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Recent progress in hypervalent organochalcogenuranes bearing four carbon ligands

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Contents

Abstract

Tetraphenyl- and 2,2′-biphenylylenediphenylsulfuranes and -selenuranes were detected directly by low-temperature NMR experiments. Bis(2,2′-biphenylylene)sulfurane was first isolated as a stable sulfurane having four carbon ligands. Kinetic studies for the ligand coupling reaction of tetraphenylchalcogen compounds Ph_4X (X = S, Se, Te) were monitored by VT-^{1}H NMR studies to estimate the activation parameters for these reactions. We also found that the pseudorotations of bis(2,2′-biphenylylene)selenurane and -tellurane take place slowly with respect to the NMR timescale at low temperature. The energy barriers for

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their pseudorotations were estimated from VT-^{13}C NMR studies. Furthermore, theoretical MO studies of chalcogenuranes(IV) bearing four carbon ligands were carried out concerning their structures, Berry pseudorotations, ligand coupling reactions and non-Berry pseudorotations using the tetramethylchalcogenuranes Me_4X (X = S, Se, Te).

Keywords: **1A** tetraphenylsulfurane; **2A** tetraphenylselenurane; **3A** tetraphenyltellurane; **1B** 2,2′-biphenylylenediphenylsulfurane; **2B** 2,2′-biphenylylenediphenylselenurane; **3B** 2,2′-biphenylylenediphenyltellurane; **1C** bis(2,2′-biphenylylene)sulfurane; **2C** bis(2,2′-biphenylylene)selenurane; **3C** bis(2,2′-biphenylylene)tellurane; **1** triphenylsulfonium hexafluorophosphate; **2** diphenyl sulfoxide; **3** diphenyl sulfide; **4** diphenyl sulfide; **5** triphenylselenonium bromide; **6** diphenyl selenoxide; **7** diphenyl selenide; **8** 2,2′-biphenylylenephenylsulfonium salt; **9** 2,2′-biphenylylenephenylselenonium salt; **10** 2,2′-biphenylylenephenyltelluronium salt; **11** dichlorodiphenyltellurane; **12** phenyl *o*-terphenyl sulfide; **13** phenyl *o*-terphenyl selenide; **14** phenyl *o*-terphenyl telluride; **15** dibenzothiophene; **16** dibenzoselenophene; **17** dibenzotellurophene; **18** dibenzothiophene *S*-oxide; **19** 2,2′-dilithobiphenyl

1. Introduction

Studies on hypervalent organic compounds of chalcogens (chalcogenuranes) have attracted attention because they seem to open a new frontier in chemistry [1–4]. Several stable organic hypervalent compounds having group 16 elements as a central atom have been reported [5–9]. Most of these compounds have strong electronegative ligands (oxygen, nitrogen, halogen) as an apical ligand in order to stabilize the three-center, four-electron (3c–4e) bond. In particular, 1,1,1,3,3,3-hexafluorocumyloxy and 2-acyloxyaryl ligands, which were found by Martin et al. and Kapovitz et al., have been used to synthesize a number of organo-hypervalent compounds and have contributed to the development of organic hypervalent chemistry [10–13]. In contrast, those having only carbon ligands [10–S–4(C4)] [13][1] have been believed to be unstable, and hence are less popular. The formation of tetraphenyl sulfurane was first suggested by Wittig in 1952 [14], and since then numerous works have been presented on the formation of tetraaryl sulfuranes in the reactions of tricoordinated organosulfur compounds with organolithium or Grignard reagents. Among hypervalent sulfur compounds bearing four carbon ligands, only tetra(pentafluorophenyl)sulfurane has been observed as an intermediate by ^{19}F NMR experiments at low temperature [15,16]. Andersen, Oae and Mislow studied the coupling reactions of triarylsulfonium salts with organolithium reagents, and reported indirect evidences for the formation of tetracoordinated sulfur species (σ-sulfuranes) as intermediates [17–19]. Further, the reactions of 2,2′-biphenylylene aryl sulfonium salts with aryllithiums were studied extensively by

[1]Compounds in this paper are designated by the *N–X–L* formalism, where *N* is the number of valence-shell electrons in the atom *X* which are formally involved in bonding *L* as ligands to *X*.

Trost and Hori in order to detect 2,2′-biphenylylene diaryl sulfuranes as intermediates. However, they did not succeed in the direct detection or isolation of these compounds [20–23]. The problem of whether σ-sulfuranes are intermediates or transition states remains unresolved.

In the case of the σ-selenurane bearing four carbon ligands, the reactions of triaryl selenonium salts with organometallic reagents have also long been believed to proceed via the initial formation of the corresponding σ-selenurane. Several stable σ-selenuranes bearing electronegative ligands such as oxygen or halogen atoms have been reported [24–33]. However, these species are fewer than those for the corresponding sulfurane species. No evidence for the formation of σ-selenuranes bound to four carbon ligands had been presented before Hellwinkel isolated bis(2,2′-biphenylylene)selenurane derivatives [34,35]. Recently, Ogawa et al. and the present authors found that diaryl selenoxides undergo facile ligand exchange and coupling reactions upon treatment with organolithium reagents, finally affording diaryl selenide and biaryl via the possible formation of σ-selenurane bearing four carbon ligands [36]. However, the question as to whether tetraphenylselenurane is actually an intermediate or a transition state has also remained unresolved.

Thus, both σ-sulfurane [10–S–4(C4)] and σ-selenurane [10–Se–4(C4)] have been considered as an intermediate or a transition state for the reaction of the corresponding onium salts or oxides with various organometallic reagents. In particular, in the case of the σ-sulfurane species [10–S–4(C4)], no one has succeeded in direct detection, except for one example. Therefore, little is known about the character of these compounds.

On the other hand, the synthesis and structures of the corresponding σ-tellurane species [10–Te–4(C4)] have been reported and characterized by some chemists [6]. Generally, telluranes bearing four carbon ligands are metastable and can be isolated in an inert gas. Since tetraphenyltellurane was reported as the first σ-tellurane species [10–Te–4(C4)] by Wittig in 1952, several σ-tellurane compounds [10–Te–4(C4)] have been synthesized over the past 20 years [37–44]. Of the σ-chalcogenurane species having four carbon ligands, only the structure of tetraphenyltellurane has been determined by X-ray crystallographic analysis [45]. This compound has a distorted trigonal bipyramidal structure. Further, some reactivities of σ-tellurane compounds [10–Te–4(C4)] have been reported by Barton et al. and others [46–49]. Thus, these tellurane species are more popular as compared with the corresponding sulfuranes and selenuranes.

On the basis of the above background, we tried to synthesize and characterize hypervalent organochalcogen(IV) compounds having only carbon ligands in order to solve the remaining problems for the isolation of σ-chalcogen(IV) species having four carbon ligands. Several manipulations should be required in the carbon ligands, namely (1) four simple aryl groups should be used; and (2) five-membered annelation, such as biphenylylene, should be used. We carried out the preparation of the nine target compounds as shown in Fig. 1.

For these compounds, we studied the direct detection of unstable species by the NMR experiments at low temperature, while stable and metastable compounds

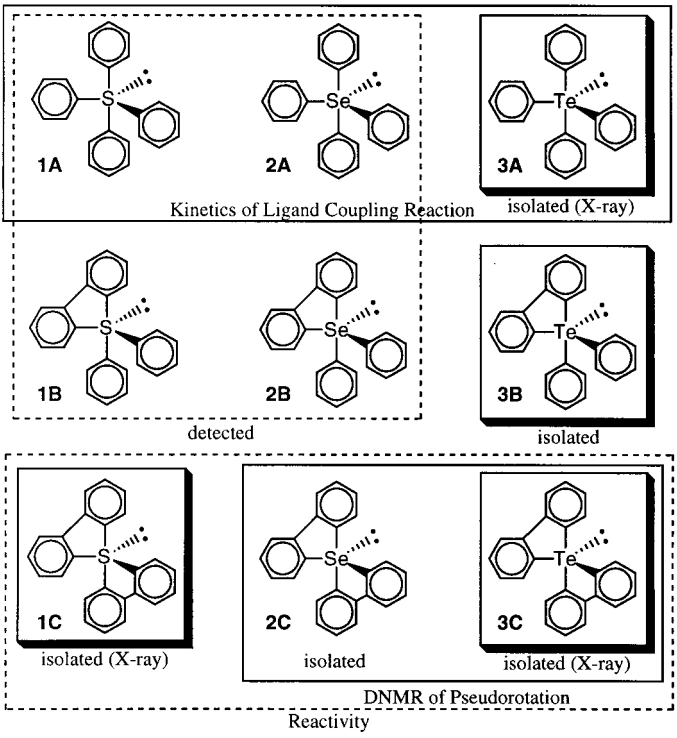


Fig. 1. The target compounds of tetraarylchalcogenurane(IV).

were isolated and their structures were determined by X-ray crystallographic analysis. In the article, we report the characteristic properties of the σ-chalcogen(IV) species having four carbon ligands. Further, the theoretical studies of σ-chalcogenuranes having only carbon ligands are presented.

2. Tetraphenylchalcogenuranes [10–X–4(C4), X = S, Se, Te]

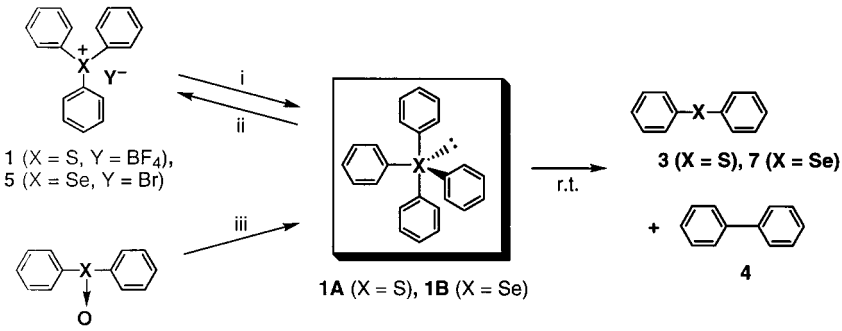
Tetraphenylchalcogenuranes are the most simple, but unstable, among the tetraarylchalcogenurane species. Although only tetraphenyltellurane has been isolated and its crystal structure has been determined, tetraphenylsulfurane and -selenurane have neither been detected directly, nor isolated in the earlier studies. We reinvestigated the reactions of the triphenyl sulfonium salt and diphenyl sulfoxides with phenyllithium (PhLi) in tetrahydrofuran (THF), in order to detect tetraphenylsulfurane [10−S−4(C4)] directly by ^{1}H, ^{13}C and CH-COSY NMR experiments at low temperature. Further, we also tried to obtain the crucial evidence for the formation of tetraphenyl selenurane [10−Se−4(C4)] in the reactions of the triphenyl selenonium salt and diphenyl selenoxide with phenyllithium (PhLi) in a

tetrahydrofuran (THF) solution by the same manners, with NMR experiments employed in the case of the detection of tetraphenylsulfurane. We have succeeded in the detection of tetraphenyl sulfuranes and selenuranes by low temperature NMR studies, while tetraphenyl tellurane has also been isolated.

One of the prominent reactions observed for these species is the ligand coupling reactions [46–49] in the hypervalent compounds, incipiently formed in the reactions between triphenyl chalcogen onium salts with aryllithium [50]. The mechanism for the reaction is considered to take place concertedly between the two ligands on the central atom of chalcogenuranes. However, no kinetic studies on the coupling reactions of the unstable hypervalent compounds have been reported, and it is still unsolved as to whether this reaction proceeds via a concerted unimolecular process, or whether it involves other multi-step processes. Therefore, we carried out kinetic studies of the ligand coupling reactions for these hypervalent chalcogen compounds, in order to determine the order of thermal stability among the chalcogenuranes using tetraphenyl derivatives. Here, we also describe the results on the kinetic studies for the ligand coupling reactions of tetraphenylsulfurane (**1A**), tetraphenylselenurane (**2A**) and tetraphenyltellurane (**3A**), using the variable temperature NMR technique.

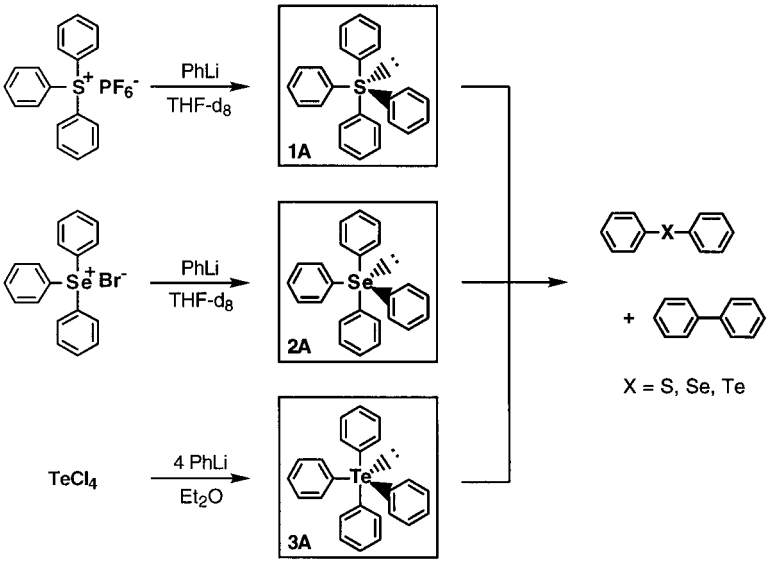
2.1. Detection of tetraphenylsulfurane (Ph_4S) and -selenurane (Ph_4Se) [10–X–4(C4), X = S, Se] [51–53]

When an equimolar amount of PhLi (1.02 M in a cyclohexane/ether solution) was added to a suspension of triphenylsulfonium hexafluorophosphate (**1**) or triphenylselenonium bromide (**5**) in anhydrous tetrahydrofuran (THF) under a N_2 at-



i, 1.0 eq. PhLi, THF, –100 (X = S) or –78 (X = Se) °C
ii, X = S: 0.2 M aq. HPF_6 (Y=PF_6)
X = Se: 0.2 M aq. HBr (Y=Br)
iii, X = S: 1) 1.0eq. $CF_3SO_3Si(CH_3)_3$, THF, -78 °C, 2) 2.0 eq. PhLi, –100 °C.
X = Se: 2.0 eq. PhLi, –78 °C.

Scheme 1.



Scheme 2.

mosphere at −78 °C, each mixture turned to yellowish homogeneous solution. Subsequently, the mixture was treated with a 0.2 M aqueous hexafluorophosphate acid (HPF_6) or a 1 N aqueous HBr solution, to give the recovered sulfonium salt **1**, or the selenonium salt **5**, quantitatively. Similarly, diphenyl sulfoxide (**2**) was treated with trimethylsilyl trifluoromethanesulfonate and two equivalents of PhLi in anhydrous THF under a N_2 atmosphere at −78 °C, and then a 0.2 M aqueous HPF_6 solution was added, which afforded the sulfonium salt **1**, quantitatively. On the other hand, diphenyl selenoxide (**6**) was treated with only two equivalents of PhLi, and then with a 1 N aqueous HBr solution at −78 °C, which afforded the same selenonium salt **5**. Further treatment of **1** and **2** or **5** and **6** with PhLi led to the ligand coupling products, diphenyl sulfide (**3**) and biphenyl (**4**) in 99 and 96%

Table 1
^1H and ^{13}C NMR chemical shifts of tetraphenylsulfurane (**1A**) and -selenurane (**2A**)

	Nuclei	Position and chemical shift (δ)			
	(THF-d_8)	*ipso* (**1**)	*ortho* (**2**)	*meta* (**3**)	*para* (**4**)
1A (−105 °C)	^1H[a]	–	7.27	7.13	7.05
		–	(d, J = 7.3 Hz)	(t, J = 7.3 Hz)	(t, J = 7.3 Hz)
	^{13}C	Not detected	130.1	128.9	127.5
2A (−70 °C)	^1H	–	7.33	7.16	7.12
		–	(t, J = 7.0 Hz)	(t, J = 7.0 Hz)	(d, J = 7.0 Hz)
	^{13}C	Not detected	132.2	130.0	129.0

[a] Coupling constants were calculated by a resolution-enhanced spectrum at −105 °C.

yields, respectively, or diphenyl selenide (**7**) and **4** in 85 and 87% yields, respectively, at an elevated temperature, as shown in Schemes 1 and 2, suggesting that an intermediate like σ-sulfurane **1A** or σ-selenurane **2A** should be formed at a low temperature.

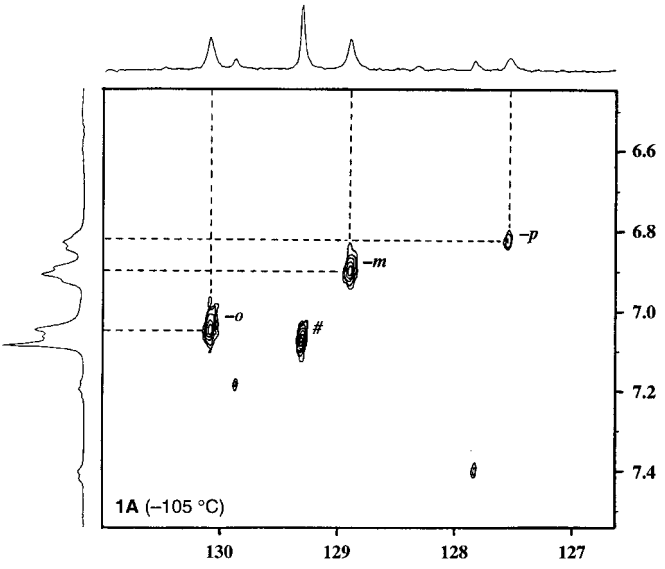


Fig. 2. CH-COSY spectrum of **1A** at low temperature in THF-d_8. (#: benzene).

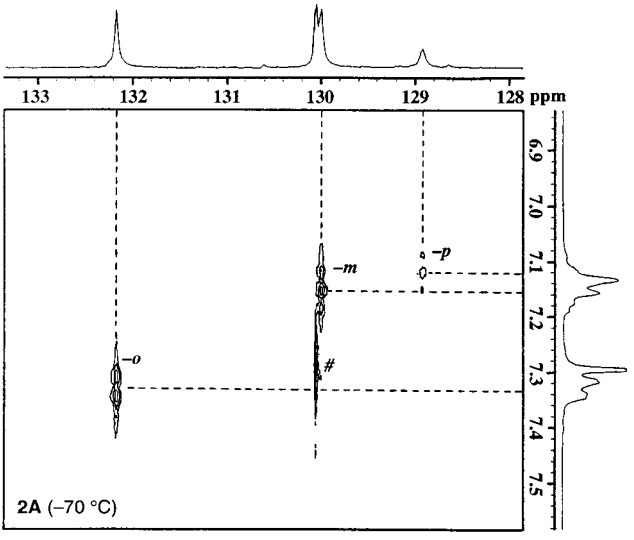


Fig. 3. CH-COSY spectrum of **2A** at low temperature in THF-d_8. (#: benzene).

In order to confirm the formation of this σ-sulfurane or σ-selenurane as a discrete intermediate, the ^{1}H and ^{13}C NMR spectra of the reaction mixture were measured at -105 or $-70\,^{\circ}C$. The temperature-dependent ^{1}H and ^{13}C NMR chemical shifts due to the phenyl groups were assigned to the corresponding *ortho*-, *meta*- and *para*-hydrogens and carbons of **1A** at $-105\,^{\circ}C$, or **2A** at $-70\,^{\circ}C$. The corresponding data are summarized in Table 1. *Ipso* carbon signals of both **1A** and **2A** may not be detected, because they have a long spin-lattice relaxation time (T_1).

The coupling constants of each proton could be determined by taking its resolution enhanced spectrum. Further, the ^{1}H and ^{13}C NMR chemical shifts of **1A** or **2A** were determined by the cross peaks observed in the two-dimensional CH shift correlation (CH-COSY) NMR spectrum, as shown in Figs. 2 and 3. Both the ^{1}H and ^{13}C spectra of the reaction mixture changed gradually upon elevating the temperature, and finally were consistent with those of approximately a 1:1 mixture of **3** or **7**, and **4**, at 15 or 20 °C. When **2** in THF-d_8 was treated with trimethylsilyl trifluoromethanesulfonate, and subsequently with two equivalents of PhLi at $-105\,^{\circ}C$, the same NMR signals due to **1A** were also observed.

These NMR experiments at low temperature, and the product analysis, indicate that both the **1** and **5** salts, and **2** and **6**, react with PhLi to give identical **1A** or **2A** as a discrete intermediate at low temperature, which on warming to room temperature decomposes to **3**, or **7** and **4**. Interestingly, the four phenyl groups formed in **1A** or **2A** become an identical formula, suggesting that pseudorotation takes place rapidly even at a low temperature, such as -105 or $-70\,^{\circ}C$. This result agrees well with the behavior of the known hypervalent compounds of group 16 elements, such as tetraarylselenuranes and tetraaryltelluranes.

^{77}Se NMR of the selenonium bromide **5** could not be obtained in THF, because of its insolubility in THF (the chemical shift of **5** is observed at 483.7 ppm in $CDCl_3$ at 22 °C). Careful treatment of the selenonium salt **5** in an anhydrous THF solution with an equimolar amount of PhLi at $-100\,^{\circ}C$ resulted in a new ^{77}Se NMR signal which appeared at 373.7 ppm. No other signals were observed in the range between 1600 and -200 ppm at $-100\,^{\circ}C$. Upon raising the temperature of the solution to 22 °C, the ^{77}Se NMR signal of **2A** shifted significantly downfield as a new singlet peak at 414.2 ppm, which was consistent with that of **7** at 22 °C (the chemical shift of **7** observed at 401.6 ppm in THF at $-100\,^{\circ}C$). Further, upon similar treatment of **6** with PhLi in THF at $-100\,^{\circ}C$, the ^{77}Se NMR signal appeared initially at 827.0 ppm, shifted to 373.7 ppm, corresponding to that of the intermediate **2A,** which was shifted again to 414.2 ppm as a sharp singlet, suggesting the formation of **7**.

Consequently, the present studies on the temperature-dependent NMR experiments provide the first and discrete evidence for the formation of **1A** and **2A** in the reaction of the salts **1** or **2**, and **2** or **6** with PhLi.

2.2. Isolation of tetraphenyltellurane (Ph_4Te) [10–Te–4(C4)]

Although tetraphenyltellurane (**3A**) has already been isolated by Wittig [14], the detailed ^{1}H and ^{13}C NMR data have not been reported. Therefore, we tried to

Table 2
^{1}H and ^{13}C NMR chemical shifts of tetraphenyltellurane (**3A**)

Nuclei	Position and chemical shift (δ)			
(25 °C, THF-d_8)	*ipso* (**1**)	*ortho* (**2**)	*meta* (**3**)	*para* (**4**)
^{1}H	–	7.32	7.04	7.03
	–	(d, J = 7.0 Hz)	(t, J = 7.0 Hz)	(t, J = 7.0 Hz)
^{13}C	Not detected	134.1	129.0	128.1

synthesize **1C** according to the usual methods, and measured using high-resonance resolution NMR spectroscopy. None of the signals change during the variable temperature measurements. The *ipso* carbon signals of **3A** may again not be detected because of their long spin-lattice relaxation time (T_1). The ^{1}H and ^{13}C chemical shifts of **3A** are summarized in Table 2.

2.3. Kinetic studies for the ligand coupling reaction of tetraphenylchalcogen compounds Ph_4X (X = S, Se, Te) [54]

1A and **2A** were generated in situ by the reactions of the corresponding salt, **1** or **5**, in THF-d_8, with an equivalent of phenyllithium (PhLi) under an argon atmosphere at −105 °C and −78 °C, respectively. **3A**, which was prepared from tellurium tetrachloride by the known method, was dissolved in toluene-d_8 at room temperature under an Ar atmosphere, as shown in Scheme 2.

The ^{1}H NMR spectra of **1A**, **2A** and **3A** in solution reveal the presence of three kinds of protons (*ortho*-, *meta*- and *para*-protons), as shown in Fig. 4, and clearly

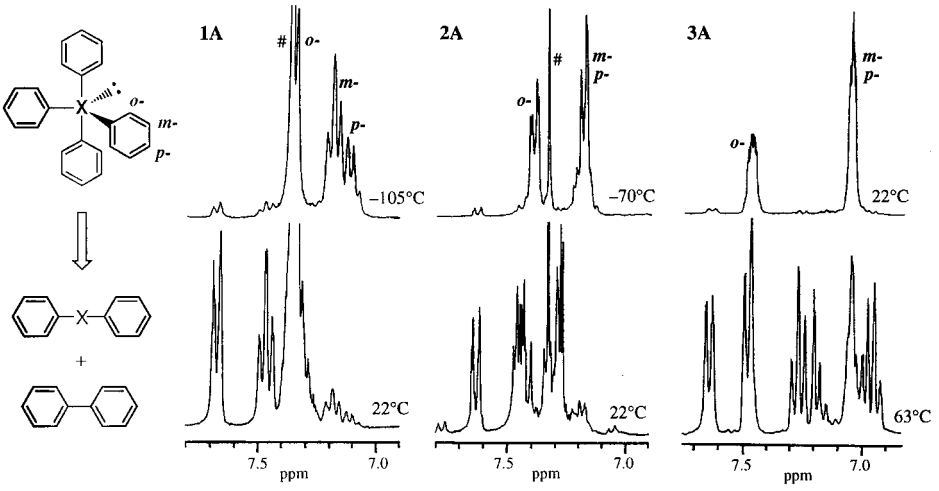
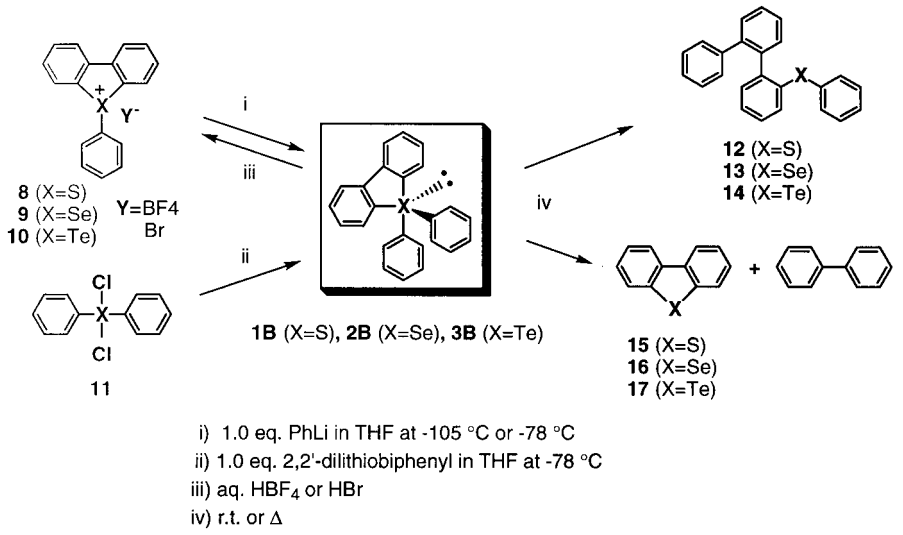


Fig. 4. Temperature-dependent ^{1}H NMR spectra of **1A**, **2A** and **3A**: initial (upper) and final (lower) spectra at present temperature; X = S, Se and Te (#: benzene).

Table 3
^{1}H and ^{13}C NMR chemical shifts of **1B** and **2B**

	Nuclei	Position and chemical shifts (δ)									
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1B	^{1}H	–	–	6.88 (d, J = 7.6 Hz)	7.21 (t, J = 7.6 Hz)	7.37 (t, J = 7.6 Hz)	8.14 (d, J = 7.6 Hz)	–	7.11 (d, J = 7.3 Hz)	7.21 (t, J = 7.3Hz)	7 (t,
	^{13}C	134.8	156.8	128.4	128.0	128.8	121.9	152.6	129.4	129.0	128
2B	^{1}H	–	–	7.17 (d, J = 9.0 Hz)	7.13 (t, J = 9.0 Hz)	7.40 (t, J = 9.0 Hz)	8.14 (d, J = 9.0 Hz)	–	7.13 (d, J = 8.5 Hz)	7.17 (t, J = 8.5Hz)	7 (t,
	^{13}C	138.1	156.2	129.5	128.6	129.9	122.7	151.9	130.9	129.1	128



Scheme 3.

indicate the formation of tetracoordinated **1A**, **2A** and **3A**. Thermolysis of tetraphenylchalcogen compounds **1A**, **2A** and **3A** in THF or toluene, gives biphenyl and diphenyl chalcogenides, quantitatively (Scheme 3).

The ligand coupling reactions were monitored by ^{1}H NMR spectroscopy at the following temperatures (**1A**: −82, −77, −72, −67 °C; **2A**: −15, −11, −5, 0 °C; **3A**: 52, 63, 74, 84 °C) as a function of time. The decay of the protons of **1A** (*meta* and *para*), **2A** (*meta* and *para*) and **3A** (*ortho*), was monitored by the peak areas of protons in the parentheses, and followed by a simple first-order kinetic equation under the present temperatures employed. Plots of ln ($[a]/[a-X]$) versus time, where $[a]$ is an initial concentration at time t_0 and $[a-X]$ was that at time after t_x, gave good straight lines. The measured rate constants, k_1, are listed in Table 3. Activation parameters for the ligand coupling reactions of tetraphenyl chalcogen compounds **1A**, **2A** and **3A** were determined from the temperature dependence of the rate constants k_1. Arrhenius plots were linear and gave the values for activation energy, E_{act}. Eyring plots were also linear, as shown in Fig. 5, and allowed the determination of the activation parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ (Table 4).

A comparison with the activation parameters for the ligand coupling reactions of **2A** and **3A** reveals, that besides a small entropic contribution in both cases, a higher energy barrier to C–chalcogen bond scission is required in **3A**. This result would be ascribed to a reduced stabilization of the hypervalent molecules among chalcogenuranes (S > Se > Te). Both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values support the unimolecularity of the rate determining step. While E_{act} of **1A** is in the expected value for decreasing the stability of the hypervalent compound of sulfur, compared with those of **2A** and **3A**, $\Delta S^{\neq}$ for the reaction of **1A** is relatively large and negative,

Table 4
Activation parameters of ligand coupling reaction of tetraphenyl chalcogen compounds[a]

Compound (solvent)	k_1 (s^{-1})		E_{act} (kcal mol^{-1})	$\Delta G^{\neq}_{298}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	Δ
Ph_4S(**1A**) (THF-d_8)	2.48×10^{-4} (−67 °C)	1.22×10^{-4} (−72 °C)	10.9	17.5	10.5	
	5.00×10^{-5} (−77 °C)	3.25×10^{-5} (−82 °C)				
Ph_4Se(**2A**) (THF-d_8)	2.20×10^{-4} (0 °C)	1.30×10^{-4} (−5 °C)	21.3	20.4	21.3	
	5.31×10^{-5} (−11 °C)	2.21×10^{-5} (−15 °C)				
Ph_4Te(**3A**) (Toluene-d_8)	3.91×10^{-4} (84 °C)	1.77×10^{-4} (74 °C)	29.0	26.9	28.4	
	3.00×10^{-5} (63 °C)	8.26×10^{-6} (52 °C)				

[a] Values shown are least-square treatments of Arrhenius and Eyring plots.

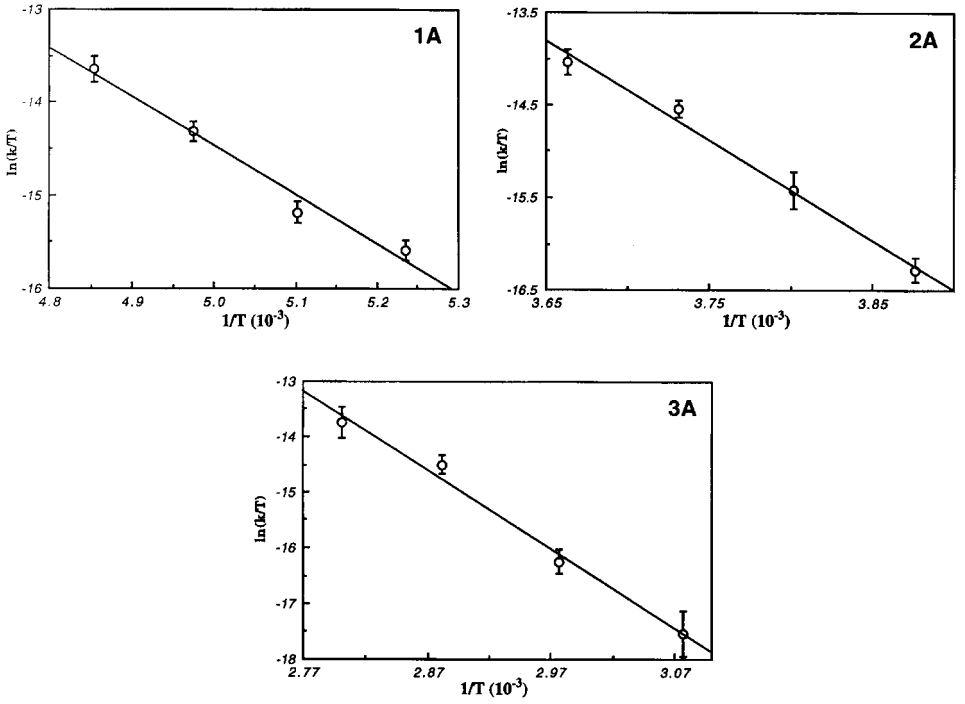


Fig. 5. Eyring plots with standard deviation for the ligand coupling reactions of **1A**, **2A** and **3A**.

compared with those of **2A** and **3A**, suggesting a highly ordered transition state in which the C–C bond should be formed simultaneously with the scission of two C–S bonds in **1A**. However, the reason for this ordering is unclear at this time.

3. 2,2′-Biphenylylenediphenylchalcogenuranes [10–X–4(C4), X = S, Se, Te] [55]

Formation of 2,2′-biphenylylenediphenylsulfurane (**1B**) [10–S–4(C4)] has already been postulated by Trost et al. and Hori et al. as an intermediate for the reaction of the 2,2′-biphenylylenephenylsulfonium salt with PhLi [20–23]. However, they could not directly prove the existence of the corresponding sulfurane as an intermediate. Therefore, we tried to obtain the first crucial evidence for the formation of not only **1B**, but also the corresponding selenurane in the reactions of 2,2′-biphenylylenephenylsulfonium and 2,2′-biphenylylenephenylselenonium salts with PhLi in THF by low temperature ^{77}Se, ^{1}H, ^{13}C and CH-COSY NMR experiments. Further, we tried to isolate 2,2′-biphenylylenediphenyltellurane (**3B**) which had never been known. Here, we describe the results on the direct detection of the 2,2′-biphenylylenediphenylchalcogenuranes, **1B** and 2,2′-biphenylylenediphenylselenurane (**2B**), using the low-temperature NMR technique, and on the isolation of **3B.**

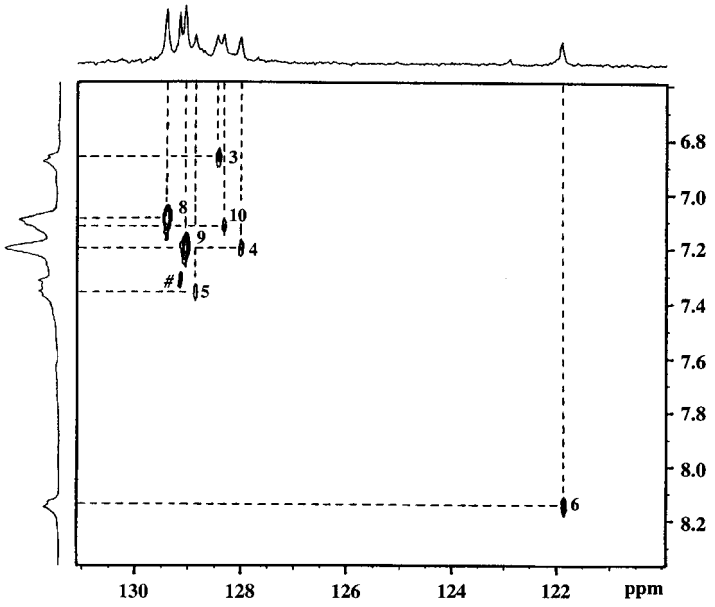


Fig. 6. CH-COSY spectrum of **1B** in THF-d_8 at −95 °C (#: benzene).

3.1. Detection of 1B and 2B [10–X–4(C4), X = S, Se]

2,2′-Biphenylylenephenylsulfonium salt (**8**), or 2,2′-biphenylylene-phenylselenonium salt (**9**), was prepared according to the general method. When an equimolar amount of PhLi (1.02 M in a cyclohexane/ether solution) was added to a suspension of **8** or **9** in anhydrous THF under an Ar atmosphere at −100 or −78 °C, the mixture turned to a yellowish homogeneous solution. Subsequently, the mixture was treated at −100 or −78 °C with a 0.2 M aqueous tetrafluoroboric acid (HBF_4) or a bromic acid (HBr) solution to give quantitatively the recovered chalcogenium salt **8** or **9**. By elevating the temperature of the THF solution to room temperature, each solution became colorless, to give phenyl *o*-terphenyl sulfide (**12**) or phenyl *o*-terphenyl selenide (**13**), quantitatively, after work up, as shown in Scheme 3.

The present results suggest that a stable intermediate, such as *σ*-sulfurane **1B** or *σ*-selenurane **2B**, should be formed in solution at low temperature. In order to confirm the formation of this *σ*-sulfurane **1B** or **2B** as a discrete intermediate, the ^{1}H and ^{13}C NMR spectra of the reaction mixture were measured in THF-d_8 at −100 or −70 °C: new sets of each spectrum differed from that of the substrate and ligand coupling products were observed. The ^{1}H and ^{13}C NMR chemical shifts of **1B** or **2B** were determined by each cross peak observed in the $^{13}C^{1}H$-COSY NMR spectra, as shown in Fig. 6, and the corresponding chemical shifts of the hydrogens and carbons of **1B** or **2B** are summarized in Table 3.

The ^{77}Se NMR spectrum of **2B** was taken under −100 °C in anhydrous THF. A sharp singlet peak due to the **2B** was observed at 397.1 ppm, which is a different chemical shift from either that of the starting compound or that of the corresponding coupling product **13** (390.0 ppm) and dibenzoselenophene (**16**) (445.9 ppm) at −100 °C.

3.2. Preparation of 3B [10−Te−4(C4)] [55]

Dichlorodiphenyltellurane (**11**) was prepared according to the general method. When an equimolar amount of 2,2′-dilithiobiphenyl was added to a suspension of **11** in anhydrous ether under an Ar atmosphere at −78 °C, the mixture turned to a yellowish homogeneous solution at room temperature. After filtration of the residue, the solvent was evaporated to leave the pale yellow solid estimated as a *σ*-tellurane **3B**. On similar treatment as with **1B** and **2B**, **3B** reacted with a 0.2 M aqueous tetrafluoroboric acid (HBF_4) solution to give the corresponding 2,2′-biphenylylenephenyltelluronium salt (**10**), quantitatively. At a higher temperature of approximately 140 °C in situ, it decomposed to give the coupling product, phenyl *o*-terphenyl telluride (**14**) (80%) (Scheme 3). In order to confirm the structure of this *σ*-tellurane **3B**, the ^{1}H, ^{13}C and ^{125}Te NMR spectra of **3B** were measured in THF-d_8 and THF at room temperature, to give new sets of the spectrum different from that of the substrate **11** and the ligand coupling product **14**. The ^{1}H and ^{13}C NMR chemical shifts of **3B** were determined similarly (Figs. 7 and 8), and the

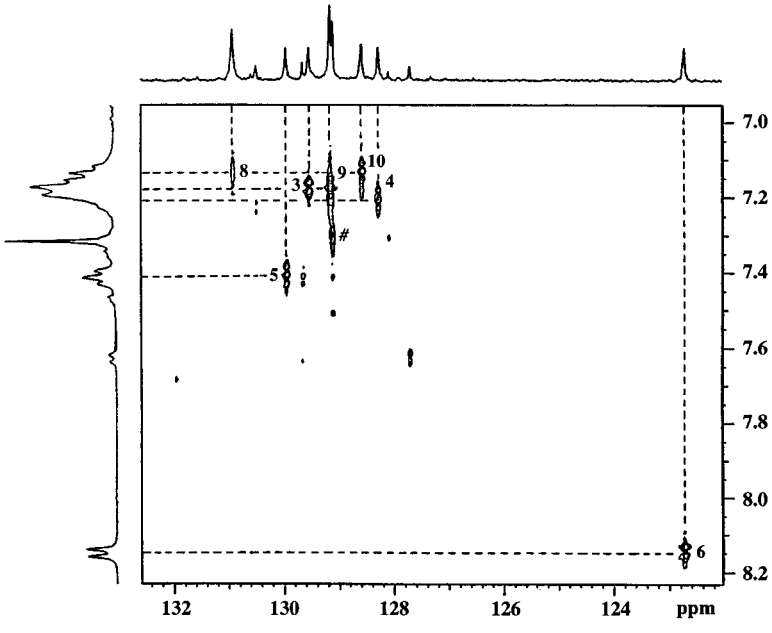


Fig. 7. CH-COSY spectrum of **2B** in THF-d_8 at −70 °C. (#: benzene).

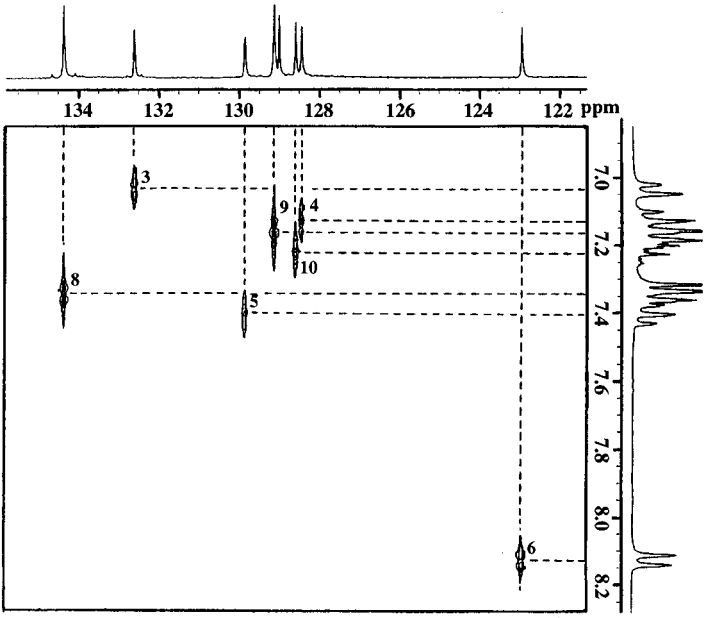


Fig. 8. CH-COSY spectrum of **3B** in THF-d_8 at 22 °C.

corresponding chemical shifts of the hydrogens and carbons of **3B** are summarized in Table 5.

The ^{125}Te NMR spectrum of **3B** appeared at 439.0 ppm [**11**: 981.0 ppm ($CDCl_3$); **14**: 638.0 ppm ($CDCl_3$)], reveals that the structure of **3B** agrees with a structure bound to four aryl ligands in solution, because this ^{125}Te value is roughly identical with that of known telluranes [37–44], **3A**: 509.7 ppm (THF); bis(2,2′-biphenylylene)tellurane: 482.1 ppm (THF).

Interestingly, the ^{1}H and ^{13}C NMR spectra of 2,2′-biphenylylene and phenyl groups in these hypervalent compounds, **1B**, **2B** and **3B** were identical, with one set of spectra suggesting that the pseudorotation takes place rapidly even under as low a temperature as −100 °C. This result agrees with the behavior of the tetraphenylchalcogen compounds.

Consequently, the present studies of the temperature-dependent NMR experiments provide the first and discrete evidence for the formation of **1B** and **2B** in the reaction of salts **8** and **9**, while **3B** was isolated as a stable derivative. These compounds, **1B**, **2B** and **3B**, are more stable than the corresponding tetraphenylchalcogenuranes, **1A**, **2A** and **3A**.

4. Bis(2,2′-biphenylylene)chalcogenuranes [10–X–4(C4), X = S, Se, Te]

Although the tetraphenylsulfurane species has been detected as an intermediate in the substitution reactions of the corresponding triphenyl sulfonium salts or

Table 5
^{1}H and ^{13}C NMR chemical shifts of **3B**

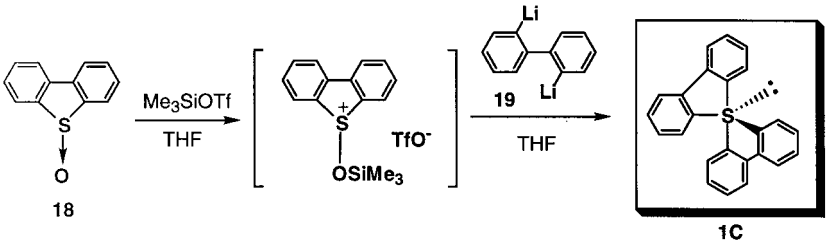
Nuclei	Position and chemical shifts (δ)									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
^{1}H	–	–	7.04	7.13	7.40	8.13	–	7.35	7.16	7
	–	–	(d, J = 7.3 Hz)	(t, J = 7.3 Hz)	(t, J = 7.3 Hz)	(d, J = 7.3 Hz)	–	(d, J = 7.3 Hz)	(t, J = 7.3 Hz)	(t, J
^{13}C	140.2	149.7	132.6	128.5	129.9	123.0	142.7	134.4	129.1	128

diphenyl sulfoxides, with organometallic reagents at low temperature, as described above, no one has succeeded in the isolation of such a species. As an isolable sulfurane, we tried to synthesize tetraarylsulfurane bearing a 2,2′-biphenylylene ligand, which may stabilize the hypervalent bond. Earlier, **1C** was predicted by Trost et al. [21], but to date its synthesis has not been successful. Recently, the first synthesis and structural characterization of a new stable sulfurane with four C–S bonds, bis(2,2′-biphenylylene)sulfurane (**1C**) have successfully been performed in our laboratory. On the other hand, bis(2,2′-biphenylylene)selenurane (**2C**) and bis(2,2′-biphenylylene)tellurane (**3C**) have already been isolated by Hellwinkel et al. We succeeded in determining the structure of **3C** by X-ray crystallographic analysis. Further, we found that the pseudorotation of these compounds, **2C** and **3C**, takes place in the NMR time scale at low temperature. The energy barriers for their pseudorotation were calculated by variable-temperature NMR studies. The results are described below.

4.1. Preparation of 1C [10–S–4(C4)] [56,57]

1C was synthesized as follows (Scheme 4): dibenzothiophene *S*-oxide (**18**) (200 mg, 1.0 mmol) in anhydrous tetrahydrofuran (THF, 10 ml), was treated with trimethyl-
silyl trifluoromethanesulfonate (0.25 ml, 1.3 mmol) under a N_2 atmosphere at −78 °C. After stirring at 0 °C for 30 min, the mixture was cooled to −78 °C and was treated with 1.0 M 2,2′-dilithiobiphenyl (**19**) (1.0 ml, 1.0 mmol) in a diethyl ether solution. The whole mixture was stirred at −78 °C for 1 h and at 0 °C for 30 min under a N_2 atmosphere. After evaporation of the solvent, the residue was washed with anhydrous diethyl ether (10 ml) under a N_2 atmosphere. The solvent was removed under reduced pressure and the crude product was recrystallized from anhydrous THF at −20 °C, to give **1C** as orange, rod-shaped crystals in 96% yield.

The structure of **1C** in a THF solution was characterized by NMR spectroscopy (Table 6). From the ^1H and ^{13}C NMR spectra, it can be seen that each aryl ring of the biphenylylene was magnetically equivalent at room temperature. Further, these signals were unchanged at −100 °C, suggesting that Berry pseudorotation should



Scheme 4.

Table 6
^{1}H and ^{13}C NMR chemical shifts of **1C**

Nuclei	Position and chemical shifts (δ)					
	1	**2**	**3**	**4**	**5**	**6**
^{1}H	–	–	7.71	7.23	7.42	8.15
	–	–	(d, J = 7.6 Hz)	(t, J = 7.6 Hz)	(t, J = 7.6 Hz)	(t, J = 7.6 Hz)
^{13}C	134.5	148.6	128.2	127.3	128.8	122.9

take place rapidly in the NMR time scale even at a low temperature, in contrast to the corresponding selenium and tellurium compounds.

The crystal structure of **1C** was confirmed by X-ray diffraction (Fig. 9). The equatorial S(1)–C(8′) and S(1)–C(8) bond lengths have normal S–C values of 1.823(2) and 1.814(2) Å, respectively. The apical S(1)–C(2) bond length is 1.926(2) Å and is the longest sulfur-aryl-carbon bond known. The equatorial–equatorial, C(8)–S(1)–C(8′), bond angle is 121.52(9)° and is the largest ever known for the tetracoordinated sulfur compounds. The apical–apical, C(2)–S(1)–C(2′), bond angle of 175.19(9)° is approximately linear. Thus, **1C** in the solid state has a slightly distorted pseudo-trigonal-bipyramidal (Ψ-TBP) geometry, with two apical S–C bonds, two equatorial S–C bonds, and the lone-pair electrons

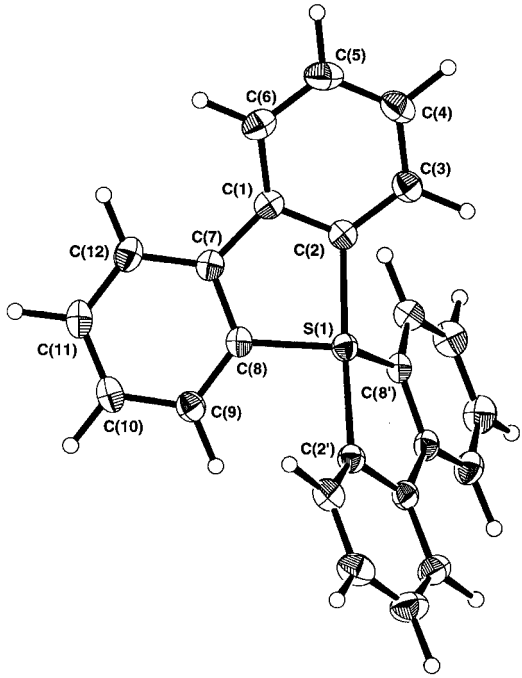


Fig. 9. ORTEP (30% probability ellipsoids) view of **1C**.

Table 7
^{13}C NMR chemical shifts of bis(2,2′-biphenylylene)selenurane (**2C**) and -tellurane (**3C**) in THF-d_8

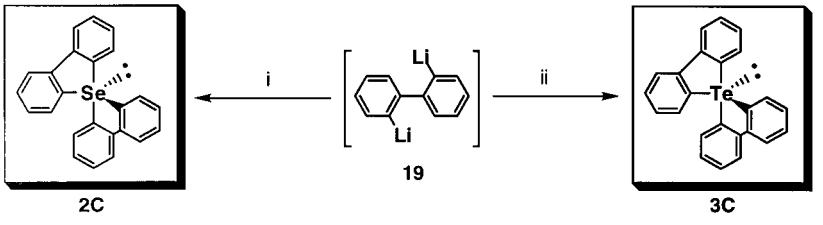
Compound	Temperature (°C)	Position and chemical shift (δ)					
		1, **1′**	**2**, **2′**	**3**, **3′**	**4**, **4′**	**5**, **5′**	**6**, **6′**
2C	50	137.5	Not detected	129.8	128.0	Not detected	123.6
2C	−45	136.6	163.5	130.4	128.2	132.0	123.7
		135.5	138.0	129.3	128.1	128.1	123.9
3C	25	141.5	Not detected	133.8	128.8	130.6	124.6
3C	−105	141.2	153.1	134.0	128.7	131.7	124.2
		140.3	128.0	133.0	128.2	128.8	124.5

as the third equatorial position. The results represent the first structural characterization of an organosulfurane consisting of two different kinds of S–C bonds. X-Ray crystallographic data of **1C** are summarized in Table 7.

4.2. Preparation of 2C and 3C [10–X–4(C4), X = Se, Te]

2C and **3C** were prepared by the modified method of Hellwinkel [10], as shown in Scheme 5. The ^{77}Se and ^{125}Te NMR chemical shifts of **2C** and **3C** appeared at 427.5 and 483.9 ppm, respectively, revealing that **2C** and **3C** remain as tetracoordinated structures bound to four aryl ligands in solution [41]. Further, as it was shown for **2C** and **3C** by the ^{1}H, ^{13}C and CH-COSY NMR, the four aryl rings of the two biphenylylene groups are magnetically equivalent at room temperature.

The crystal structure of **3C** was confirmed by X-ray diffraction, as shown in Fig. 10. The apical Te(1)–C(2) and Te(1)–C(14) bond distances are 2.23(1) Å, while the equatorial Te(1)–C(8) and Te(1)–C(20) bond distances are 2.14(1) and 2.16(1) Å, respectively. Bond angles between C(2)–Te(1)–C(14), C(2)–Te(1)–C(8), C(8)–Te(1)–C(20) and C(2)–Te(1)–C(14) are 158.9(5), 77.4(5), 107.9(4) and 89.6(5)°, indicating that **3C** is a considerably distorted TBP structure which is nearly identical with that of **3A**, reported by Ziolo and Titus [58,59]. X-Ray crystallographic data of **3C** are summarized in Table 8.



i) dibenzoselenophene-5-oxide/Et_2O/-78 °C~r.t.
ii) tetrachlorotellurane/Et_2O/-78 °C~r.t.

Scheme 5.

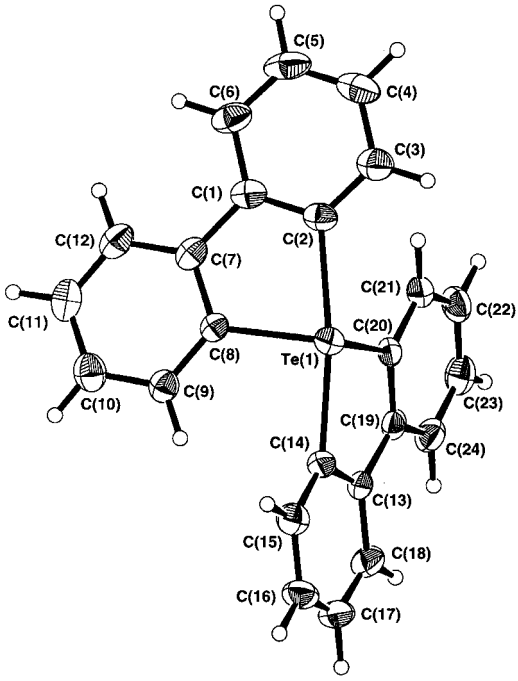


Fig. 10. ORTEP (30% probability ellipsoids) view of **3C**.

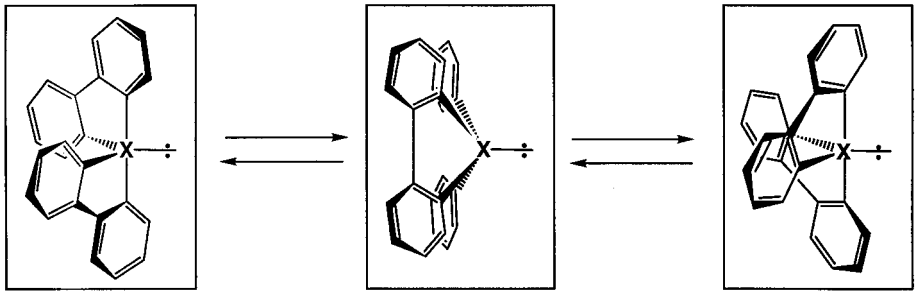


Fig. 11. Mechanism of Berry pseudorotation on **2C** and **3C**.

4.3. DNMR studies of bis(2,2′-biphenylylene)chalcogenuranes [10−X−4(C4), X = S, Se, Te] [60]

We described that the four phenyl groups in tetraarylchalcogen compounds are in equivalent states and hence, intramolecular ligand exchange (pseudorotation) [61–63] takes place rapidly even at −105 °C in solution by NMR studies. However,

Table 8
X-ray crystallographic data for diffraction studies of **1C** and **3C**

Compd	**1C**	**3C**
Formula	C24H16S	C24H16Te
fw	336.46	432.00
Cryst. syst.	Triclinic	Monoclinic
Space group	C2/*c* (No. 2)	P21/*n* (No. 14)
a (Å)	20.957(1)	4.540(0)
b (Å)	10.372(1)	18.808(0)
c (Å)	7.845(1)	20.226(0)
β (deg.)	99.01(0)	91.48(0)
V (Å^3)	1684.250	1726.6
Z	4	4
D_{calcd} (g/cm^3)	1.33	1.66
F(000)	704	848
Temp. (°C)	23 ± 1	23 ± 1
Radiation (λ, Å)	Mo K α (0.709 30)	Mo K α (0.710 73)
Cryst. dimen. (mm)	0.20 × 0.20 × 0.30	0.20 × 0.40 × 0.40
μ (cm^{-1})	1.8	17.3
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Scan rate	2–20°/min	2–20°/min
Scan width (deg.)	0.8 + 0.350 tan θ	0.5 + 0.580 tan θ
Maximun 2θ (deg.)	46.0	50.0
Total no. of rflns	2486	6910
No. of unique rflns	1250	3541
No. of params refined	138	226
Reflections included	1483 with $F_0^2 > 3.0\sigma(F_0^2)$	2804 with $F_0^2 > 3.0\sigma(F_0^2)$
Agreement factors[a]		
R	0.033	0.063
Rw	0.033	0.066

[a] $R = \Sigma\,||F_0| - |F_c||/\Sigma\,|F_0|$; $Rw = [\,\Sigma\, w(|F_0| - |F_c|^2]/\Sigma\, wF_0^2]^{1/2}$.

there are no reports on the kinetic studies for the pseudorotation of such tetracoordinated group 16 elements having four carbon ligands [64]. Hellwinkel reported the synthesis of relatively stable **2C** and **3C** [34–36], but little was

Table 9
^{1}H NMR chemical shifts of **2C** and **3C** in THF-d_8

Compound	Temperature (°C)	Position and chemical shift (δ, Hz)			
		3, **3′**	**4**, **4′**	**5**, **5′**	**6**, **6′**
2C	50	7.84 (7.4)	7.23 (7.4)	7.42 (7.4)	8.09 (7.4)
2C	−45	8.04 (4.9)	7.22 (4.9)	7.55 (4.9)	8.19 (4.9)
		7.70 (4.9)	7.36 (4.9)	7.41 (4.9)	8.18 (4.9)
3C	25	8.14 (7.3)	7.51 (7.3)	7.65 (7.3)	8.33 (7.3)
3C	−105	8.10 (7.0)	7.32 (7.0)	7.58 (7.0)	8.27 (7.0)
		7.90 (7.0)	7.49 (7.0)	7.49 (7.0)	8.26 (7.0)

investigated about the physical behaviors of these species. The structure of **3A** has been determined by X-ray crystallographic analysis, showing a distorted *Ψ*-trigonal bipyramidal (TBP) geometry [45]. Here we described the first results of the solution state structures of **2C** and **3C**, and the energy barriers for their pseudorotations by variable-temperature NMR studies. The mechanism of Berry pseudorotation on bis(2,2′-biphenylylene)chalcogenurane compounds is shown in Fig. 11.

It is shown for **2C** and **3C**, by the ^{1}H, ^{13}C and CH-COSY NMR, that the aryl rings of the biphenylylene groups are magnetically equivalent at room temperature. However, at −45 (**2C**) and −105 °C (**3C**), each signal of the aryl rings splits into two sets of signals with equal intensities, and the positions of protons and carbons have been assigned on the basis of NMR parameter values (chemical shift, coupling constant, homo-spin decoupling, and CH-shift correlation), as shown in Tables 7 and 9. Interestingly, the ^{13}C NMR of the one *ipso* carbon at the 2′-position was observed at an exceptionally low field, while the other chemical shifts at the 2-position appeared strongly downfield. These unexpected ^{13}C chemical shifts can be ascribed to the hypervalent apical bonds and the development of a negative charge on the apical ligands, as predicted by the MO calculation of a TBP structure [65–73]. From these ^{13}C NMR results we concluded that the tetracoordinated **2C** and **3C** should exist as the TBP structures in solution, and that the pseudorotations take place slowly with respect to the NMR time scale at a low temperature.

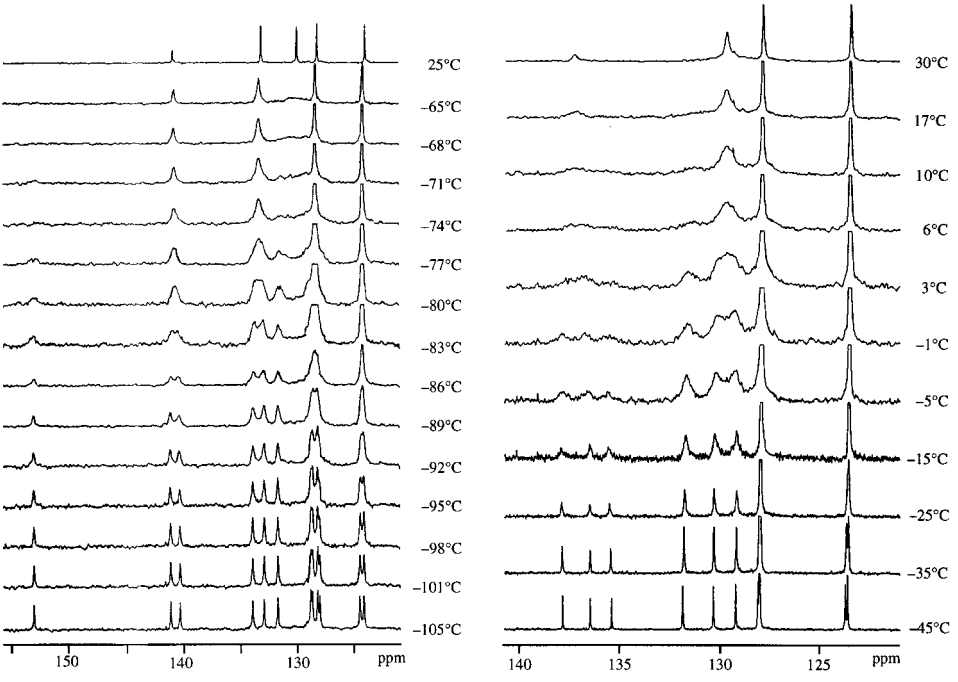


Fig. 12. Variable-temperature ^{13}C NMR spectra of **2C** and **3C** in THF-d_8.

Table 10
Activation parameters of pseudorotation determined by ^{13}C DNMR

Compound	Position	Temperature range (°C)	T_c[a] (°C)	Δn (Hz)	$\Delta H^{\neq}$[b] (kcal mol^{-1})	$\Delta S^{\neq}$[b] (eu)	$\Delta G_c^{\neq}$[c] (kcal mol^{-1})	ΔG_c (kca
2C	1,1′	−45 ~ 50	6	137.8	13.5	1.4	13.1	13.0
2C	3,3′	−45 ~ 50	3	107.8	13.5	1.4	13.1	13.2
3C	1,1′	−105 ~ 25	−80	82.5	7.4	−9.1	9.1	9.2
3C	3,3′	−105 ~ 25	−77	100.0	7.2	−10.5	9.2	9.1

[a] Coalescence temperature.
[b] From the line shape analysis.
[c] $\Delta G_c^{\neq} = \Delta H^{\neq} - T_c \Delta S^{\neq}$.
[d] The values were obtained from the equation $\Delta G_c^{\neq} = 4.57 \times 10^{-3} T_c[10.32 + \log(T_c/2/\pi\Delta\nu)]$.

The variable-temperature ^{13}C NMR spectra of **2C** and **3C** were measured as shown in Fig. 12. Their spectral changes are interpretable in terms of pseudorotation processes, where the lone electrons pair acts as the pivotal ligand. Further, the results of ^{13}C DNMR studies on **2C** and **3C** are summarized in Table 7, and the activation parameters of the pseudorotation have been evaluated from the simulation of the experimental spectra by analyzing the simple two-site exchange model [74,75]. The first-order rate constant k for the pseudorotation was obtained for each temperature, by comparing experimental spectra with simulated ones. The plots of $\log(k/T)$ against $1/T$ gave good straight lines, and the activation enthalpy ($\Delta H^{\neq}$) and the activation entropy ($\Delta S^{\neq}$) were calculated by a least-square treatment using the Eyring model.

These results indicate that the activation energies ($\Delta G^{\neq}$) of **2C** and **3C** are almost governed by the activation enthalpies ($\Delta H^{\neq}$), and the activation entropies ($\Delta S^{\neq}$) are nearly zero or small negative values (Table 10). The activation energies ($\Delta G^{\neq}$) for pseudorotation of **2C** and **3C** are 13.1 and 9.2 kcal mol^{-1} and are not significantly different, but are lower than that of the same row elements of group 15 bound to only aryl ligands, bis(biphenylylene)arylpnyctogenuranes [10−X−4(C5), X = P, As, Sb] (X = P, 15.7; X = As, 15.4; X = Sb, 11.5 kcal/mol) [76]. These results suggest that the configurations of the ground state in pseudorotational processes of **2C** and **3C** form the structure between TBP and SP.

The results of the lower activation energy of pseudorotation of **3C** indicate that its TBP structure is nearly an SP configuration identical as an intermediate of pseudorotation, as shown in Fig. 11. The present studies on the variable-temperature NMR experiments provide the first examples of the solution state structure and the activation parameters of tetraaryl selenurane and tellurane.

5. Theoretical studies of chalcogenuranes(IV) bearing four carbon ligands

Tetraarylchalcogenuranes are too large to be investigated by ab initio calculations in detail. To date, ab initio studies on tetra-carbon-coordinated chalcogenuranes are reported only for tetramethyl species Me_4X (X = S, Se, Te) [77–79], although Me_4S and Me_4Se have not yet been prepared. These studies have elucidated the probable structure, energy barrier for the Berry pseudorotation, and thermodynamic stability of the Me_4X molecules. In this section, we briefly review the results of these theoretical studies. In addition, we describe our recent results on the ligand coupling reactions (kinetic stabilities) of these molecules. Moreover, the possibility of non-Berry pseudorotation, in which one apical and two equatorial ligands mutate, is proposed.

5.1. Structure

Me_4Te has recently been prepared [80] and its structure has been disclosed by X-ray diffraction and electron diffraction (ED) experiments [78]. Both experiments show that this molecule adopts a distorted trigonal bipyramidal (TBP) structure.

Ab initio calculations [77–79] consistently predict a distorted TBP structure for Me_4S, Me_4Se and Me_4Te. Marsden and Smart [78] found that the calculated bond angles of Me_4Te (at the MP2/PSP level) appreciably deviate from the ED results, whereas they agree well with the X-ray values. This result was ascribed to the extraordinary fluxional nature of the Me_4Te molecule (see below).

The calculated equilibrium structures of Me_4S, Me_4Se and Me_4Te have C_{2v} symmetry, both apical and equatorial methyl groups being staggered with respect to the lone pair of the central chalcogen atom. The lengths of the equatorial bonds are very close to those of the corresponding dimethyl chalcogenides (Me_2X), and the apical bonds are longer than the equatorial bonds. The $C_{ax}–X–C_{ax}$ angles reduce in the order $Me_4S > Me_4Se > Me_4Te$; the MP2/PSP values, for example, are 173.2°, 167.4° and 158.7°, for Me_4S, Me_4Se and Me_4Te, respectively [79].

5.2. Berry pseudorotation

The Berry pseudorotation (BPR) of a chalcogenurane molecule is the apical–equatorial ligand interchange. The two apical ligands become equatorial ligands and the two equatorial ligands become apical ligands by BPR. The lone pair of the central chalcogen atom remains in an equatorial position.

The calculations [77–79] for Me_4S, Me_4Se and Me_4Te predict that the square pyramidal (SP) geometry (C_4 or C_{4v} symmetry) corresponds to the transition state (TS) along the BPR pathway. The TS for Me_4S was predicted to have C_4 symmetry, whereas the TS for Me_4Te has C_{4v} symmetry, with the four methyl groups being staggered with respect to the lone pair. The symmetry of the TS for Me_4Se depends on the methods of calculations. These results reflect the difference in steric crowding among the three molecules. The C_4 structure of Me_4S results from methyl rotation, by which the repulsions between hydrogen atoms on neighboring methyl groups are reduced. The four methyl groups are equivalent in the TS's of BPR, and the chalcogen–C bond lengths lie between the apical and equatorial bond lengths of the TBP minimum structure.

The barriers to BPR are calculated to reduce in the order $Me_4S > Me_4Se > Me_4Te$. Marsden and Smart predicted the barriers for Me_4S, Me_4Se and Me_4Te to be approximately 5, 3.5 and 0.7 kcal mol^{-1}, respectively [79]. This trend is in good agreement with the experimental results for tetraarylchalcogenuranes described in Section 4.3. It should be noted that the barrier to BPR of Me_4Te is extremely low and, hence, this molecule is very fluxional. Indeed, its ^{13}C spectrum stays as a single spectrum down to $-90\,°C$ [80].

5.3. Ligand coupling

Marsden and Smart [79] investigated the thermodynamical stabilities (binding energies with respect to Me_2X and ethane) of the three Me_4X molecules. The estimated binding energies are approximately -84, -72 and -54 kcal mol^{-1} for Me_4S, Me_4Se and Me_4Te, respectively. Thus, all three species are thermodynamically unstable with respect to Me_2X and ethane, though the instability decreases from Me_4S to Me_4Te.

Morokuma and coworkers [81] investigated H_2 elimination from XH_4 species (X = S, Se, Te), which are hypothetical molecules. It should be noted that the XH_4 molecules adopt SP structures of C_{4v} symmetry, whereas actual chalcogenurane molecules adopt distorted TBP structures. Two types of H_2 elimination from XH_4 can be envisaged. One corresponds to the coupling between adjacent hydrogen atoms, and the other to the coupling between opposite hydrogen atoms. The former corresponds to the apical–equatorial coupling in the TBP case and is symmetry-forbidden (in C_s symmetry); the latter corresponds to the equatorial–equatorial coupling and is symmetry-allowed (in C_{2v} symmetry). Morokuma and coworkers located two transition states for each XH_4 molecule: one is highly polarized with C_1 symmetry corresponding to apical–equatorial coupling, and the other has C_{2v} symmetry. The C_1 TS's are much more favored over the C_{2v} TS's, although the latter corresponds to a symmetry-allowed pathway.

Although the above results for H_2 elimination from the XH_4 species suggest that ligand coupling reactions of chalcogenuranes proceed in the apical–equatorial fashion, calculations on more realistic molecules are desirable in order to elucidate

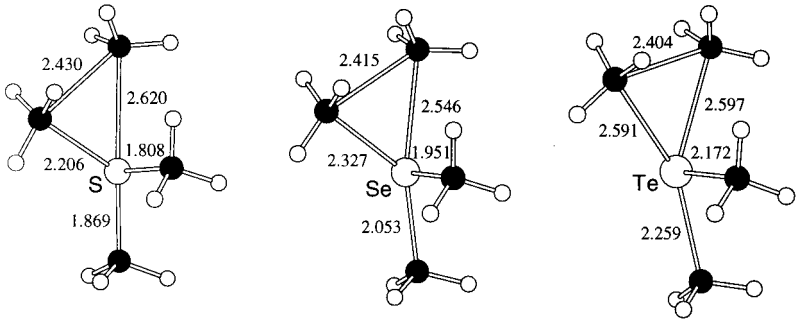


Fig. 13. The transition states for the apical–equatorial ligand coupling of Me_4S, Me_4Se and Me_4Te located by RHF/3-21G(*) calculations. The values shown are skeletal bond lengths (Å).

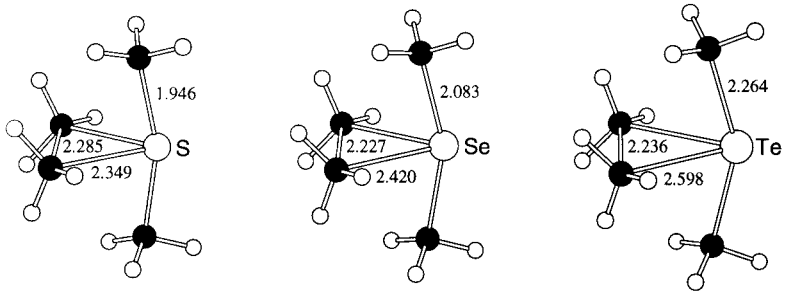


Fig. 14. The transition states (C_2 symmetry) for the equatorial–equatorial ligand coupling of Me_4S, Me_4Se and Me_4Te located by RHF/3-21G(*) calculations. The values shown are skeletal bond lengths (Å).

the mechanism of actual ligand coupling reactions. We therefore performed ab initio calculations on the ligand coupling reactions of the tetramethyl derivatives, Me_4X (X = S, Se, Te).

One can envisage three types of ligand coupling modes for chalcogenuranes which adopt TBP structures: apical–equatorial (a–e), equatorial–equatorial (e–e) and apical–apical (a–a) couplings. If the two apical ligands move in the direction opposite to the lone pair, the molecule will undergo the Berry pseudorotation; therefore, the a–a coupling corresponds to the motion of the two apical ligands in the direction opposite to one equatorial bond. However, we could not locate any TSs of a–a coupling for Me_4S, Me_4Se and Me_4Te. Instead, we accidentally found the TSs for non-Berry pseudorotation in which one apical and two equatorial ligands mutate in one step (see Section 5.4). We believe that there is no pathway corresponding to a direct a–a coupling.

The TS's for the a–e and e–e couplings of Me_4S, Me_4Se and Me_4Te could be located by RHF/3-21G(*) calculations. They are shown in Figs. 13 and 14. The barriers to the a–e couplings of Me_4S, Me_4Se and Me_4Te are calculated to be 50.0, 57.0 and 69.2 kcalssmol^{-1}, respectively, while those to the e–e couplings are 95.0, 92.3 and 90.4 kcal mol^{-1}, respectively. Thus, the barriers to the e–e couplings are much higher than those to the corresponding a–e couplings. This result is in line with that for the XH_4 species [81], and we predict that the ligand coupling reactions of chalcogenuranes proceed by the apical–equatorial coupling.

Why are the barriers to the e–e couplings so high, in spite of the fact that they are symmetry-allowed? It should be noted that the C–X–C angles of the incipient Me_2X in the e–e coupling TS's are much larger than those of the Me_2X molecules in their equilibrium geometries. The C–X–C angles in the TSs are 161.4°, 157.6° and 152.8° for X = S, Se, and Te, respectively. The RHF/3-21G(*) energy of Me_2S, for example, increases by about 59 kcal mol^{-1} when the C–S–C angle is increased to 160° from the energy-minimum structure in which the angle is 99.5°. Thus, a large part of the very high activation barriers of the e–e couplings can be ascribed to the large C–X–C angles in the TSs.

The calculated a–e coupling barriers increase in the order $Me_4S < Me_4Se < Me_4Te$. This trend is in good agreement with the experimental results for tetraphenylchalcogenuranes described in Section 2.3, and with the computational results for the XH_4 species [81]. At the RHF/3-21G(*) level, the relative energies of the Me_2X and ethane products of the ligand coupling reactions with respect to the Me_4X reactants, are −98.3, −78.8, and −56.3 kcal mol^{-1} for X = S, Se and Te, respectively. This trend is parallel to the results of more sophisticated calculations [79]. The stabilities increase in the order $Me_4S < Me_4Se < Me_4Te$, both thermodynamically and kinetically.

The TS's for the a–e coupling of Me_4S were also located by the RHF/6-31G*, RHF/6-31 + G* and MP2/6-31 + G* calculations. The results are shown in Fig. 15. The activation barriers are calculated to be 48.3, 45.5 and 38.1 kcal mol^{-1} by the RHF/6-31G*, RHF/6-31 + G* and MP2/6-31 + G* methods, respectively. The activation barrier decreases by inclusion of diffuse functions and electron correlation.

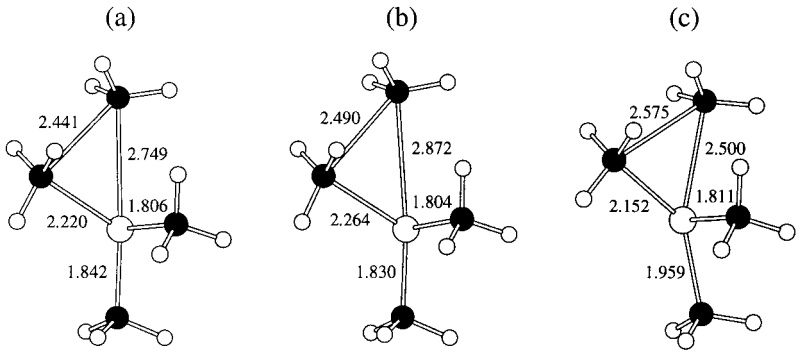


Fig. 15. The transition states for the apical–equatorial ligand coupling of Me_4S located by RHF/6-31G* (a), RHF/6-31 + G* (b), and MP2/6-31 + G* (c) calculations. The values shown are skeletal bond lengths (Å).

In conclusion, the ligand coupling reactions of chalcogenuranes are predicted to proceed in the apical–equatorial (a–e) fashion. Although there is no direct evidence for a–e ligand coupling of chalcogenuranes, such a coupling mode has often been postulated [82–85]. The calculated barrires to the a–e couplings increase in the order $Me_4S < Me_4Se < Me_4Te$. This trend is in good agreement with the experimental results for tetraphenylchalcogenuranes, although the barriers of the tetraphenyl derivatives are much lower than those of the tetramethyl derivatives.

5.4. Non-Berry pseudorotation

In the course of the attempts of locating the TS's of apical–apical ligand coupling for tetramethylchalcogenuranes, we accidentally found the TS's of non-Berry pseudorotation (NBPR) which have C_s symmetry. The TS's located by RHF/3-21G(*) calculations are shown in Fig. 16.

These TSs are those for the mutation of one apical and two equatorial ligands, as exemplified in Fig. 17. The corresponding TS's were also located by the RHF/6-

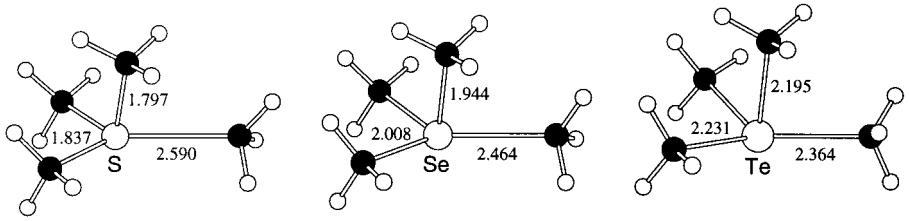


Fig. 16. The transition states (C_s symmetry) for the non-Berry pseudorotation of Me_4S, Me_4Se and Me_4Te located by RHF/3-21G(*) calculations. The values shown are skeletal bond lengths (Å).

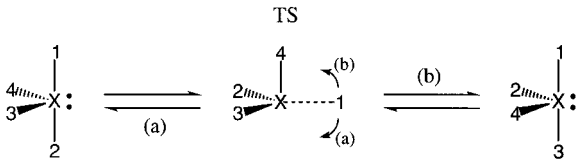


Fig. 17. Non-Berry pseudorotation of a chalcogenurane molecule.

31G*, RHF/6-31 + G* and MP2/6-31 + G* calculations for Me_4S. The barriers to NBPR calculated by RHF/3-21G(*) are 37.0, 36.7 and 35.7 kcal mol^{-1} for Me_4S, Me_4Se and Me_4Te, respectively. Those calculated for Me_4S by RHF/6-31G*, RHF/6-31 + G* and MP2/6-31 + G* are 32.1, 25.0 and 32.0 kcal mol^{-1}, respectively. It should be noted that the barriers to NBPR are lower than those to the (apical–equatorial) ligand couplings. Namely, it is predicted that the ligand mutation by NBPR occurs preceding the ligand coupling.

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