lected, 9658 independent reflections, GOF = 1.049, $R = 0.0526$, $wR^2 = 0.1196$. **2**: $C_{96}H_{156}N_8O_{13}K_3U_2$, $M_r = 2223.65$, triclinic, space group $P\bar{1}$, $a = 17.325(1)$, $b = 18.258(1)$, $c = 19.616(2)$ Å, $\alpha = 108.527(2)$, $\beta = 90.998(2)$, $\gamma = 105.658(2)°$, $V = 5628.9(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.312$ Mg m^{-3}, $\mu = 3.039$ mm^{-1}, $F(000) = 2266$, 44317 reflections collected, 16076 independent reflections, GOF = 1.021, $R = 0.0723$, $wR^2 = 0.1947$. **3**: $C_{94}H_{102}N_8O_{12}K_4SiU_2$, $M_r = 2196.34$, monoclinic, space group $P2_1/m$, $a = 16.322(1)$, $b = 17.691(2)$, $c = 19.772(2)$ Å, $\beta = 98.956(2)°$, $V = 5643.4(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.293$ Mg m^{-3}, $\mu = 3.076$ mm^{-1}, $F(000) = 2184$, 44186 reflections collected, 6134 independent reflections, GOF = 1.058, $R = 0.0529$, $wR^2 = 0.1737$. **4**: $C_{96}H_{156}N_{10}O_{12}K_5U_2$, $M_r = 2313.87$, monoclinic, space group $P2_1/n$, $a = 13.111(1)$, $b = 22.953(3)$, $c = 17.976(2)$ Å, $\beta = 91.634(2)°$, $V = 5407(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.421$ Mg m^{-3}. $\mu = 3.241$ mm^{-1}, $F(000) = 2354$, 12592 reflections collected, 6924 independent reflections, GOF = 1.002, $R = 0.0383$, $wR^2 = 0.0908$. CCDC-177345, -177346, -177347, -177348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[1] a) J. Jubb, S. Gambarotta, *J. Am. Chem. Soc.* **1994**, *116*, 4477; b) T. Dubé, S. Conoci, S. Gambarotta, G. P. A. Yap, G. Vaspollo, *Angew. Chem.* **1999**, *111*, 3890; *Angew. Chem. Int. Ed.* **1999**, *38*, 3657; c) T. Dubé, J. Guan, S. Gambarotta, G. P. A. Yap, *Chem. Eur. J.* **2001**, *7*, 374; d) T. Dube, M. Ganesan, S. Conoci, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 3716.

[2] W. J. Evans, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1988**, *110*, 6877.

[3] a) C. E. Laplaza, C. C. Cummins, *Science* **1995**, *268*, 862; b) C. E. Laplaza, M. J. A. Johnson, J. C. Peters, A. C. Odom, E. Kim, C. C. Cummins, G. N. George, I. J. Pichering, *J. Am. Chem. Soc.* **1996**, *118*, 709; c) B. G. K. Clentsmith, F. G. H. Cloke, *J. Am. Chem. Soc.* **1999**, *121*, 10444; d) A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzoli, A. Chiesi-Villa, *J. Am. Chem. Soc.* **2000**, *122*, 365; e) P. Berno, S. Gambarotta, *Angew. Chem.* **1995**, *107*, 871; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 822; f) M. Tayebani, K. Feghali, S. Gambarotta, C. Bensimon, *Organometallics* **1997**, *16*, 5084.

[4] a) T. Dube, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 115; b) T. Dube, S. Conoci, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 1182; c) M. Ganesan, S. Gambarotta, G. P. A. Yap, *Angew. Chem.* **2001**, *113*, 788; *Angew. Chem. Int. Ed.* **2001**, *40*, 766; d) M. Ganesan; M. P. Lalonde, S. Gambarotta, G. P. A. Yap, *Organometallics* **2001**, *20*, 2443; e) T. Dube, J. Guan, S. Gambarotta, G. P. A. Yap, *Organometallics* **2001**, *20*, 374.

[5] a) P. Roussel, P. Scott, *J. Am. Chem. Soc.* **1998**, *120*, 1070; b) A. L. Odom, P. L. Arnold, C. C. Cummins, *J. Am. Chem. Soc.* **1998**, *120*, 5836.

[6] P. Diaconescu, P. L. Arnold, T. Baker, D. Mindiola, C. C. Cummins, *J. Am. Chem. Soc.* **2000**, *122*, 6108.

[7] a) I. Korobkov, S. Gambarotta, G. P. A. Yap, *Organometallics* **2001**, *20*, 2552; b) an example of DME demethylation has also been recently found: I. Korobkov, J. Guan, S. Gambarotta, G. P. A. Yap, unpublished results.

[8] D. S. J. Arney, C, J. Burns, *J. Am. Chem. Soc.* **1993**, *115*, 9840.

[9] I. Korobkov, S. Gambarotta, G. P. A. Yap, L. Thompson, J. Hay, *Organometallics* **2001**, *20*, 5440.

Are Ate Complexes True Intermediates in Lithium–Metalloid Exchange? Subtle Effects of Ion-Pair Structure in Lithium–Tellurium and Lithium–Selenium Exchange Reactions[**]

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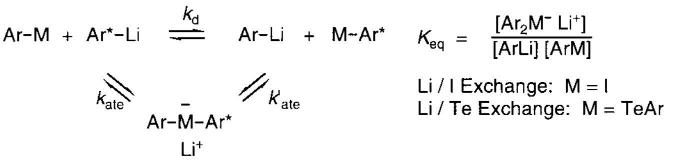
Birgir Ö. Gudmundsson, and Craig L. Puckett

The lithium–metalloid exchange reaction is widely used to prepare synthetically valuable organolithium reagents. The full synthetic potential of one of the most important of these reactions, the Li/I exchange, was not realized (e.g., in the synthesis of alkyllithium reagents) until mechanistic studies showed that it was a well-behaved polar process without a significant radical component.[1a,b,2] Ate complexes, first proposed by Wittig and Schöllkopf,[3] are presumptive intermediates in these reactions [Eq. (1)]. Ate complexes of iodine,[1a,b,4] tellurium,[1b,5] selenium,[1c,5] tin,[1d,6] and silicon[7] having only alkyl and aryl ligands have been characterized in solution and in the solid state, and probed by high-level calculations.[8] Their presence, however, is not proof that they are intermediates in the exchange. No direct evidence has been reported for any Li/M exchange which shows that all of the exchange proceeds along path k_{ate}, and none by the direct exchange path k_d, which bypasses the ate complex [Eq. (1)]. To perform such an experiment with dynamic NMR (DNMR) spectroscopy, the three reactants (monomeric ArLi, ArM, and Ar_2MLi) in the triangular equilibrium of Equation (1) must be present in detectable concentrations under conditions for which the rates k_d, k_{ate}, and k'_{ate} can each be measured.



(1)

A number of Li/I and Li/Te exchanges we investigated failed to provide a clear answer. Exchanges of PhI and Ph_2Te with PhLi could not be analyzed because no solvent of appropriate polarity was found such that all species were detectable. In THF both monomer and dimer were observable, but the equilibrium constant K_{eq} [Eq. (1)] for the ate complex was so high that insufficient PhLi and/or PhI/Ph_2Te (whichever was stoichiometrically limiting) was present.[1b] In less polar, mixed solvents, the concentration of PhLi monomer was too low for proper line-shape analysis[1e,9] (the dimer of PhLi is not active in the exchange process[1b]). A problem which prevents kinetic analysis of Li/I exchanges is the fast reaction between ArI and the ate complex, in which the latter

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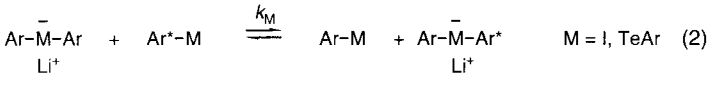
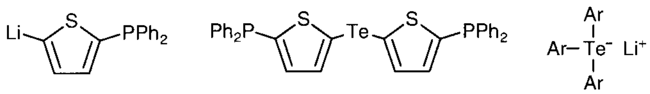
acts as an anion donor [k_M, Eq. (2)], which causes the ArI and $Ar_2I^-Li^+$ signals to coalesce at temperatures down to −130 °C.[1a]



$$\underset{Li^+}{Ar\text{–}\overset{-}{M}\text{–}Ar} + Ar^*\text{–}M \underset{}{\overset{k_M}{\rightleftharpoons}} Ar\text{–}M + \underset{Li^+}{Ar\text{–}\overset{-}{M}\text{–}Ar^*} \qquad M = I,\ TeAr \qquad (2)$$

We now report that a high-quality test of this mechanism can be performed on the exchange of 5-(diphenylphosphanyl)-2-lithiothiophene (**1**) with the telluride **2**, provided that the



1 **2** **3**

somewhat unusual solvent mixture 1,3-dioxolane/2-methyltetrahydrofuran (4/1) is used.[10] In this solvent the lithium reagent is completely monomeric, and the equilibrium constant K_{eq} [Eq. (1)] is ideal in the temperature range in which rates can be measured. A major advantage is the availability of ^{31}P NMR spectroscopy for the DNMR analysis, which provides excellent signal-to-noise ratio and dispersion of signals.

The low-temperature ^{31}P NMR spectrum of roughly equimolar ArLi and Ar_2Te showed well-resolved ArLi and Ar_2Te signals, as well as the characteristic 2:1 ratio of signals for apical and equatorial groups in the T-shaped ate complex **3** (Figure 1).[1b,5] On warming, all four signals coalesced to a single peak at about −40 °C.

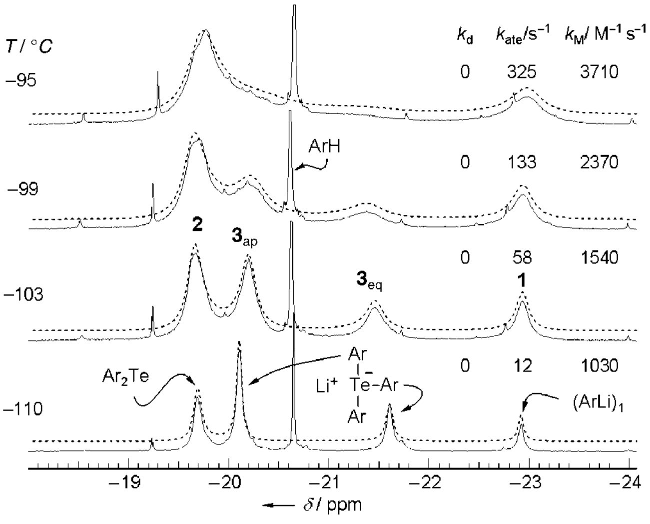
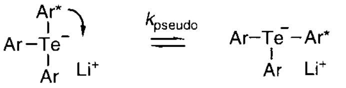
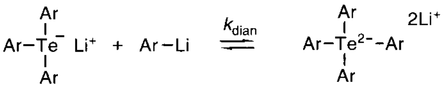


Figure 1. Variable-temperature 145.8 MHz ^{31}P NMR study of the exchange of **1** (0.033 M) and **2** (0.039 M) with **3** in 1,3-dioxolane/2-methyltetrahydrofuran (4/1) solution (Ar = 5-diphenylphosphanyl-2-thienyl). Temperatures were measured with the $(Me_3Si)_3CH$ ^{13}C chemical-shift thermometer.[1j] The thermodynamics and kinetics of Equation (1) at −99 °C are: for k_{ate}, $\Delta G^{\neq} = 8.3$ kcal mol^{-1}, $\Delta H^{\neq} = 11.5$ kcal mol^{-1}, $\Delta S^{\neq} = 18$ cal K^{-1} mol^{-1}; for K_{eq}, $\Delta H^0 = -6.5$ kcal mol^{-1}, $\Delta S^0 = -30.2$ cal K^{-1} mol^{-1}.

Analysis of these spectra is potentially complicated by several exchange processes: 1) The ate-complex mechanism, which averages all of the signals [k_{ate} in Eq. (1)]; 2) the ate complex as an aryl-anion donor[1a] [k_M in Eq. (2)], which would average the signals of **2** and **3**; 3) pseudorotation of **3**,[1f] which would average the signals of the ate complex **3** [Eq. (3)]; 4) reversible formation of a square-planar intermediate **4**, which would average the signals of **1** and **3** [k_{dian} in Eq. (4)];[11] and 5) direct exchange between telluride and lithium reagent, which would average the signals of **1** and **2** [k_d in Eq. (1)].



$$\underset{Ar\ \ Li^+}{Ar\text{–}\overset{Ar^*}{Te^-}} \overset{k_{pseudo}}{\rightleftharpoons} \underset{Ar\ \ Li^+}{Ar\text{–}Te^-\text{–}Ar^*} \qquad (3)$$



$$\underset{Ar}{Ar\text{–}\overset{Ar}{Te^-}}\ Li^+ + Ar\text{–}Li \overset{k_{dian}}{\rightleftharpoons} \underset{Ar}{Ar\text{–}\overset{Ar}{Te^{2-}}\text{–}Ar}\ 2Li^+ \qquad (4)$$

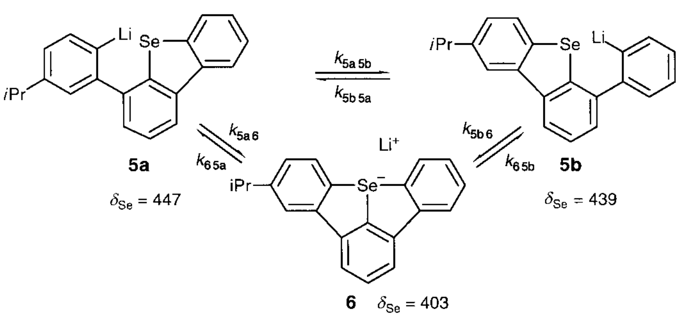
4

Experiments on solutions containing hexamethylphosphoramide (HMPA), in which the formation constant of the ate complex is very high,[12] allowed us to address interference from processes 3 and 4. In the presence of excess ArLi and 8 equiv of HMPA, the ^{31}P NMR signals of the ate complex remained sharp, and the signal of ArLi broadened only slightly up to −50 °C. Thus, neither the normal Li/Te exchange (process 1) or the pseudorotation (process 3), nor exchange via **4** (process 4) proceed at a significant rate, even at temperatures more than 40 K higher than those used in the experiment of Figure 1. Solutions containing HMPA also allowed process 2, mutual exchange between the ate complex and telluride signals, to be detected and quantified (e.g., at −95 °C with 10 equiv of HMPA and excess telluride: $k_M = 2900$ s^{-1}M^{-1}, $\Delta G^{\neq}_{-95} = 7.4$ kcal mol^{-1}, $\Delta H^{\neq} = 6.6$ kcal mol^{-1}, $\Delta S^{\neq} = -4.6$ cal K^{-1} mol^{-1}).[13]

Accurate simulations for the spectra in Figure 1 were achieved[14] in using only process 1 (k_{ate}) and a small (20–35 %) contribution to the total rate from process 2 (k_M), which manifests itself as a line broadening of the ArLi signal, slightly smaller than expected, when only k_{ate} is allowed.[1h] No contribution from non-ate-complex exchange by process 5 (k_d) was detected. Hence, the ate complex is a kinetic intermediate in this Li/Te exchange, and there is no significant exchange between ArLi and Ar_2Te by any mechanism other than via the ate complex.

While characterizing a selenium ate complex[1c] we found that **5** also met the requirements for testing the ate-complex mechanism for an Li/Se exchange. Here ^{77}Se NMR spectroscopy could be used to detect the interconversion of **5a**, **5b**, and **6**. In dimethyl ether/diethyl ether the intramolecular Li/Se exchange was fast on the NMR timescale down to −100 °C (Figure 2a). At lower temperatures the ^{77}Se NMR signals of lithium reagents **5a** and **5b** decoalesced in a 1:3 ratio.

The addition of 12 % THF to this sample caused the appearance of a new signal at $\delta = 403$ ppm (Figure 2b) which we assigned to the ate complex **6**.[15] At −149 °C k_{ate} (k_{65}) is slow on the NMR timescale, but no decoalescence of the two lithium reagents can be detected. Thus, Li/Se exchange (**5a**⇌**5b**) is still fast under conditions for which exchange with the ate complex **6** is slow on the NMR timescale (we



$$\begin{array}{cc}
 & \begin{array}{cccc} \text{A (ate-apical)} & \text{B (ate-eq)} & \text{C (ArLi)} & \text{D (Ar}_2\text{Te)} \end{array} \\
\begin{array}{c} \text{A} \\ \\ \text{B} \\ \\ \text{C} \\ \\ \text{D} \end{array} &
\left[\begin{array}{cccc}
\begin{array}{c} i2\pi(\nu_A) \\ -1/T\text{-}\Sigma k_{AX} \end{array} & k_{AB} & k_{AC} & k_{AD} \\
k_{BA} & \begin{array}{c} i2\pi(\nu_B) \\ -1/T\text{-}\Sigma k_{BX} \end{array} & k_{BC} & k_{BD} \\
k_{CA} & k_{CB} & \begin{array}{c} i2\pi(\nu_C) \\ -1/T\text{-}\Sigma k_{CX} \end{array} & k_{CD} \\
k_{DA} & k_{DB} & k_{DC} & \begin{array}{c} i2\pi(\nu_D) \\ -1/T\text{-}\Sigma k_{DX} \end{array}
\end{array}\right] = \boldsymbol{E}
\end{array}$$

$$\begin{aligned}
k_{AB} &= \frac{k_{pseudo}}{2} + \frac{k_{dian}\,[\mathbf{1}]}{4} \\
k_{AC} &= \frac{k_{ate}}{2} + \frac{k_{dian}\,[\mathbf{1}]}{4} \\
k_{AD} &= \frac{k_{ate} + k_M\,[\mathbf{2}]}{2} \\
k_{BC} &= \frac{k_{dian}\,[\mathbf{1}]}{4} \\
k_{BD} &= k_{ate} + k_M\,[\mathbf{2}] \\
k_{CD} &= k_d\,[\mathbf{2}]
\end{aligned}$$

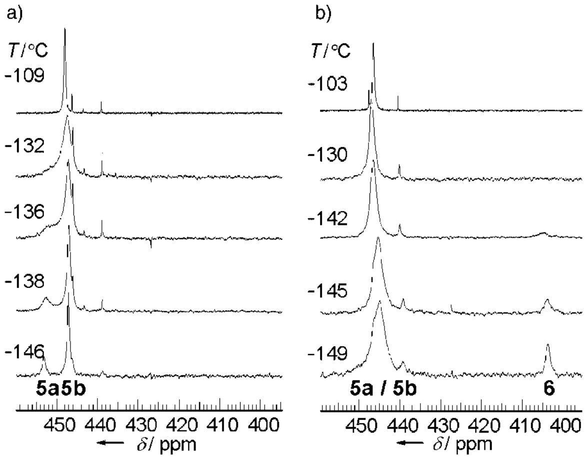


Figure 2. Variable-temperature 68.68 MHz ^{77}Se NMR spectra of **5a**/**5b**/**6**. a) In Me$_2$O/Et$_2$O (54/46). b) With addition of THF (Me$_2$O/Et$_2$O/THF 48/40/12). Line-shape simulation of the spectra on the left gave $\Delta G^{\ddagger}_{-136\,^{\circ}\mathrm{C}} =$ 6.2 kcal mol^{-1}, $\Delta H^{\ddagger} = 6.4 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -0.7 \pm 4$ cal K^{-1} mol^{-1} for k_{5b5a}. The small impurity signals at $\delta = 439$ and $\delta = 447$ ppm are due to compounds formed by protonation of **5a** and **5b**.

assume that addition of 12% THF will appreciably affect neither the ^{77}Se chemical shifts of **5a** and **5b** nor their ratio).

The dynamics can be quantified by performing three-spin DNMR simulations,[1h] as shown in Figure 3.[14] Simulation 1 fits the spectrum of the sample containing no THF and no detectable ate complex. If we attempt to fit the spectrum in the solution containing 12% THF (bottom spectrum in Figure 3) and allow exchange only via the ate complex ($k_{5a5b} = k_d = 0$), then the lithium reagent isomers **5a** and **5b** are predicted to be well below coalescence when the signal of the ate complex has the correct line shape (Figure 3, simulation 2). Increasing the rate of exchange broadens this signal (simulation 3). Only when a substantial rate of direct exchange between the two lithium reagents is included can a successful simulation be performed (simulation 4, $k_{5a5b} \geq 45 k_{5a6}$). There is thus an alternate pathway for exchange of **5a** and **5b** [k_d in Eq. (1)] which is at least 45 times as fast as that involving **6**.

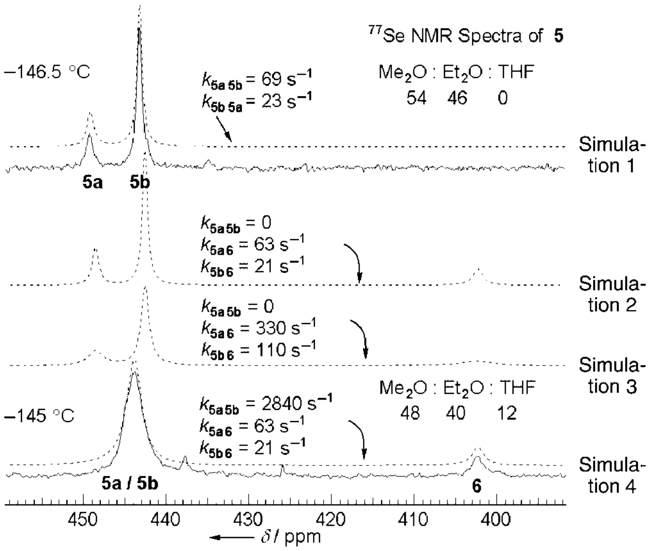
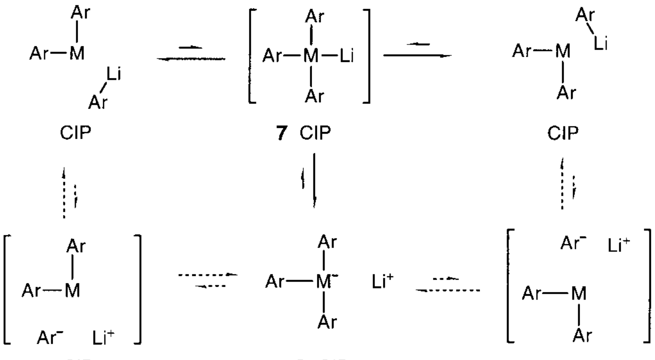


Figure 3. ^{77}Se NMR spectra of solutions of **5**/**6** with simulations (dotted lines).[1h]

How can we explain the different behavior of systems **1**/**2**/**3** and **5**/**6**? We considered single-electron transfer (SET) mechanisms, but the absence of decomposition in solutions in which tens of millions of Li/Te, Li/Se, or Li/I exchanges have occurred argues strongly against radical intermediates. A more satisfactory explanation is as follows: Since organometalloid ate complexes in THF and more polar solvents are separated ion pairs (SIPs),[1b,e] and ArLi reagents are strong contact ion pairs (CIPs),[1e,i] a mechanism for ArLi/ArM exchange which involves the observable ate complex requires ion-pair separation of either ArLi or the ate complex (vertical arrows in Scheme 1). We propose that the Li/Se exchange of **5a**/**5b** proceeds along the top row of Scheme 1 much faster than dissociation of the CIP ate complex **7** to the more stable SIP ate complex **8**. The observable ate complex **8** (= **6**) is then just a parasitic equilibrium on the actual exchange pathway, which has more the character of an S$_N$2 substitution. The Li/Te exchange of **1** probably involves the same pathway as for **5**,



Scheme 1. CIP and SIP intermediates in the Li/M exchange (M = Te, Se). Species in brackets are not observable for either the **1**/**2**/**3** or **5a**/**5b**/**6** systems.

except that the rates to and from CIP **7** are slow enough that dissociation of **7** to **8** is faster than the exchange process (**5a**/**5b** exchange is faster than the dissociation of **3** by about a factor of 10^3).

In summary, DNMR studies have shown that the Li/Te exchange of the lithiothiophene **1** with the telluride **2** proceeds exclusively through the ate complex **3**. The very fast intramolecular Li/Se exchange of **5a** and **5b**, on the other hand, does not proceed appreciably through the observable SIP ate complex **6**. We propose that here the SIP/CIP interconversion is slower than the Li/Se exchange rate, and this allows the intramolecular substitution to bypass the SIP of **6**.

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[1] a) H. J. Reich, D. P. Green, N. H. Phillips, *J. Am. Chem. Soc.* **1989**, *111*, 3444–3445; b) H. J. Reich, D. P. Green, N. H. Phillips, *J. Am. Chem. Soc.* **1991**, *113*, 1414–1416; H. J. Reich, D. P. Green, N. H. Phillips, J. P. Borst, I. L. Reich, *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *67*, 83–97; c) H. J. Reich, B. Ö. Gudmundsson, R. R. Dykstra, *J. Am. Chem. Soc.* **1992**, *114*, 7937–7938; d) H. J. Reich, N. H. Phillips, *J. Am. Chem. Soc.* **1986**, *108*, 2102–2103; e) H. J. Reich, D. P. Green, M. A. Medina, W. S. Goldenberg, B. Ö. Gudmundsson, R. R. Dykstra, N. H. Phillips, *J. Am. Chem. Soc.* **1998**, *120*, 7201–7210; f) such a pseudorotation has been studied for the isoelectronic triaryliodine compounds: H. J. Reich, C. S. Cooperman, *J. Am. Chem. Soc.* **1973**, *95*, 5077–5088; g) H. J. Reich, N. H. Phillips, I. L. Reich, *J. Am. Chem. Soc.* **1985**, *107*, 4101–4103; h) simulations were performed with a version of the computer program WINDNMR (H. J. Reich, *J. Chem. Educ. Software* **1996**, 3D, 2; http://www.chem.wisc.edu/areas/reich/plt/windnmr.htm); i) H. J. Reich, J. P. Borst, R. R. Dykstra, D. P. Green, *J. Am. Chem. Soc.* **1993**, *115*, 8728–8741; j) W. H. Sikorski, A. W. Sanders, H. J. Reich, *Magn. Reson. Chem.* **1998**, *36*, S118–S124.

[2] W. F. Bailey, J. J. Patricia, *J. Organomet. Chem.* **1988**, *352*, 1–46, and references therein.

[3] G. Wittig, U. Schöllkopf, *Tetrahedron* **1958**, *3*, 91–93.

[4] W. B. Farnham, J. C. Calabrese, *J. Am. Chem. Soc.* **1986**, *108*, 2449–2451; V. Schulze, M. Brönstrup, V. P. W. Böhm, P. Schwerdtfeger, M. Schimeczek, R. W. Hoffmann, *Angew. Chem.* **1998**, *110*, 869–871; *Angew. Chem. Int. Ed.* **1998**, *37*, 824–826.

[5] Y. Masutomi, N. Furukawa, T. Erata, *Heteroat. Chem.* **1995**, *6*, 19–27.

[6] A. J. Ashe III, L. L. Lohr, S. M. Al-Taweel, *Organometallics* **1991**, *10*, 2424–2431; A. Maercker, H. Bodenstedt, L. Brandsma, *Angew. Chem.* **1992**, *104*, 1387; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1339–1341.

[7] A. H. J. F. de Keijzer, F. J. J. de Kanter, M. Schakel, V. P. Osinga, G. W. Klumpp, *J. Organomet. Chem.* **1997**, *548*, 29–32.

[8] G. Boche, M. Schimeczek, J. Cioslowski, P. Piskorz, *Eur. J. Org. Chem.* **1998**, 1851–1860; J. Cioslowski, P. Piskorz, M. Schimeczek, G. Boche, *J. Am. Chem. Soc.* **1998**, *120*, 2612–2615; K. B. Wiberg, S. Sklenak, W. F. Bailey, *Organometallics* **2001**, *20*, 771–774.

[9] W. Bauer, W. R. Winchester, P. von R. Schleyer, *Organometallics* **1987**, *6*, 2371–2379.

[10] The telluride was insufficiently soluble in conventional solvents such as THF mixed with ether, toluene, or dimethyl ether. In solvents containing a large fraction of THF, K_{eq} [Eq. (1)] was too large to allow measurement of rates.

[11] The analogous dianionic halotellurates TeX_4^{2-} are known: S. Pohl, W. Saak, B. Krebs, *Z. Naturforsch. B* **1985**, *40*, 251–257.

[12] HMPA preferentially solvates and stabilizes the weakly coordinated Li cation of the ate complex over that of ArLi, in which lithium bears the very strong carbanion donor ligand.[1g]

[13] The exchange of Ar_2Te with Ar_3TeLi in 1,3-dioxolane/2-methyltetrahydrofuran/HMPA solution was shown to be first order in [Ar_2Te] by DNMR experiments with variable telluride concentrations, as expected for process 2. Under conditions for which the formation constant of the ate complex is large, such as in the presence of several equivalents of HMPA,[1g] the exchange between Ar_2Te and the ate complex by process 1 would be zero order in [Ar_2Te].

[14] The exchange matrix for the simulations in Figure 1 and Figure 3 and the relationship between the NMR rate constants (k_{AB}, k_{AC}, etc.) and the physical rate constants of Equations (1)–(4) (k_{ate} is first order; k_{pseudo}, k_{dian}, k_M, and k_d are second order) are given below (in the simulations of Figure 1, k_{pseudo}, k_{dian}, and k_d were set to zero).

[15] The appearance of the signal assigned to **6** was fully reversible and strongly temperature dependent (in 1/1/1 ether/dimethyl ether/THF at −60 °C: > 80 % **5**; at −143 °C: ca. 60 % **6**). Conversion to **6** (δ_{Se} = 403 ppm) was quantitative if excess HMPA was added (δ_{Se} = 409 ppm), an effect also seen for the parent system (without the isopropyl substituent)[1c] and for other Te, I, and Sn ate complexes.[1a,d,g] The signals of the two apical C atoms of **6** were characteristically shifted downfield (δ = 181.9, 187.2 ppm), as was also seen for numerous other ate complexes.[1b] Quenching of the HMPA solution of **6** with bromotrimethylstannane cleanly gave the stannylated precursors (2:1 mixture), that is, no structural changes had occurred.

Generation of Polyunsaturated Cumulene Chains by Unprecedented Insertions of the Ynamine MeC≡CNEt$_2$ in Ruthenium(II) Allenylidene Complexes[**]

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Allenylidene (propadienylidene) complexes [ML$_n$]=C=C=CR^{1}R^2, which belong to the series of unsaturated carbenes [ML$_n$]=C(=C)$_i$=CR^{1}R^2 ($i > 0$) have received increasing interest during the last few years.[1] These derivatives have a great potential to promote novel carbon–carbon and carbon–heteroatom coupling reactions, because of the electrophilic (C_α and C_γ) and nucleophilic (C_β) character of the carbon nuclei of the allenylidene chain. While simple nucleophilic and electrophilic additions are well-studied, cycloaddition processes are scarce, in particular those involving C≡C dipolar substrates.[2] In 1998 Fischer and co-workers reported the synthesis of cyclobutenylidene and alkenylallenylidene Group 6 metal complexes which are formed as a mixture by the cycloaddition of ynamines to both the C_α=C_β and C_β=C_γ bonds of an

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