies. The same procedure was used for both sulfur and selenium lithium compounds and will be referred to as the *General Procedure* for such sample preparations. Samples in THF/Et_2O 80:20 were prepared as follows: all equipment, a 10-ml NMR tube, two 5-ml round-bottom flasks, two 5-ml conical flasks, syringes, needles, and cannulas were oven-dried and either allowed to cool in a desiccator (syringes, needles, cannulas) or purged with N_2. The flasks and NMR tube were fitted with septa, and N_2 pressure was kept on the whole system throughout the sample preparation. For making 0.10M solns., 0.40 mmol of the starting material (trimethylstannane compounds) was dissolved in 0.5 ml of dry Et_2O in one of the 5-ml conical flasks. The cannula was flushed with *ca.* 1 ml of MeLi (in Et_2O) between the two 5-ml round-bottom flasks. MeLi (0.5 equiv.) was added into the NMR tube, which was shaken and cooled in a dry-ice bath (–78°). The Et_2O soln. containing the stannane was transferred *via* cannula into the NMR tube which was shaken and kept at –78°. No color change should be seen at this point. Into the remaining 5-ml conical flask was added dry THF (3.2 ml) and MeLi (0.6 equiv.). The THF/MeLi soln. was slowly transferred *via* cannula into the NMR tube. The color of the soln. turned yellow immediately as THF was added and then darker in the case of selenium compounds (ate-complex formation). Solns. of 3% THF/Et_2O were made in the same way.

Solns. with Me_2O as the main solvent were made similarly, with the following changes. Slightly more than the desired amount of Me_2O was condensed into a graduated vial cooled to –78° and fitted with a septum. MeLi (*ca.* 0.5 ml) was added to the vial, and the dried Me_2O was condensed *via* cannula into the NMR tube containing the starting material/MeLi soln. (see above). The remaining solvent (THF and/or Et_2O) to be used in an experiment was dried with enough MeLi to give a total of at least 1 equiv. used in the reaction (generally 10–20% excess MeLi was used). The dried solvent was added *via* cannula into the NMR tube cooled to –78°.

The above methods gave solns. that were almost free of any protonated product. Significant protonation occurred if MeLi was not added to the THF before adding the THF to the Et_2O soln. containing the stannane. The Li/Sn exchange in Et_2O is very slow and MeLi completely dries the Et_2O before it starts to react with the stannane. The lithium reagents were quenched with Me_3SnBr and combined with quenched fractions from other experiments to be purified later. A typical recovery of stannanes was 80%.

*Variable-Temperature ^{7}Li- and ^{13}C-NMR Spectroscopy of 4-(2-Lithiophenyl)dibenzothiophene (***12-S***) in THF/Et$_2$O 80:20.* A sample of **12-S** in THF/Et$_2$O 80:20 was prepared according to the *General Procedure* with **18-S** (0.22 g, 0.51 mmol), THF (3.2 ml), Et$_2$O (0.4 ml), and 1.43M MeLi (0.45 ml). The sample turned yellow upon the addition of MeLi to the trimethylstannane and stayed that way during the experiment. ^{13}C- and ^{7}Li-NMR spectra were taken at temps. between r.t. and $-78°$. The sample was stable at $-78°$ for a week, after which time very little protonation had taken place. Addition of HMPA to the sample resulted in decomposition. NMR data before addition of HMPA: ^{1}H-NMR (360.14 MHz, $-78°$): 8.19 (*m*, 1 H); 8.02 (*d*, *J* = 7.8, 1 H); 7.94 (*d*, *J* = 7.2, 1 H); 7.76 (*m*, 1 H); 7.47 (*d*, *J* = 7.8, 1 H); 7.40 (*t*, *J* = 7.8, 1 H); 7.33 (*m*, 2 H); 7.16 (*d*, *J* = 7.2, 1 H); 6.77 (*m*, 2 H). ^{13}C-NMR (90.56 MHz, $-78°$): spectra and data in *Fig. 3*. ^{7}Li-NMR (139.96 MHz, $-115°$): 0.66 (*s*).

In THF/Et$_2$O 3:97: ^{13}C-NMR (90.56 MHz, 170 K): 196.3 (br. *s*); 151.6 (*s*); 147.3 (*s*); 143.0 (*s*); 142.3 (*d*); 139.5 (*s*); 136.5 (*s*); 135.9 (*s*); 126.5 (*d*); 125.6 (*d*); 125.0 (*d*); 124.8 (*d*); 123.9 (*d*); 123.5 (*d*); 122.4 (*d*); 122.4 (*d*); 121.9 (*d*); 117.9 (*d*). A spectrum is shown in *Fig. 4*.

*Variable Temperature ^{7}Li-, ^{77}Se-, and ^{13}C-NMR Spectroscopy of 4-(2-Lithiophenyl)dibenzoselenophene (***12-Se***) **20-Se** in THF/Et2O 80:20.* The *General Procedure* was followed, with **18-Se** (0.16 g, 0.33 mmol), THF (3.2 ml), Et$_2$O (0.6 ml), and 1.56M MeLi (0.25 ml, 1.2 equiv.). ^{77}Se-, ^{13}C-, and ^{7}Li-NMR spectra were taken at temps. between $+6°$ and $-135°$. After the variable temp. study (spectra in *Figs. 6* and *7*), the sample was treated with 5.0 equiv. of HMPA, and ^{13}C- and ^{7}Li-NMR spectra were taken. The sample was quenched with Me$_3$SnBr to give 0.13 g (80%) of **18-Se** with less than 10% protonated product present: ^{1}H-NMR (200 MHz, CDCl$_3$): 8.2–7.3 (*m*, 11 H); -0.1 (*s*, *J*(H,Sn) = 54, 52, 9 H).

The following is selected NMR data for the lithium reagent and the ate complex: **12-Se**. ^{13}C-NMR (90.56 MHz, $+6°$): 170.6 (*s*, 2 C); 145.1 (*s*, 2 C); 142.9 (*s*, 2 C); 140.1(*s*); 133.5 (*d*, 2 C); 125.3 (*d*); 124.8 (*d*, 2 C); 123.5 (*d*, 2 C); 123.2 (*d*, 2 C); 121.0 (*d*, 2 C). ^{77}Se-NMR (68.68 MHz, $+6°$): 444.8 (*s*). ^{13}C-NMR (90.56 MHz, $-78°$): 176.7 (*s*, 2 C); 142.3 (*s*, 2 C); 140.6 (*s*, 2 C); 140.2 (*s*); 131.5 (*d*, 2 C); 124.4 (*d*); 124.4 (*d*, 2 C); 123.0 (*d*, 2 C); 122.0 (*d*, 2 C); 119.6 (*d*, 2 C). ^{77}Se-NMR (68.68 MHz, $-78°$): 432.6 (br. *s*). ^{7}Li-NMR (139.96 MHz): at $-113°$, -0.87 (br. *s*). at $-125°$, -1.0 (br. *s*).

Solution of **12-Se** *in 3% THF.* ^{13}C-NMR (90.56 MHz, $-78°$): 169.4 (br. *s*, 2 C); 145.1 (*s*, 2 C); 142.9 (*s*, 2 C); 140.1 (*s*); 133.5 (*d*, 2 C); 125.6 (*d*); 125,0 (*d*, 2 C); 123.7 (*d*, 2 C); 123.5 (*d*, 2 C); 121.1 (*d*, 2 C). ^{7}Li-NMR (139.96 MHz): at $-78°$, 0.4 (br. *s*); at 160 K, 0.2 (br. *s*). ^{77}Se-NMR (68.68 MHz, $-78°$): 447.0 (*s*). A spectrum is shown in *Fig. 4*.

Solution of **20** *in THF/Et$_2$O 20:80 with 5 equiv. of HMPA*. ^{13}C-NMR (90.56 MHz, $-78°$): data in *Fig. 6*. ^{1}H-NMR (360.14 MHz, $-78°$): 7.88 (*d*, *J* = 7.4, 2 H); 7.84 (*d*, *J* = 7.4, 2 H); 7.75 (*d*, *J* = 6.4, 2 H); 7.25 (*t*, *J* = 7.3, 1 H); 6.96 (*t*, *J* = 7.0, 2 H); 6.84 (*t*, *J* = 6.9, 2 H). ^{77}Se-NMR (68.68 MHz, $-78°$): 414.0 (*s*); at $-128°$. 411.0 (*s*). ^{7}Li-NMR (139.96 MHz, $-115°$): -0.5 (*quint.*). See *Fig. 6,b*.

In THF/Me$_2$O/Et$_2$O 8:67:25. A sample of **12-Se** was made following the *General Procedure* (Me$_2$O instead of THF), with **18-Se** (0.18 g, 0.38 mmol), Me$_2$O (3.0 ml), Et$_2$O (0.8 ml), THF (0.3 ml), and MeLi (0.25 ml, 0.38 mmol). ^{13}C-, ^{77}Se-, and ^{7}Li-NMR spectra were taken between $-141°$ and $-79°$.

*Variable-Temperature NMR Spectroscopy of an Isomer Mixture of 8-Isopropyl-4-(2-lithiophenyl)dibenzoselenophene and 4-(5-Isopropyl-2-lithiophenyl)dibenzoselenophene (***21a**/**21b***) in Me$_2$O/Et$_2$O 54:46 and in Me$_2$O/Et$_2$O/THF 48:40:12.* A sample of **21-Se** in Me$_2$O/Et$_2$O 54:46 was prepared according to the *General Procedure* (with Me$_2$O instead of THF), with an isomer mixture of **25a**/**25b** (0.27 g, 0.52 mmol), Me$_2$O (1.5 ml), Et$_2$O (0.9 ml), and MeLi (0.4 ml, 0.52 mmol). ^{77}Se-NMR spectra were taken at temps. between $-146°$ and $-41°$ (see *Fig. 8,a*). Dry THF (400 µl) was added to a 5-ml conical flask fitted with a septum. To the THF was added a few drops of MeLi, and the dried THF was transferred *via* cannula into the NMR tube cooled at $-78°$. ^{77}Se-NMR spectra were taken at temps. between $-157°$ and $-49°$ (see *Fig. 8,b*). The sample was quenched with Me$_3$SnBr (200 µl). After aq. workup, 0.22 g (82%) of the isomeric stannanes (*ca.* 3:2) were obtained with less than 5% contamination of the protonated species: ^{1}H-NMR (300 MHz, CDCl$_3$): 8.25–7.25 (*m*, 20 H); 3.11 (*sept.*, *J* = 7.0, 1 H); 2.98 (*sept.*, *J* = 7, 1 H); 1.39 (*d*, *J* = 7.0, 6 H); 1.33 (*d*, *J* = 7.0, 6 H); -0.08 (*s*, *J*(H,Sn) = 55.0, 52.7, 9 H); -0.09 (*s*, *J*(H,Sn) = 55.0, 52.5, 9 H).

In THF/Et$_2$O/Me$_2$O (36:36:28. A sample of **21a**/**21b** in THF/Et$_2$O/Me$_2$O 36:36:28 was prepared according to the *General Procedure* except of a 5-mm NMR tube, with a *ca.* 1:6 isomer mixture **25a**/**25b** (0.031 g, 0.0605 mmol), THF (0.25 ml), Et$_2$O (0.25 ml), Me$_2$O (0.20 ml), and BuLi (0.07 ml, 0.069 mmol). ^{13}C-, ^{77}Se-, and ^{7}Li-NMR spectra were taken at temps. between $-60°$ and $-143°$. HMPA (0.075 ml, 0.431 mmol, 7 equiv.) was added at $-78°$. ^{13}C-, ^{77}Se-, and ^{7}Li-NMR spectra were taken at $-138°$. The sample was quenched with Me$_3$SnBr to give a 2:1 isomer mixture **25a**/**25b**.

Preparation of p-*Tolyllithium*. A flask containing 15 ml of THF was cooled to $-78°$ under N$_2$, 2.0M *tert*-butyllithium (5.4 ml, 10.8 mmol) was added followed by dropwise addition of a soln. of *p*-bromotoluene

(0.924 g, 5.4 mmol) in THF (3.5 ml). The flask was warmed to 0° for 10 min and stored in the freezer at −20°. Titrations of the sample diluted in propan-1-ol with 1,10-phenanthroline as an indicator [37] showed the soln. to be 0.194M in *p*-tolyllithium. This soln. contains 1 equiv. of LiBr.

Determination of the Exchange Rate between Diphenyl Selenide and p-*Tolyllithium* (TolLi) [6a][26]. A stirred soln. of 0.194M *p*-tolyllithium (0.80 ml, 0.155 mmol) in THF was cooled to 0° under N_2 in a long-necked, round-bottom flask. Ph_2Se (27 µl, 0.155 mmol) was added. After 5 min, Me_3SiCl (20 µl, 0.158 mmol) was added followed by pentylbenzene (13.3 mg, 0.0897 mmol) as a GC standard and sat. NH_4Cl soln. (24 µl). The org. soln. was stirred vigorously, dried (Na_2SO_4), and analyzed by GC. The amounts of $PhSiMe_3$ (20.9% reaction) and *p*-$TolSiMe_3$ were determined (corrected for response factor), total recovery was 91%. Similar experiments were run for 10 (34.3% reaction), 20 (52.6%), and 40 min (66.4%), and the infinity point was taken after 180 min (79.4% of $PhSiMe_3$). The rate constant of exchange (second-order approach to equilibrium), rate of appearance of PhLi/$PhSiMe_3$) was calculated with *Eqn. 3*; where t = time in s, K = equilibrium constant = 14.9 (R = Ph or Tol), C_0 = initial concentration of TolLi, and x = molarity of product ($PhSiMe_3$). The exchange rate constant k_2 was calculated to be 0.00490 ± 0.00017 M^{-1} s^{-1} at 0°.

$$k_2 t = \frac{K^{0.5}}{2C_0} \cdot \ln\left[\frac{x - x/K - C_0 - C_0/K^{0.5}}{x - x/K - C_0 + C_0/K^{0.5}}\right] - \ln\left[\frac{C_0 + C_0/K^{0.5}}{C_0 - C_0/K^{0.5}}\right] \tag{3}$$

$$K = \frac{[\text{RSeTol}][\text{PhLi}]}{[\text{RSePh}][\text{TolLi}]} = \frac{[\text{PhSiMe}_3]^2}{[\text{TolSiMe}_3]^2}$$

Determination of Exchange Rate between Bromobenzene and p-*Tolyllithium.* A similar series of experiments with PhBr instead of Ph_2Se were performed at −20° ($K = 3.22$, $k_2 = 0.0109 \pm 0.0002$ M^{-1} s^{-1}), −30° ($K = 3.19$, $k_2 = 0.00487 \pm 0.00011$ M^{-1} s^{-1}), and −50° ($K = 3.32$, $k_2 = 0.000768 \pm 0.000039$ M^{-1} s^{-1}). An *Eyring* plot is shown in *Fig. 10*.

Determination of Exchange Rate between Diphenyl Sulfide and p-*Tolyllithium*. Done as described for Ph_2Se. After 17 h at 0°, a small peak amounting to 0.27% was seen on GC analysis with the correct retention time for $PhSiMe_3$. At this point, the material recovery was 60%. On this basis, the rate was calculated with the equilibrium constant determined for the Ph_2Se exchange: $k_2 = 2.0 \cdot 10^{-7}$ M^{-1} s^{-1} at 0°. This rate constant can be considered to be an upper limit.

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