J. Am. Chem. Soc. **1992**, *114*, 7937–7938

The First Organoselenium Ate Complex

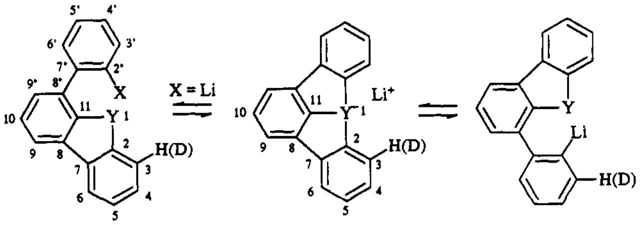
Hans J. Reich,* Birgir Örn Gudmundsson, and
Robert R. Dykstra

Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

Received June 8, 1992

We report here spectroscopic evidence for the first organoselenium ate complex and for a lithium–sulfur exchange that is fast on the NMR time scale. Ate complexes of non-first-row elements with electronegative substituents are common, but those with only carbon ligands are rare. Ate complexes of the fourth-row elements iodine,[1a–c] tellurium,[1a,c,d] and tin[1a,e,2] (but not of sulfur and selenium[1f]) have been detected kinetically and spectroscopically and are firmly established as intermediates in the lithium–metalloid exchange. The preparation of dialkoxy sulfuranide anions,[3] as well as the recent spectroscopic detection of related neutral compounds tetraphenylsulfurane[4a] and tetraphenylselenurane,[4b] species that have been implicated as reaction intermediates in earlier studies,[5] provided hope that direct observation of even the all-carbon anionic analogs might be possible.

Hypervalent molecules can be dramatically stabilized by molecular frameworks that favor trigonal bipyramidal or square pyramidal structures,[6,7] so we have undertaken the synthesis of rigid molecules with ideal geometry for the presumed T-shaped structure of sulfur and selenium ate complexes. We chose a *m*-terphenyl grouping[8] and were delighted that conversion of the deuterium-labeled bromide **1**-S (**1**, Y = S) to the lithium reagent **3**-S resulted in equilibration of isotopic label in less than 1 min at −78 °C in THF.[9] Variable temperature ^{13}C NMR spectra of **3**-S in 80% THF/ether are shown in Figure 1A–C. All ^{13}C NMR signals were assigned with the aid of deuterium isotope shifts, $^3J_{\mathrm{CH}}$, C–H COSY, and homonuclear ^{1}H decoupling experiments. At −78 °C (Figure 1C) all 18 resonances were resolved, and thus the structure is static on the NMR time scale.[10] At higher temperatures most of the signals broadened, until at −18 °C only the two nonexchanging carbons C-10 (125.0 ppm) and C-11 (139.6 ppm) remained sharp. At −18 °C the $\Delta G^{\ddagger}$ for the equilibration **3**-S ⇄ **3′**-S is 11.9 kcal/mol (k = 350 s^{-1}).[11] It is of interest to compare this rate with analogous intermolecular Li/S,[1d,9] Li/Se,[1d] and Li/Te[1c,h] exchanges of Ph$_2$Y with phenyl- or *p*-tolyllithium. The **3**-S/**3′**-S exchange at 0 °C is $\approx 10^9$ times faster than the intermolecular Li/S exchange ($\Delta G^{\ddagger}$ = 23 kcal/mol) and $\approx 10^5$ faster than the Li/Se exchange ($\Delta G^{\ddagger}$ = 19 kcal/mol at 0 °C), although not as fast as the Li/Te exchange ($\Delta G^{\ddagger}$ = 7.5 kcal/mol at −110 °C) by a factor of about 10^4.



1 X = Br
2 X = SnMe$_3$
3 X = Li

4
Y = S, Se

3′

Encouraged by these results, we prepared the selenium analog **3**-Se. The NMR behavior of **3**-Se was complex. Figure 1D–F shows key ^{13}C NMR spectra, and Figure 2, ^{77}Se NMR spectra. Figure 1D is a ^{13}C NMR spectrum in 3% THF/ether at −78 °C. There are only 10 signals, two of them with half-intensity. We believe that under these conditions the solution contains essentially pure lithium reagent **3**-Se undergoing rapid degenerate exchange, **3**-Se ⇄ **3′**-Se. The half-intensity signals at 125.6 and 140.1 ppm can be assigned to the two carbons in the middle ring, C-10 and C-11. Their chemical shifts are close to those of the nonexchanging signals in **3**-S. The C–Li signal (C-2/2′, 169.4 ppm) is very near the average of the corresponding signals in **3**-S (197.3 and 143.0 ppm).

Figure 1E is the ^{13}C spectrum in 80% THF/ether at −78 °C. A number of signals are substantially shifted (>1 ppm) from those in 3% THF (Figure 1D). This is in contrast to **3**-S, for which only C-2′ was shifted more than 1 ppm on going from 3% to 80% THF/ether. The C-2/C-2′ signal at 177 ppm is especially affected. These changes can be interpreted in terms of a rapidly equilibrating mixture of **3**-Se and the selenium ate complex **4**-Se.

Figure 1F presents the ^{13}C spectrum in THF/HMPA. All of the chemical shift changes observed on going from 3% to 80% THF continue in the same direction, and with a magnitude consistent with conversion of the ≈1:1 mixture of **3**-Se/**4**-Se in 80% THF to pure **4**-Se. Two key aspects of the spectrum are the shift of C-2/2′ at 187 ppm, which cannot be the average of C-2 (near 140 ppm) and C-2′ (∼195 ppm) of structure **3**-Se/**3′**-Se, and the selenium–carbon coupling constant of **4**-Se ($^1J_{\mathrm{SeC}}$ = 85 Hz), which similarly cannot be the average of the selenium coupling to C-2 (∼100 Hz[12]) and C-2′ (∼0 Hz) predicted for a **3**-Se/**3′**-Se average. The ^{7}Li NMR spectrum at −115 °C shows complete conversion of the broad singlet at −0.8 ppm for **3**-Se/**4**-Se to the characteristic quintet of Li(HMPA)$_4^+$ at −0.5 ppm, as expected for a separated ion **4**-Se, with lithium coupled to four phosphorus nuclei.[1i,j]

Supporting evidence for this interpretation of Figure 1D–F is provided by the variable temperature ^{77}Se NMR spectra shown in Figure 2. These spectra demonstrate the conversion of lithium reagent **3**-Se at high temperature (Figure 2A) to increasing

---

(1) (a) Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101. (b) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444. (c) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414. (d) Reich, H. J.; Green, D. P.; Phillips, N. H.; Borst, J. P.; Reich, I. L. *Phosphorus Sulfur* **1992**, *67*, 83. (e) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102. Reich, H. J.; Phillips, N. H. *Pure Appl. Chem.* **1987**, *59*, 1021. (f) Unpublished results from these laboratories. (g) Reich, H. J.; Cooperman, C. S. *J. Am. Chem. Soc.* **1973**, *95*, 5077. (h) Green, D. P. Ph.D. Thesis, University of Wisconsin, Madison, 1989. (i) Reich, H. J.; Green, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 8729. (j) Reich, H. J.; Borst, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1835.

(2) Ashe, A. J.; Lohr, L. L.; Al-Tawee, S. M. *Organometallics* **1991**, *10*, 2424.

(3) Perkins, C. W.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3209. Ohkata, K.; Ohnishi, M.; Yoshinaga, K.; Akiba, K.; Rongione, J. C.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 9270.

(4) (a) Ogawa, S.; Matsunaga, Y.; Sato, S.; Erata, T.; Furukawa, N. *Tetrahedron Lett.* **1992**, *33*, 93. (b) Ogawa, S.; Sato, S.; Erata, T.; Furukawa, N. *Tetrahedron Lett.* **1991**, *32*, 3179. (c) Ogawa, S.; Sato, S.; Erata, T.; Furukawa, N. *Tetrahedron Lett.* **1992**, *33*, 1915.

(5) Trost, B. M.; Arndt, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 5288. Wittig, G.; Fritz, H. *Justus Liebigs Ann. Chem.* **1952**, *577*, 39. Iwama, Y.; Aragi, M.; Sugiyama, M.; Matsui, K.; Ishii, Y.; Ogawa, M. *Bull. Soc. Chem. Jpn.* **1981**, *54*, 2065.

(6) Sulfuranes,[3,7a] selenanes,[4b,7b] iodinanes,[1g,7c] phosphoranes,[7d,e] siliconates,[7f] stannates.[7g,h]

(7) (a) Walter, W.; Krische, B.; Juergen, V. *J. Chem. Res., Synop.* **1978**, 332. (b) Hellwinkel, D.; Fahrbach, G. *Justus Liebigs Ann. Chem.* **1968**, *715*, 68. (c) Wittig, G.; Clauss, K. *Justus Liebigs Ann. Chem.* **1952**, *578*, 136. Clauss, K. *Chem. Ber.* **1955**, *88*, 268. Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1972**, *37*, 1516. (d) Hellwinkel, D. *Top. Curr. Chem.* **1983**, *109*, 1. (e) Hellwinkel, D.; Krapp, W. *Chem. Ber.* **1978**, *111*, 13. Culley, S. A.; Arduengo, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 1164. (f) Stevenson, W. H., III; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340. (g) Jurkschat, K.; Tzschach, A. *J. Organomet. Chem.* **1984**, *272*, C13. (h) Van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C. *J. Organomet. Chem.* **1978**, *148*, 233.

(8) The only previous use of an all-carbon framework such as **4** is in triarylamines with Y$^-$ = N (Buchanan, C.; Tucker, S. H. *J. Chem. Soc.* **1958**, 2750). Similar ligands with axial heteroatoms have been used to stabilize hypervalent sulfur,[3,7a] phosphorus,[7e] and tin[7h] compounds.

(9) Schlosser, M.; Kadibelban, T.; Steinhoff, G. *Justus Liebigs Ann. Chem.* **1971**, *743*, 25. The cleavage of C–S bonds with alkyllithium reagents (Li/S exchange) occurs only in unusual circumstances: Meinwald, J.; Knapp, S.; Obendorf, S. K.; Hughes, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 6643. Cohen, T.; Yu, L. C. *J. Org. Chem.* **1985**, *50*, 3266. Seebach, D.; Meyer, N.; Beck, A. K. *Justus Liebigs Ann. Chem.* **1977**, 846.

(10) In THF/HMPA solution, compound **3**-S gave no signals attributable to **4**-S.

(11) The **3**-S/**3′**-S degenerate exchange rate was calculated from the broadening of several pairs of carbons at −48 °C ($\Delta G^{\ddagger}$ = 11.5 kcal/mol), −31 °C ($\Delta G^{\ddagger}$ = 11.7 kcal/mol), and −18 °C ($\Delta G^{\ddagger}$ = 11.9 kcal/mol).

(12) The $^1J_{\mathrm{CSe}}$ in dibenzoselenophene is 99.8 Hz; for compound **2**-Se it is 100.2 Hz for C-2 and 98.2 Hz for C-11 (numbering as shown for **3**).

0002-7863/92/1514-7937$03.00/0

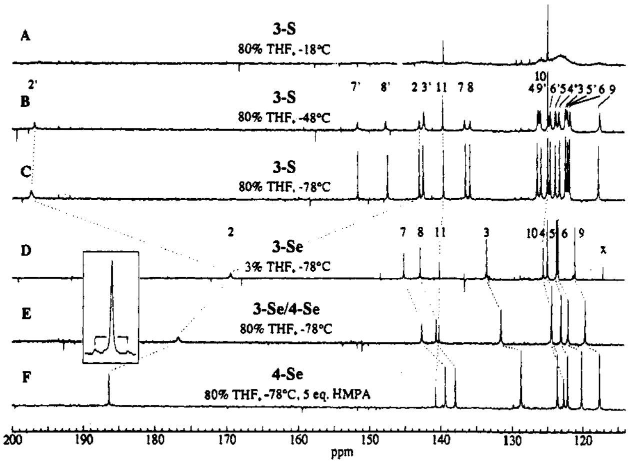


Figure 1. ^{13}C NMR spectra (90.56 MHz) of solutions of 3-S and 3-Se. The inset in spectrum F shows the ^{77}Se satellites of C-2 (J_{SeC} = 85 Hz).

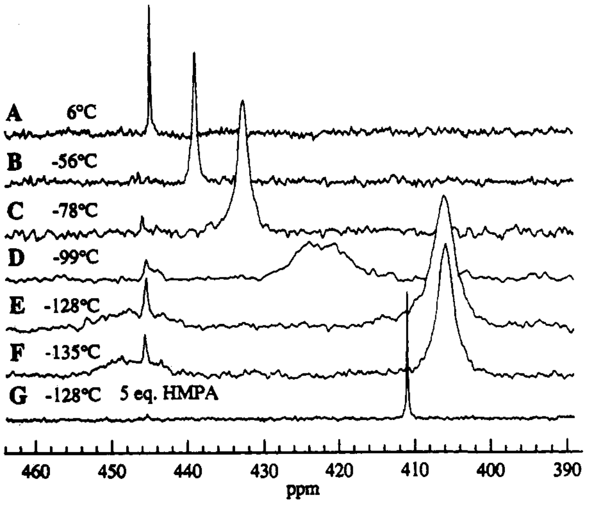


Figure 2. ^{77}Se NMR spectra (68.68 MHz) of solutions of 3-Se and 4-Se in 80% THF/ether (A–F) and THF/ether/HMPA (G). Chemical shifts are referenced to Me_2Se in $CDCl_3$ at 25 °C.

proportions of 4-Se at lower temperatures. The ^{77}Se spectrum broadened and decoalesced at ≈−128 °C (Figure 2E) to a broad signal at 447 ppm for 3-Se and one at 406 ppm for 4-Se.[13] The sharp signal at 446 ppm is the protonation product of 3-Se. The spectra in Figure 2A–F and corresponding ^{13}C spectra (not shown) can be used to determine the temperature dependence of the 3-Se/4-Se equilibrium. A plot of $\Delta G°$ vs T gives $\Delta H° = -2.5 \pm 1$ kcal/mol, $\Delta S° = -14 \pm 5$ eu. Equilibria between solvent-separated and contact lithium ion pairs in ether solvents are temperature dependent, with lower temperatures favoring separated ions.[14] Equilibria between aryllithium reagents (contact ions) and the ate complexes Ph_2ILi and Ph_3TeLi (separated ions in THF) also follow this pattern.[1c] Figure 2G shows the spectrum of the ate complex 4-Se in THF/HMPA.

Summary. The enormous rate acceleration of the intramolecular Li/S exchange 3-S/3'-S and the unusual stability of the selenium ate complex 4-Se suggest that the structure of 4 is close to the ideal geometry of such ate complexes, and provides support for the intermediacy of ate complexes in Li/S and Li/Se exchanges.

Acknowledgment. We thank the National Science Foundation for support of this work.

---

[13] Upfield ^{125}Te and ^{77}Se shifts are found for the conversion of Ph_2Te (688 ppm) to Ph_3TeLi (327 ppm),[1c,d] and Ph_2Se (402 ppm) to Ph_4Se (373.7 ppm)[4b] as well as their dibenzoselenophene analogs.[4c] However, the conversion Ph_4Te (529 ppm) to Ph_5TeLi (622 ppm) results in a downfield shift.[1d]

[14] For the equilibration of lithium fluorenide contact and separated ion pairs in THF: $\Delta H° = -7.5$ kcal/mol and $\Delta S° = -22$ eu;[14a] for equilibration of PhLi/PhI with Ph_2ILi, $\Delta H° = -9.9$ kcal/mol and $\Delta S° = -44$ eu.[1c] Rate studies for the PhLi/ArBr exchange in ether ($\Delta H^* = 14$ kcal/mol, $\Delta S^* = -24$ eu)[14b] and THF (223 K, $\Delta H^* = 9.5$ kcal/mol, $\Delta S^* = -30$ eu)[1f] show negative entropies of activation. (a) Hogen-Esch, T. E. *Adv. Phys. Org. Chem.* **1977**, *15*, 153. O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633. (b) Winkler, H. J. S.; Winkler, H. *J. Am. Chem. Soc.* **1966**, *88*, 964, 969. Rogers, H. R.; Houk, J. *J. Am. Chem. Soc.* **1982**, *104*, 522.

X-ray Crystallographic and NMR Studies on the Origins of High Enantioselectivity in Diels-Alder Reactions Catalyzed by a Chiral Diazaaluminolidine

E. J. Corey* and Sepehr Sarshar

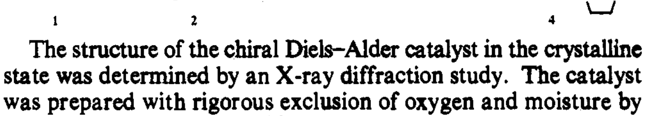
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Jon Bordner

Medical Research Laboratories, Pfizer, Inc.
Groton, Connecticut 06340

Received July 8, 1992

The use of chiral aluminum-containing catalysts for enantioselective Diels-Alder reactions has recently been reported.[1] For instance, the reaction of 5-(benzyloxymethyl)-1,3-cyclopentadiene (**1**) and 3-acryloyl-1,3-oxazolidin-2-one (**2**), when catalyzed by the (*S*,*S*)-diazaaluminolidine 3 (ca. 10 mol %) at −78 °C, produced after 18 h the adduct 4 in 93% yield and with ca. 97:3 enantioselectivity.[2] This useful and interesting process has now been examined for mechanistic detail on the control of enantioselectivity within the catalytic transition-state assembly. We present herein X-ray crystallographic and NMR evidence for the basis of enantioselectivity in this system.



The structure of the chiral Diels-Alder catalyst in the crystalline state was determined by an X-ray diffraction study. The catalyst was prepared with rigorous exclusion of oxygen and moisture by the method used earlier,[1,3] and crystals were grown from a methylene chloride–heptane bilayer at 23 °C. A crystal of size 0.21 × 0.31 × 0.35 mm was sealed in a glass capillary for X-ray analysis, which revealed that two units of the diazaaluminolidine system 3 are associated as shown in structure **5**.[4] In the dimer

---

[1] (a) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, X. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493–5495. (b) Corey, E. J.; Imai, N.; Pikul, S. *Tetrahedron Lett.* **1991**, *32*, 7517–7520.

[2] For a review of this and other applications of chiral 1,2-diphenyl-1,2-diaminoethane-derived reagents, see: Corey, E. J. *Pure Appl. Chem.* **1990**, *62*, 1209–1216.

[3] For details of the preparation of the catalyst and its use in a Diels–Alder reaction, see: Pikul, S.; Corey, E. J. *Org. Synth.*, in press. A flame-dried, 250-mL, three-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with 1.31 g (2.75 mmol) of the bistriflamide of (*S*,*S*)-1,2-diphenyl-1,2-diaminoethane (dried at 80 °C and 1 mmHg) and placed under dry argon. 1,2-Dichloroethane (20 mL) was added, and the mixture was heated to 80 °C with stirring to effect solution, cooled to ambient temperature, and treated dropwise with 1.37 mL (2.74 mmol) of 2 M trimethylaluminum in toluene. After the evolution of gases ceased, the homogeneous mixture was heated to 80 °C (oil bath) for 3 h. The mixture was cooled to ambient temperature, and the solvent was removed under vacuum, which was maintained for an additional 30 min. The resulting solid was dissolved in 10 mL of dry methylene chloride and overlayered with 50 mL of dry heptane. Colorless, clear crystals of catalyst were deposited after 20 h. The supernatant was drawn off by syringe. Since trimethylaluminum can also catalyze Diels–Alder reactions of 2 with dienes, it is essential that this and other Lewis acids be removed from catalyst 3.

[4] Detailed X-ray crystallographic data are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, U.K. Data for empirical formula $Al_2C_{34}H_{30}N_4O_8S_4F_{12}$ (1032.9): space group $P2_1$, $a = 10.798$ (5) Å, $b = 16.264$ (9) Å, $c = 12.406$ (7) Å, $\alpha = 90.00°$, $\beta = 92.87$ (4)°, $\gamma = 90.00°$, $V = 2176$ (2) Å^3, 2 molecules per unit cell, $d = 1.58$ g/cm^3; Mo Kα radiation (23 °C); 2341 reflections obtained (1643 with $I > 3\sigma$), R index = 0.069; GOF = 1.04.

0002-7863/92/1514-7938$03.00/0