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Low-Temperature ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR Studies on the Apical-Apical Ligand Exchange via the Hypervalent Tellurium and Selenium Ate Complexes [10-M-3(C3); M = Se, Te] in the Reactions of Diaryl Tellurides and Selenides with Aryllithium Reagents

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ABSTRACT

*Pentafluorophenyl phenyl telluride (**1**) and 3,5-dichloro-2,4,6-trifluorophenyl phenyl telluride (**2**) react with pentafluorophenyllithium or 3,5-dichloro-2,4,6-trifluorophenyllithium in THF at low temperatures to form the corresponding tellurium ate complexes (**A**) and (**B**) as sole intermediates in the ligand exchange on the hypervalent tellurium atom. The corresponding selenides (**3**) and (**4**) also react with identical aryllithium reagents in THF to form the discrete intermediates, selenium ate complexes (**C**) and (**D**), in the exchange reactions. In these ligand exchange reactions of tellurides and selenides, electron-withdrawing ligands occupy the apical positions and the exchange takes place between these apical-oriented groups. The low-temperature ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopic techniques are effective methods for detection of unstable tellurium and selenium ate complexes.*

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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INTRODUCTION

Recently, diaryl tellurides have been found to undergo tellurium-lithium exchange reactions on treatment with organolithium reagents. These tellurium-lithium exchange reactions have attracted considerable attention, since the reactions provide a convenient procedure for the generation of numerous, synthetically useful organolithium reagents, as presented by Sonoda and co-workers [1]. Furthermore, the mechanism of the exchange reaction has been investigated by Reich *et al.* [2] and Furukawa *et al.* [3]. They have confirmed that the exchange reaction proceeds via two steps involving the initial formation of discrete intermediates, ate complexes of [10-Te-3(C3)], using ^{1}H, ^{13}C, and ^{125}Te NMR techniques at low temperatures. However, there still remains a question regarding the structure of the hypervalent intermediate formed in each reaction, namely, the apicophilicity of the ligands attached to the central atom [4]. The substitution reactions hitherto have been conducted by the employment of substrates bearing strongly electronegative halogen or oxygen ligands as a leaving group, which always occupies the apical position. However, in the reaction of chalcogenides with organolithium reagents [5], both the leaving and attacking groups are carbon ligands, and hence,

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it has been difficult to predict the apicophilicity among the ligands.

In order to decide the apicophilic priority of the carbon ligands bearing substituents, ligand exchange reactions of pentafluorophenyl phenyl telluride (**1**) and 3,5-dichloro-2,4,6-trifluorophenyl phenyl telluride (**2**) were carried out with pentafluorophenyllithium in tetrahydrofuran (THF). The reactions were monitored by ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy at low temperature. Actually, when the reactions were carried out in an NMR tube at low temperature, the ^{125}Te NMR spectra of tellurides (**1**) and (**2**), respectively, appeared as a singlet peak shifted upfield at −105°C by addition of aryllithiums. Similar high-field shifts of the ^{125}Te chemical shift have been observed in the reaction of diphenyl telluride with phenyllithium at −78°C [2a,2b,3]. Consequently, the NMR chemical shifts observed in the present reactions indicate that the hypervalent telluranes [ate complexes, 10-Te-3(C3)] are also formed in the reactions of tellurides (**1**) and (**2**) with pentafluorophenyllithium. Alternatively, when pentafluorophenyl phenyl and 3,5-dichloro-2,4,6-trifluorophenyl phenyl selenides (**3**) and (**4**) were treated with pentafluorophenyllithium or 3,5-dichloro-2,4,6-trifluorophenyllithium at −78°C, similar ^{1}H, ^{13}C, ^{19}F, and ^{77}Se NMR behavior was observed in the reactions of selenides with aryllithiums. This is the first observation of the formation of selenium ate complexes [10-Se-3(C3)] having three carbon ligands. This article describes the formation of ate complexes of tellurium and selenium bearing carbon ligands and clarifies the observation that the electronegative ligands always occupy the apical positions, and the exchange should take place at the apical-apical geometry.

RESULTS AND DISCUSSION

Formation of Tellurium Ate Complexes in the Reactions of Tellurides with Aryllithiums

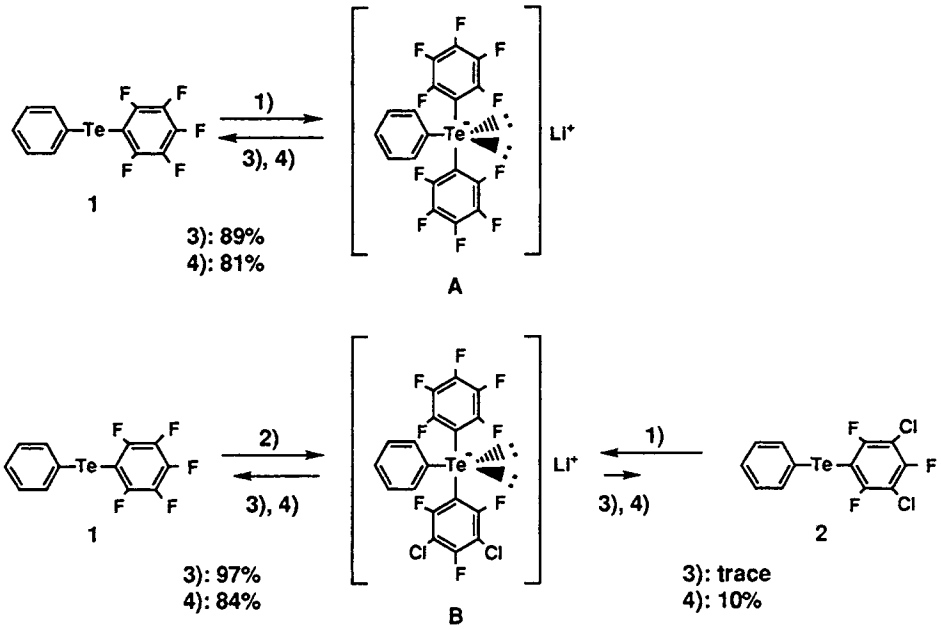
The tellurides employed in the reactions were pentafluorophenyl phenyl (**1**) and 3,5-dichloro-2,4,6-trifluorophenyl phenyl (**2**) tellurides, which were prepared by the reaction of diphenyl ditelluride with pentafluorophenylmagnesium bromide and with 3,5-dichloro-2,4,6-trifluorophenyllithium, respectively.

Telluride (**1**) in THF was treated with an equimolar amount of 3,5-dichloro-2,4,6-trifluorophenyllithium in THF under an argon atmosphere for 15 minutes at −78°C, and then the mixture was treated with water. After the usual workup procedure, the residue was purified by column chromatography, followed by preparative liquid chromatography, to afford a mixture of tellurides (**1**) and (**2**) in quantitative yields. However, by changing the temperature at which the workup was carried out, the mixture obtained was composed of tellurides (**1**) and (**2**) in a different ratio; namely, at −78°C, telluride (**1**) was recovered along with a trace of telluride (**2**), while at room temperature, the products obtained were a mixture of tellurides (**1**) and (**2**) in 84 and 10% yields, respectively. On the other hand, when telluride (**2**) was allowed to react with pentafluorophenyllithium by the same procedure as that used for (**1**), telluride (**1**) was formed quantitatively, as shown in Scheme 1. Meanwhile, on treatment of telluride (**1**) with an equimolar amount of pentafluorophenyllithium in THF, followed by treatment with water, the telluride (**1**) was recovered quantitatively. These results clearly indicate that ligand exchange takes place completely between the more electronegative ligand attached to the tellurium and the pentafluorophenyl anion, while the phenyl group on tellurides (**1**) and (**2**) always remains unchanged. Comparison of the leaving ability between pentafluorophenyl and 3,5-dichloro-2,4,6-trifluorophenyl groups reveals that the former should be more electropositive than the latter, since 3,5-dichloro-2,4,6-trifluorophenyl should be more electronegative than the pentafluorophenyl group; this trend agrees with the Hammett σ values of the two ligands; namely, the σ_m value of Cl is +0.373 and that of F is +0.337 (Scheme 1) [6].

As described in our previous article and indicated by Reich's results on the lithium-tellurium exchange, the formation of triphenyltellurium ate complex as an intermediate has been confirmed by ^{1}H, ^{13}C, ^{7}Li, and ^{125}Te NMR techniques at low temperatures [2a,2b,3]. Thus, on careful addition of pentafluorophenyl lithium at −105°C, the ^{125}Te NMR signals of tellurides (**1**) and (**2**) in THF observed at 533.5 and 560.5 ppm (at −105°C) disappeared at once, and a large upfield shift of ^{125}Te NMR at 168.9 and 164.5 ppm was observed as a sole signal, respectively, as shown in Table 1 and Figure 1.

These large upfield shifts of ^{125}Te NMR indicate that the ate complexes (**A**) and (**B**) are formed as intermediates on addition of aryllithium reagents to the tellurides (**1**) and (**2**). These ^{125}Te NMR spectra are rationalized in terms of the increase in the electron density at the central tellurium atom of the hypervalent ate complexes as well as the triphenyltellurium ate complex previously reported [3]. On warming the reaction mixture in an NMR tube, these ^{125}Te NMR signals shift again to 527.5 and 549.6 ppm, which are assigned as those of tellurides (**1**) and (**2**) at room temperature, and the ratios are nearly identical to those of the isolated tellurides, demonstrating that the exchange reaction between two carbon ligands takes place at room temperature.

Furthermore, the formation of ate complexes (**A**) and (**B**) was confirmed by measuring the ^{1}H, ^{19}F, and ^{13}C NMR spectra. Both the ^{1}H and ^{19}F NMR



SCHEME 1 1) One equivalent of pentafluorophenyllithium at −78°C in THF under an argon atmosphere. 2) One equivalent of 3,5-dichloro-2,4,6-trifluorophenyllithium at −78°C in THF under an argon atmosphere. 3) Quenched with H_2O at −78°C and usual workup. 4) Quenched with H_2O at room temperature and usual workup.

TABLE 1 ^{125}Te, ^{1}H, and ^{19}F NMR Data at −105°C

		Positions and Chemical Shifts, δ					
		^{1}H			*^{19}F*		
Compound (THF-d_8)	*^{125}Te*	*ortho*	*meta*	*para*	*ortho*	*meta*	*para*
1	533.5	7.84	7.26	7.34	−116.9	−162.6	−155.0
2	560.5	7.85	6.93	7.01	−88.8	—	−109.8
A	168.9	7.87	6.95	7.04	−117.1	−162.7	−162.6
B	164.5	7.85	7.01	6.93	−128.5	−163.9	−163.8[a]
					−108.3	—	−115.4[b]

[a]pentafluorophenyl group.
[b]3,5-dichloro-2,4,6-trifluorophenyl group.

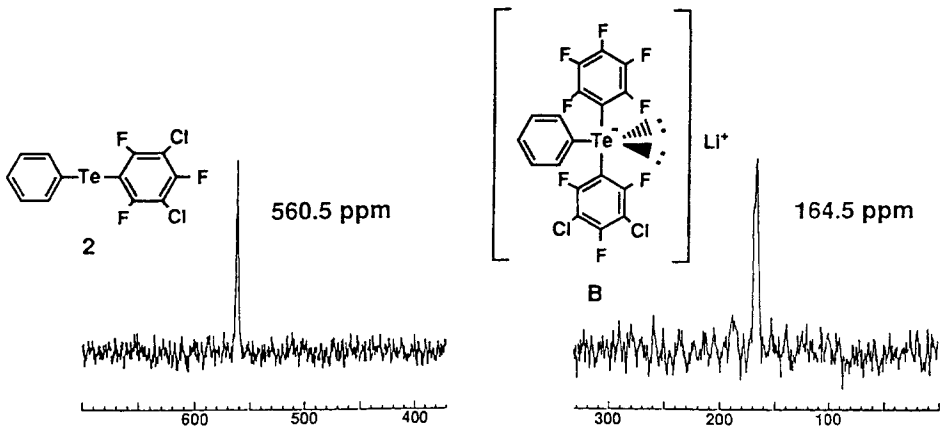


FIGURE 1 ^{125}Te NMR spectra (126 MHz) of 3,5-dichloro-2,4,6-trifluorophenyl phenyl telluride (left) and ate complex **B** (right) at −100°C in THF.

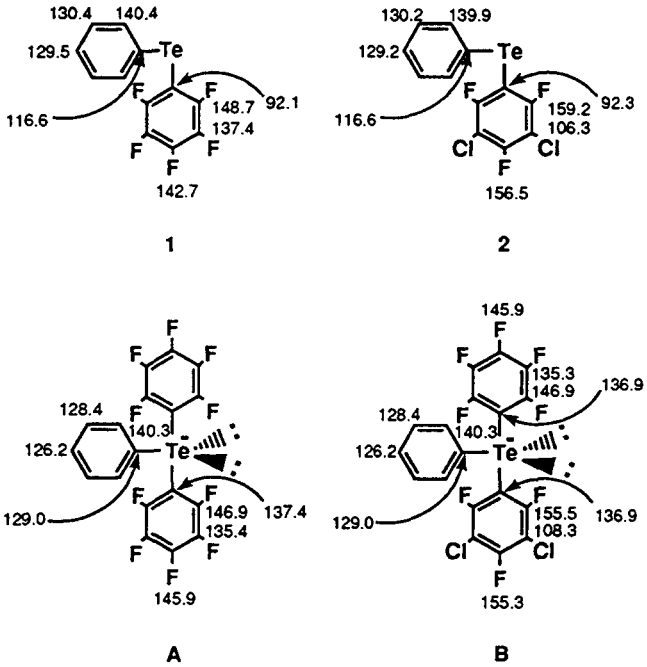


FIGURE 2 ^{13}C NMR chemical shifts in THF-d_8 at −105°C.

data reveal the arrangement of the three aryl ligands around the hypervalent tellurium center, as shown in Table 1. The ^{1}H NMR spectra of (**A**) and (**B**) demonstrate the presence of only one kind of phenyl ring attached to the tellurium atom at −105°C. The ^{19}F NMR spectrum of (**A**) at −105°C indicates that the pentafluorophenyl rings should occupy the two apical positions. Contrariwise, in the case of ate complex (**B**), the arrangement of the three aryl rings could not be determined by ^{1}H and ^{19}F NMR spectra. However, we assumed that the equatorial positions are occupied by one phenyl group and two lone pairs of electrons, while the two apical positions should be occupied by the two electronegative groups, pentafluorophenyl and 3,5-dichloro-2,4,6-trifluorophenyl, because the ^{1}H and ^{19}F NMR spectra of ate complex (**B**) are quite similar to those of ate complex (**A**). This assumption is also supported by measuring the ^{13}C NMR spectra of complexes (**A**) and (**B**).

Low-temperature ^{13}C NMR spectra (−105°C) of these ate complexes (**A**) and (**B**) in THF-d_8 were measured, and the chemical shifts were compared with those of tellurides (**1**) and (**2**). The data support strongly the validity of the assigned structures of (**A**) and (**B**), as shown in Figure 2. Namely, in the ^{13}C NMR spectra, the chemical shift for one ipso carbon at the equatorial position (from 116.6 to 129.0 ppm) shows a small downfield shift similar to that of five other carbons at the phenyl ring, while the other two ipso chemical shifts for the apical position appear strongly downfield (from 92.1 to 137.4 ppm (**A**) or 92.3 to 136.9 ppm (**B**)]. These ^{13}C NMR chemical shifts can be ascribed to the formation of hypervalent apical bonds and the development of negative charge on the electron-withdrawing apical ligands analogously observed in the triphenyltellurium ate complex [2a,2b,3] and as predicted by MO calculations [7]. These results clearly indicate (1) that, in ate complexes (**A**) and (**B**), the equatorial positions are occupied by one phenyl group and two lone pairs of electrons, and the apical positions are occupied by two electronegative aryl groups and (2) that ligand exchange should always take place between apical-oriented groups (Figure 2).

Interestingly, these results support our understanding that there is no symptom for ligand interchange, namely, pseudorotation, even in the triphenyltellurium ate complex, although the phenomenon of pseudorotation has been observed in general in hypervalent tellurium and selenium compounds, such as tetraphenyltellurane [5g,8] and bis(2,2′-biphenylylene)tellurane [5d,9]. In these tricoordinated ate complexes, higher energy should be required for pseudorotation than in tetracoordinated hypervalent compounds, since, for conversion, at least one lone electron pair must be placed at the apical position, thus preventing pseudorotation in these ate complexes.

Present observations seem to favor the interpretation that the process of nucleophilic substitution at the tellurium atom proceeds via the attack of the organolithium reagent from the backside of the leaving group, with formation of the trigonal bipyramidal compound as an intermediate in which the two electronegative carbon ligands should be situated at the apical positions of the most stable isotopomer.

First Formation of Se-Ate Complexes in the Reactions of Diaryl Selenides with Aryllithiums

In diaryl chalcogenides, tellurides undergo facile ligand exchange reactions with organolithium reagents and the intermediary tellurium ate complexes can be detected as described earlier. On the other hand, diaryl selenides do not, in general, react with organolithium reagents except in the case of a few selenides having strongly electron-withdrawing substituents on the α-carbon, such as silyl or diselenoacetal groups [10]. For example, diphenyl selenide did not react at all with butyllithium or phenyllithium. However, we have noticed that selenides having pentafluorophenyl or 3,5-dichloro-2,4,6-trifluorophenyl groups undergo ligand exchange reactions on treatment with organolithium reagents. Hence, by employing low-temperature NMR techniques, we have succeeded in detecting the intermediary ate complexes of diaryl selenides in THF in the presence of hexamethylphosphoric triamide (HMPA).

The compounds used in these experiments were pentafluorophenyl phenyl (**3**) and 3,5-dichloro-2,4,6-trifluorophenyl phenyl (**4**) selenides, which were prepared according to the same method employed in the synthesis of tellurides (**1**) and (**2**).

When selenide (**3**) was treated with an equimolar amount of pentafluorophenyllithium or 3,5-dichloro-2,4,6-trifluorophenyllithium at −78°C in THF in the presence of HMPA, the selenide (**3**) was recovered quantitatively after hydrolysis. On the other hand, the reaction of selenide (**4**) with pentafluorophenyllithium also gave selenide (**3**); however, the product ratio depends on the temperature at which the reactions are carried out, as shown in Scheme 2.

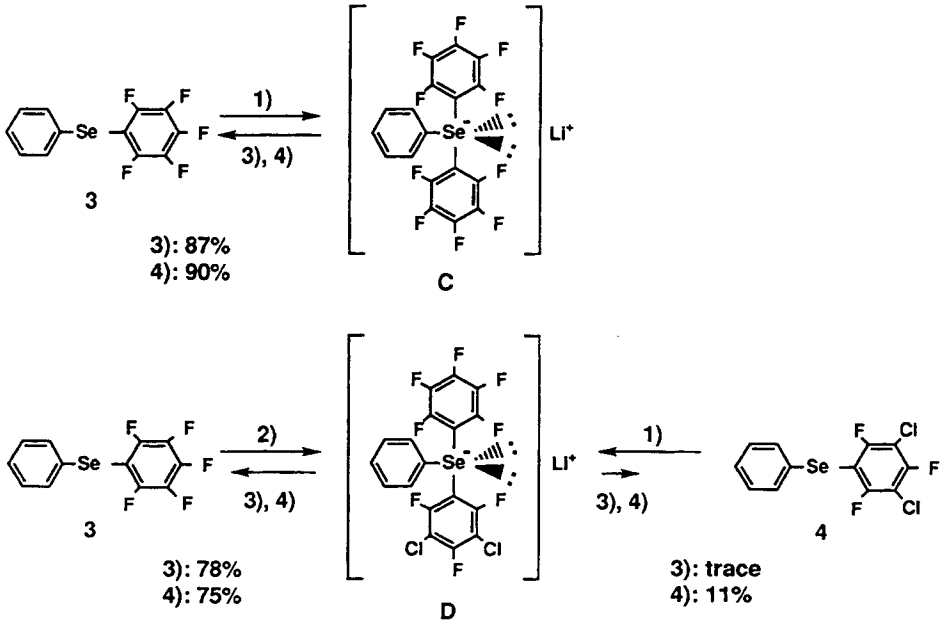
The results imply that this lithium-selenium exchange reaction takes place via the formation of an ate complex of Se [10-Se-3(C3)]. We tried to detect the formation of a selenium ate complex, which is an intermediate for the ligand exchange reaction, by ^{77}Se NMR spectroscopy. The ^{77}Se NMR chemical shift of selenide (**3**), which appeared at 259.1 ppm at −105°C (270.2 ppm at 20°C), disappeared at once, and new chemical shifts appeared at 256.8 or 257.9 ppm, these being assigned to the ate complexes (**C**) and (**D**), respectively, upon the addition of pentafluorophenyllithium or 3,5-dichloro-2,4,6-trifluorophenyllithium at −105°C to this solution. Similar treatment of selenide (**4**) (^{77}Se: 274.4 ppm) with an equimolar amount of pentafluorophenyllithium showed a singlet peak at 257.9 ppm corresponding to a signal of selenium ate complex (**D**).

Moreover, the ^{77}Se NMR signal of selenide (**3**) was observed at room temperature in the reaction of selenide (**3**) with pentafluorophenyllithium when a variable temperature NMR experiment was conducted, as shown in Figure 3. Consequently, the chemical shifts of ^{77}Se NMR, although the changes of chemical shifts are small but significant, suggest that the selenium ate complexes (**C**) and (**D**) are formed as intermediates in the reactions.

Furthermore, ^{19}F, ^{13}C, and ^{1}H NMR spectra of ate complexes (**C**) and (**D**) in THF-d_8 at −105°C were measured, and the results are shown in Table 2 and Figure 4.

These ^{19}F, and ^{13}C NMR data reveal that the ate complex (**C**) should have only one kind of phenyl group and two pentafluorophenyl ligands, while the ate complex (**D**) should have both pentafluorophenyl and 3,5-dichloro-2,4,6-trifluorophenyl groups.

A similar small change of the chemical shifts of ^{77}Se NMR has been observed in the reaction of a triphenylselenonium salt with phenyllithium, where the formation of tetraphenylselenurane has been observed [11]. The trend of the ^{13}C NMR behavior of (**C**) and (**D**), in comparison with that of the starting phenyl aryl selenides, resembles that of the intermediary formed ate complexes observed in the Te-Li exchange reaction; hence, these results imply the formation of selenium ate complexes in the reactions of pentafluorophenyl phenyl



SCHEME 2 1) One equivalent of pentafluorophenyllithium at −78°C in THF under an argon atmosphere. 2) One equivalent of 3,5-dichloro-2,4,6-trifluorophenyllithium at −78°C in THF under an argon atmosphere. 3) Quenched with H_2O at −78°C and usual workup. 4) Quenched with H_2O at room temperature and usual workup.

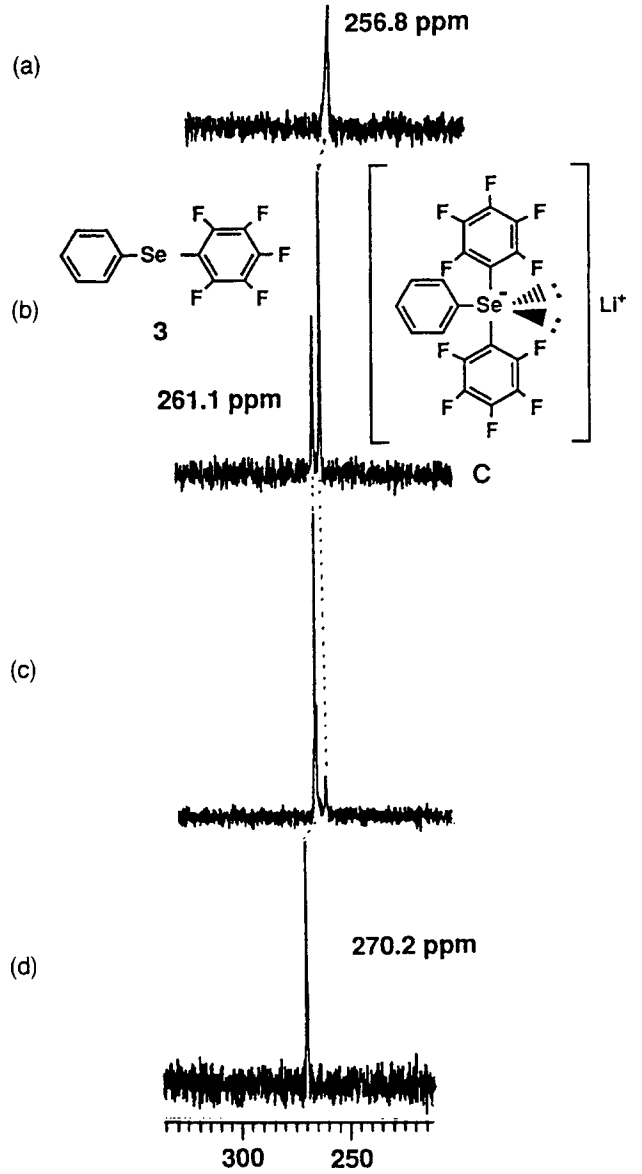


FIGURE 3 Variable temperature ^{77}Se NMR of C: (a) 173, (b) 183, (c) 193, and (d) 293 K.

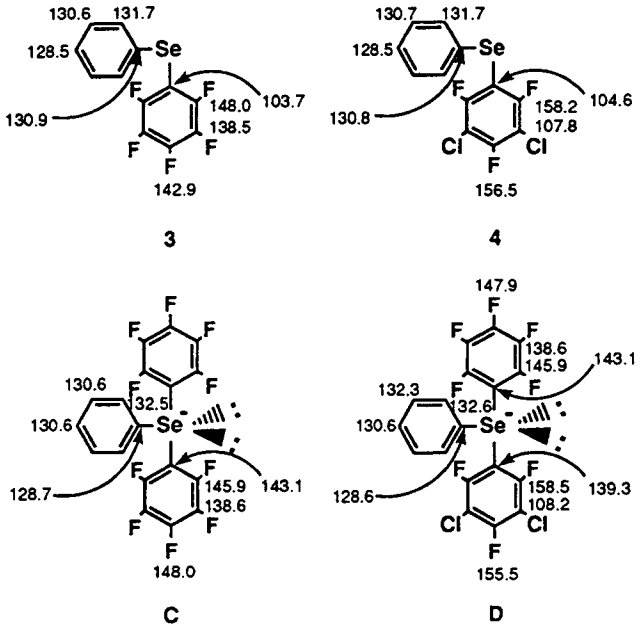


FIGURE 4 ^{13}C NMR chemical shifts in THF-d_8 at −105°C.

selenide and 3,5-dichloro-2,4,6-trifluorophenyl phenyl selenide with pentafluorophenyllithium or 3,5-dichloro-2,4,6-trifluorophenyllithium. The NMR spectral data suggest that the selenium ate complexes (**C**) and (**D**) have one phenyl group and two lone pairs electrons in the equatorial positions, with two electronegative groups in the apical positions. Consequently, these results demonstrate that the apical-directing exchange reactions proceed via a selenium ate complex [10-Se-3(C3)] as an intermediate.

As a novel result of the formation of a selenium ate complex, Reich and his co-workers have reported that 4-deuterio-6-(2-trimethyltinphenyl)-dibenzoselenophene affords the selenium ate complex (**5**) on treatment with methyllithium, as shown in Figure 5 [12].

Normally, a dicoordinated diaryl sulfide does not react at all with organometallic reagents. However, both the corresponding diaryl selenides and tellurides react with organolithium reagents to give the hypervalent ate complexes, which have never been isolated but only detected by low-temperature NMR techniques. Thus, the qualitative stability of the hypervalent ate complexes among chalcogen elements lies in the order Te > Se > S.

EXPERIMENTAL

All melting points are uncorrected. NMR spectra were obtained with a JEOL EX-270 or a Bruker AM-500 or Bruker MSL-400 spectrometer. Mass spectra were taken with a Shimadzu GCMS QP-2000A mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center at the University of Tsukuba. All reagents were obtained from Wako Pure Chemical Industries, Ltd. or Aldrich Chemical Co. The reaction solvents were further purified and dried by general methods.

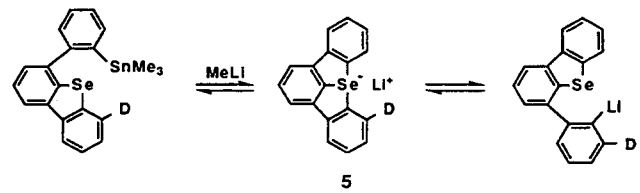


FIGURE 5

TABLE 2 ^{77}Se, ^1H, and ^{19}F NMR Data in −105°C

Compound (THF-d_8)	^{77}Se	Positions and Chemical Shifts, δ				
		^1H		^{19}F		
		ortho	meta-para	ortho	meta	para
3	259.1	7.69	7.48	−128.8	−163.1	−154.7
4	274.4	7.66	7.50	−100.9	—	−112.3
C	256.8	7.69	7.48	−128.5	−163.1	−154.7
D	257.9	7.67	7.48	−128.5	−163.1	−154.7[a]
				−107.8	—	−115.5[b]

[a]Pentafluorophenyl group.
[b]3,5-Dichloro-2,4,6-trifluorophenyl group.

Preparation of Diaryl Tellurides

Diphenyl ditelluride, which was used as a starting material for the synthesis of unsymmetrical diaryl tellurides, was obtained by the following procedure. To a solution of 1.09M phenylmagnesium bromide (0.38 mol, 350 mL) was added dry tellurium powder (50 g, 0.39 mol) under an N_2 atmosphere. After having been stirred for 30 minutes at room temperature, the mixture was treated with oxygen gas for 30 minutes. The mixture was poured onto cracked ice (200 g), and the solution was neutralized with aqueous HCl. The cold mixture was separated by filtration, and the filtrate was extracted with chloroform (200 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was recrystallized from hexane to give 58 g (73%) of diphenyl ditelluride as red crystals: mp 64–65°C [13]; ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, J = 7.6 Hz, 4H, 3,5-PhH), 7.23 (t, J = 7.6 Hz, 2H, 4-PhH), 7.78 (d, J = 7.6 Hz, 4H, 2,6-PhH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.9, 128.1, 129.3, 137.6; MS (m/z) 414 (M^+). A stirred solution of diphenyl ditelluride (1.43 g, 3.5 mmol) in THF (20 mL) was cooled to 0°C under an argon atmosphere. To the solution was added bromine (0.2 mL, 3.88 mmol). To the mixture was added dropwise 0.44M pentafluorophenylmagnesium bromide (16.04 mL, 6.99 mmol) at 0°C, and the mixture was stirred for 30 minutes at room temperature. After neutralization with 2M HCl solution, the solution was treated with aqueous ammonium chloride and extracted with ether (100 mL × 3). The combined ether layer was dried over anhydrous magnesium sulfate, and solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent hexane) to give pure pentafluorophenyl phenyl telluride. 3,5-Dichloro-2,4,6-trifluorophenyl phenyl telluride was prepared by a similar procedure.

Pentafluorophenyl Phenyl Telluride. Yield 2.4 g (93%); pale yellow crystals; mp 30–31°C; ^1H NMR (400 MHz, THF-d_8) δ 7.23 (t, J = 7.4 Hz, 2H, 3,5-PhH), 7.32 (t, J = 7.4 Hz, 1H, 4-PhH), 7.85 (d, J = 7.4 Hz, 2H, 2,6-PhH); ^{19}F NMR (376 MHz, THF-d_8) δ −163.1 (t, J = 19.7 Hz, 2F, 3,5-ArF), −155.2 (t, J = 19.7 Hz, 1F, 4-ArF), −117.0 (d, J = 19.7 Hz, 2F, 2,6-ArF); ^{13}C NMR (101 MHz, THF-d_8) δ 89.4, 114.2, 129.6, 130.3, 137.6, 140.2, 143.1, 148.8; ^{125}Te NMR (126 MHz, THF) δ 530.9; MS m/z 374 (M^+). Anal. found: C, 38.53; H, 1.43%. Calcd for $C_{12}H_5F_5Te$: C, 38.77; H, 1.36%.

3,5-Dichloro-2,4,6-trifluorophenyl Phenyl Telluride. Yield 1.38 g (49%); pale yellow crystals; mp 47–48°C; ^1H NMR (400 MHz, THF-d_8) δ 7.23 (t, J = 7.3 Hz, 2H, 3,5-PhH), 7.32 (t, J = 7.3 Hz, 1H, 4-PhH), 7.85 (d, J = 7.3 Hz, 2H, 2,6-PhH); ^{19}F NMR (376 MHz, THF-d_8) δ −109.8 (s, 1F, 4-ArF), −88.8 (s, 2F, 2,6-ArF), ^{13}C NMR (101 MHz, THF-d_8) δ 89.4, 106.8, 114.4, 129.4, 130.2, 140.0, 157.0, 159.5; ^{125}Te NMR (126 MHz, THF) δ 553.2; MS m/z 406 (M^+). Anal. found: C, 35.70; H, 1.47%. Calcd for $C_{12}H_5Cl_2F_3Te$: C, 35.35; H, 1.24%.

Preparation of Diaryl Selenides

A stirred solution of diphenyl diselenide (4.80 g, 15.36 mmol) in THF (20 mL) was cooled to 0°C under an argon atmosphere. To the solution was added bromine (0.8 mL, 16 mmol). To the mixture was added dropwise 0.61M pentafluorophenyllithium (52.5 mL, 32 mmol) at 0°C, and the mixture was stirred for 30 minutes at room temperature. After neutralization with 2M HCl solution, the solution was treated with aqueous ammonium chloride and extracted with chloroform (100 mL × 3). The combined chloroform layer was dried over anhydrous magnesium sulfate, and solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent hexane) to give pure pentafluorophenyl phenyl selenide. 3,5-Dichloro-2,4,6-trifluorophenyl phenyl selenide was prepared by a similar procedure.

Pentafluorophenyl Phenyl Selenide. Yield 5.7 g

(55%); pale yellow oil; ^{1}H NMR (270 MHz, THF-d_8) δ 7.29 (m, 3H, 3,4,5-PhH), 7.57 (m, 2H, 2,6-PhH); ^{19}F NMR (254 MHz, THF-d_8) δ −163.3 (t, J = 18.3 Hz, 2F, 3,5-ArF), −155.0 (t, J = 18.3 Hz, 1F, 4-ArF), −128.6 (d, J = 18.3 Hz, 2F, 2,6-ArF); ^{13}C NMR (67 MHz, THF-d_8) δ 104.4, 129.1, 129.5, 130.3, 133.8, 138.5, 142.9, 148.1; ^{77}Se NMR (51 MHz, THF-d_8) δ 264.9; MS m/z 324 (M^+). Anal. found: C, 44.44; H, 1.44%. Calcd for $C_{12}H_5F_5Se$: C, 44.61; H, 1.56%.

3,5-Dichloro-2,4,6-Trifluorophenyl Phenyl Selenide. Yield 1.7 g (68%); pale yellow oil; ^{1}H NMR (270 MHz, THF-d_8) δ 7.29 (m, 3H, 3,4,5-PhH), 7.53 (m, 2H, 2,6-PhH); ^{19}F NMR (254 MHz, THF-d_8) δ −111.5 (s, 1F, 4-ArF), −100.4 (s, 2F,2,6-ArF); ^{13}C NMR (67 MHz, THF-d_8) δ 104.7, 107.9, 129.0, 129.7, 130.3, 133.6, 155.7, 159.3; ^{77}Se NMR (51 MHz, THF-d_8) δ 278.6; MS m/z 356 (M^+). Anal. found: C, 40.34; H, 1.30%. Calcd for C_{12} $H_5U_2F_3Se$: C, 40.48; H, 1.42%.

Ligand Exchange Reactions of Diaryl Tellurides with ArLi

In a typical procedure, to a stirred solution of 3,5-dichloro-2,4,6-trifluorophenyl phenyl telluride (40 mg, 0.1 mmol) in 5 mL THF at −78°C was added 0.76M pentafluorophenyllithium (0.13 mL, 0.1 mmol) in ether solution under an argon atmosphere at −78°C during 15 minutes. After hydrolysis and extraction with chloroform (20 mL × 3), the extract was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Diaryl tellurides were obtained in the ligand exchange reaction and then structures were determined by ^{1}H, ^{13}C, and ^{19}F NMR experiments.

Measurement of the ^{125}Te NMR Spectra

A typical procedure is as follows. Pentafluorophenyl phenyl telluride (185.8 mg, 0.5 mmol) was placed in a 10 mmφ NMR tube under an argon atmosphere. Then, THF (1.7 mL) was added to the tube and the solution was cooled to −105°C. To the solution was added 0.95M pentafluorophenyllithium (0.63 mL, 0.6 mmol) in ether solution at −105°C. The ^{125}Te NMR spectrum was measured by a Bruker MSL-400 spectrometer.

Measurement of the ^{1}H, ^{13}C, and ^{19}F NMR Spectra

A typical procedure is as follows. Pentafluorophenyl phenyl telluride (13 mg, 0.035 mmol) was placed in a 5 mmφ NMR tube under an argon atmosphere. Then, THF-d_8 (0.3 mL) was added to the tube, and the solution was cooled to −105°C. To the solution was added 0.76M pentafluorophenyllithium (0.1 mL, 0.076 mmol) in ether solution at −105°C. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured by a Bruker MSL-400 spectrometer.

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