Heteroatom Chemistry
Volume 3, Number 4, 1992

# NMR Studies on the Ligand Exchange Reactions Between Diaryl Tellurides and Phenyllithium: Detection of Hypervalent Triaryl Tellurium Ate Complexes

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*Received 3 February 1992.*

ABSTRACT

*Diaryl tellurides undergo rapid ligand exchange and disproportionation reactions on treatment with phenyllithium at −78°C. Triaryltelluranes [10-Te-3($C_3$)]$^-$ $Li^+$ were identified as discrete intermediates during the reactions by $^{125}Te$, $^1H$, $^{13}C$, and CH-COSY NMR studies.*

## *INTRODUCTION*

Hypervalent compounds of group 16 elements have become currently attractive species for organic chemists. Recently, many stable hypervalent compounds have been prepared according to Martin's requisites for the ligands attached to the central chalcogen elements, namely, the hypervalent compounds should have two electronegative substituents for the apical ligands and two $\pi$- or electron-donating equatorial ligands [1]. In a series of group 16 elements, the stability of the hypervalent compounds has been known to have the following order: Te > Se > S. Indeed, no hypervalent sulfur compound ($\sigma$-sulfurane) bearing four electropositive carbon ligands has been reported except Sheppard's $(C_6F_5)_4S$ [2]. Recently, we have succeeded in detecting tetraphenylsulfurane ($Ph_4S$) and selenurane ($Ph_4Se$) as unstable intermediates in ligand exchange and coupling reactions [3] of triarylsulfonium (selenonium) salts or diaryl sulfoxides (selenoxides) with phenyllithium [4]. In the case of tellurium, tetraphenyltellurane ($Ph_4Te$) has been isolated and its structure determined by X-ray crystallographic analysis [5].

As another standard for comparison of the reactivity among the organochalcogen compounds and the stability of their intermediates, we reported previously that facile ligand exchange and disproportionation reactions took place via the initial formation of $\sigma$-sulfuranes [10-S-4($C_3$, $O_1$)] or $\sigma$-selenuranes [10-Se-4($C_3$, $O_1$)] as intermediates in the reactions of tricoordinated diaryl sulfoxides or selenoxides with organometallic reagents such as organolithium or Grignard reagents [6, 7]. On the other hand, although dicoordinated diaryl sulfides do not react at all with organolithium or Grignard reagents, diaryl or alkyl aryl selenides and tellurides react readily with organometallic reagents [8], suggesting the possible formation of tiarylselenuranes [10-Se-3($C_3$)]$^-$ $M^+$ or telluranes [10-Te-3($C_3$)]$^-$ $M^+$ ($M^+$ = $Li^+$ or $MgBr^+$) as intermediates. The first mechanistic study of these lithium-calcogen exchange reactions was performed by Reich and his coworkers [9]. Recently, they have reported lith-

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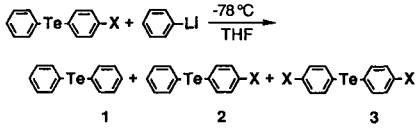
ium-tellurium exchange reactions as evidenced by $^{13}C$ and $^{7}Li$ NMR spectroscopy and disclosed the formation of a triphenyl-tellurium ate complex [10]. Sonoda *et al.* have reported novel generation and synthetic applications of acyl- and aroyl-lithium by lithium-tellurium exchange reactions [11].

As one of the developments of our investigation on the reactions of tri- and di-coordinated organochalcogen compounds, these results prompted us to attempt to detect or to isolate the hypervalent ate complexes of selenium and tellurium compounds in the ligand exchange reactions involving treatment of diaryl selenides and tellurides with organo-lithium reagents. After several trials, we found that the hypervalent ate complexes $[10\text{-}Te\text{-}3(C_3)]^- Li^+$ were formed in the ligand exchange reactions of diaryl tellurides with phenyllithium. This paper reports the detection of $(Ar_3Te)^- Li^+$ together with the facile ligand exchange reactions of diaryl tellurides with phenyllithium by low-temperature $^{125}Te$, $^{1}H$, and $^{13}C$ NMR spectroscopy [12].

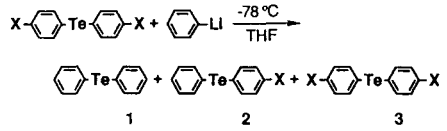
## *RESULTS AND DISCUSSION*

When diaryl tellurides were treated with an equivalent of phenyllithium (PhLi) in tetrahydrofuran (THF) at −78°C, facile ligand exchange reactions took place to give a mixture of three disproportionated tellurides. It has been known that PhLi exists as an equilibrium mixture of monomer and dimer in THF solution. Therefore, we tried the reactions with monomeric PhLi. When diaryl tellurides were treated with a 1:1 mixture of PhLi and hexamethyl-phosphoramide (HMPA) in which PhLi exists as a monomer, [13] three disproportionated tellurides were obtained. The exchange reactions proceeded readily even with 0.2 equivalent of PhLi (Schemes 1 and 2, Tables 1 and 2).

The low-temperature NMR studies were performed in order to obtain reliable evidence for the formation of the intermediates, hypervalent triaryl ate complexes, in the ligand exchange reactions. We chose the reaction of diphenyl telluride with PhLi as a model system of ligand exchange reactions (Scheme 3). The $^{125}Te$ NMR chemical shift of diphenyl telluride appeared at $\delta$ = 670.8 at −100°C. On careful addition of PhLi at −100°C to this solution the peak at $\delta$ = 670.8 disappeared at once to shift enormously upfield to $\delta$ = 310.5 (Figure 1, Table 3). A similar characteristic change of the chemical shift also appeared in the presence of 1




**SCHEME 1**




**SCHEME 2**

equivalent of HMPA or 2 equivalents of tetramethylethylenediamine (TMEDA). The role of HMPA is described above and TMEDA may act as a chelating reagent to lithium cation [14]. These dramatic shifts of $^{125}Te$ NMR reveal that the ate complex **A** is formed on addition of PhLi to diphenyl telluride as an intermediate for the ligand exchange reactions. This large upfield shift of the $^{125}Te$ NMR is explained rationally in terms of the increase in the electron density at the central tellurium atom of the hypervalent ate complex. This peak shifts to $\delta$ = 697.4 when the mixture was warmed to room temperature, which is assigned as that of diphenyl telluride at this temperature.

Furthermore, the low temperature (−100°C) $^{13}C$ NMR spectrum of this ate complex **A** in THF-$d_8$ was measured (Figure 2, Table 3). In these spectra, one ipso carbon shift was similar to those of other carbons, while the other ipso shift was strongly down-field. These unexpected $^{13}C$ chemical shifts can be ascribed to the formation of hypervalent apical bonds and the development of negative charge on the apical ligands, as predicted by MO calculation of trigonal bipyramidal (TBP) structures [15, 16]. These $^{13}C$ NMR results are in satisfactory agreement with the values reported by Reich [10] within experimental error. The $^{1}H$ NMR data (in the presence of 1 equivalent of HMPA) reveal the aromatic protons and their coupling constants in the ate complex **A** (Figure 3 and Table 4).

The chemical shifts of the $^{13}C$ and $^{1}H$ NMR signals were assigned by the cross peaks obtained in two dimensional C—H shift correlation (CH—COSY) spectrum (Figure 4). The CH—COSY spectrum indicates the relative positions of both the protons and the carbon atoms by the chemical shifts and the corresponding cross peaks in the spectrum.

**TABLE 1** Ligand Exchange Reactions of Unsymmetrical Diaryl Tellurides with PhLi

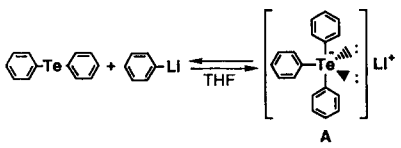
| X | PhLi (eq.) | HMPA (eq.) | Yield (%) 1 | 2 | 3 |
|---|---|---|---|---|---|
| $CH_3$ | 0.2 | 0 | 25 | 50 | 19 |
| $CH_3$ | 1.0 | 0 | 39 | 37 | 17 |
| $CH_3$ | 1.0 | 1.0 | 35 | 50 | 15 |
| $CH_3O$ | 1.0 | 0 | 44 | 41 | 8 |
| $CH_3O$ | 1.0 | 1.0 | 43 | 30 | 8 |
| Cl | 0.2 | 0 | 23 | 62 | 6 |
| Cl | 1.0 | 0 | 36 | 46 | 1 |
| Cl | 1.0 | 1.0 | 24 | 55 | 8 |

**TABLE 2** Ligand Exchange Reactions of Symmetrical Diaryl Tellurides with PhLi

| X | PhLi (eq.) | HMPA (eq.) | Yield (%) 1 | 2 | 3 |
|---|---|---|---|---|---|
| $CH_3$ | 1.0 | 0 | 14 | 45 | 39 |
| $CH_3$ | 1.0 | 1.0 | 11 | 23 | 27 |
| $CH_3O$ | 1.0 | 0 | 15 | 48 | 25 |
| $CH_3O$ | 1.0 | 1.0 | 11 | 48 | 40 |
| Cl | 1.0 | 0 | 23 | 69 | 8 |
| Cl | 1.0 | 1.0 | 13 | 77 | 9 |

Both the $^1H$ and $^{13}C$ NMR spectra indicate that the three phenyl rings attached to the central tellurium atom gave different patterns dependent on the two apical and one equatorial groups and that interchange between these two sets of phenyl groups does not take place at this temperature. It is suggested that pseudorotation does not take place at −100°C due to the stability of the present conformation in which the equatorial positions are occupied by one phenyl group and two lone electron pairs while the apical positions are occupied by two relatively electronegative phenyl groups.

Furthermore, we tried to confirm the formation of the ate complexes as intermediates in the ligand exchange and disproportionation reactions of p-substituted diaryl tellurides and PhLi. $^1H$ and $^{13}C$ NMR data were complicated and could not be assigned for their chemical shifts. Therefore, the $^{125}Te$ NMR spectra of these reactions were measured similarly (in the presence of 1 equivalent HMPA) as described above. In a typical example, the six peaks in the $^{125}Te$ NMR spectra were observed for a 1:1 mixture of 4-methylphenyl phenyl telluride (or bis(4-methylphenyl) telluride) and PhLi in the presence of an equivalent amount of HMPA in THF at −100°C (Scheme 4 and Figure 5). Although the hypervalent ate complex formed in the first stage of the nucleophilic attack of PhLi on the tellurium center could not be observed, these spectral data revealed that the ate complexes **A–F** were formed as a consequence of the rapid ligand exchange reactions between the telluride and PhLi. These peaks shifted to the downfield at room temperature and hence they were assigned as the corresponding three disproportionated tellurides (diphenyl, 4-methylphenyl phenyl, and bis(4-methylphenyl) telluride at $\delta$ = 695.6, 680.6, and 667.8, respectively) by comparison with those of the authentic samples in HMPA/THF solution.




**SCHEME 3**

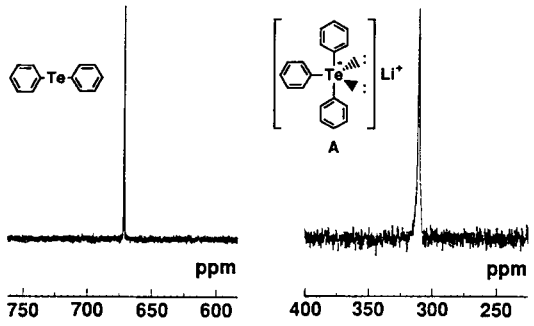



**FIGURE 1** $^{125}Te$ NMR spectra (126 MHz) of diphenyl telluride (left) and ate complex **A** (right) at −100°C in THF.

## *EXPERIMENTAL*

All melting points are uncorrected. NMR spectra were obtained with a Bruker MSL-400 or a Bruker AM-500 instrument. Mass spectra were taken with a Shimadzu GCMS QP-2000A mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center of this University. 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.

### *Preparation of Symmetrical Diaryl Tellurides*

Diaryltellurium dichlorides which were used as starting materials for the synthesis of symmetrical diaryl tellurides were obtained by the modified method of Günther *et al.* [17]. In a typical procedure, a mixture of tellurium tetrachloride (26.6 g, 0.1 mol) and aluminum trichloride (40 g, 0.3 mol) in benzene (300 mL) was heated to reflux with stirring under a $N_2$ atmosphere. The HCl produced immediately in the reaction was swept into aqueous phenolphthalein and NaOH (8.0 g, 0.2 mol) solution. Then, the mixture was poured into ice-water (400 mL) after two equivalents of HCl had evolved

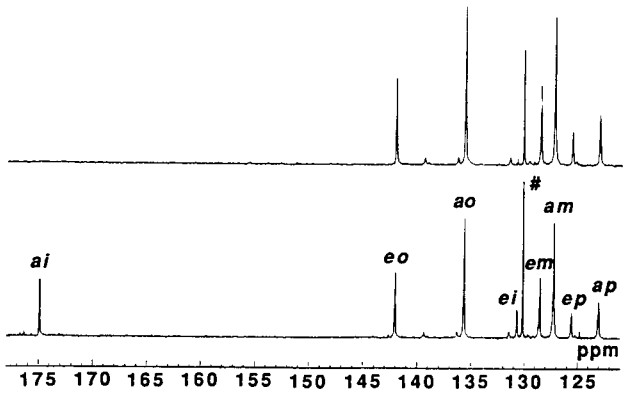



**FIGURE 2** $^{13}C$ NMR spectra (100 MHz) of **A** at −100°C in THF-$d_8$; complete decoupling (lower) and DEPT 90 (upper); [*a*: apical, *e*: equatorial; *i*: ipso, *o*: ortho, *m*: meta, *p*: para; #: benzene].

**TABLE 3** $^{125}$Te and $^{13}$C NMR Data at −100°C

| Compd (THF) or THF-$d_8$) | $\delta^{125}$Te | $\delta^{13}$C apical ipso | ortho | meta | para | equatorial ipso | ortho | meta | para |
|---|---|---|---|---|---|---|---|---|---|
| **A** | 310.5 | 173.9 | 134.7 | 126.3 | 122.1 | 129.8 | 141.1 | 127.6 | 124.6 |
| **A** / HMPA | 320.6 | 174.9 | 135.6 | 127.2 | 123.0 | 130.7 | 142.0 | 128.5 | 125.5 |
| **A** / TMEDA | 310.7 | | | | | | | | |
| $Ph_2Te$ / HMPA | 670.4 | 115.2 | 137.2 | 129.3 | 127.4 | | | | |
| $Ph_2Te$ | 670.8(697.4)[a] | | | | | | | | |

[a] At room temperature.

(the color of the monitoring solution changed from red to colorless). The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. The solid that was obtained on concentration of the solution was recrystallized from ethanol to give 7.2 g (20%) of diphenyltellurium dichloride as colorless crystals: mp 159–160°C (lit. [18] mp 159°C), $^1$H NMR (500 MHz, $CDCl_3$) δ 7.50–7.55 (m, 6H, 3,4,5 PhH), 8.07–8.10 (m, 4H, 2,6 PhH), $^{13}$C NMR (125 MHz, $CDCl_3$) δ 130.1, 131.8, 133.7, 135.5 MS (m/z) 319 ($M^+$-Cl). To a refluxed solution of diphenyltellurium dichloride (3.56 g, 0.01 mol) in ethanol/water (75/8 mL) was added hydrazine (1.67 g, 0.05 mol) in ethanol (10 mL). The mixture was stirred for 5 min, water added (100 mL), and extracted with ether (3 × 100 mL). The combined ether layer was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane) to give pure diphenyl telluride. Other symmetrical diaryl tellurides were prepared by a similar procedure.

*Diphenyl Telluride.* Yield 2.7 g (96%); red liquid [19]; $^1$H NMR (500 MHz, THF-$d_8$) δ 7.20 (t, $J$ = 7.6 Hz, 4H, 3.5-PhH), 7.27 (t, $J$ = 7.6 Hz, 2H, 4-PhH), 7.69 (d, $J$ = 7.6 Hz, 4H, 2,6-PhH); $^{13}$C NMR (125 MHz, THF-$d_8$) δ 115.2, 127.4, 129.3, 137.2; MS (m/z) 284 ($M^+$).

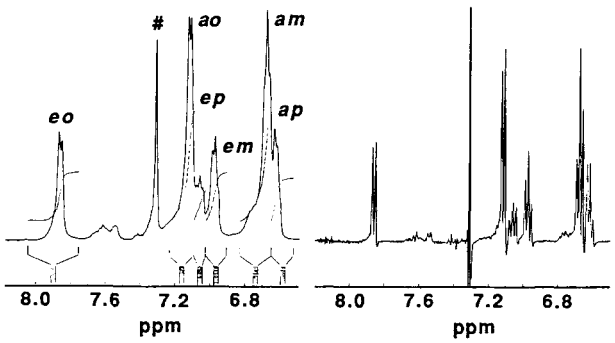



**FIGURE 3** $^1$H NMR spectra (400 MHz) of **A** at −100°C in THF-$d_8$; normal (left) and resolution enhanced (right); [*a*: apical, *e*: equatorial; *o*: ortho, *m*: meta, *p*: para; #: benzene].

*Bis(4-methylphenyl) Telluride.* Yield 309 mg (92%); Colorless crystals; mp 60°C (lit. [18] mp 64°C); $^1$H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 6H, $CH_3$), 7.02, 7.58 (ABq, $J$ = 7.9 Hz, 8H, ArH); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 21.2, 110.7, 130.4, 137.8, 138.1; MS (m/z) 312 ($M^+$).

*Bis(4-chlorophenyl) Telluride.* Yield 590 mg (71%); Colorless crystals; mp 97–98°C (lit. [20] mp 98°C); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.20, 7.60 (ABq, $J$ = 8.3 Hz, 8H, ArH); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 112.0, 129.9, 139.4, 142.6; MS (m/z) 352 ($M^+$).

*Bis(4-methoxyphenyl) Telluride.* Yield 318 mg (93%); Colorless crystals; mp 52°C (lit. [19] mp 55–57°C); $^1$H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 6H, $CH_3O$), 6.77, 7.63 (ABq, $J$ = 8.8 Hz, 8H, ArH); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 55.2, 104.3, 115.4, 139.7, 159.7; MS (m/z) 344 ($M^+$).

## *Preparation of Unsymmetrical Diaryl Tellurides*

Preparation of 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 powdered tellurium (50 g, 0.39 mol) under a $N_2$ atmosphere. After having been stirred for 30 min at room temperature, the mixture was treated with oxygen gas for 30 min. The mixture was poured upon cracked ice (200 g) and neutralized with aqueous HCl. The cold mixture was filtered, and the filtrate was extracted with chloroform (3 × 200 mL). 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-orange crystals: mp 64–65°C (lit. [17] mp 65°C), $^1$H 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,

**TABLE 4** $^1$H NMR Data at −100°C

| Compd (THF-$d_8$) | Chemical Shift, δ | |
|---|---|---|
| | *Apical* | *Equatorial* |
| **A** / HMPA | 6.62 (t, 2H, *J* = 6.9 Hz, *para*)<br>6.68 (t, 4H, *J* = 6.9 Hz, *meta*)<br>7.12 (d, 4H, *J* = 6.9 Hz, *ortho*) | 7.06 (t ,1H, *J* = 7.3 Hz, *para*)<br>6.97 (t, 2H, *J* = 7.3 Hz, *meta*)<br>7.86 (d, 2H, *J* = 7.3 Hz, *ortho*) |
| $Ph_2Te$[a] | 7.20 (t, 4H, *J* = 7.6 Hz, *meta*),<br>7.69 (d, 4H, *J* = 7.6 Hz, *ortho*) | 7.27 (t, 2H, *J* = 7.6 Hz, *para*), |

[a] 25°C in $CDCl_3$.

137.6. MS (m/z) 414 ($M^+$). A stirred solution of diphenyl ditelluride (3.37 g, 8.24 mmol) in THF (20 mL) was cooled to 0°C under an argon atmosphere. To the solution was added bromine (0.5 mL, 9.69 mmol). To the mixture was added dropwise 0.74M 4-methylphenylmagnesium bromide (33.8 mL, 25 mmol), and the mixture was stirred for 30 min at room temperature. After neutralization with 2M HCl solution, the mixture was treated with aqueous ammonium chloride and extracted with ether (3 × 100 mL). The combined ether layer was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane) to give pure 4-methylphenyl phenyl telluride. Other unsymmetrical diaryl tellurides were prepared by similar procedures.

*4-Methylphenyl Phenyl Telluride.* Yield 4.16 g (86%); red liquid [21]; $^1$H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3H, $CH_3$), 7.04, 7.63 (ABq, *J* = 7.8 Hz, 4H, ArH), 7.17 (t, *J* = 7.6 Hz, 2H, 3,5-PhH), 7.23 (t, *J* = 7.6 Hz, 1H, 4-PhH), 7.63 (d, *J* = 7.6 Hz, 2H, 2,6-PhH); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 21.2, 110.2, 115.2, 127.5, 129.3, 130.4, 137.2, 138.0, 138.7; MS (m/z) 298 ($M^+$).

*4-Methoxyphenyl Phenyl Telluride.* Yield 1.83 (52%); Colorless crystals; mp 59–60°C (lit. [21] mp 60–61°C); $^1$H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 3H, $CH_3O$), 6.80, 7.74 (ABq, *J* = 8.7 Hz, 4H, ArH), 7.16 (t, *J* = 7.1 Hz, 2H, 3,5-PhH), 7.21 (t, *J* = 7.1 Hz, 1H, 4-PhH), 7.56 (d, *J* = 7.1 Hz, 2H, 2,6-PhH); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 55.2, 103.2, 115.5, 115.9, 127.3, 129.3, 136.4, 141.2, 160.0; MS (m/z) 314 ($M^+$).

*4-Chlorophenyl Phenyl Telluride.* Yield 2.0 g (99%); Red liquid [22]; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.2 Hz, 2H, 3,5-PhH), 7.30 (t, *J* = 7.2 Hz, 1H, 4-PhH), 7.17, 7.59 (ABq, *J* = 8.4 Hz, 4H, ArH), 7.69 (d, *J* = 7.2 Hz, 2H, 2,6-PhH); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 112.4, 114.4, 128.1, 129.6, 129.7, 134.3, 138.2, 139.2; MS (m/z) 318 ($M^+$).

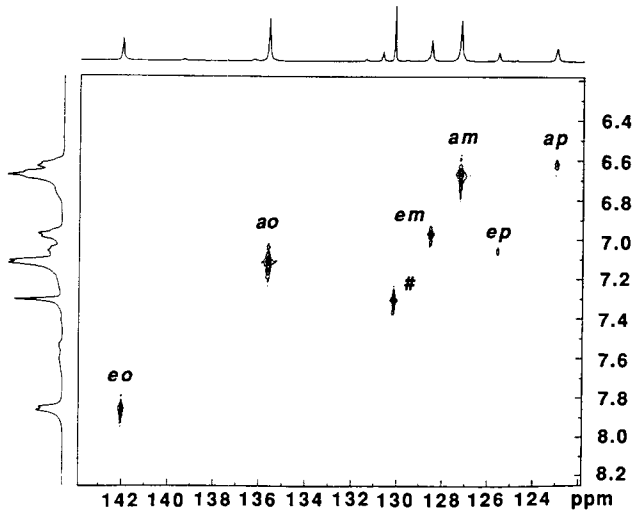
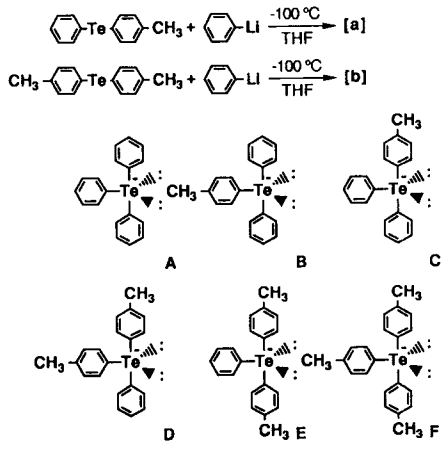



**FIGURE 4** CH-COSY spectrum of **A** at −100°C in THF-$d_8$; [*a*: apical, *e*: equatorial; *o*: ortho, *m*: meta, *p*: para; #: benzene].

## *Ligand Exchange Reactions of Diaryl Tellurides with PhLi*

In a typical run, to a stirred solution of 4-methylphenyl phenyl telluride (74 mg, 0.25 mmol) in THF




**SCHEME 4**

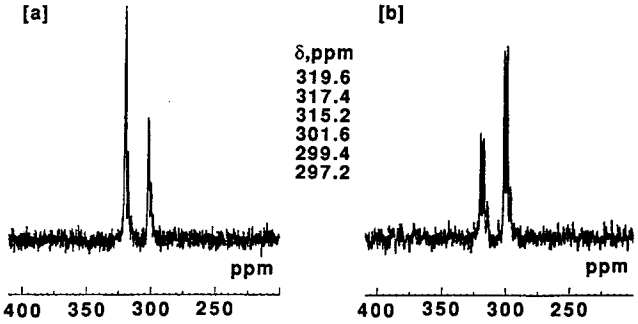



**FIGURE 5** $^{125}$Te NMR spectra (126 MHz) of the reaction mixture of 4-methylphenyl phenyl telluride (bis(4-methylphenyl) telluride) with PhLi at −100°C in THF.

(5 mL) at −78°C was added 1.8M PhLi (0.139 mL, 0.25 mmol) in ether/cyclohexane solution under an argon atmosphere at −78°C. The mixture was stirred at −78°C for 15 min under an argon atmosphere. After hydrolysis and extraction with chloroform (3 × 20 mL), the extract was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The yields of disproportionated diaryl tellurides were determined by GC analysis.

### *Measurement of the $^{125}$Te NMR Spectra*

A typical procedure is as follows. Diphenyl telluride (140.8 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 −100°C. To the solution was added 1.02M PhLi (0.5 mL, 0.51 mmol) in ether/cyclohexane solution at −100°C. The $^{125}$Te NMR spectrum was measured by use of a Bruker MSL-400 instrument.

### *Measurement of the $^{1}$H and $^{13}$C NMR Spectra*

A typical procedure is as follows. Diphenyl telluride (28.2 mg, 0.1 mmol) was placed in a 5 mmφ NMR tube under an argon atmosphere. Then, THF-$d_8$ (0.34 mL) was added to the tube and the solution was cooled to −100°C. To the solution was added 1.02 M PhLi (0.1 mL, 0.102 mmol) in ether/cyclohexane solution at −100°C. $^{1}$H, $^{13}$C, and CH-COSY NMR spectra were measured by use of a Bruker MSL-400 instrument.

## *ACKNOWLEDGMENT*

This work was supported by a Grant-in-Aid for Scientific Research in the Priority area of Organic Unusual Valency, No. 03233101 from the Ministry of Education, Science and Culture, Japan. We thank Professor H. J. Reich, Department of Chemistry, University of Wisconsin, for his helpful discussions of this work.

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