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Osaka University

**STUDIES ON  
ELECTROPHILIC SUBSTITUTION  
REACTIONS WITH  
PHENYLTHALLIUM CROWN ETHER  
COMPLEXES**

（フェニルタリウム-クラウンエーテル錯体による  
求電子置換反応に関する研究）

**FUMITOSHI KAKIUCHI**

**OSAKA UNIVERSITY**

**1993**

## Preface

The work presented in this thesis was carried out under the guidance of Professor Shinji Murai at the Department of Applied Chemistry, Faculty of Engineering, Osaka University, and Professor Yoshikane Kawasaki, at the Department of Applied Chemistry, Osaka Institute of Technology.

A handwritten signature in black ink, appearing to read 'F. Kakiuchi', with a large, stylized flourish at the end.

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January 1993

## List of Publications

- (1) Electrophilic Thallation of Phenol and Its Derivatives with Phenylthallium(III) Crown Ether Complexes  
F. Kakiuchi, Y. Kawasaki, N. Enomoto, H. Akita, K. Ohe, N. Chatani, H. Kurosawa, and S. Murai,  
*Organometallics*, **10**, 2056-2060, (1991).
- (2) Electrophilic Thallation of Aniline Derivatives and Nitrogen Heterocycles with Phenylthallium(III) 18-Crown-6 Diperchlorate  
F. Kakiuchi, K. Ohe, N. Chatani, H. Kurosawa, S. Murai, and Y. Kawasaki,  
*Organometallics*, **11**, 752-756, (1992).
- (3) Electrophilic Thallation of Thiophene Derivatives and Furan with Phenylthallium(III) 18-Crown-6 Diperchlorate  
F. Kakiuchi, S. Murai, and Y. Kawasaki,  
*Organometallics*, **11**, 4352-4355, (1992).
- (4) Highly Selective Methyl Transfer from Methyl Silanes to Phenylthallium(III) Crown Ether Complexes  
F. Kakiuchi, K. Furuta, S. Murai, and Y. Kawasaki,  
*Organometallics*, in press.

## Supplementary List of Publication

Completely Selective Synthesis of (*E*)- $\beta$ -(Triethylsilyl)styrenes by Fe<sub>3</sub>(CO)<sub>12</sub>-Catalyzed Reactions of Styrenes with Triethylsilane  
F. Kakiuchi, Y. Tanaka, N. Chatani, and S. Murai,  
*J. Organomet. Chem.*, in press.

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## General Introduction

Increasing attention has been paid to electrophilic aromatic substitution reactions with inorganic salts, examples being Tl(III),<sup>1</sup> Hg(II),<sup>2</sup> Pb(IV),<sup>3</sup> Rh(III),<sup>4</sup> and Pt(IV).<sup>5</sup> Reactions of the Tl(III) ion with aromatic compounds have been extensively investigated from the viewpoint of organic synthesis because the thallium moiety in the product monoarylthallium(III) ion can be easily converted to other functional groups.<sup>1</sup> Although it can be presumed that monoarylthallium(III) ions have enough electrophilicity for further aromatic substitution, there are only a few examples of diarylthallium(III) compound formed by the reaction of monoarylthallium(III) ions with aromatic compounds.<sup>1c</sup>

Previously, in our laboratory Kawasaki and co-workers found that the otherwise unstable monoarylthallium(III) compounds can be isolated by the coordination of crown ethers to the thallium ion.<sup>6</sup> For example, (dibenzo-18-crown-6)(phenyl)(iodo)thallium(III) perchlorate,  $[\text{Ph(I)Tl}^{\text{III}}(\text{DBC})](\text{ClO}_4)$  (DBC = dibenzo-18-crown-6), having a Tl-I bond was isolated by the reaction of  $[\text{PhTl}^{\text{III}}(\text{DBC})](\text{ClO}_4)_2$  with sodium iodide 15-crown-5 complex,  $[\text{Na}(15\text{-crown-5})]\text{I}$ , without decomposition of the phenylthallium(III) ion.<sup>7</sup>

I expected that (crown ether)phenylthallium(III) complexes could exhibit unique reactivities and good selectivities owing to the steric effect of the crown ether and the dicationic nature of the thallium ion.

I describe in Chapter 1 preparations of diarylthallium(III) complexes by the reaction of (18-crown-6)phenylthallium(III) diperchlorate with several aromatic compounds (phenols and anilines). Chapter 2 deals with direct synthesis of unsymmetrical diorganothallium(III) perchlorate complexes from the reaction of (18-crown-6)phenylthallium(III) diperchlorate with heteroaromatics (pyrroles, thiophenes, furan, and pyrazole). In Chapter 3, I present the selective cleavage of silicon-methyl bond in tetraorganosilanes, e.g. trimethylsilyl containing group such as benzyltrimethylsilane, phenyltrimethylsilane, and vinyltrimethylsilane. Chapter 4 deals with analysis of ionic character of the thallium-carbon

bonds on the basis of spin-spin coupling constants between thallium nucleus and ortho protons of the phenyl group.

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## Chapter 1

### Electrophilic Thallations of Phenols and Anilines by the Reaction of (18-Crown-6)phenylthallium(III) Diperchlorate

#### 1-1 Introduction

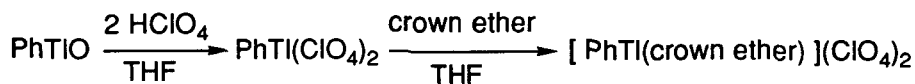
There are many examples of electrophilic substitution of various aromatic compounds with thallium(III) ion to give arylthallium(III) compounds.<sup>1</sup> However, these thallation reactions do not work with phenols and anilines because of the strong oxidizing ability of thallium(III) ions; these substrates are oxidized to quinones and diazo compounds, respectively. For example, when the reaction of  $Tl(NO_3)_3$  with 2,6-di-*tert*-butylphenol was carried out, the phenol converted to the 2,6-di-*tert*-butylquinone.<sup>2</sup> In the case of the reaction of  $Tl(OOCCH_3)_3$  with aniline, aniline was oxidized to azobenzene.<sup>3</sup>

I expected that an introduction of phenyl group and crown ether to the thallium ion could reduce the oxidizing ability of the thallium ion. On the basis of this assumption, I tried to prepare unsymmetrical diarylthallium compounds, which are difficult to be prepared by conventional methods, by the reaction of (crown ether)phenylthallium(III) diperchlorate (also called phenylthallium(III) (crown ether) diperchlorate) with phenols or anilines.

#### 1-2 Preparation of (Crown ether)phenylthallium(III) Diperchlorates.

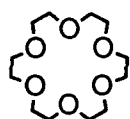
Five (crown ether)phenylthallium(III) diperchlorate complexes were prepared. The preparation of the complexes was performed by the following way (Scheme I). To a THF suspension of phenylthallium oxide was slowly added perchloric acid at 0 °C and then the mixture was stirred at the same temperature. After stirring for 6 h, a clear brown solution was obtained. The resulting solution was added into a THF solution of crown ethers (**A-E**) at 0 °C. After stirring for 1 h, colorless or pale yellow solids precipitated. Purification of the solids from acetonitrile/diethyl ether affords pure (crown ether) phenylthallium diperchlorate complexes (**1-5**) in 70-90% yields.

### Scheme I



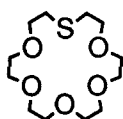
crown ether = 18-crown-6	: 1	90 %
MTC	: 2	70 %
1,4-DTC	: 3	80 %
1,7-DTC	: 4	70 %
1,10-DTC	: 5	80 %

crown ether :



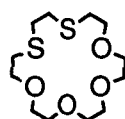
18-crown-6

A



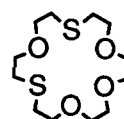
MTC

B



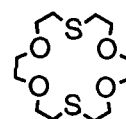
1,4-DTC

C



1,7-DTC

D



1,10-DTC

E

### 1-3 Reaction of Phenol with (Crown ether)phenylthallium(III) Diperchlorates.

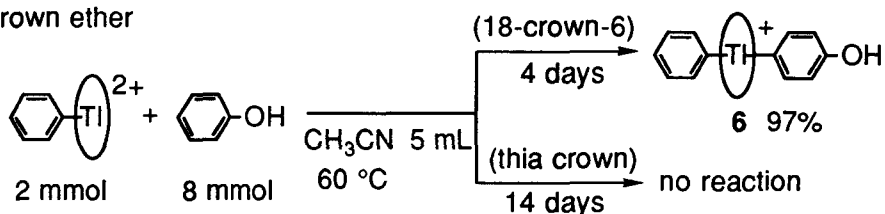
Reactions of five phenylthallium(III) diperchlorate complexes of 18-crown-6 (**1**) and thia crown ethers (**2-5**) with phenol were carried out at 60 °C in CH<sub>3</sub>CN (Scheme II). Interestingly, of the five complexes **1-5** examined, only **1** completed the aromatic thallation within 4 days to give a high yield of (18-crown-6)(4'-hydroxyphenyl)phenylthallium(III) perchlorate (**6**). The others did not undergo the thallation even after 14 days. The failure of the reaction of **2-5** with phenol may be due to the coordination of the sulfur atoms in the crown ethers to the thallium atom from the opposite side of the phenyl group, preventing the approach of phenol.

Complex **6** was isolated in 97% yield. In the <sup>1</sup>H NMR spectrum of **6**, three kinds of phenyl protons (H<sub>2</sub>, H<sub>3</sub>, and H<sub>4</sub>) and two kinds of protons bonding to the aromatic ring of the hydroxyaryl group (hydroxyaryl protons: H<sub>2'</sub> and H<sub>3'</sub>) were observed (for the numbering, see structures **7** and **8** in Scheme III). Each proton split by the spin coupling with the thallium nucleus. These observations indicate that the thallation occurred at the position para to the OH group and the amount of the ortho thallated

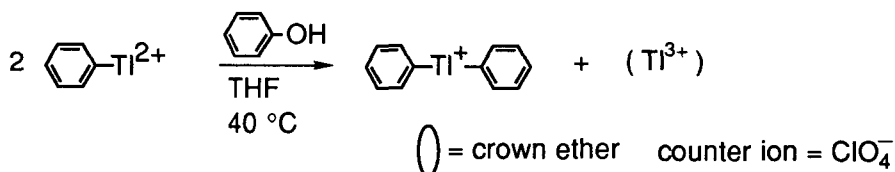
product is very small if present at all. The NMR signal of the OH proton was not observed owing to overlap with other signals, although a strong IR absorption of the OH stretching was observed at  $3360\text{ cm}^{-1}$ .

### Scheme II

with crown ether



without crown ether



The reaction of phenylthallium(III) diperchlorate,  $\text{PhTl}^{\text{III}}(\text{ClO}_4)_2$ , with phenol was carried out in tetrahydrofuran (THF) at  $40\text{ }^\circ\text{C}$ . In the  $^1\text{H}$  NMR study, the phenyl proton signals of  $\text{PhTl}^{\text{III}}(\text{ClO}_4)_2$  disappeared and new signals owing to diphenylthallium(III) ion,  $\text{Ph}_2\text{Tl}^{\text{III}}(\text{ClO}_4)$ , appeared after 5 days. Thallation product of phenol was not observed.

#### 1-4 Reaction of (18-Crown-6)phenylthallium(III) diperchlorate with Methyl Substituted Phenols.

The reactions of **1** with 2-, 3-, and 4-methylphenols and 2,6-, and 3,5-dimethylphenols were carried out in a similar manner at  $60\text{ }^\circ\text{C}$  in  $\text{CH}_3\text{CN}$  (Scheme III). In the case of the reaction with 2- and 3-methylphenols and 2,6-dimethylphenol, the  $^1\text{H}$  NMR spectra indicate the formation of thallated complexes, **7-9**, as revealed by the reduction of the spin-spin coupling constants of the phenyl protons with the thallium nucleus and the appearance of thallated hydroxyaryl proton signals (440-

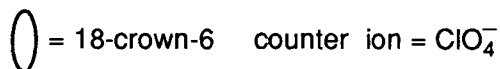
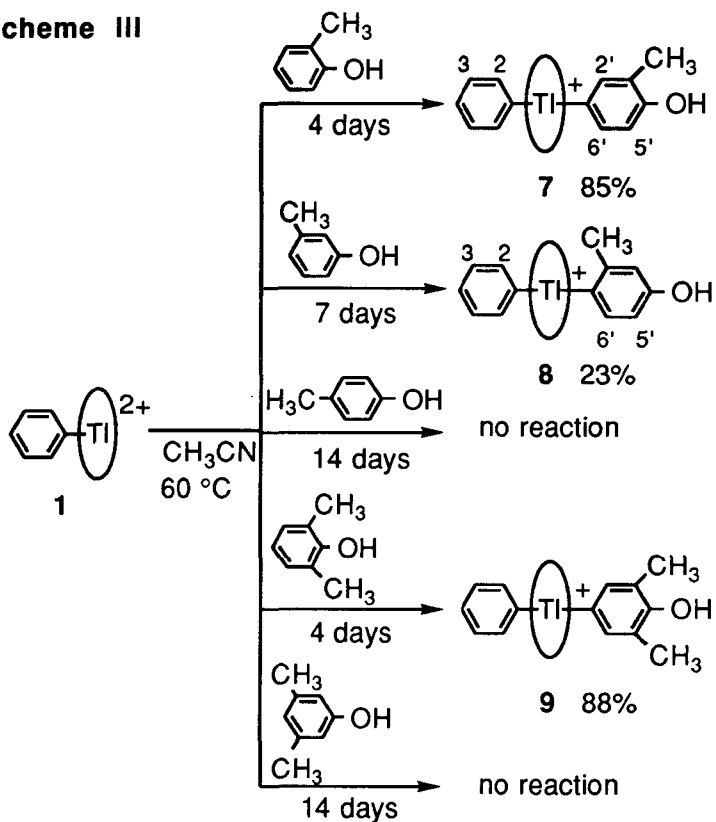
480 Hz).<sup>4</sup> The complexes **7-9** were isolated in 85, 23, and 88% yields, respectively.

The aromatic thallation of the ortho substituted phenols (2-methylphenol and 2,6-dimethylphenol) required about 4 days and the meta compound (3-methylphenol) about 7 days. The longer reaction time was necessary for 3-methylphenol possibly owing to the steric repulsion between the methyl group and the crown ether in an intermediate. In the case of the reaction with 4-methylphenol, no aromatic substitution was observed, although it was conceivable that the thallation could occur at the ortho position. The thallation at the ortho position, however, was reported in the reaction of  $\text{Tl}(\text{OOCF}_3)_3$  with anisole.<sup>1e</sup> The reaction between **1** and 3,5-dimethylphenol did not occur because of the blocking the position para to the OH group with two methyl groups against the thallium atom.

Determination of the thallated position in (18-crown-6)(4-hydroxyaryl)phenylthallium(III) perchlorate, **7-9** was carried out by the following procedure. The  $^1\text{H}$  NMR spectrum of the hydroxyaryl protons of **9** was observed as a doublet having a coupling with the thallium nucleus ( $J_{\text{TlH}} = 446$  Hz, 2H). This observation indicates that the thallation also occurred at the position para to the OH group and the two methyl groups located at the position meta to the thallium atom. In this complex, the spin-spin coupling constant between the thallium nucleus and the methyl protons,  $J_{\text{TlCH}_3}$ , was found to be 22 Hz. In complex **7**, three kinds of the hydroxyaryl protons were observed: one doublet,  $J_{\text{TlH}} = 444$  Hz; two doublet-doublets,  $J_{\text{TlH}} = 436$  Hz,  $J_{\text{TlH}} = 124$  Hz with same intensity. In **8** also three kinds of the hydroxyaryl protons were observed: one doublet-doublets,  $J_{\text{TlH}} = 480$  Hz; one doublet,  $J_{\text{TlH}} = 158$  Hz; one doublet-doublets,  $J_{\text{TlH}} = 152$  Hz. These spectral data suggest that there are two kinds of ortho protons and one kind of the meta proton in **7**, and one kind of the ortho proton and two kinds of meta protons in **8**, respectively. The thallated position relative to the OH and  $\text{CH}_3$  groups in **7** and **8** was determined by comparing the coupling constant  $J_{\text{TlCH}_3}$  with that of **9**. The  $J_{\text{TlCH}_3}$  value of **7** was observed to be 22 Hz and the same as that of **9**. The methyl group, therefore, is decided to be located at the position meta and the OH group at

the position para to the thallium atom. In the complex **7**, the slightly large  $J_{\text{TlCH}_3}$  value (26 Hz) was observed, suggesting that the methyl group is at the position ortho to the thallium atom. In both complexes **7** and **8** the thallation occurred at the position para to the hydroxy group.

**Scheme III**



The result that the thallation of **1** exhibited high para selectivity with regard to the OH group deserves special comment. This selectivity may be due to preference that the positive charge induced on the OH group be separated as far as possible from the thallium ion in the intermediate.

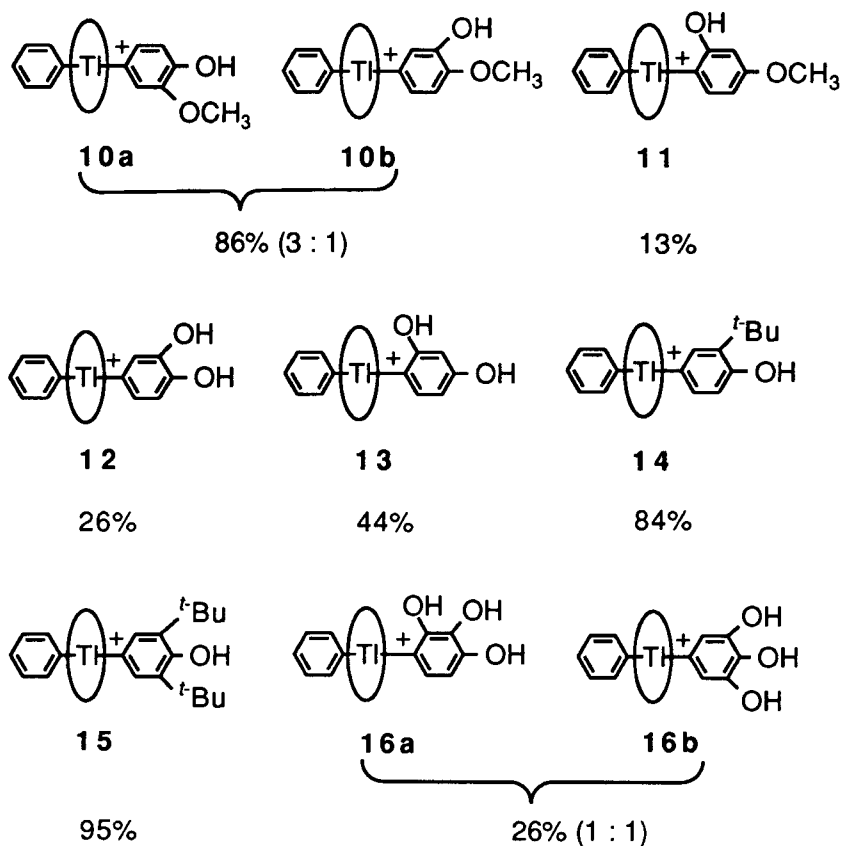
### 1-5 Reaction of (18-Crown-6)phenylthallium(III) Diperchlorate with Phenols Containing Good Electron Donating Group.

The reaction of **1** with 2-methoxyphenol, 3-methoxyphenol, catechol, resorcinol, 2-*tert*-butylphenol, 2,6-di-*tert*-butylphenol, and pyrogallol gave thallated complexes **10-16**, respectively. The complexes **10** and **16** were obtained as a mixture. Yields and the structures of the isolated products are listed in Chart I.

McKillop et al.<sup>2</sup> have reported that the reaction of thallium trinitrate with 2,6-di-*tert*-butylphenol gave 2,6-di-*tert*-butyl-*p*-benzoquinone in high yield. In contrast to this observation, the reaction of **1** with 2,6-di-*tert*-butylphenol proceeded without oxidation of the substrate to give (18-crown-6)(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)phenylthallium(III) per-chlorate (**15**). Furthermore, catechol and pyrogallol, which are easily oxidizable and known as good antioxidants, were also thallated by **1** to give **12** and **16**. The difference in reactivity of **1** for phenols from that of Tl(NO<sub>3</sub>)<sub>3</sub> is weakening of an oxidizing ability of the thallium(III) ion of **1** as a result of the binding of the phenyl group and the coordination of 18-crown-6.

The thallated positions in **12-16** were determined in a similar to that described above. NOE experiments were also used for determination of the thallated position in **10a**, **10b**, and **11**.<sup>5</sup> From the above result on **10**, (18-crown-6)(4'-hydroxy-3'-methoxyphenyl)phenylthallium(III) perchlorate (**10a**) was found to be a major product and (18-crown-6)(3'-hydroxy-4'-methoxyphenyl)phenylthallium(III) perchlorate (**10b**) was found to be a minor product. In the case of 3-methoxyphenol the thallation occurred only at the position para to the methoxy group, affording **11**. The selectivity of the thallation position of 2-methoxyphenol was mainly controlled by an electronic factor in the intermediate, which places two positive charges furthest apart as described above. On the other hand, in the thallation of 3-methoxyphenol, a steric factor dominates the thallation position; a steric repulsion of the crown ether with the OH group at 2'-position is smaller than that with the OCH<sub>3</sub> group at 2'-position.

Chart I

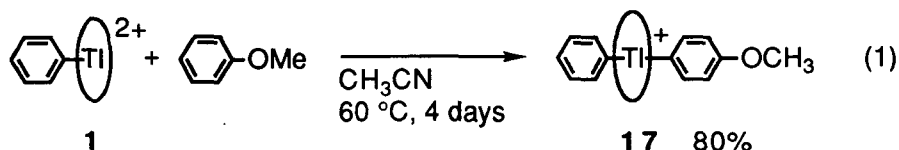


#### 1-6 Reaction with Anisole and Alkylbenzenes.

The reaction **1** with anisole was carried out under the same reaction conditions as described above. The thallation also took place at the position para to the methoxy group, affording (18-crown-6)(4'-methoxyphenyl)phenylthallium(III) perchlorate (**17**) in 80% yield (eq 1). However, when the reaction of **1** with benzene, toluene, and *tert*-butylbenzene were examined under the similar reaction conditions, the aromatic thallation was not observed even after 14 days. McKillop et al.<sup>1g</sup> have reported electrophilic aromatic thallation of benzene, toluene, and halobenzenes with thallium(III) trifluoroacetate. The electrophilicity of **1**,

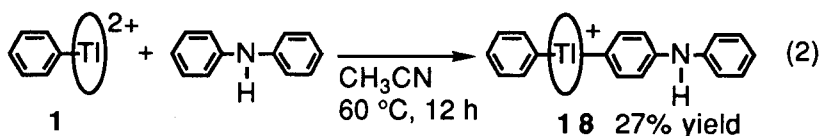


therefore, is not strong enough to cause the thallation of unactivated aromatics.



### 1-7 Reaction of (18-Crown-6)phenylthallium(III) Diperchlorate with Anilines

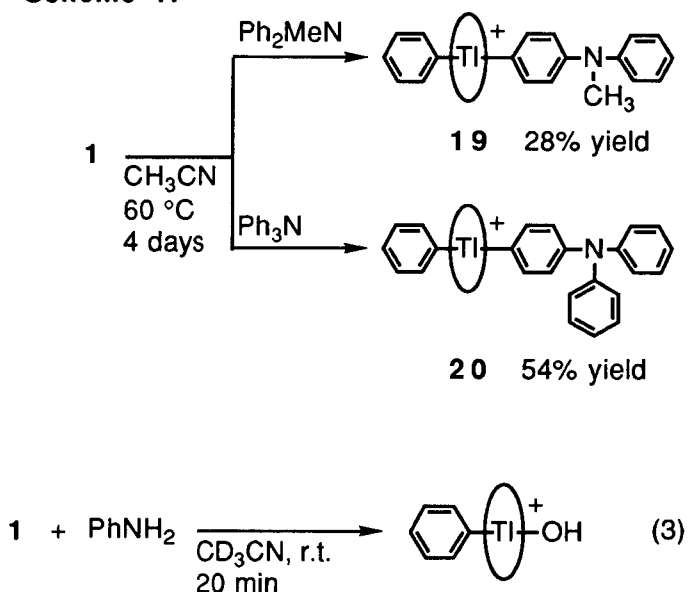
The reaction of **1** with diphenylamine was carried out in acetonitrile at 60 °C for 12 h to give (18-crown-6)[(4'-phenylamino)phenyl]phenylthallium(III) perchlorate (**18**) in 27% yield (eq 2). In the  $^1\text{H}$  NMR spectrum of **18**, the resonances of one phenyl ring ( $\text{H}_2'$  and  $\text{H}_3'$ ) of the diphenylamino group exhibited spin-spin coupling with the thallium nucleus, and the proton resonances of the other phenyl ring were observed as multiplets at  $\delta$  6.6-7.5 ppm without spin-spin coupling with thallium nucleus. Chemical shifts of  $\text{H}_2$ ,  $\text{H}_3$ ,  $\text{H}_2'$ , and  $\text{H}_3'$  were assigned by the following procedure. Signals of  $\text{H}_2$  and  $\text{H}_2'$  were observed as a doublet of doublets and the  $\text{H}_3$  and  $\text{H}_3'$  signals could be distinguished by the spectral pattern ( $\text{H}_3$ , doublet of triplets;  $\text{H}_3'$ , doublet of doublets). In order to assign the  $\text{H}_2$  and  $\text{H}_2'$ , the strong irradiation of either higher field or lower field component of the  $\text{H}_3$  triplet pair proton separated by  $J_{\text{Tl}}$  was performed. This irradiation resulted in, besides disappearance of the other component of the  $\text{H}_3$  pair, collapse of the corresponding one component of the  $\text{H}_2$  doublet pair into a singlet. An N-H stretching frequency,  $\nu(\text{N-H})$ , was observed at  $3364\text{ cm}^{-1}$  in the solid state in IR spectroscopy. These results suggest that the thallation occurred only in one phenyl group at the position para to the amino group. The  $^1\text{H}$  NMR spectra of a reaction mixture between **1** and diphenylamine in  $\text{CD}_3\text{CN}$  showed almost exclusive formation of **18**, without any multithallation product having been detected within an accuracy of the  $^1\text{H}$  NMR spectral measurement.



Analogous reactions with diphenylmethanamine and triphenylamine also led to the thallation only on one phenyl group and at the position para to the amino group (Scheme IV). The thallated positions in the products were determined by the same procedure as that described above. The products, (18-crown-6)[(4'-methylphenylamino)phenyl]phenylthallium(III) perchlorate (**19**) and (18-crown-6)[(4'-diphenylamino)phenyl]phenylthallium(III) perchlorate (**20**), were isolated in 28% and 54% yields, respectively.

Contrary to these, aniline did not undergo thallation with **1** but gave only  $[\text{Ph}(\text{OH})\text{Tl}^{\text{III}}(18\text{-crown-6})](\text{ClO}_4)_6$  at room temperature (eq 3). This compound may have been formed by deprotonation from  $\text{H}_2\text{O}$  coordinated to thallium atom in **1**.<sup>7</sup>

Scheme IV



## 1-8 Experimental Section

**General Considerations.** The  $^1\text{H}$  NMR spectra were recorded on a JEOL PS-100 and JEOL GSX-270 spectrometer operating at 100 and 270 MHz, respectively. Chemical shifts of  $^1\text{H}$  NMR signals are quoted relative to internal tetramethylsilane. Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, c = complex, br = broad), coupling constant (Hz), relative intensity, and interpretation. IR spectra were measured on a Hitachi 215 or a Hitachi 270-50 infrared spectrometer. Melting points were determined in open capillaries on a Mitamura Riken Kogyo melting points apparatus and are uncorrected.

**Materials.** Crown ethers, 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6),<sup>8</sup> 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane (1,10-DTC),<sup>9</sup> 1,7-dithia-4,10,13,16-tetraoxacyclooctadecane (1,7-DTC),<sup>10</sup> 1,4-dithia-7,10,13,16-tetraoxacyclooctadecane (1,4-DTC),<sup>10</sup> and 1-thia-4,7,10,13,16-pentaoxacyclooctadecane (MTC)<sup>10</sup> were prepared by literature methods. Phenols and alkylbenzenes were used without further purification. Aniline was purified by distillation under nitrogen atmosphere. Diphenylamine and triphenylamine were purified by recrystallization. Triethylamine and pyridine were dried over  $\text{CaH}_2$  and purified by distillation under nitrogen atmosphere. Solvents except for acetonitrile were used for without purification. Acetonitrile was dried over  $\text{P}_2\text{O}_5$  and was purified by distillation.

**Caution!** *Thallium compounds are highly toxic. The use of rubber gloves is strongly recommended for handling thallium compounds, whether inorganic or organic. Special care must also be taken in handling potentially explosive perchloric acid as well as perchlorate salts; chemists must prudently exercised safe practices in their manipulation and disposal.*

**(18-Crown-6)phenylthallium(III) Diperchlorate (1).** In a typical preparation, into a suspension of phenylthallium(III) oxide (2.97 g, 10 mmol) in 30 mL of THF was added a THF (10 mL) solution of 60% perchloric acid (5.01 g, 30 mmol). After stirring for 6 h, the resulting clear brown solution was added into a THF (30 mL) solution of 18-crown-6 (2.65 g, 10 mmol) at 0 °C.

After further stirring for 1 h at 0 °C, 200 mL of diethyl ether was added and then colorless solids precipitated. Addition of 100 mL of diethyl ether to an acetonitrile (5 mL) solution of the precipitate gave pure colorless [phenylthallium(III)(18-crown-6)] diperchlorate (**1**) (6.70 g, 9.0 mmol, 90% yield), mp 181 °C dec. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.67 (s, 24 H, 18-crown-6), 7.49 (dd,  $J_{\text{TlH}} = 1173$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.66 (dt,  $J_{\text{TlH}} = 494$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.65 (dt,  $J_{\text{TlH}} = 166$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 6.12 (s, 2 H, H<sub>2</sub>O). IR (Nujol): ν(OH) 3400 (s), ν(C-O-C and ClO<sub>4</sub>) 1085 (s) cm<sup>-1</sup>. Anal. Calcd for (C<sub>18</sub>H<sub>29</sub>Cl<sub>2</sub>O<sub>14</sub>Tl)H<sub>2</sub>O: C, 28.35; H, 4.10. Found: C, 28.21; H, 4.26.

**(MTC)phenylthallium(III) diperchlorate (2)** was prepared by the following method. To a reaction mixture formed from a reaction of phenylthallium(III) oxide, 60% perchloric acid, and MTC was added 200 mL of diethyl ether to give colorless solids. Addition of 100 mL of diethyl ether to an acetonitrile (5 mL) solution of the solids gave a colorless oil. The oil was washed with 10 mL of dichloromethane. Colorless solids precipitated successively and were purified by an addition of 100 mL of diethyl ether to an acetonitrile (5 mL) solution of the solids, affording a colorless [phenylthallium(III)(MTC)] diperchlorate (**2**) (5.33 g, 7.0 mmol, 70% yield), mp 178-179 °C dec. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 4.02 (dt,  $J_{\text{TlH}} = 290$  Hz, 4 H, SCH<sub>2</sub>), δ 3.72-3.91 (c, 16 H, OCH<sub>2</sub>CH<sub>2</sub>O), 4.35 (dt,  $J_{\text{TlH}} = 23$  Hz, 8 H, SCH<sub>2</sub>CH<sub>2</sub>), 7.59 (dd,  $J_{\text{TlH}} = 994$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.65 (dt,  $J_{\text{TlH}} = 424$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.60 (dt,  $J_{\text{TlH}} = 153$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>). IR (Nujol): ν(C-O-C and ClO<sub>4</sub>) 1075 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>29</sub>Cl<sub>2</sub>O<sub>13</sub>STl: C, 28.42; H, 3.84. Found: C, 28.50; H, 3.83.

**(1,4-DTC)phenylthallium(III) diperchlorate (3)**, a colorless solid, mp 166 °C dec, was obtained (6.21 g, 8.0 mmol, 80% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.72 (br d,  $J_{\text{TlH}} = 170$  Hz, 8 H, SCH<sub>2</sub>), δ 3.75 (s, 8 H, OCH<sub>2</sub>CH<sub>2</sub>O), 4.01 (br d,  $J_{\text{TlH}} = 15$  Hz, 8 H, SCH<sub>2</sub>CH<sub>2</sub>), 7.61 (dd,  $J_{\text{TlH}} = 965$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.65 (dt,  $J_{\text{TlH}} = 403$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.59 (dt,  $J_{\text{TlH}} = 149$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>). IR (Nujol): ν(C-O-C and ClO<sub>4</sub>) 1060-1080 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>29</sub>Cl<sub>2</sub>O<sub>12</sub>S<sub>2</sub>Tl: C, 27.83; H, 3.76. Found: C, 28.16; H, 3.75.

**(1,7-DTC)phenylthallium(III) diperchlorate (4)**, a pale yellow solid, mp 148 °C dec, was obtained (5.44 g, 7.0 mmol, 70% yield).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  3.40 (br d,  $J_{\text{TlH}} = 54$  Hz, 8 H,  $\text{SCH}_2$ ),  $\delta$  3.56 (br t,  $J_{\text{HH}} = 4$  Hz, 4 H,  $\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}$ ), 3.8-3.9 (m, 8 H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 4.0 (br d,  $J_{\text{HH}} = 4$  Hz, 4 H,  $\text{SCH}_2\text{CH}_2\text{O}$ ), 7.56 (dd,  $J_{\text{TlH}} = 1008$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_2$ ), 7.59 (dt,  $J_{\text{TlH}} = 419$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_3$ ), 7.53 (dt,  $J_{\text{TlH}} = 160$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H,  $\text{H}_4$ ). IR (Nujol):  $\nu(\text{C-O-C}$  and  $\text{ClO}_4)$  1060-1080 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $(\text{C}_{18}\text{H}_{29}\text{C}_{12}\text{O}_{12}\text{S}_2\text{Tl})_3\text{CH}_3\text{CN}$ : C, 28.36; H, 3.83; N, 0.59. Found: C, 28.30; H, 3.83; N, 0.40.

**(1,10-DTC)phenylthallium(III) diperchlorate (5)**, a colorless solid, mp 195-196 °C dec, was obtained (6.21 g, 8.0 mmol, 80% yield).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  3.72 (br d,  $J_{\text{TlH}} = 170$  Hz, 8 H,  $\text{SCH}_2$ ),  $\delta$  3.75 (m, 8 H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 4.01 (br d,  $J_{\text{TlH}} = 15$  Hz, 8 H,  $\text{SCH}_2\text{CH}_2$ ) 7.74 (dd,  $J_{\text{TlH}} = 987$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H  $\text{H}_2$ ), 7.72 (dt,  $J_{\text{TlH}} = 432$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_3$ ), 7.69 (dt,  $J_{\text{TlH}} = 156$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H,  $\text{H}_4$ ). IR (Nujol):  $\nu(\text{C-O-C}$  and  $\text{ClO}_4)$  1060-1080 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{29}\text{C}_{12}\text{O}_{12}\text{S}_2\text{Tl}$ : C, 27.83; H, 3.76. Found: C, 28.04; H, 3.76.

**Reactions of 1-5 with phenol in NMR tubes.** The complexes (1-5) (0.1 mmol) were dissolved in 0.3 mL of acetonitrile in NMR tubes. An acetonitrile (0.3 mL) solution of phenol (0.038 g, 0.4 mmol) was added into the solutions of the complexes. The solutions were degassed three times by freeze (liquid nitrogen bath)-thaw (water bath) cycles. The tubes were sealed under reduced pressure. The solution was heated at 60 °C in the darkness and progress of the reaction was monitored by  $^1\text{H}$  NMR spectrum.

**(18-Crown-6)(4'-hydroxyphenyl)phenylthallium(III) Perchlorate (6).** In a typical procedure, the complex **1** (1.49 g, 2.00 mmol) was dissolved in 3 mL of acetonitrile in a test tube (18 mm i.d. X 180 mm length). An acetonitrile (2 mL) solution of phenol (0.755 g, 8.02 mmol) was added into the solution of **1**. The solution was degassed three times by freeze (liquid nitrogen bath)-thaw (water bath) cycles. The reaction tube was sealed under reduced pressure. The solution was heated at 60 °C for 4 days in the darkness. Into the reaction mixture was added 120 mL of diethyl ether and

then colorless solids precipitated. Addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solids gave a colorless (18-crown-6)(4'-hydroxyphenyl)phenylthallium(III) perchlorate (**6**) (1.43 g, 1.94 mmol, 97% yield), mp 207 °C dec. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.66 (s, 24 H, 18-crown-6), 7.74 (dd,  $J_{\text{TlH}} = 447$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.56 (dt,  $J_{\text{TlH}} = 140$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.39 (dt,  $J_{\text{TlH}} = 51$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.50 (dd,  $J_{\text{TlH}} = 436$  Hz,  $J_{\text{HH}} = 4.5$  Hz, 2 H, H<sub>2</sub>), 7.04 (dd,  $J_{\text{TlH}} = 111$  Hz,  $J_{\text{HH}} = 4.5$  Hz, 2 H, H<sub>3</sub>). IR (Nujol): ν(OH) 3360 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>34</sub>ClO<sub>11</sub>Tl: C, 38.99; H, 4.77. Found: C, 39.02; H, 4.66.

**(18-Crown-6)(3'-methyl-4'-hydroxyphenyl)phenylthallium(III) perchlorate (7)**, a colorless solid, mp 190 °C dec, was obtained (1.28 g, 1.70 mmol, 85% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2.37 (d,  $J_{\text{TlH}} = 22$  Hz, 3 H, CH<sub>3</sub>), 3.66 (s, 24 H, 18-crown-6), 7.73 (dd,  $J_{\text{TlH}} = 445$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.53 (dt,  $J_{\text{TlH}} = 140$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.36 (dt,  $J_{\text{TlH}} = 50$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.41 (d,  $J_{\text{TlH}} = 444$  Hz, 1 H, H<sub>2</sub>), 6.99 (dd,  $J_{\text{TlH}} = 124$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>5</sub>), 7.34 (dd,  $J_{\text{TlH}} = 436$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>6</sub>). IR (Nujol): ν(OH) 3400 (s) cm<sup>-1</sup>. Anal. Calcd for (C<sub>25</sub>H<sub>36</sub>ClO<sub>11</sub>Tl)<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub>: C, 38.53; H, 4.69. Found: C, 38.84; H, 4.79.

**(18-Crown-6)(2'-methyl-4'-hydroxyphenyl)phenylthallium(III) perchlorate (8)**, a colorless solid, mp 195 °C dec, was obtained (0.35 g, 0.46 mmol, 23% yield) by the reaction of **1** with 2-methylphenol for 7 days and by the same purification as described above. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2.32 (d,  $J_{\text{TlH}} = 26$  Hz, 3 H, CH<sub>3</sub>), 3.66 (s, 24 H, 18-crown-6), 7.78 (dd,  $J_{\text{TlH}} = 480$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.53 (dt,  $J_{\text{TlH}} = 157$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.37 (dt,  $J_{\text{TlH}} = 59$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.19 (d,  $J_{\text{TlH}} = 158$  Hz, 1 H, H<sub>3</sub>), 6.93 (dd,  $J_{\text{TlH}} = 152$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>5</sub>), 7.53 (dd,  $J_{\text{TlH}} = 480$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>6</sub>). IR (Nujol): ν(OH) 3400 (s) cm<sup>-1</sup>. Anal. Calcd for (C<sub>25</sub>H<sub>36</sub>ClO<sub>11</sub>Tl)<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub>: C, 38.53; H, 4.69. Found: C, 38.38; H, 4.72.

**(18-Crown-6)(3',5'-dimethyl-4'-hydroxyphenyl)phenylthallium(III) perchlorate (9)**, a colorless solid, mp 190 °C dec, was obtained (1.30 g, 1.70 mmol, 85% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2.25 (d,  $J_{\text{TlH}} = 22$  Hz, 6 H, CH<sub>3</sub>), 3.66 (s, 24 H, 18-crown-6), 6.26 (s, 1 H, OH), 7.68 (dd,  $J_{\text{TlH}} = 442$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.54 (dt,  $J_{\text{TlH}} = 138$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.39

(dt,  $J_{\text{T1H}} = 54$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.25 (d,  $J_{\text{T1H}} = 450$  Hz, 2 H, H<sub>2</sub>). IR (Nujol):  $\nu(\text{OH})$  3420 (s)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>26</sub>H<sub>38</sub>ClO<sub>11</sub>Tl: C, 40.75; H, 5.00. Found: C, 40.60; H, 5.06.

**(18-Crown-6)(4'-hydroxy-3'-methoxyphenyl)phenylthallium(III) perchlorate (10a) and (18-crown-6)(3'-hydroxy-4'-methoxyphenyl)phenylthallium(III) perchlorate (10b)**, a colorless solid, mp 188 °C dec, was obtained (1.32 g, 1.72 mmol, 86% yield) as a mixture (**10a/10b** = 3/1). This mixture could not be separated by column chromatography. The ratio of **10a/10b** was determined by a comparison of the intensity ratio of H<sub>2'</sub> in **10a** and **10b**. **10a**: <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.60 (s, 24 H, 18-crown-6), 3.90 (s, 3 H, OCH<sub>3</sub>), 7.75 (dd,  $J_{\text{T1H}} = 453$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.35 (d,  $J_{\text{T1H}} = 484$  Hz, 1 H, H<sub>2'</sub>), 7.20 (dd,  $J_{\text{T1H}} = 451$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>6'</sub>). The chemical shifts of H<sub>3</sub>, H<sub>4</sub>, and H<sub>5'</sub> could not be determined because these signals overlapped with other signals. **10b**: <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.60 (s, 24 H, 18-crown-6), 3.90 (s, 3 H, OCH<sub>3</sub>), 7.80 (dd,  $J_{\text{T1H}} = 453$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.26 (d,  $J_{\text{T1H}} = 466$  Hz, 1 H, H<sub>2'</sub>), 7.20 (dd,  $J_{\text{T1H}} = 451$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>6'</sub>). The chemical shifts H<sub>3</sub>, H<sub>4</sub>, and H<sub>5'</sub> could not be determined because these signals overlapped with other signals. IR (Nujol):  $\nu(\text{OH})$  3900 (s)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>25</sub>H<sub>36</sub>ClO<sub>12</sub>Tl: C, 39.08; H, 4.72. Found: C, 38.59; H, 4.77.

**(18-Crown-6)(2'-hydroxy-4'-methoxyphenyl)phenylthallium(III) perchlorate (11)**. The reactants were resolved in a similar way and the solution was heated at 60 °C for 7 days in the darkness. Into the solution was added 120 mL of diethyl ether when a brown oil produced. This oil was purified through silica gel column (eluent: dichloromethane, 18 mm i.d. X 150 mm length, Wako gel C-200). After evaporation of the solvent, a colorless solid remained. Addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solid gave a pure colorless (18-crown-6)(2'-hydroxy-4'-methoxyphenyl)phenylthallium(III) perchlorate (**11**), mp >235 °C dec, (0.200 g, 0.26 mmol, 13% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.60 (s, 24 H, 18-crown-6), 7.83 (dd,  $J_{\text{T1H}} = 486$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.59 (dt,  $J_{\text{T1H}} = 158$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.38 (dt,  $J_{\text{T1H}} = 64$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 6.61 (d,  $J_{\text{T1H}} = 194$  Hz, 1 H, H<sub>3'</sub>), 7.02 (dd,  $J_{\text{T1H}} = 144$  Hz,  $J_{\text{HH}} = 8.0$

Hz, 1 H, H<sub>5</sub>'), 7.58 (dd,  $J_{\text{T1H}} = 460$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>6</sub>'). IR (Nujol):  $\nu(\text{OH})$  3390 (s)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>25</sub>H<sub>36</sub>ClO<sub>12</sub>Tl: C, 39.08; H, 4.72. Found: C, 38.91; H, 4.81.

**(18-Crown-6)(3',4'-dihydroxyphenyl)phenylthallium(III) perchlorate (12)**, a colorless solid, mp 212 °C dec, was obtained (0.39 g, 0.52 mmol, 26% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.59 (s, 24 H, 18-crown-6), 6.85 (s, 2 H, OH), 7.69 (dd,  $J_{\text{T1H}} = 448$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.53 (dt,  $J_{\text{T1H}} = 135$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.36 (dt,  $J_{\text{T1H}} = 68$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.22 (d,  $J_{\text{T1H}} = 474$  Hz, 1 H, H<sub>2</sub>'), 7.01 (dd,  $J_{\text{T1H}} = 151$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>5</sub>'), 7.08 (dd,  $J_{\text{T1H}} = 443$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>6</sub>'). IR (Nujol):  $\nu(\text{OH})$  3370 (s)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>24</sub>H<sub>34</sub>ClO<sub>12</sub>Tl: C, 38.21; H, 4.54. Found: C, 38.33; H, 4.62.

**(18-Crown-6)(2',4'-dihydroxyphenyl)phenylthallium(III) perchlorate (13)**, a colorless solid, mp 230 °C dec, was obtained (0.66 g, 0.88 mmol, 44% yield) by the reaction of **1** with resorcinol for 7 days and by the same purification as described above. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 3.66 (s, 24 H, 18-crown-6), 7.69 (dd,  $J_{\text{T1H}} = 481$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.48 (dt,  $J_{\text{T1H}} = 156$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 6.47 (d,  $J_{\text{T1H}} = 197$  Hz, 1 H, H<sub>3</sub>'), 6.92 (dd,  $J_{\text{T1H}} = 146$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H H<sub>5</sub>'), 7.43 (dd,  $J_{\text{T1H}} = 464$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H H<sub>6</sub>'). The chemical shift of H<sub>4</sub> could not be determined because the signal overlapped with other signals. IR (Nujol):  $\nu(\text{OH})$  3310s  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>24</sub>H<sub>34</sub>ClO<sub>12</sub>Tl: C, 38.21; H, 4.54. Found: C, 38.01; H, 4.63.

**(18-Crown-6)(3'-tert-butyl-4'-hydroxyphenyl)phenylthallium(III)**

**perchlorate (14)**, a colorless solid, mp >235 °C dec, was obtained (1.34 g, 1.68 mmol, 84% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  1.14 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 3.60 (s, 24 H, 18-crown-6), 7.79 (dd,  $J_{\text{T1H}} = 447$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.57 (dt,  $J_{\text{T1H}} = 137$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.44 (dt,  $J_{\text{T1H}} = 57$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.62 (dd,  $J_{\text{T1H}} = 465$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>2</sub>'), 7.01 (dd,  $J_{\text{T1H}} = 133$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>5</sub>'), 7.32 (d,  $J_{\text{T1H}} = 434$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>6</sub>'). IR (Nujol):  $\nu(\text{OH})$  3270 (s)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>28</sub>H<sub>42</sub>ClO<sub>11</sub>Tl: C, 42.33; H, 5.33. Found: C, 42.54; H, 5.38.

**(18-Crown-6)(3',5'-di-tert-butyl-4'-hydroxyphenyl)phenylthallium(III)**

**perchlorate (15)**, a colorless solid, mp 173-174 °C dec, was obtained (1.62



g, 1.90 mmol, 95% yield).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  1.47 (s, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 3.57 (s, 24 H, 18-crown-6), 7.73 (dd,  $J_{\text{TiH}} = 441$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_2$ ), 7.57 (dt,  $J_{\text{TiH}} = 137$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_3$ ). 7.38 (dt,  $J_{\text{TiH}} = 59$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H,  $\text{H}_4$ ), 7.68 (d,  $J_{\text{TiH}} = 480$  Hz, 2 H,  $\text{H}_2$ ). IR (Nujol):  $\nu(\text{OH})$  3420 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{32}\text{H}_{50}\text{ClO}_{11}\text{Ti}(\text{H}_2\text{O})$ : C, 44.25; H, 6.03. Found: C, 44.35; H, 5.92.

**(18-Crown-6)(2',3',4'-trihydroxyphenyl)phenylthallium(III) perchlorate (16a) and (18-crown-6)(3,4,5-trihydroxyphenyl)phenylthallium(III) perchlorate (16b)**. The reaction of **1** with pyrogallol carried out at 60 °C for 1 day. When to the reaction mixture was added 120 mL of diethyl ether, a brown oil produced. This oil was purified through a silica gel column chromatography (eluent:  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2 = 1/2$ , 20 mm i.d. X 200 mm length, Wako gel C-300). After evaporation of the solvent, a colorless solid remained. Addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solids gave (18-crown-6)(2',3',4'-trihydroxyphenyl)phenylthallium(III) perchlorate (**16a**) and (18-crown-6)(3,4,5-trihydroxyphenyl)phenylthallium(III) perchlorate (**16b**) as a mixture (**16a/16b** = 1/1), mp 173-175 °C dec, (0.408 g, 0.52 mmol, 26% yield). **16a**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  3.57 (s, 24 H, 18-crown-6), 7.73 (dd,  $J_{\text{TiH}} = 450$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_2$ ), 7.09 (dd,  $J_{\text{TiH}} = 150$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H,  $\text{H}_5$ ), 7.10 (dd,  $J_{\text{TiH}} = 441$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H,  $\text{H}_6$ ). The chemical shift of  $\text{H}_3$  and  $\text{H}_4$  could not be determined because these signals overlapped with other signals. **16b**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  3.57 (s, 24 H, 18-crown-6), 7.73 (dd,  $J_{\text{TiH}} = 450$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_2$ ), 7.24 (d,  $J_{\text{TiH}} = 471$  Hz, 2 H,  $\text{H}_2$ ). The chemical shift of  $\text{H}_3$  and  $\text{H}_4$  could not be determined because these signals overlapped with other signals. IR (Nujol):  $\nu(\text{OH})$  3400 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $(\text{C}_{24}\text{H}_{34}\text{ClO}_{13}\text{Ti})_2(\text{C}_2\text{H}_5)_2\text{O}$ : C, 38.68; H, 4.87. Found: C, 38.29; H, 4.59.

**(18-Crown-6)(4'-methoxyphenyl)phenylthallium(III) perchlorate (17)**, a colorless, (1.204 g, 1.6 mmol, 80% yield), mp 216 °C dec.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  3.60 (s, 24 H, 18-crown-6), 7.80 (dd,  $J_{\text{TiH}} = 454$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_2$ ), 7.59 (dt,  $J_{\text{TiH}} = 142$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_3$ ). 7.44 (dt,  $J_{\text{TiH}} = 58$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H,  $\text{H}_4$ ), 7.68 (dd,  $J_{\text{TiH}} = 433$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2

H, H<sub>2</sub>) 7.16 (dd,  $J_{\text{TH}} = 110$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>3</sub>). IR (Nujol):  $\nu(\text{C-O-C}$  and  $\text{ClO}_4)$  1080 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{25}\text{H}_{36}\text{ClO}_{11}\text{Tl}$ : C, 39.91; H, 4.82. Found: C, 39.63; H, 4.90.

**Attempted Reactions of 1 with Alkylbenzenes.** The complex **1** (0.074 g, 0.1 mmol) was dissolved in 0.3 mL of acetonitrile in an NMR tube. Into the solution of **1** was added an acetonitrile (0.3 mL) solution of alkylbenzene (0.4 mmol). This solution was degassed three times by freeze (liquid nitrogen bath)-thaw (water bath) cycles. The reaction tube was sealed under reduced pressure. The solution was heated at 60 °C in the darkness, and progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy.

**Reaction of phenylthallium(III) diperchlorate with phenol.** Into a suspension of phenylthallium(III) oxide (0.297 g, 1.0 mmol) in 3 mL of THF was added THF (2 mL) solution of 60% perchloric acid (0.335 g, 2.0 mmol). After stirring for 6 h, a clear brown solution was obtained. To NMR tube (5 mm o.d.) was transferred 0.5 mL (0.1 mmol of  $\text{PhTl}(\text{ClO}_4)_2$ ) of the resulting solution. Phenol (0.038 g, 0.4 mmol) was added to the solution and then the solution was degassed three times by freeze (liquid nitrogen bath)-thaw (water bath) cycles. The tube was sealed under reduced pressure, and then the solution was heated at 40 °C for 5 days in the darkness. Progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy.

**Preparation of (18-Crown-6)[(4'-phenylamino)phenyl]phenylthallium(III) Perchlorate (18).** To a test tube containing **1** (0.372 g, 0.50 mmol) were added 5 mL of acetonitrile and diphenylamine (0.338 g, 2.0 mmol). The solution was degassed three times by freeze (liquid nitrogen bath)-thaw (water bath) cycles and the tube was sealed under reduced pressure. The reaction mixture was heated at 60 °C for 12 h in the darkness and to this solution was added 100 mL of diethyl ether. Oils produced were decanted and purified through silica gel column chromatography (eluent:  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2 = 2/1$ , 20 mm i.d. X 250 mm length, Nakarai Tesque mesh 70-230) to give light purple solids. These were purified by dissolution in acetonitrile (5 mL), followed by addition of 100 mL of diethyl ether to afford **18** as light purple solids, in 27% yield (0.110 g, 0.14 mmol): mp >260 °C dec. <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ ): 3.63 (s, 24 H, 18-crown-6), 6.6-7.5 (m, 5 H,

NC<sub>6</sub>H<sub>5</sub>), 7.78 (dd,  $J_{\text{TIH}} = 440$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.60 (dd,  $J_{\text{TIH}} = 435$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>2</sub>), 7.33 (dd,  $J_{\text{TIH}} = 117$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>3</sub>) (chemical shifts of H<sub>3</sub>, H<sub>4</sub>, and NH resonances could not be determined because these signals overlapped with other signals); IR (Nujol):  $\nu$  (N-H) 3364 (m) cm<sup>-1</sup>. Anal. Calcd for (C<sub>30</sub>H<sub>39</sub>ClNO<sub>10</sub>Tl)<sub>2</sub>H<sub>2</sub>O: C, 43.81; H, 4.90; N, 1.70. Found: C, 43.65; H, 4.89; N, 1.73.

**Preparation of (18-Crown-6)[(4'-methyphenylamino)phenyl]phenylthallium(III) Perchlorate (19).** In a 20-mL round-bottomed flask was placed **1** (0.372 g, 0.5 mmol) and the flask was charged with nitrogen. To this were added 5 mL of acetonitrile and diphenylmethanamine (0.367 g, 2.0 mmol). This solution was heated at 60 °C for 4 days. The reaction mixture was transferred into 100-mL flask. To the reaction mixture was added 100 mL of diethyl ether to give purple oils. These oils were purified by silica gel column chromatography (eluent : CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> = 1/5, 20-mm i.d. X 250-mm length, Nakarai Tesque mesh 70-230). Light purple solids obtained were dissolved in dichloromethane (10 mL). Addition of 100 mL of diethyl ether to this afforded pure **19** as light purple solids in 28% yield (0.116 g, 0.14 mmol), mp 239 °C dec. <sup>1</sup>H NMR (CD<sub>3</sub>CN) 3.38 (s, 3 H, CH<sub>3</sub>), 3.60 (s, 24 H, 18-crown-6), 7.1-7.2 (m, 5 H, NC<sub>6</sub>H<sub>5</sub>), 7.77 (dd,  $J_{\text{TIH}} = 444$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.54 (dt,  $J_{\text{TIH}} = 140$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>3</sub>), 7.52 (dd,  $J_{\text{TIH}} = 429$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>2</sub>), 7.02 (dd,  $J_{\text{TIH}} = 114$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>3</sub>) (chemical shift of the H<sub>4</sub> resonance could not be determined because it overlapped with other signals); IR (Nujol):  $\nu$ (C-O-C and ClO<sub>4</sub>) 1084 (s) cm<sup>-1</sup>. Anal Calcd for C<sub>31</sub>H<sub>41</sub>ClNO<sub>10</sub>Tl: C, 45.00; H, 4.99; N, 1.69. Found: C, 44.60; H, 5.02; N, 1.64.

**Preparation of (18-Crown-6)[(4'-diphenylamino)phenyl]phenylthallium(III) Perchlorate (20).** An acetonitrile (20 mL) solution of **1** (0.745 g, 1.0 mmol) and triphenylamine (0.981 g, 4.0 mmol) was heated at 60 °C for 4 days under nitrogen atmosphere. To the reaction mixture was added 200 mL of diethyl ether. Dark green oils obtained were dissolved in dichloromethane (50 mL), and this solution of oils was washed with two 50 mL portions of deionized water. The dichloromethane layer was dried over MgSO<sub>4</sub> and evaporated in vacuo at room temperature to give green solids. Addition of

100 mL of diethyl ether to an acetonitrile (10 mL) solution of the solids afforded pure **20** as green solids in 54% yield (0.481 g, 0.54 mmol): mp >285 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) 3.69 (s, 24 H, 18-crown-6), 7.0-7.5 (m, 10 H, N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>), 7.67 (dd,  $J_{\text{TiH}} = 440$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.54 (dt,  $J_{\text{TiH}} = 142$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.44 (dd,  $J_{\text{TiH}} = 425$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>2</sub>), 7.12 (dd,  $J_{\text{TiH}} = 112$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>3</sub>) (chemical shift of the H<sub>4</sub> resonance could not be determined because it overlapped with other signals); IR (Nujol):  $\nu(\text{C-O-C and ClO}_4)$  1084 (s) cm<sup>-1</sup>. Anal. Calcd for (C<sub>36</sub>H<sub>43</sub>ClNO<sub>10</sub>Ti)<sub>2</sub>CH<sub>3</sub>CN: C, 48.83; H, 4.93; N, 2.31. Found: C, 48.95; H, 5.04; N, 2.45.

**Reaction of 1 with Aniline.** Into an acetonitrile-*d*<sub>3</sub> (0.6 mL) solution of **1** (0.074 g, 0.1 mmol) was added aniline (0.037 g, 0.4 mmol). <sup>1</sup>H NMR spectra of the reaction mixture were measured after 20 min at room temperature. The complex **1** completely changed to [Ph(OH)Ti<sup>III</sup>(18-crown-6)](ClO<sub>4</sub>).

## 1-9 References and Note

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## Chapter 2

### Electrophilic Thallation of Heteroaromatic Compounds Using (18-Crown-6)phenylthallium(III) Diperchlorate

#### 2-1 Introduction

Electrophilic substitution reactions of heteroaromatic compounds have been widely investigated. Electron rich heteroaromatic compounds such as five-membered heterocycles tend to undergo poly substitution.<sup>1</sup> For example, halogenation reaction pyrrole afford tetrahalogenated pyrrole. Polymercuration<sup>2</sup> of pyrrole,<sup>2c,d</sup> and indole<sup>2e</sup> also occurred by the use of HgX<sub>2</sub> (X = OAc, NCO), which are the only examples of metallation of nitrogen containing heteroaromatic derivatives.

I described in chapter 1 the electrophilic thallation of several phenols and anilines using (18-crown-6)phenylthallium(III) diperchlorate (**1**).<sup>3</sup> In these reactions the thallation occurred exclusively at the position para to electron-donating group such as OH, OCH<sub>3</sub>, and NR<sub>2</sub> and no polythallated product was observed. This result may be traced to steric and/or electronic origins. The electronic origin of the exclusive monothallation may be attributed to electronic repulsion between the positive charge induced at the aromatic ring of the monothallation product and the second molecule of **1**. On the basis of this consideration, it was interesting to examine if monothallation predominates even for more electron rich compounds such as five-membered heteroaromatic compounds.

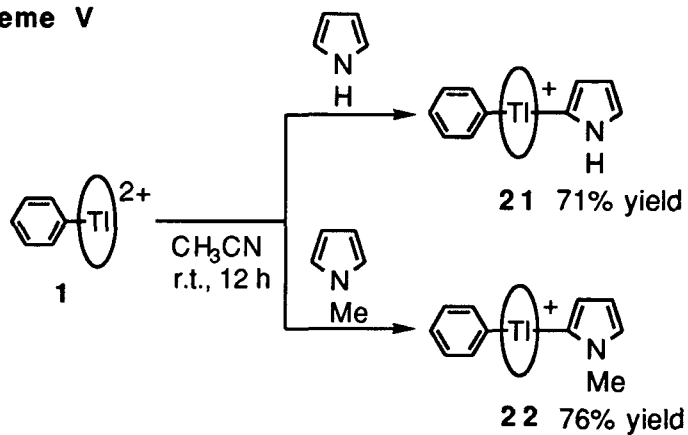
Described herein is a further exploitation of the new method applied to the thallation of pyrroles, pyrazole, thiophenes, and furan. The results indicate that these heteroaromatics also undergo thallation with a feature of typical aromatic substitution and provide a series of new compounds that will be important in the future structural study of organothallium compounds.

## 2-2 Reaction of (18-Crown-6)phenylthallium(III) Diperchlorate with Five-Membered Nitrogen Heterocycles.

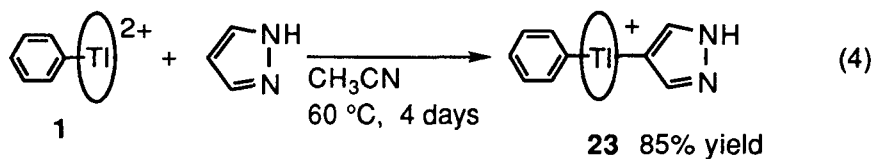
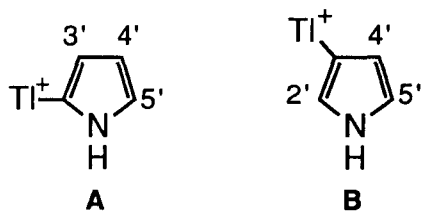
The thallation of pyrrole with **1** in acetonitrile at room temperature for 12 h occurred only at the  $\alpha$ -position to give (18-crown-6)(2'-pyrrolyl)phenylthallium(III) perchlorate (**21**) in 71% isolated yield (Scheme V). Determination of the thallated position in **21** was made by the values of the spin-spin coupling constant between the thallium nucleus and pyrrolyl group protons. On strong irradiation of one component of each pair of the signals separated by  $J_{Tl}$ , the intensity of the other component of the pair decrease. Thus, this observation indicates that saturation transfer occurred from the proton signal irradiated to the signals spin coupled with the thallium nucleus. This saturation transfer method is useful for determination of each pair of the spin separated proton signals. When the thallation occurs at the  $\alpha$ -position (see **A** of Chart II), three resonances of the pyrrolyl group ( $H_{3'}$ ,  $H_{4'}$ , and  $H_{5'}$ ) with  $^3J_{Tl}$  (Tl-C-C-H),  $^4J_{Tl}$  (Tl-C-C-C-H), and  $^4J_{Tl}$  (Tl-C-N-C-H), respectively, would be observed; i.e. one large and two small spin-spin coupling constants. In the case of thallation at the  $\beta$ -position (**B**), three resonances of the pyrrolyl group ( $H_{2'}$ ,  $H_{4'}$ ,  $H_{5'}$ ) with  $^3J_{Tl}$  (Tl-C-C-H),  $^3J_{Tl}$  (Tl-C-C-H), and  $^4J_{Tl}$  (Tl-C-C-C-H), respectively, would be observed: i.e. two large and one small spin-spin coupling constant. The spin-spin coupling constants observed in **21** are 212, 76, and 55 Hz. One large and two small  $J$  values suggest that the thallium moiety is located at the  $\alpha$ -position (**A**). Formation of multiply thallated complexes were not detected in the reaction mixture, even if a 4-fold excess of **1** was used. The thallation of *N*-methylpyrrole also took place at the  $\alpha$ -position, and the complex was isolated in 76% yield (Scheme V).

The thallation of pyrazole took place at the 4-position to give (18-crown-6)(4'-pyrazolyl)phenylthallium(III) perchlorate (**23**) in 85% isolated yield (eq 4). An IR absorption at  $3108\text{ cm}^{-1}$  indicated the presence of an N-H bond in **23**. In the  $^1\text{H}$  NMR spectrum of **23**, only one kind of C-H signal of the pyrazole moiety was observed. This result suggests that there is a rapid movement of the N-H hydrogen as shown in Scheme VI.

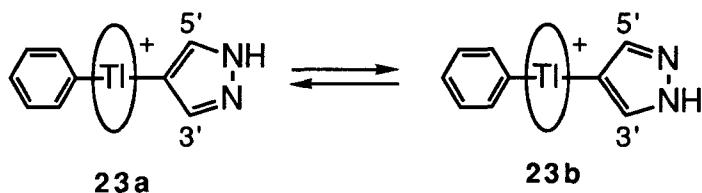
**Scheme V**



**Chart II**



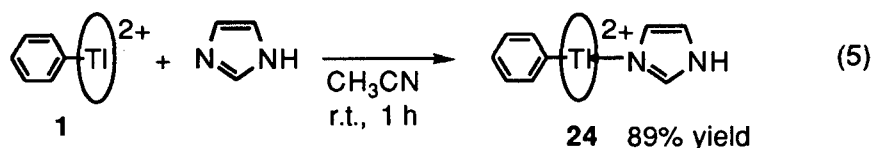
**Scheme VI**



**2-3 Reaction of (18-Crown-6)phenyltitanium(III) Diperchlorate with Imidazole and *N*-methylimidazole.**



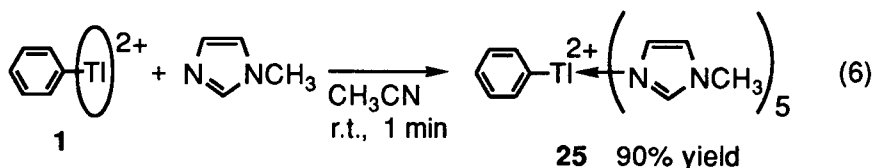
The reaction with imidazole was carried out at room temperature for 1 h. Colorless solids were obtained by addition of diethyl ether to the reaction mixture. The elemental analysis of the product agrees with the formula  $[\text{PhTi}^{\text{III}}(18\text{-crown-6})(\text{imidazole})](\text{ClO}_4)_2$  (**24**), and the isolated yield of the adduct was 89% after recrystallization from  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$  (eq 5). In an IR measurement in Nujol mull, the  $\nu(\text{N-H})$  band was observed at  $3160\text{ cm}^{-1}$ .



Reactions of **24** with NaCl and triethylamine were carried out in  $\text{CD}_3\text{CN}/\text{D}_2\text{O}$  and  $\text{CD}_3\text{CN}$ , respectively, at room temperature. In the former reaction, the imidazole ligand was substituted with chloride ion, giving  $[\text{Ph}(\text{Cl})\text{Ti}^{\text{III}}(18\text{-crown-6})](\text{ClO}_4)$ .<sup>4</sup> In the latter, however, the product was  $[\text{Ph}(\text{OH})\text{Ti}^{\text{III}}(18\text{-crown-6})](\text{ClO}_4)$ ,<sup>5</sup> which may be formed by a reaction of **1** with  $\text{OH}^-$  which was generated by triethylamine and moisture in  $\text{CD}_3\text{CN}$ . The coordinated imidazole, however, was not substituted with pyridine even after heating at  $60\text{ }^\circ\text{C}$  for 1 day in acetonitrile containing a large excess of pyridine. The steric bulk of imidazole and 18-crown-6 would have prohibited the approach of a large ligand such as pyridine. We cannot rule out the alternative possibility that the substitution reaction by pyridine is thermodynamically unfavored. However, the reaction of **1** with pyridine afforded only  $[\text{Ph}(\text{OH})\text{Ti}^{\text{III}}(18\text{-crown-6})](\text{ClO}_4)$ , which is produced by a deprotonation reaction from **1**.

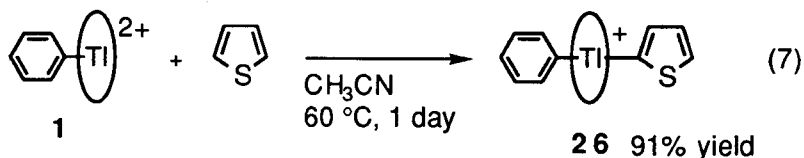
When the reaction of **1** with 10 equiv of *N*-methylimidazole<sup>6</sup> was carried out at room temperature, colorless precipitates appeared immediately. In contrast to the reaction with imidazole, the complex obtained was found to be crown ether free pentakis(*N*-methylimidazole)phenylthallium(III) diperchlorate (**25**) (90% yield) (eq 6) on the basis of an elemental analysis.

This complex may be produced by coordination of *N*-methylimidazole to the phenylthallium(III) ion which was generated by dissociation of 18-crown-6 from **1**. It is uncertain why the reaction of **1** with imidazole gives adduct **24** and the reaction of **1** with *N*-methylimidazole gives the crown ether free complex **25**.



#### 2-4 Reaction of (18-Crown-6)phenylthallium(III) Dip perchlorate with Thiophenes and Furan.

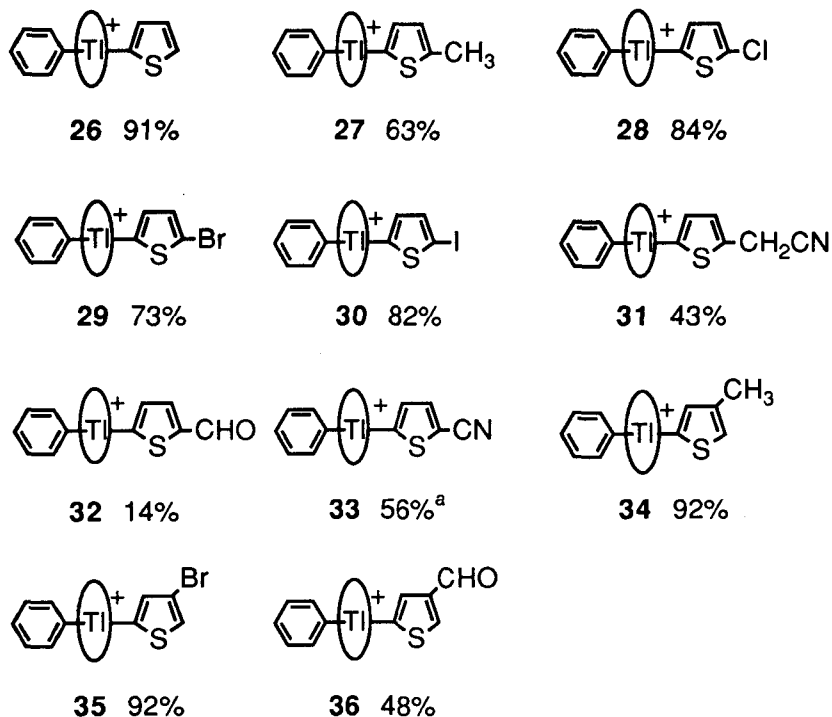
The electrophilic thallation of thiophene with **1** was carried out at 60 °C for 1 day to afford (18-crown-6)(2'-thienyl)phenylthallium(III) perchlorate (**26**) in 91% yield after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (eq 7).



The thallated position in **26** was determined by the <sup>1</sup>H NMR spectrum. Assignment of the chemical shifts and the *J*<sub>TlH</sub> values for H<sub>2</sub>-H<sub>4</sub> and H<sub>3</sub>'-H<sub>5</sub>' was done by examining the Tl-H spin-spin coupling patterns and utilizing the double-irradiation technique, as described above. In this compound one low-field signal and the two high field signals for the protons in the thienyl group (δ 7.89, *J*<sub>TlH</sub> = 165 Hz; δ 7.54, *J*<sub>TlH</sub> = 255 Hz; δ 7.45, *J*<sub>TlH</sub> = 78 Hz) were observed.<sup>7</sup> The assignment of the two β-protons (H<sub>3</sub>' and H<sub>4</sub>') was made by comparison of the *J*<sub>TlH</sub> values (<sup>3</sup>*J*<sub>TlH</sub> = 255 and <sup>4</sup>*J*<sub>TlH</sub> = 78 Hz, respectively) with those of thienylmercury compounds.<sup>8</sup>

The reaction of **1** with 4 equiv of thiophene in acetonitrile- $d_3$  at 60 °C was monitored by  $^1\text{H}$  NMR spectroscopy for 24 h. The observed product was only **26**, indicating the exclusive thallation at the position  $\alpha$  to the sulfur atom.

Chart III

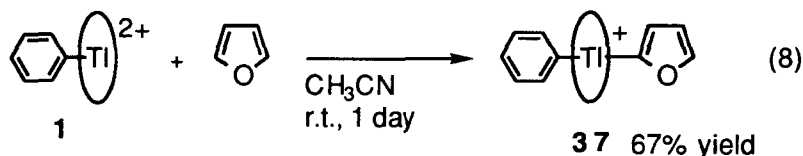


<sup>a</sup>The reaction was carried out under reflux conditions.

The reactions of **1** with several substituted thiophenes were carried out, and the results are given in Chart III. The thallated positions in the products, **27-36**, were determined by the same procedure as described above. The thallations of 2-methyl-, 2-chloro-, 2-bromo-, and 2-iodothiophenes, 2-thiopheneacetonitrile, and 2-thiophenecarboxaldehyde gave the corresponding  $\alpha$ -thallated complexes in good yields. A higher reaction temperature (reflux conditions) was required to accomplish the thallation of

2-thiophenecarbonitrile. In the case of 3-methylthiophene, 3-bromothiophene, and 3-thiophenecarboxaldehyde,  $\alpha$ -thallated compounds **33-36** were isolated in good to excellent yields. The reaction of furan with **1** gave the  $\alpha$ -thallated product, (18-crown-6)(2'-furyl)phenylthallium(III) perchlorate (**37**), in 67% yield under mild reaction conditions (room temperature) (eq 8).

The fact that the CHO group remained intact in **32** and **36** may be related to the weak oxidizing ability of the thallium atom in **1**, which was also observed in the reaction with catechol and pyrogallol.<sup>9</sup> It is also interesting to note that **1** reacted even with 2-thiophenecarbonitrile 2- and 3-thiophenecarboxaldehydes having strong electron-withdrawing groups.



## 2-5 Experimental Section

**General Consideration.** The <sup>1</sup>H NMR spectra were recorded on a JEOL PS-100 and JEOL GSX-270 spectrometer operating at 100 and 270 MHz, respectively. Chemical shifts of <sup>1</sup>H NMR signals are quoted relative to internal tetramethylsilane. Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant (Hz), relative intensity, and interpretation. IR spectra were measured on a Hitachi 215 or a Hitachi 270-50 infrared spectrometer. Melting points were determined in open capillaries on a Mitamura Riken Kogyo melting points apparatus and are uncorrected.

**Materials.** Pyrrole, *N*-methylpyrrole, thiophene, and furan were purified by distillation under nitrogen atmosphere. Triethylamine and pyridine were dried over CaH<sub>2</sub> and purified by distillation under nitrogen atmosphere. Solvents except for acetonitrile were used without further purification. Acetonitrile was dried over P<sub>2</sub>O<sub>5</sub> and purified by distillation under nitrogen atmosphere.

**Preparation of (18-Crown-6)(2'-pyrrolyl)phenylthallium(III) Perchlorate (21).** A 20-mL round-bottomed flask containing **1** (1.489 g, 2.0 mmol) was charged with nitrogen. To this were added 5 mL of acetonitrile and pyrrole (0.537 g, 8.0 mmol). After the mixture was stirred at room temperature for 12 h, colorless solids precipitated. The solids were filtered with suction (**A**). An additional amount of brown solids was obtained by addition of 100 mL of diethyl ether to the filtrate. A dichloromethane (30 mL) solution of the brown solids was washed with two 50 mL portions of deionized water, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure at room temperature. Addition of 100 mL of diethyl ether to the concentrated solution afforded colorless solids (**B**). Both **A** and **B** are pure **21** (71% yield, 1.00 g, 1.42 mmol): mp 312 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) 3.64 (s, 24 H, 18-crown-6), 7.71 (dd, *J*<sub>TIH</sub> = 449 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>2</sub>), 7.57 (dt, *J*<sub>TIH</sub> = 141 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>3</sub>), 7.42 (dt, *J*<sub>TIH</sub> = 67 Hz, *J*<sub>HH</sub> = 8.0 Hz, 1 H, H<sub>4</sub>), 6.62 (d, *J*<sub>TIH</sub> = 212 Hz, 1 H, H<sub>3'</sub>), 6.80 (d, *J*<sub>TIH</sub> = 76 Hz, 1 H, H<sub>4'</sub>), 6.71 (d, *J*<sub>TIH</sub> = 55 Hz, 1 H, H<sub>5'</sub>); IR (Nujol) ν(N-H) 3352 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>33</sub>ClNO<sub>10</sub>Tl: C, 37.15; H, 4.68; N, 1.97. Found: C, 37.12; H, 4.69; N, 1.96.

**Preparation of (18-Crown-6)(2'-N-methylpyrrolyl)phenylthallium(III) Perchlorate (22).** Reactants (**1**, 0.372 g, 0.50 mmol; N-methylpyrrole, 0.162 g, 2.0 mmol) were dissolved in 5 mL of acetonitrile in a 20-mL round-bottomed flask. This solution was stirred at room temperature under nitrogen atmosphere in the darkness for 12 h. To the reaction mixture was added 100 mL of diethyl ether. Pale yellow solids that precipitated were dissolved in 50 mL of dichloromethane, and the resulting solution was washed with four 50 mL portions of deionized water. The organic layer was dried over MgSO<sub>4</sub> and evaporated in vacuo at room temperature to give colorless solids. Addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solids afforded **22** as colorless solids in 76% yield (0.273 g, 0.38 mmol): mp >260 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) 3.69 (s, 24 H, 18-crown-6), 7.76 (dd, *J*<sub>TIH</sub> = 450 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>2</sub>), 7.61 (dt, *J*<sub>TIH</sub> = 146 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>3</sub>), 7.38 (dt, *J*<sub>TIH</sub> = 60 Hz, *J*<sub>HH</sub> = 8.0 Hz, 1 H, H<sub>4</sub>), 3.79 (d, *J*<sub>TIH</sub> = 6 Hz, 3 H, CH<sub>3</sub>), 6.56 (d, *J*<sub>TIH</sub> = 217 Hz, 1 H, H<sub>3'</sub>),

6.72 (d,  $J_{\text{T1H}} = 94$  Hz, 1 H, H<sub>4</sub>), 7.20 (d,  $J_{\text{T1H}} = 65$  Hz, 1 H, H<sub>5</sub>); IR (Nujol)  $\nu$  (C-O-C and ClO<sub>4</sub>) 1095 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>35</sub>ClNO<sub>10</sub>Tl: C, 38.09; H, 4.86; N, 1.91. Found: C, 37.70; H, 4.92; N, 2.33.

**Preparation of (18-Crown-6)(4'-pyrazolyl)phenylthallium(III) Perchlorate (23).** Reactants (**1**, 0.372 g, 0.50 mmol; pyrazole, 0.136 g, 2.00 mmol) were dissolved in 5 mL of acetonitrile in a test tube. The solution was degassed three times by freeze (liquid nitrogen bath)-thaw (water bath) cycles, and then the tube was sealed under reduced pressure. This solution was heated at 60 °C for 4 days in the darkness. To the reaction mixture was added 100 mL of diethyl ether to give colorless precipitates. Addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solids afforded **23** as colorless solids in 85% yield (0.303 g, 0.43 mmol): mp 225 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) 3.66 (s, 24 H, 18-crown-6), 7.75 (dd,  $J_{\text{T1H}} = 562$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.65 (dt,  $J_{\text{T1H}} = 187$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.57 (dt,  $J_{\text{T1H}} = 65$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 8.30 (d,  $J_{\text{T1H}} = 104$  Hz, 2 H, H<sub>3</sub>), 10.80 (s, 1 H, N-H); IR (Nujol)  $\nu$  (N-H) 3108 (w) cm<sup>-1</sup>. Anal. Calcd for (C<sub>21</sub>H<sub>32</sub>ClN<sub>2</sub>O<sub>10</sub>Tl)CH<sub>2</sub>Cl<sub>2</sub>: C, 33.14; H, 4.30; N, 3.51. Found: C, 33.25; H, 4.59; N, 3.26.

**Preparation of (18-Crown-6)(imidazole)phenylthallium(III) Diperchlorate (24).** In a 20-mL round-bottomed flask was placed **1** (1.489 g, 2.00 mmol), and the flask was charged with nitrogen. To this were added 5 mL of acetonitrile and imidazole (0.545 g, 8.00 mmol). The solution was stirred at room temperature for 1 h. To the reaction mixture was added 100 mL of diethyl ether to give colorless precipitates. The solids were filtered and washed with 50 mL of diethyl ether. Addition of 100 mL of diethyl ether to an acetonitrile (5 mL) solution of the solids afforded pure **24** as colorless solids in 89% yield (1.443 g, 1.78 mmol): mp 246 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) 3.65 (s, 24 H, 18-crown-6), 7.75 (dd,  $J_{\text{T1H}} = 953$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.65 (dt,  $J_{\text{T1H}} = 377$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.67 (dt,  $J_{\text{T1H}} = 127$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 8.57 (d,  $J_{\text{T1H}} = 41$  Hz, 1 H, H<sub>2</sub>), 7.14 (d,  $J_{\text{T1H}} = 52$  Hz, 1 H, H<sub>4</sub>), 8.35 (d,  $J_{\text{T1H}} = 41$  Hz, 1 H, H<sub>5</sub>); IR (Nujol)  $\nu$  (N-H) 3160 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>21</sub>H<sub>33</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>14</sub>Tl: C, 31.03; H, 4.09; N, 3.45. Found: C, 31.39; H, 3.94; N, 3.44.

**Preparation of Pentakis(*N*-methylimidazole)phenylthallium(III) Dipерchlorate (25).** Reactants (**1**, 0.372 g, 0.50 mmol; *N*-methylimidazole, 0.430 g, 5.0 mmol) were resolved in a similar way as in **24** and the solution was stirred at room temperature for 1 min in the darkness. Colorless solids precipitated. To the reaction mixture was added 100 mL of diethyl ether to enforce precipitation of all amount of the product. The solids obtained were washed with 100 mL of diethyl ether. Addition of 150 mL of diethyl ether to an acetonitrile (30 mL) solution of the solids afforded pure **25** as colorless solids in 90% yield (0.409 g, 0.45 mmol): mp 197 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) 7.38 (dd,  $J_{\text{TIH}} = 903$  Hz,  $J_{\text{HH}} = 7.5$  Hz, 2 H, H<sub>2</sub>), 7.52 (dt,  $J_{\text{TIH}} = 335$  Hz,  $J_{\text{HH}} = 7.5$  Hz, 2 H, H<sub>3</sub>), 7.47 (dt,  $J_{\text{TIH}} = 116$  Hz,  $J_{\text{HH}} = 7.5$  Hz, 1 H, H<sub>4</sub>), 3.73 (s, 15 H, CH<sub>3</sub>), 7.60 (s, 5 H, H<sub>2'</sub>), 7.18 (s, 5 H, H<sub>4'</sub>), 6.86 (s, 5 H, H<sub>5'</sub>); IR (Nujol)  $\nu$  (C-O-C and ClO<sub>4</sub>) 1097 (s) cm<sup>-1</sup>. Anal. Calcd for (C<sub>26</sub>H<sub>35</sub>Cl<sub>2</sub>N<sub>10</sub>O<sub>8</sub>Tl)H<sub>2</sub>O: C, 34.36 ; H, 4.10; N, 15.41. Found: C, 34.31; H, 3.88; N, 15.39.

**Reaction of 24 with NaCl in CD<sub>3</sub>CN/D<sub>2</sub>O Mixed Solvent.** Into an acetonitrile-*d*<sub>3</sub> (0.5 mL) solution of **24** (0.0816 g, 0.1 mmol) was added D<sub>2</sub>O (0.2 mL) solution of NaCl (0.0040 g, 0.1 mmol). An <sup>1</sup>H NMR spectrum of the reaction mixture was measured after 20 min at room temperature showed that complex **24** completely changed to [Ph(Cl)Tl<sup>III</sup>(18-crown-6)](ClO<sub>4</sub>) and free imidazole.

**Reaction of 24 with Triethylamine.** Into an acetonitrile-*d*<sub>3</sub> (0.6 mL) solution of **24** (0.0816 g, 0.1 mmol) was added triethylamine (0.0010 g, 0.1 mmol). An <sup>1</sup>H NMR spectrum of the reaction mixture was measured after twenty minutes at room temperature showed that complex **24** completely changed to [Ph(OH)Tl<sup>III</sup>(18-crown-6)](ClO<sub>4</sub>) and free imidazole.

**Reaction of 24 with Pyridine.** Into an acetonitrile-*d*<sub>3</sub> (0.6 mL) solution of **24** (0.0816 g, 0.1 mmol) was added pyridine (0.079 g, 1.0 mmol). An <sup>1</sup>H NMR spectrum of the reaction mixture measured after heating at 60 °C for 1 day showed no ligand exchange reaction.

**Preparation of (18-Crown-6)(2'-thienyl)phenylthallium(III) Perchlorate (26).** In a typical preparation procedure, to a test tube containing **1** (0.745 g, 1.00 mmol) were added 2.5 mL of acetonitrile and thiophene (0.337 g, 4.00

mmol). This solution was degassed three times by freeze (liquid nitrogen bath)-thaw (water bath) cycles and then the tube was sealed under reduced pressure. The solution was heated at 60 °C for 24 h in the dark and to the reaction mixture was added 100 mL of diethyl ether to enforce the precipitation of the product. These resulting solids were filtered and the purification was carried out by addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solids. The solids produced were filtered and the these solids dissolved in 5 mL of acetonitrile. Addition of 100 mL of diethyl ether to the solution gave pure **26**, in 91% yield (0.663 g, 0.91 mmol), mp 271 °C dec. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.65 (s, 24 H, 18-crown-6), 7.67 (dd,  $J_{\text{T1H}} = 529$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.61 (dt,  $J_{\text{T1H}} = 173$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.46 (dt,  $J_{\text{T1H}} = 63$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.54 (dd,  $J_{\text{T1H}} = 255$  Hz,  $J_{\text{HH}} = 2.0$  Hz, 1 H, H<sub>3'</sub>), 7.45 (dd,  $J_{\text{T1H}} = 78$  Hz,  $J_{\text{HH}} = 5.0$  Hz, 1 H, H<sub>4'</sub>), 7.89 (dd,  $J_{\text{T1H}} = 165$  Hz,  $J_{\text{HH}} = 5.0$  Hz, 1 H, H<sub>5</sub>). IR (Nujol): ν (C-O-C and ClO<sub>4</sub>) 1090 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>32</sub>ClO<sub>10</sub>STl: C, 36.28; H, 4.43. Found: C, 36.30; H, 4.39.

**(18-Crown-6)(5'-methyl-2'-thienyl)phenylthallium(III) perchlorate (27)**, mp 306 °C dec, was isolated in 63% yield (0.468 g, 0.63 mmol) after silica gel column chromatography (20 mm i.d. X 200 mm, eluent 1/2 CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>, Wako gel C-200) and recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.64 (s, 24 H, 18-crown-6), 7.66 (dd,  $J_{\text{T1H}} = 521$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.59 (dt,  $J_{\text{T1H}} = 173$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.45 (dt,  $J_{\text{T1H}} = 61$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.28 (d,  $J_{\text{T1H}} = 275$  Hz, 1 H, H<sub>3'</sub>), 7.28 (d,  $J_{\text{T1H}} = 98$  Hz, 1 H, H<sub>4'</sub>), 2.60 (d,  $J_{\text{T1H}} = 9$  Hz, 3 H, CH<sub>3</sub>). IR (Nujol): ν (C-O-C and ClO<sub>4</sub>) 1090 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>34</sub>ClO<sub>10</sub>STl: C, 37.21; H, 4.62. Found: C, 37.71; H, 4.62.

**(18-Crown-6)(5'-chloro-2'-thienyl)phenylthallium(III) perchlorate (28)**, mp 195 °C dec, was isolated in 84% yield (0.64 g, 0.84 mmol) after recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.66 (s, 24 H, 18-crown-6), 7.72 (dd,  $J_{\text{T1H}} = 544$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.63 (dt,  $J_{\text{T1H}} = 185$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.51 (dt,  $J_{\text{T1H}} = 72$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.63 (d,  $J_{\text{T1H}} = 288$  Hz, 1 H, H<sub>3'</sub>), 7.30 (d,  $J_{\text{T1H}} = 100$



Hz, 1 H, H<sub>4</sub>). IR (Nujol):  $\nu$  (C-O-C and ClO<sub>4</sub>) 1086 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>31</sub>Cl<sub>2</sub>O<sub>10</sub>STl: C, 34.64; H, 4.10. Found: C, 34.96; H, 4.20.

**(18-Crown-6)(5'-bromo-2'-thienyl)phenylthallium(III) perchlorate (29)**, mp 222 °C dec, was isolated in 73% yield (0.590 g, 0.73 mmol) after recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.67 (s, 24 H, 18-crown-6), 7.72 (dd,  $J_{\text{TlH}} = 546$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.60 (dt,  $J_{\text{TlH}} = 184$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.48 (dt,  $J_{\text{TlH}} = 65$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.31 (d,  $J_{\text{TlH}} = 284$  Hz, 1 H, H<sub>3</sub>), 7.43 (d,  $J_{\text{TlH}} = 96$  Hz, 1 H, H<sub>4</sub>). IR (Nujol):  $\nu$  (C-O-C and ClO<sub>4</sub>) 1087 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>31</sub>BrClO<sub>10</sub>STl: C, 32.73; H, 3.87. Found: C, 32.99; H, 3.99.

**(18-Crown-6)(5'-iodo-2'-thienyl)phenylthallium(III) perchlorate (30)**, mp 268 °C dec, was isolated in 82% yield (0.700 g, 0.82 mmol) after recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.65 (s, 24 H, 18-crown-6), 7.66 (dd,  $J_{\text{TlH}} = 545$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.61 (dt,  $J_{\text{TlH}} = 186$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.57 (dt,  $J_{\text{TlH}} = 61$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.22 (d,  $J_{\text{TlH}} = 274$  Hz, 1 H, H<sub>3</sub>), 7.63 (d,  $J_{\text{TlH}} = 88$  Hz, 1 H, H<sub>4</sub>). IR (Nujol):  $\nu$  (C-O-C and ClO<sub>4</sub>) 1089 (s) cm<sup>-1</sup>. Anal. Calcd for (C<sub>22</sub>H<sub>31</sub>ClIO<sub>10</sub>STl)H<sub>2</sub>O: C, 30.29; H, 3.81. Found: C, 30.35; H, 3.63.

**Preparation of (18-Crown-6)(5'-cyanomethyl-2'-thienyl)phenylthallium(III) Perchlorate (31)**. The reaction of **1** with 2-thiopheneacetonitrile was carried out in acetonitrile under refluxing condition for 24 hours. The complex **31**, mp 238 °C dec, was isolated in 43% yield (0.320 g, 0.43 mmol) after silica gel column chromatography (25 mm i.d. X 180 mm, eluent 1/5 CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>, Wako gel C-200) and recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.67 (s, 24 H, 18-crown-6), 7.70 (dd,  $J_{\text{TlH}} = 540$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 2 H, H<sub>2</sub>), 7.64 (dt,  $J_{\text{TlH}} = 177$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.44 (dt,  $J_{\text{TlH}} = 56$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 1 H, H<sub>4</sub>), 7.40 (dd,  $J_{\text{TlH}} = 270$  Hz,  $J_{\text{HH}} = 4$  Hz, 1 H, H<sub>3</sub>), 7.38 (d,  $J_{\text{TlH}} = 95$  Hz,  $J_{\text{HH}} = 4$  Hz, 1 H, H<sub>4</sub>), 4.14 (d,  $J_{\text{HH}} = 4$  Hz, 2 H, CH<sub>2</sub>CN). IR (Nujol):  $\nu$  (CN) 2252 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>33</sub>ClNO<sub>10</sub>STl: C, 37.56; H, 4.33; N, 1.83. Found: C, 37.31; H, 4.33; N, 1.67.

**(18-Crown-6)(5'-formyl-2'-thienyl)phenylthallium(III) perchlorate (32)**, mp 295 °C dec, was isolated in 48% yield (0.363 g, 0.48 mmol) after silica gel

column chromatography (20 mm i.d. X 150 mm, eluent 1/2 CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>, Nakarai Tesque mesh 70-230) and recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.64 (s, 24 H, 18-crown-6), 7.70 (dd, *J*<sub>TIH</sub> = 544 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>2</sub>), 7.59 (dt, *J*<sub>TIH</sub> = 182 Hz, *J*<sub>TIH</sub> = 7.0 Hz, 2 H, H<sub>3</sub>), 7.45 (dt, *J*<sub>TIH</sub> = 65 Hz, *J*<sub>HH</sub> = 8.0 Hz, 1 H, H<sub>4</sub>), 7.79 (d, *J*<sub>TIH</sub> = 258 Hz, 1 H, H<sub>3'</sub>), 8.65 (d, *J*<sub>TIH</sub> = 157 Hz, 1 H, H<sub>5</sub>'), 10.20 (d, *J*<sub>TIH</sub> = 66 Hz, 1 H, CHO). IR (Nujol): ν (C=O) 1680 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>32</sub>ClO<sub>11</sub>STl: C, 36.52; H, 4.26. Found: C, 36.24; H, 4.18.

**Preparation of (18-Crown-6)(5'-cyano-2'-thienyl)phenylthallium(III) Perchlorate (33).** The reaction of **1** with 2-thiophenecarbonitrile was carried out in acetonitrile under refluxing condition for 24 h. The complex **33**, mp 254 °C dec, was isolated in 56% yield (0.422 g, 0.56 mmol) after silica gel column chromatography (25 mm i.d. X 180 mm, eluent 1/5 CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>, Wako gel FC-40) and recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.67 (s, 24 H, 18-crown-6), 7.72 (dd, *J*<sub>TIH</sub> = 536 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>2</sub>), 7.62 (dt, *J*<sub>TIH</sub> = 177 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>3</sub>), 7.40 (dt, *J*<sub>TIH</sub> = 64 Hz, *J*<sub>HH</sub> = 8.0 Hz, 1 H, H<sub>4</sub>), 7.38 (d, *J*<sub>TIH</sub> = 267 Hz, 1 H, H<sub>3'</sub>), 7.38 (d, *J*<sub>TIH</sub> = 98 Hz, 1 H, H<sub>4'</sub>). IR (Nujol): ν (CN) 2252 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>31</sub>ClNO<sub>10</sub>STl: C, 36.67; H, 4.15; N, 1.86. Found: C, 36.84; H, 4.16; N, 1.80.

**(18-Crown-6)(4'-methyl-2'-thienyl)phenylthallium(III) perchlorate (34)**, mp 234 °C dec, was isolated in 92% yield (0.683 g, 0.92 mmol) after recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.65 (s, 24 H, 18-crown-6), 7.74 (dd, *J*<sub>TIH</sub> = 522 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>2</sub>), 7.60 (dt, *J*<sub>TIH</sub> = 170 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>3</sub>), 7.45 (dt, *J*<sub>TIH</sub> = 63 Hz, *J*<sub>HH</sub> = 8.0 Hz, 1 H, H<sub>4</sub>), 7.27 (d, *J*<sub>TIH</sub> = 255 Hz, 1 H, H<sub>3'</sub>), 7.43 (d, *J*<sub>TIH</sub> = 168 Hz, 1 H, H<sub>5</sub>'), 2.36 (d, *J*<sub>TIH</sub> = 26 Hz, 3 H, CH<sub>3</sub>). IR (Nujol): ν (C-O-C and ClO<sub>4</sub>) 1089 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>34</sub>ClO<sub>10</sub>STl: C, 37.21; H, 4.62. Found: C, 37.45; H, 4.64.

**(18-Crown-6)(4'-bromo-2'-thienyl)phenylthallium(III) perchlorate (35)**, mp 223 °C dec, was isolated in 92% yield (0.743 g, 0.92 mmol) after recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.62 (s, 24 H, 18-crown-6), 7.64 (dd, *J*<sub>TIH</sub> = 547 Hz, *J*<sub>HH</sub> = 7.0 Hz, 2 H, H<sub>2</sub>),

7.56 (dt,  $J_{\text{T1H}} = 183$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.41 (dt,  $J_{\text{T1H}} = 66$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.34 (d,  $J_{\text{T1H}} = 244$  Hz, 1 H, H<sub>3</sub>), 7.74 (d,  $J_{\text{T1H}} = 160$  Hz, 1 H, H<sub>5</sub>). IR (Nujol):  $\nu$  (C-O-C and ClO<sub>4</sub>) 1086 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>31</sub>BrClO<sub>10</sub>STl: C, 32.73; H, 3.87. Found: C, 32.58; H, 3.99.

**(18-Crown-6)(4'-formyl-2'-thienyl)phenylthallium(III) perchlorate (36)**, mp 295 °C dec, was isolated in 48% yield (0.363 g, 0.48 mmol) after silica gel column chromatography (20 mm i.d. X 150 mm, eluent 1/2 CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>, Nakarai Tesque mesh 70-230) and recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.64 (s, 24 H, 18-crown-6), 7.70 (dd,  $J_{\text{T1H}} = 544$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.59 (dt,  $J_{\text{T1H}} = 182$  Hz,  $J_{\text{T1H}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.45 (dt,  $J_{\text{T1H}} = 65$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.79 (d,  $J_{\text{T1H}} = 258$  Hz, 1 H, H<sub>3</sub>), 8.65 (d,  $J_{\text{T1H}} = 157$  Hz, 1 H, H<sub>5</sub>), 10.20 (d,  $J_{\text{T1H}} = 66$  Hz, 1 H, CHO). IR (Nujol):  $\nu$  (C=O) 1680 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>32</sub>ClO<sub>11</sub>STl: C, 36.52; H, 4.26. Found: C, 36.24; H, 4.18.

**Preparation of (18-Crown-6)(2'-furyl)phenylthallium(III) Perchlorate (37).**

The reaction of **1** (0.745 g, 1.00 mmol) with furan (0.272 g, 8.00 mmol) was carried out at room temperature for 1 day. The complex **37** (0.477 g, 67%), mp >230 °C dec, was isolated after recrystallization from 5 mL/100 mL CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  3.67 (s, 24 H, 18-crown-6), 7.69 (dd,  $J_{\text{T1H}} = 527$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>2</sub>), 7.66 (dt,  $J_{\text{T1H}} = 170$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H, H<sub>3</sub>), 7.42 (dt,  $J_{\text{T1H}} = 64$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H, H<sub>4</sub>), 7.37 (d,  $J_{\text{T1H}} = 200$  Hz, 1 H, H<sub>3</sub>), 6.90 (d,  $J_{\text{T1H}} = 62$  Hz, 1 H, H<sub>4</sub>), 7.31 (d,  $J_{\text{T1H}} = 38$  Hz, 1 H, H<sub>5</sub>). IR (Nujol):  $\nu$  (C-O-C and ClO<sub>4</sub>) 1080 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>32</sub>ClO<sub>11</sub>Tl: C, 37.10; H, 4.53. Found: C, 37.04; H, 4.59.

## 2-6 Reference and Notes

- (1) Bird, C. W.; Cheeseman, G. W. H. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 4, Chapter 3.
- (2) (a) Makarova, L. G.; Nesmeyanov, A. N. In *Methods of Elemento-Organic Chemistry*; Nesmeyanov, A. N.; Kocheshkov, K. A., Eds.; North-Holland: Amsterdam, 1967; Vol. 4, Chapter 5. Originally published as: *Metody Elemento-Organicheskoy Khimii*; Nauka: Moscow, 1965. (b) Mahapatra, S.;

Ghosh, J. L.; Guha Sircar, S. S. *J. Indian. Chem. Soc.* **1955**, *32*, 613. (c) Ciusa, R.; Grillo, G. *Gazz. Chim. Ital.* **1927**, *57*, 323. (d) Söderbäck, E. *Acta Chem. Scand.* **1959**, *13*, 1221. (e) Mingoia, Q. *Gazz. Chim. Ital.* **1930**, *60*, 509.

(3) The complex **1** is isolated as a monohydrate.

(4) Unpublished result. The values of spin-spin coupling constants between the thallium nucleus and phenyl protons in  $[\text{Ph}(\text{Cl})\text{Tl}^{\text{III}}(\text{18-crown-6})](\text{ClO}_4)$  were 930 ( $J_{\text{TlH}_2}$ ), 359 ( $J_{\text{TlH}_3}$ ), and 122 Hz ( $J_{\text{TlH}_4}$ ). These values agreed with those of the product obtained by the reaction of **1** with sodium chloride.

(5) Kawasaki, Y.; Enomoto, N.; Tomioka, J.; Akita, H. *J. Coord. Chem.* **1988**, *18*, 157. Kawasaki, Y.; Yokota, W.; Enomoto, N. *Chem. Lett.* **1982**, 941.

(6) When the reaction of **1** with 4 equiv of *N*-methylimidazole was carried out under the same conditions as in the NMR tube, the complexes **1** and **9** were observed.

(7) In general, the  $^1\text{H}$  NMR resonances of the  $\alpha$ -protons in thiophenes will be observed at lower fields than those of  $\beta$ -protons.

For thiophenes and furans, see: (a) Gronowitz, S.; Hörnfeldt, A. In *The Chemistry of Heterocyclic Compounds*; Taylor, E. C., Weissberger, A., Eds.; John Wiley & Sons: New York, 1991; pp 52-96. (b) Kellogg, R. M. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon Press: Oxford, U.K., 1984; pp 728-733. For metal-substituted thiophenes and furans see: (c) Bulman, M. J. *Tetrahedron* **1969**, *25*, 1443. (d) Lunazzi, L.; Tiecco, M.; Boicelli, C. A.; Taddei, F. *J. Mol. Spectrosc.* **1970**, *35*, 190. (e) Ebdon, A. P.; Huckerby, T. N.; Thorpe, F. G. *Tetrahedron Lett.* **1971**, 2921.

(8) These observations are in agreement with those in 2-thienylmercuric chloride. In 2-thienylmercuric chloride, the spin-spin coupling constants between the mercury nucleus and H<sub>5</sub> proton of the thienyl moiety were found to be larger than that between the mercury nucleus and H<sub>4</sub> proton.<sup>7c-e</sup>

(9) See, Chapter 1.

## Chapter 3

### Highly Selective Methyl Transfer from Methylsilanes to (Crown ether)phenylthallium(III) Complexes

#### 3-1 Introduction

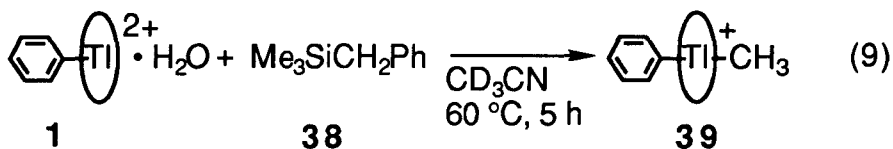
During the course of our study on the unique carbophilic property of  $\text{PhTl}^{\text{III}}(\text{crown ether})$  complexes,<sup>1</sup> e.g., (18-crown-6)phenylthallium(III) diperchlorate monohydrate (**1**) attacks not an oxygen but a carbon atom of phenols<sup>1b</sup> and not a nitrogen but a carbon atom of anilines,<sup>1c</sup> I have now found that the thallium(III) complexes can cause methyl group transfer to  $\text{Tl}(\text{III})$  from methylsilicon compounds of the unactivated trialkyl- and tetraalkylsilanes type. The selectivity for the carbon-silicon bond cleavage is extremely high so that virtually only the methyl-silicon bond is cleaved in the presence of ethyl-, vinyl-, or phenyl-silicon bonds.

The present reaction is unique since generally the cleavage of a carbon-silicon bond is confined to ethynyl-, vinyl-, phenyl-, and allyl-silicon bonds, in which the carbon atoms are activated.<sup>2</sup> That unactivated tetraalkylsilanes are stable toward various reagents is best exemplified by the popular use of tetramethylsilane as an NMR reference. There have been a limited number of examples of the cleavage of an alkyl-silicon bond in unactivated tetraalkylsilane using electrophilic metal reagents<sup>3-11</sup> with varying degrees of efficiency and selectivity. The reaction described below stands out from the rest in the degree of efficiency and selectivity.

#### 3-2 Reaction of (Crown ether)phenylthallium(III) Diperchlorate with Benzyltrimethylsilane

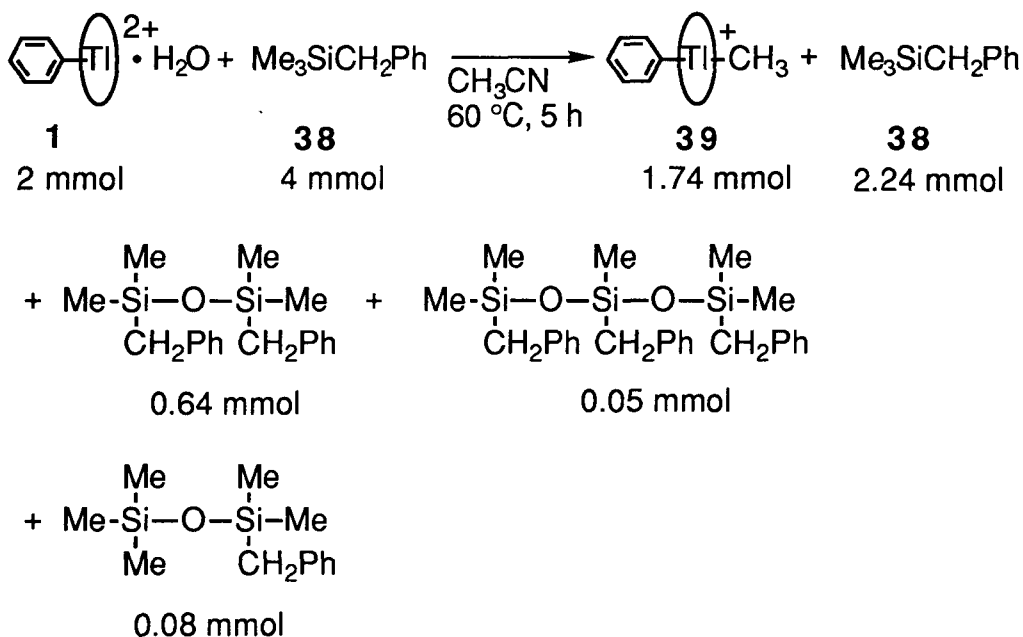
A representative example of a methyl-transfer reaction mediated by **1** is shown in eq 9. The reaction of **1**<sup>12</sup> with benzyltrimethylsilane (**38**) (1:2) in  $\text{CD}_3\text{CN}$  at 60 °C resulted in quantitative formation of (18-crown-6)(methyl)phenylthallium(III) perchlorate (**39**) as revealed by the  $^1\text{H}$  NMR spectrum. As will be discussed later the reaction also gave products arising from the hydrolysis of **38**. The observed high methyl selectivity is

noteworthy since the benzyl group is generally more reactive than a methyl group either in electrophilic or nucleophilic displacement.<sup>13</sup>



The silicon containing products of reaction 9 were siloxanes. From the reaction of **1** (2.0 mmol) with PhCH<sub>2</sub>SiMe<sub>3</sub> (4.0 mmol) in CH<sub>3</sub>CN at 60 °C for 5 h, 0.64 mmol of (PhCH<sub>2</sub>Me<sub>2</sub>Si)<sub>2</sub>O, 0.05 mmol of Me<sub>2</sub>(PhCH<sub>2</sub>)SiOSi(CH<sub>2</sub>Ph)MeOSi(CH<sub>2</sub>Ph)Me<sub>2</sub>, and 0.08 mmol of Me<sub>3</sub>SiOSi(CH<sub>2</sub>Ph)Me<sub>2</sub> were obtained in addition to unreacted **38** (2.24 mmol) and **39** (1.74 mmol) (Scheme VII). The material balance with respect to Si was 96%. The formation of a siloxane having SiMe<sub>3</sub> indicated that cleavage of the PhCH<sub>2</sub>-Si bond took place to a small extent with a cleaved PhCH<sub>2</sub>/CH<sub>3</sub> ratio of 1:20.

### Scheme VII



### 3-3 Reaction with Various Organosilanes Containing Trimethylsilyl Group

The selective methyl transfer has been found general for several organosilicon compounds, and the results are given in Table I. Tetramethylsilane did react. Therefore, CHD<sub>2</sub>CN contained in CD<sub>3</sub>CN was used as an internal standard for NMR throughout these experiments. Within the accuracy of <sup>1</sup>H NMR spectroscopy any products obtainable by ethyl, phenyl,<sup>14</sup> or even vinyl transfer were not detected.<sup>15</sup> The high selectivity for a methyl group may be attributed to the steric congestion of the crown ether ligand in **1**. A disilane and a siloxane reacted similarly.

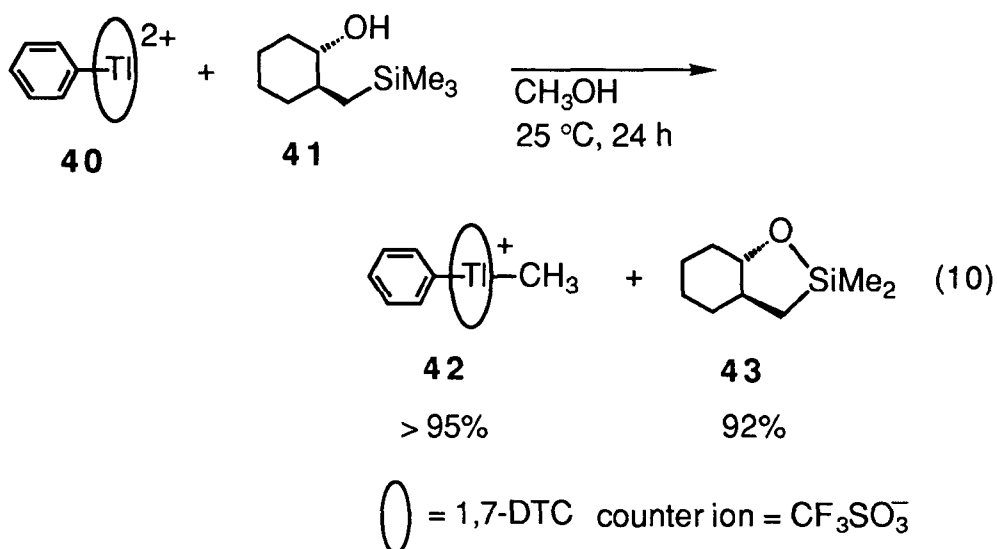
Table I. Reaction of **1** with Alkylsilanes and Siloxane<sup>a</sup>

silane	temp., °C	time, h	yield of <b>39</b> <sup>b</sup> , %
PhCH <sub>2</sub> SiMe <sub>3</sub>	60	15 (5) <sup>c</sup>	60 (>95) <sup>c</sup>
Me <sub>4</sub> Si	r. t.	240	34 <sup>d</sup>
Me <sub>3</sub> SiEt	60	12	80
Me <sub>3</sub> SiPh	60	15	70
Me <sub>3</sub> Si $\text{---}\text{C}(\text{C}_2\text{H}_5)=\text{C}(\text{C}_2\text{H}_5)_2$	60	15	50 <sup>e</sup>
Me <sub>3</sub> SiSiMe <sub>3</sub>	60	5	83
Me <sub>3</sub> SiOSiMe <sub>3</sub>	60	42	77

<sup>a</sup>Reaction conditions: **1** (0.1 mmol), silane (0.1 mmol), CD<sub>3</sub>CN (0.5 mL). <sup>b</sup>Yields were quantified by <sup>1</sup>H NMR spectra by the use of CHD<sub>2</sub>CN as an internal standard. <sup>c</sup>Reaction conditions: **1** (0.1 mmol), silane (0.2 mmol), CD<sub>3</sub>CN (0.5 mL). <sup>d</sup>Complex **1** was recovered in 47% yield. <sup>e</sup>Diphenylthallium compound (Ph<sub>2</sub>Tl<sup>+</sup>) was also formed in 15% yield.

### 3-4 Intramolecular Trapping of the Silyl Fragment with Hydroxy Group

For the formation of these siloxanes, water contained in **1** may be responsible. It seemed to us that the use of nucleophiles other than water would be interesting and important. After various attempts I have found the reaction conditions which enable clean intramolecular trapping of the silyl fragment by a hydroxy group using  $[\text{PhTi}^{\text{III}}(1,7\text{-DTC})](\text{OTf})_2$  (**40**)<sup>16</sup> (eq 10). This result opens a new possibility for the use of tetraalkylsilanes (such as **41**) in organic synthesis, since the presence of at least one electron-negative functional group (such as that in **43**) on the silicon atom is required for the application of Tamao oxidative cleavage<sup>17</sup> and reaction 2 provides a method for the required functionalization<sup>18</sup> of tetraalkylsilanes.



### 3-5 Experimental section

**General Considerations.** The <sup>1</sup>H NMR spectra were recorded on a JEOL PS-100 and JEOL GSX-270 spectrometer operating at 100 and 270 MHz, respectively. Chemical shifts of <sup>1</sup>H NMR signals are quoted relative to internal tetramethylsilane. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, br = broad), coupling constant (Hz), relative intensity, and interpretation. IR spectra were measured on a Hitachi 270-50 infrared spectrometer. Melting points were determined in open capillaries on a Mitamura Riken Kogyo melting



points apparatus and are uncorrected. Preparative GLC was carried out on Hitachi Model 164 gas chromatograph using 2 m X 10 mm stainless steel column packed with 3% Silicone OV-1 supported on 60/80 mesh.

**Materials.** Solvents except for acetonitrile and methanol were used without further purification. Acetonitrile was dried over  $\text{CaH}_2$  and purified by distillation under nitrogen atmosphere. Methanol was dried over  $\text{Mg}(\text{OMe})_2$  and was purified by distillation under nitrogen atmosphere.

**Preparation of (18-Crown-6)(methyl)phenylthallium(III) Perchlorate (39).**

In a 20-mL two-necked flask was placed **1** (1.488 g, 2.0 mmol) and was charged argon. The solids were dissolved in 10 mL of acetonitrile and then benzyltrimethylsilane (0.656 g, 4.0 mmol) was added to this solution. This mixture was heated at 60 °C for 5 h with stirring. The reaction mixture was transferred into 300-mL flask and 200 mL of diethyl ether was added to enforce precipitation of the product. The precipitates were filtered. After purification from  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$  (5 mL/100 mL), (18-crown-6)(methyl)phenylthallium(III) perchlorate (**3**) was obtained in 87% yield (1.149 g, 1.74 mmol): mp 273 °C dec.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 100 MHz) 3.65 (s, 24 H, 18-crown-6), 1.16 (d,  $J_{\text{TH}}$  = 485 Hz, 3 H,  $\text{CH}_3$ ), 7.61 (dd,  $J_{\text{TH}}$  = 402 Hz,  $J_{\text{HH}}$  = 7.0 Hz, 2 H,  $\text{H}_2$ ), 7.55 (dt,  $J_{\text{TH}}$  = 123 Hz,  $J_{\text{HH}}$  = 7.0 Hz, 2 H,  $\text{H}_3$ ), 7.39 (dt,  $J_{\text{TH}}$  = 37 Hz,  $J_{\text{HH}}$  = 8.0 Hz, 1 H,  $\text{H}_4$ ); IR (Nujol) 1578 w, 1354 s, 1286 s, 1250 s, 1100 s, 1022 m, 1000 w, 962 s, 870 w, 836 m, 700 m, 620 s, 534 w, 450 w. Anal. Calcd for  $\text{C}_{19}\text{H}_{32}\text{ClO}_{10}\text{Tl}$ : C, 34.56; H, 4.89. Found: C, 34.55; H, 4.89.

**Preparation of (1,7-DTC)phenylthallium(III) bis(frifluoromethanesulfonate) (40).**

Into a suspension of phenylthallium(III) oxide (2.87 g, 10 mmol) in 30 mL of THF was added a cooled (0 °C) THF (20 mL) solution of trifluoromethanesulfonic acid (3.36 g, 22 mmol) at 0 °C. After stirring for 6 h at the same temperature, the resulting clear brown solution was added to a THF (30 mL) solution of 1,7-DTC at 0 °C. After further stirring for 2 h at 0 °C, 200 mL of diethyl ether was added and then pale yellow solids precipitated. Addition of 100 mL of diethyl ether to a solution of the resulting solids in acetonitrile/THF (1/1) gave pure **40** (4.53 g, 54% yield, pale yellow solids), mp 148 °C dec.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): 3.2-4.2 (m, 24 H,

1,7-DTC), 7.57 (br d,  $J_{\text{TIH}} = 1070$  Hz, 2 H, H<sub>2</sub>), 7.58 (br d,  $J_{\text{TIH}} = 457$  Hz, 2 H, H<sub>3</sub>), 7.54 (br d,  $J_{\text{TIH}} = 175$  Hz, 1 H, H<sub>4</sub>); IR (Nujol): 1564 m, 1310 s, 1280 s, 1258 s, 1234 s, 1210 s, 1176 m, 1154 s, 1122 m, 1088 m, 1068 m, 1032 s, 1016 s, 990 m, 932 w, 904 w, 878 w, 834 w, 866 w, 688 w, 636 s, 572 m, 518 m, 450 w cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>29</sub>F<sub>6</sub>O<sub>10</sub>S<sub>4</sub>Tl: C, 27.42; H, 3.34. Found: C, 27.37; H, 3.36.

**Quantification of the Products.** Quantifications of the products were performed by the GLC (Bu<sub>2</sub>O as an internal standard). Isolation of dibenzyltetramethyldisiloxane was carried out by the following procedure. After addition of 200-mL of diethyl ether to the reaction mixture to enforce the precipitation of **39**, the colorless solids precipitated were filtered. The filtrate was evaporated to remove the solvents and benzyltrimethylsilane. After the evaporation, viscous liquid remained. Separation of the products from this residue was accomplished by preparative GLC.

**Reaction of 1 with Tetramethylsilane in an NMR Tube.** The complex **1** (74.4 mg, 0.1 mmol) and tetramethylsilane (8.8 mg, 0.1 mmol) were dissolved in 0.5 mL of acetonitrile-*d*<sub>3</sub> in an NMR tube. The resulting solution was allowed to stand at 25 °C. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. After 240 h, **39** produced in 34% NMR yield and **1** was recovered in 47% yield.

**Reaction of 1 with Benzyl-, Ethyl-, Phenyl-, and Vinyltrimethylsilanes, Hexamethyldisilane, and Hexamethyldisiloxane.** In an NMR tube was placed **1** (74.4 mg, 0.1 mmol), and then the solid was dissolved in 0.5 mL of acetonitrile-*d*<sub>3</sub>. To this solution was added the silane (0.1 mmol). This tube was sealed, and the resulting solution was heated at 60 °C. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. (18-Crown-6)(methyl)phenylthallium(III) perchlorate (**39**) was obtained in 60-80% NMR yield. When the reaction was carried out in the presence of 0.2 mmol of benzyltrimethylsilane, **39** was obtained in >95% NMR yield.

**Reaction of (1,7-DTC)phenylthallium(III) Bis(trifluoromethanesulfonate) with *Trans*-2-trimethylsilylmethyl-1-cyclohexanol in an NMR Tube.** In an NMR tube were added (1,7-DTC)phenylthallium(III) bis(trifluoromethanesulfonate) (**40**) (97.5 mg, 0.1 mmol) and 0.5 mL of

acetonitrile- $d_3$ , and then *trans*-2-trimethylsilylmethyl-1-cyclohexanol (**41**) (20.1 mg, 0.1 mmol) was added to the resulting solution. The resulting solution was allowed to stand at 25 °C. The progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy. After 24 h, (1,7-DTC)(methyl)phenylthallium(III) trifluoromethanesulfonate (**42**) produced in >95% NMR yield.

**Reaction of 40 with 41.** In a 10-mL two-necked flask was placed **40** (963 mmol, 1.1 mmol) and the solids were dissolved in 5 mL of methanol. To the solution was added **41** (189 mg, 1.0 mmol) and then the mixture was stirred at 25 °C for 24 h. After addition of 100 mL of diethyl ether to enforce precipitation of **42**, the resulting solids were filtered. After evaporation of the solvent, purification of the residue was carried out by the preparative GLC to give 8-dimethylsila-7-oxa-bicyclo[4.3.0]nonane (**43**). Quantifications of the products were performed by the GLC (triethyleneglycol dimethylether as an internal standard, 92% yield based on **41**). Spectral data of **42**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.20 (s, 3 H,  $\text{SiCH}_3$ ), 0.22 (s, 3 H,  $\text{SiCH}_3$ ), 0.42 (dd,  $J_{\text{HH}} = 14$  Hz,  $J_{\text{HH}} = 13$  Hz,  $\text{SiCHH}$ ), 0.93 (dd,  $J_{\text{HH}} = 14$  Hz,  $J_{\text{HH}} = 6$  Hz, 1 H,  $\text{SiCHH}$ ), 1.05-1.4 (m, 5 H), 1.6-2.1 (m, 4 H), 3.15 (dt,  $J_{\text{HH}} = 4$  Hz,  $J_{\text{HH}} = 10$  Hz, OCH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz) -0.15 ( $\text{Si}(\text{CH}_3)_2$ ), 19.4 ( $\text{SiCH}_2$ ), 24.9, 26.2, 33.4, 34.3, 45.2 ( $\text{SiCCH}$ ), 82.0 (OCH); IR (neat) 2936 s, 2860 s, 1449 m, 1418 w, 1373 w, 1374 w, 1338 w, 1305 w, 1287 w, 1250 s, 1166 w, 1107 s, 1074 m, 1028 s, 942 m, 921 m, 865 s, 840 m, 830 m, 811 s, 775 m, 739 w, 700 w, 630 w, 577 m, 529 m, 455 w, 362 m, 327 m, 288 m. Spectral data of **43**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 270 MHz) 1.41 (d,  $J_{\text{TIH}} = 475$  Hz, 3 H,  $\text{CH}_3$ ), 2.8-3.0 (m, 8 H,  $\text{SCH}_2$ ), 3.5-3.7 (m, 16 H,  $\text{OCH}_2$ ), 7.74 (br d,  $J_{\text{TIH}} = 399$  Hz, 2 H,  $\text{H}_2$ ), 7.52 (br d,  $J_{\text{TIH}} = 125$  Hz, 2 H,  $\text{H}_3$ ), 7.37 (br d,  $J_{\text{TIH}} = 43$  Hz, 1 H,  $\text{H}_4$ ); IR (Nujol) 1566 w, 1270 s, 1222 m, 1144 s, 1104 s, 1082 s, 1030 s, 916 w, 836 w, 788 w, 698 w, 634 s 572 w, 518 m, 450 w. Anal. Calcd for  $\text{C}_{20}\text{H}_{32}\text{F}_3\text{O}_7\text{S}_3\text{Tl}$ : C, 32.37; H, 4.35. Found: C, 32.52; H, 4.24.

### 3-6 References and Notes

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- (12) The purified complex **1** contained one molecule of water in the crystal.

(13) Benzyl group in  $C_6H_5CH_2SiMe_3$  reacts also exclusively in the reaction with single electron transfer mechanism. See: Baciocchi, E.; Crescenzi, M.; Fasella, E.; Mattioli, M. *J. Org. Chem.* **1992**, *57*, 4684.

(14) To the best of our knowledge, in only one case can methyl compete with phenyl. Preferential methyl cleavage was reported in the  $H_2PtCl_4$ -catalyzed redistribution reaction of  $PhSiMe_3$  with chlorosilanes, see ref. 10. On the other hand, it was reported that platinum complexes ( $[(C_2H_4)PtCl_2]^9$  and  $H_2PtCl_6 \cdot 6H_2O^{11c,d}$ ) brought about cleavage of a phenyl-silicon bond in  $PhSiMe_3$  as usual.

(15) In an NMR tube was placed **1** (74.4 mg, 0.1 mmol), and then the solids were dissolved in 0.5 mL of acetonitrile- $d_3$ . To the solution was added the silane (0.1 mmol). This tube was sealed and the resulting solution was heated at 60 °C or was kept at 25 °C. The progress of the reaction was monitored by  $^1H$  NMR spectroscopy. Complex **39** was obtained in 60-80% NMR yield.

(16) 1,7-DTC stands for 1,7-dithia-4,10,13,16-tetraoxacyclooctadecane. Complex **40** was prepared by a modification of our published method (see Chapter 1). After the reaction of **40** with **41**, diethyl ether was added to precipitate the thallium complexes. The ether layer was washed with  $NaHCO_3(aq)$  and dried with  $MgSO_4$ . The products were isolated as usual.

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## Chapter 4

### **Analysis of Ionic Character of Thallium-Carbon Bonds Formed on the Basis of Spin-Spin Coupling Constant Between Thallium Nucleus and Protons**

#### **4-1 Introduction**

Thallium has isotopes,  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$ , both with nuclear spin  $1/2$ . These isotopes exist in 29.5% ( $^{203}\text{Tl}$ ) and 70.5% ( $^{205}\text{Tl}$ ) natural abundance, having with very similar magnetic moment. In  $^1\text{H}$  NMR spectra of organothallium compounds, these two isotopes produce large spin-spin couplings with protons. The large values of the spin-spin coupling constant,  $J_{\text{TlH}}$ , can be qualitatively understood on the basis of the Fermi contact interaction, as arising from the large effective nuclear charge of the thallium atom. The increase of the coupling constant in the series  $\text{R}_3\text{Tl}$ ,  $\text{R}_2\text{Tl}^+$ , and  $\text{RTl}^{2+}$  may be partly due to the increase in the s-character of the thallium-carbon bond and partly to the increment of the effective positive charge of the thallium atom. Since all the (crown ether)diorganothallium(III) complexes presented in this thesis have similar structure around C-Tl-C bond, the s-character of the thallium atom is nearly same among these complexes. If the s-character of the thallium atom is same, the positive charge on thallium atom mainly affects the spin-spin coupling constant. On the basis of this criterion, a large magnitude of a spin-spin coupling exhibits a large ionic character of the thallium carbon bond in diorganothallium compounds.

Described in this chapter is analysis of the thallium-carbon bond in (18-crown-6)diorganothallium(III) complexes on the basis of the spin-spin coupling constants between thallium nucleus and ortho-protons of the phenyl group.

#### **4-2 Ionic Character of Thallium-Carbon Bonds in (18-Crown-6)-diorganothallium(III) Perchlorate**

Selected  $J_{\text{TlH}}$  values for complexes **6-16** are given in Table II. The coupling constants between the thallium nucleus and  $\text{H}_2$  in **6-16** are in a

range of 435-486 Hz which are smaller than those in **44-46** and slightly larger than that in **39** (Table III). This result suggests that the ionic character of the Tl-C bond between thallium atom and hydroxy aryl group in **6-16** is much smaller than those of the Tl-halogen bonds and slightly larger than that of the Tl-CH<sub>3</sub> bond. In the complexes **6, 7, 9, 10, 12, 14, 15,** and **16a** which have no substituent at 2'-position on the aromatic ring, the  $J_{\text{TlH}_2}$  values are about 450 Hz. On the other hand in the complexes **8, 11,** and **13** in which 2'-position was substituted by methyl or hydroxy group, the  $J_{\text{TlH}_2}$  values are about 480 Hz. I consider that the steric repulsion between the substituent at 2'-position and 18-crown-6 as a ligand may cause the Tl-C bond more ionic in **8, 11,** and **13**. In the complexes **6, 7, 10a, 12,** and **14** which have electronically different substituents at 3'-position (H, CH<sub>3</sub>, OCH<sub>3</sub>, OH, *t*-Bu, respectively), the  $J_{\text{TlH}_2}$  values are independent of an electronic character of the substituents. This suggests that the character of the Tl-C bond remains almost constant in these complexes.

In the complexes **17-20**, the values of  $^3J_{\text{TlH}_2}$  are in a range of 440-450 Hz (Table IV). These values are larger than the values of **39** (402 Hz) and are comparable with those of **6** (447 Hz) and of **17** (454 Hz). It is suggested from these results that electronic factors of the substituent at the 4'-position of C<sub>6</sub>H<sub>4</sub>X group (X = NR<sup>1</sup>R<sup>2</sup>, OH, OMe) and of the substituents on nitrogen atom (NR<sup>1</sup>R<sup>2</sup> : R<sup>1</sup> = H, R<sup>2</sup> = Ph; R<sup>1</sup> = Me, R<sup>2</sup> = Ph; R<sup>1</sup> = R<sup>2</sup> = Ph) do not greatly affect the Tl-C bond character.

The values of  $^3J_{\text{TlH}_2}$  in **21** and **22** are also observed to be about 450 Hz (Table V), suggesting that the ionic character of Tl-C bonds are similar to those of Tl-C bonds in **6, 7, 9, 10, 12,** and **14-20**. The substituent on the nitrogen atom in **21** and **22** (H and Me, respectively) causes no appreciable effect on the Tl-C bonds. The value of  $^3J_{\text{TlH}_2}$  in **23** is about 110 Hz larger than that in **21**. This may be due to the increase of the ionic character of the Tl-C bond, as a result of an electron-withdrawing ability of the additional nitrogen atom.

Table II. Selected  $J_{\text{TiH}}$  Values in  $\text{C}_6\text{H}_5\text{-Ti}^+\text{-C}_6\text{H}_3(\text{R})\text{-OH}$

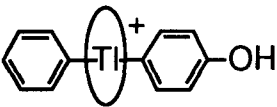
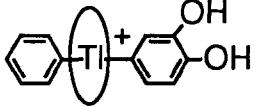
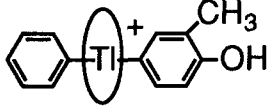
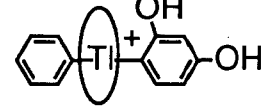
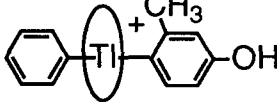
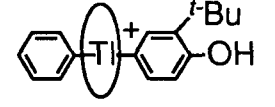
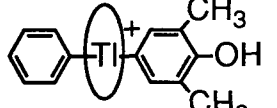
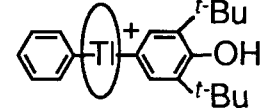
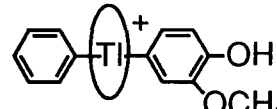
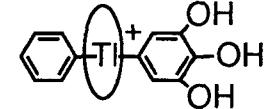
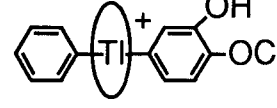
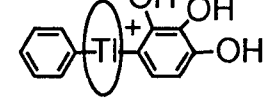
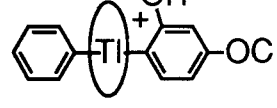
complex	$J_{\text{TiH}_2}$ (Hz)	complex	$J_{\text{TiH}_2}$ (Hz)
	447		448
<b>6</b>		<b>12</b>	
	445		481
<b>7</b>		<b>13</b>	
	480		447
<b>8</b>		<b>14</b>	
	442		441
<b>9</b>		<b>15</b>	
	435		450
<b>10a</b>		<b>16a</b>	
	453		450
<b>10b</b>		<b>16b</b>	
	480		
<b>11</b>			



Table III. Selected  $J_{\text{TlH}}$  Values

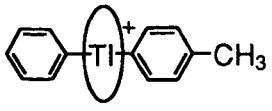
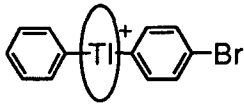
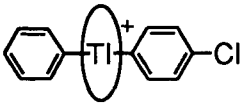
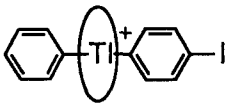
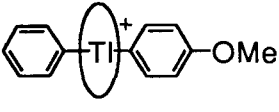
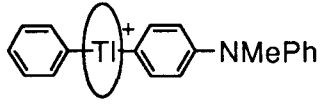
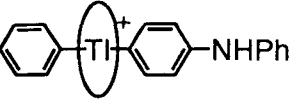
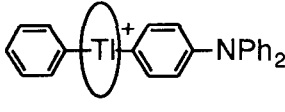
complex	$J_{\text{TlH}_2}$ (Hz)	complex	$J_{\text{TlH}_2}$ (Hz)
	402		899
<b>39</b>		<b>45</b>	
	926		824
<b>44</b>		<b>46</b>	

Table IV. Selected  $J_{\text{TlH}}$  Values

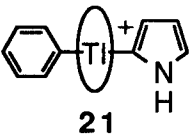
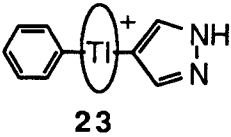
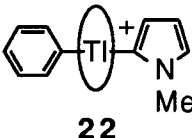
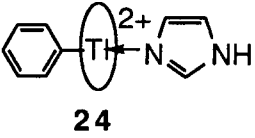
complex	$J_{\text{TlH}_2}$ (Hz)	complex	$J_{\text{TlH}_2}$ (Hz)
	454		444
<b>17</b>		<b>19</b>	
	440		440
<b>18</b>		<b>20</b>	

It is interesting that in **24** containing the Tl-N bond spin-spin couplings between the thallium nucleus and the imidazole protons through Tl-N bond (41, 52, 41 Hz) were observed. This observation indicates that the Tl-N bond in **24** has somewhat covalent bond character, which is consistent with the inertness of this complex to the ligand exchange reaction with pyridine.

The  $^1\text{H}$  NMR spectrum of **24** showed  $^3J_{\text{TlH}_2} = 953$  Hz for ortho protons of the phenyl group, which is much larger than those of **21-23** but only slightly smaller than that of **1** (1173 Hz). These observations suggest

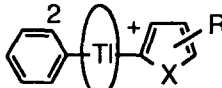
only a small reduction of effective positive charge on the thallium atom in **24** as compared to that in **1**, and the coordination of imidazole in **24** through its  $sp^2$  nitrogen atom is deduced. Bonding to the thallium ion with the other nitrogen (i.e.,  $N_1$ ) is unfavorable since the aromaticity of the ring is thereby lost.<sup>4</sup>

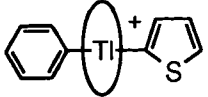
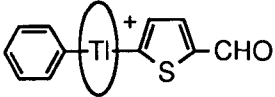
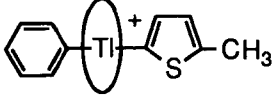
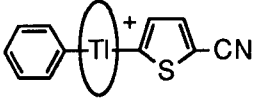
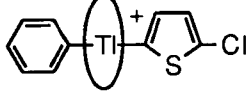
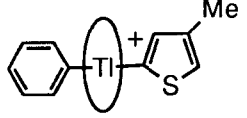
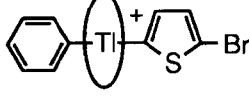
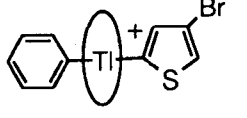
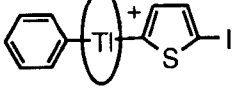
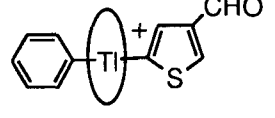
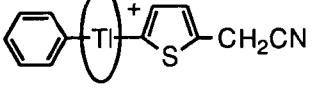
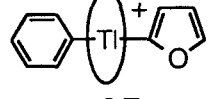
Table V. Selected  $J_{\text{TlH}}$  values

complex	$J_{\text{TlH}_2}$ (Hz)	complex	$J_{\text{TlH}_2}$ (Hz)
	449		562
	450		953

The selected spin-spin coupling constants between the thallium nucleus and the ortho protons in phenyl group in **26-37** are listed in Table VI.

The  ${}^3J_{\text{TlH}_2}$  values in **28-33** were slightly larger than those in **26** and **27**. These  ${}^3J_{\text{TlH}_2}$  values in **26-37** are about 80 Hz larger than that in the pyrrole derivative **21** ( ${}^3J_{\text{TlH}_2} = 449$  Hz). These observations suggest that the ionic character of the newly formed Tl-C bonds in **26-37** is larger than that in **21**. Somewhat larger ionic character of the Tl-C bonds in **26-37** as compared with that in **21** may be caused by larger electron-withdrawing abilities of the sulfur and the oxygen atoms than that of the nitrogen atom in the five-membered rings. I found that the ionic character in **26-37** is in the middle of that in (1,7-DTC)(phenylethynyl)phenylthallium(III) perchlorate ( ${}^3J_{\text{TlH}_2} = 647$  Hz) and that in **39** ( ${}^3J_{\text{TlH}_2} = 402$  Hz).

Table VI. Selected  $J_{\text{TiH}}$  Values in 

complex	$J_{\text{TiH}_2}$ (Hz)	complex	$J_{\text{TiH}_2}$ (Hz)
 <b>26</b>	529	 <b>32</b>	562
 <b>27</b>	521	 <b>33</b>	536
 <b>28</b>	544	 <b>34</b>	522
 <b>29</b>	546	 <b>35</b>	547
 <b>30</b>	545	 <b>36</b>	544
 <b>31</b>	540	 <b>37</b>	527

#### 4-3 References

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## Conclusions

I have provided direct preparation methods of unsymmetrical diorganothallium(III) compounds by the reaction of (18-crown-6)phenylthallium(III) diperchlorate with phenols, anilines, heteroaromatic compounds, and organosilanes.

I described the electrophilic thallation of phenols and anilines with (crown ether)phenylthallium(III) diperchlorate compounds in Chapter 1. In these reactions the thallation occurred exclusively at position para to the electron-donating groups, such as -OH and -NR<sub>2</sub>. The high para selectivity of (18-crown-6)phenylthallium(III) diperchlorate with regard to the OH and the NR<sub>2</sub> groups may be due to the electronic factor and/or steric factor, the dicationic nature of the (18-crown-6)phenylthallium(III) complex and large steric hindrance of the 18-crown-6 toward the substituent on the aromatic ring. Thus, in the intermediates formed from the electrophilic thallation of phenols and anilines, the positive charge induced on the OH group is separated as far as possible from the thallium(III) ion and the thallium(III) ion attacks the less hindered position.

The thallations took place on the carbon atom but not on the oxygen or the nitrogen atom. This high carbophilicity could be a result of the softness of the thallium atom in (18-crown-6)phenylthallium(III) diperchlorate. Thus, the introduction of the phenyl group and the coordination of 18-crown-6 to the thallium(III) ion increases the softness of the thallium ion.

In Chapter 2, I described the direct synthesis of unsymmetrical diorganothallium(III) complexes by the reaction of (18-crown-6)phenylthallium(III) diperchlorate with heteroaromatic compounds.

Highly selective methyl transfer reactions from tetraorganosilanes which contain a trimethylsilyl group to (crown ether)phenylthallium(III) complexes were mentioned in Chapter 3. These reactions gave (crown ether)(methyl)phenylthallium(III) complexes and siloxanes. Even in the presence of benzyl, phenyl, or vinyl group on the silicon atom, the silicon-methyl bond was exclusively cleaved. Intramolecular trapping of the silyl

fragment by a hydroxy group using (1,7-DTC)phenylthallium(III) bis(trifluoromethanesulfonate) was employed to *trans*-2-trimethylsilylmethyl-1-cyclohexanol, affording a thallium-methyl complex and bicyclic silyl ether. This methyl transfer reactions using (crown ether)phenylthallium(III) complexes accomplishes the functionalization of trimethylsilyl group in tetraorganosilanes.

In Chapter 4, the ionic character of the thallium-carbon bonds in (18-crown-6)diorganothallium(III) perchlorate was analyzed on the basis of spin-spin coupling constant between the thallium nucleus and the ortho-protons of the phenyl group. Among the thallium-carbon bonds in the prepared complexes, the thallium-carbon bond in thallium-methyl complex is the least ionic and the thallium-carbon bond in thallium-pyrazolyl complex is the most ionic. The steric repulsion between 18-crown-6 and the substituent on the aromatic ring enhances the ionic character of the thallium-carbon bond. The electronic effect of the substituent does not largely affect the ionic character. The order of the ionic character of the thallium-carbon bonds afford some information for the character of the metal-carbon bonds in organometallic compounds.

The crown ether, which coordinated to the thallium(III) ion, stabilizes the dicationic phenylthallium(III) compound and also compels the other organo group to a position *trans* of the phenyl group. The introduction of the phenyl group and the coordination of the crown ether to the thallium(III) ion weakens the oxidizing ability of the thallium(III) ion.

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Fumitoshi Kakiuchi