Electrophilic Thallation of Phenol and Its Derivatives with Phenylthallium(III) Crown Ether Complexes

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Received November 25, 1990

The reaction of [phenylthallium(III)(18-crown-6)] diperchlorate, [PhTl^{III}(18-crown-6)](ClO$_4$)$_2$ (**1a**), with phenol gives [phenyl(4′-hydroxyphenyl)thallium(III)(18-crown-6)] perchlorate (**2**), the phenolic OH having remained intact. The complex **1a** reacts also with alkylphenols, methoxyphenols, catechol, resorcinol, and pyrogallol to give thallated products exclusively at the para position of the electron-donating group (OH or OCH$_3$) without suffering from reduction of thallium(III). No reaction takes place with benzene, toluene, and *tert*-butylbenzene.

Introduction

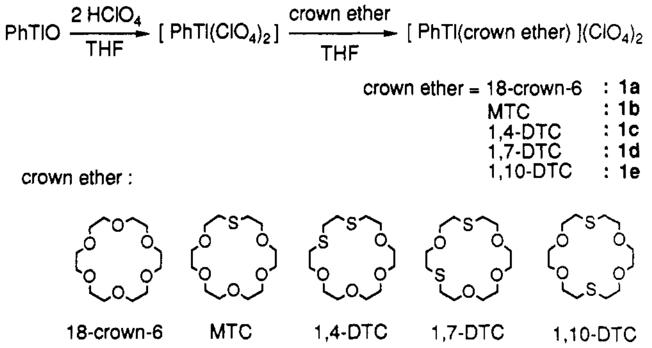
Increasing attention has been paid to electrophilic aromatic substitution reactions with inorganic salts, examples being Tl(III),[1] Hg(II),[2] Pb(IV),[3] Rh(III),[4] and Pt(IV).[5] Reactions of the Tl(III) ion with aromatic compounds have been extensively investigated from the viewpoint of organic synthesis because the thallium moiety in the product monoarylthallium(III) ion can easily be converted to other functional groups.[1] 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 formations by the reaction of monoarylthallium(III) ions with aromatic compounds.[1c]

Previously, we have found that the otherwise unstable monoarylthallium(III) compounds can be isolated by the coordination of crown ethers to the thallium ion.[6] For example, [phenyl(iodo)thallium(dibenzo-18-crown-6)] perchlorate, [Ph(I)Tl^{III}(DBC)](ClO$_4$) (DBC = dibenzo-18-crown-6), having a Tl–I bond[7] was isolated by the reaction of [PhTl^{III}(DBC)](ClO$_4$)$_2$ with the sodium iodide 15-crown-5 complex [Na(15-crown-5)]I, without decomposition of the phenylthallium(III) ion. We expected that reactions of phenylthallium(III) crown ether complexes with phenols could proceed without oxidation of phenols by the Tl(III) ion,[1e] affording complexes having Tl–O or Tl–C bonds.

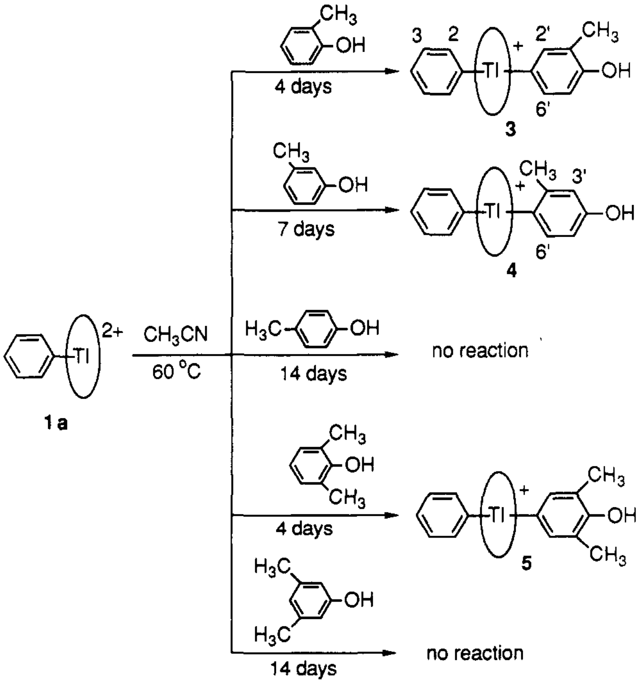
We wish to report here preparation of [phenyl(hydroxyaryl)thallium(III)(18-crown-6)] perchlorate by the reaction of [phenylthallium(III)(18-crown-6)] diperchlorate, [PhTl^{III}(18-crown-6)](ClO$_4$)$_2$ (**1a**), with phenols. There is no example of the preparations of analogous (hydroxyaryl)metal complexes except for mercuric compounds such as HOC$_6$H$_4$HgOCOCH$_3$.[2]

Results and Discussion

Scheme I

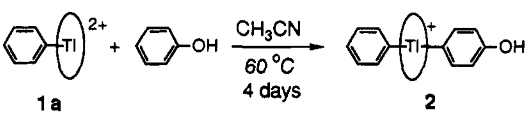


Scheme II[a]



[a] For clarity, the counterion ClO$_4^-$ is not shown.

Reaction of [PhTl^{III}(crown ether)](ClO$_4$)$_2$ with Phenol. The reactions of five phenylthallium(III) diperchlorate complexes of 18-crown-6 (**1a**) and thia crown ethers (**1b–e**) (Scheme I) with phenol were carried out at 60 °C in CH$_3$CN. Interestingly, of the five complexes **1a–e** examined, only **1a** completed the aromatic thallation within 4 days to give a high yield of [phenyl(4′-hydroxyphenyl)thallium(III)(18-crown-6)] perchlorate (**2**) (eq 1).



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0276-7333/91/2310-2056$02.50/0

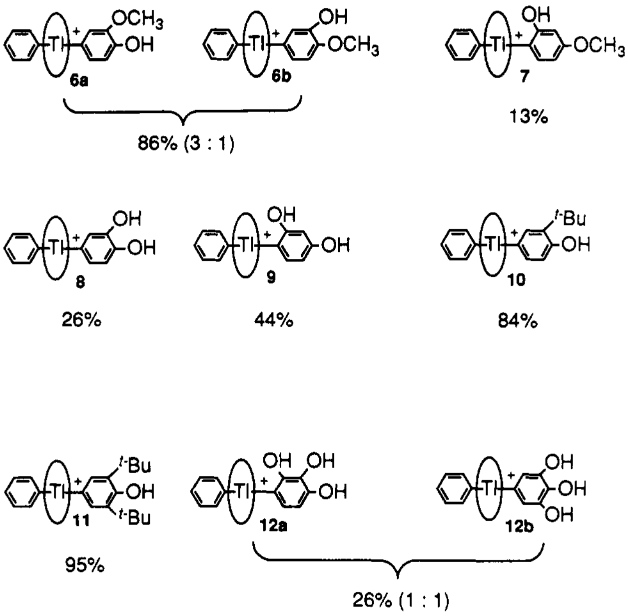
The others did not undergo the thallation even after 14 days. The failure of the reaction of **1b–e** with phenol may be due to the coordination of the sulfur atoms in the crown ethers to the thallium atom[8] from the opposite side of the phenyl group, preventing the approach of phenol.

Complex **2** was isolated in 97% yield. In the ^{1}H NMR spectrum of **2**, three kinds of phenyl protons (H_2, H_3, and H_4) and two kinds of protons bonding to the aromatic ring of the hydroxyaryl group (hydroxyaryl protons: $H_{2'}$ and $H_{3'}$) were observed (for the numbering, see structures **3** and **4** in Scheme II). Each proton was 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 orthothallated 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 strong IR absorption of the OH stretching was observed at 3360 cm^{-1}.

Reaction of 1a with Methyl-Substituted Phenols. The reactions of **1a** with 2-, 3-, and 4-methylphenols and 2,6-, and 3,5-dimethylphenols were carried out in a similar manner at 60 °C in CH_3CN (Scheme II). In the case of the reaction with 2- and 3-methylphenols and 2,6-dimethylphenol, the ^{1}H NMR spectra indicate the formation of thallated complexes **3–5**, as revealed by the reduction of the spin–spin coupling constants of the phenyl protons with the thallium nucleus and appearance of thallated hydroxyaryl proton signals (440–480 Hz).[9] Complexes **3–5** 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 of the meta compound (3-methylphenol) about 7 days. The longer reaction time necessary for 3-methylphenol was 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 $Tl(O_2CCF_3)_3$ with anisole.[1f] The reaction between **1a** and 3,5-dimethylphenol did not occur because of the blocking of the position para to the OH group with two methyl groups against the thallium atom.

Chart I[a]



[a] For clarity, the counterion ClO_4^- is not shown.

Determination of the Thallated Position in [Phenyl(hydroxyaryl)thallium(III)(18-crown-6)] Perchlorate (3–5). The ^{1}H NMR spectrum of the hydroxyaryl protons of **5** was observed as a doublet having a coupling with the thallium nucleus (J_{TlH} = 450 Hz, 2 H). This observation indicates that the thallation also occurred at the para position of the OH group and the two methyl groups located at the meta position relative to the thallium atom. In this complex, the spin–spin coupling constant between the thallium nucleus and the methyl protons, J_{TlCH_3}, was found to be 22 Hz. In complex **3**, three kinds of the hydroxyaryl protons were observed: one doublet, J_{TlH} = 444 Hz; two doublet–doublets, J_{TlH} = 436 Hz, J_{TlH} = 124 Hz, with same intensity. In **4** also three kinds of the hydroxyaryl protons were observed: one doublet–doublet, J_{TlH} = 480 Hz; one doublet, J_{TlH} = 158 Hz; one doublet–doublet, J_{TlH} = 152 Hz. These spectral data suggest that there are two kinds of ortho protons and one kind of meta proton in **3** and one kind of ortho proton and two kinds of meta protons in **4**, respectively. The thallated position relative to the OH and CH_3 groups in **3** and **4** was determined by comparing the coupling constant J_{TlCH_3} with that of **5**. The J_{TlCH_3} value of **3** was observed to be 22 Hz and the same as that of **5**. The methyl group, therefore, is decided to be located at the meta position and the OH group at the position para to the thallium atom. In complex **4**, the slightly large J_{TlCH_3} value (26 Hz) was observed, suggesting that the methyl group is at the position ortho to the thallium atom. In both complexes **3** and **4** the thallation occurred at the position para to the hydroxy group.

The result that the thallation of **1a** 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.

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(8) The spin–spin couplings between the thallium nucleus and methylene protons of SCH_2 groups were observed in a range of 260–180 Hz. This observation suggests that the Tl–S bonds have some covalent character.

(9) In monoarylthallium compounds coupling constants between the thallium nucleus and ortho protons of the aryl group are observed in a range of 950–1100 Hz, whereas in diarylthallium compounds the corresponding values are in a range of 430–460 Hz.

Reaction of 1a with Phenols Containing a Good Electron-Donating Group. The reaction of **1a** with 2-methoxyphenol, 3-methoxyphenol, catechol, resorcinol, 2-*tert*-butylphenol, 2,6-di-*tert*-butylphenol, and pyrogallol gave thallated complexes **6–12**, respectively. Complexes **6** and **12** were obtained as a mixture. Yields and the structures of the isolated products are listed in Chart I.

McKillop et al.[1e] 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 **1a** with 2,6-di-*tert*-butylphenol proceeded without oxidation of the substrate to give [phenyl(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)thallium(III)(18-crown-6)](ClO_4) (**11**). Furthermore, catechol and pyrogallol, which are easily oxidizable and known as good antioxidants, were also thallated by **1a** to give **8** and **12**. The difference in reactivity of **1a** for phenols from that of $Tl(NO_3)_3$ is weakening of an oxidizing ability of the thallium(III) ion of **1a** as a result of the binding of the phenyl group and the coordination of the 18-crown-6.

The thallated positions in **8–12** were determined in a manner similar to that described above. NOE experiments were also used for determination of the thallated position in **6a**, **6b** and **7**.[10] From the above result on **6**, [phenyl(4′-hydroxy-3′-methoxyphenyl)thallium(III)(18-crown-6)] perchlorate (**6a**) was found to be a major product and [phenyl(3′-hydroxy-4′-methoxyphenyl)thallium(III)(18-crown-6)] perchlorate (**6b**) 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 **7**. 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 the 2′-position is smaller than that with the OCH_3 group at the 2′-position.

Reaction of Phenylthallium(III) Diperchlorate with Phenol. The reaction of phenylthallium(III) diperchlorate, $PhTl(ClO_4)_2$, with phenol was carried out in tetrahydrofuran (THF) at 40 °C. In the ^1H NMR study, the phenyl proton signals of $PhTl(ClO_4)_2$ disappeared and new signals owing to the diphenylthallium(III) ion, $Ph_2Tl(ClO_4)$, appeared after 5 days. The thallation product of phenol was not observed.

Reactions of 1a with Benzene, Toluene, and *tert*-Butylbenzene. The reactions of **1a** with benzene, toluene, and *tert*-butylbenzene were examined under similar reaction conditions. The aromatic thallation, however, was not observed even after 14 days. McKillop et al.[1g] have reported electrophilic aromatic thallation of benzene, toluene, and halobenzenes with thallium(III) trifluoroacetate. The electrophilicity of **1a**, therefore, is not strong enough to cause the thallation of unactivated aromatics.

Table I. Selected J_{TlH} (Hz) and J_{TlCH_3} (Hz) Data for 2–12

complex	J_{TlH_2}	$J_{TlH_{2'}}$	$J_{TlH_{6'}}$	J_{TlCH_3}
2	447	436		
3	445	444	436	22
4	480		471	26
5	442	450		22
6a	453	484	451	
6b	453	466	451	
7	486		460	
8	448	474	443	
9	481		464	
10	447	465	434	
11	441	480		
12a	450		441	
12b	450	471		

Consideration of the Character of Newly Formed Tl-C Bonds by Comparing the J_{TlH_2} Values. Selected J_{TlH} values for complexes **2–12** are given in Table I (see Experimental Section for complete NMR data). In general, Tl–H spin–spin coupling constants in R_2Tl^+ are numerically very large, and the magnitude of the values has been explained qualitatively on the basis of a Fermi contact mechanism.[11-13] We have been investigating the ionic character of the Tl–X bonds in [Ph(X)Tl^{III}(crown ether)](ClO_4) by comparing the coupling constants between the thallium nucleus and phenyl protons.[6] We have found that the spin–spin coupling constants between the thallium nucleus and the ortho protons of the phenyl group in [Ph(X)Tl(18-crown-6)](ClO_4) (X = Cl (**13**), Br (**14**), I (**15**), CH_3 (**16**)) increase with increasing ionic character of the Tl–X (X = Cl, Br, I, CH_3) bond.[14] The J_{TlH_2} values in **13–16** were observed to be 926, 899, 824, and 401 Hz, respectively.

The coupling constants between the thallium nucleus and H_2 in **2–12** are in a range of 441–486 Hz, which are smaller than those in **13–15** and slightly larger than that in **16**. This result suggests that the ionic character of the Tl–C bond between the thallium atom and hydroxy aryl group in **2–12** is much smaller than those of the Tl–halogen bonds and slightly larger than that of the Tl–CH_3 bond. In complexes **2**, **3**, **5**, **6**, **8**, **10**, **11**, and **12a**, which have no substituent at the 2′-position on the aromatic ring, the J_{TlH_2} values are about 450 Hz. On the other hand in complexes **4**, **7**, and **9** in which the 2′-position was substituted by a methyl or hydroxyl group, the J_{TlH_2} values are about 480 Hz. We consider that the steric repulsion between the substituent at the 2′-position and 18-crown-6 as a ligand may cause the Tl–C bond to be more ionic in **4**, **7**, and **9**. In complexes **2**, **3**, **6a**, **8**, and **10**, which have electronically different substituents at the 3′-position (H, CH_3, OCH_3, OH, ^tBu, respectively), the J_{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.

Experimental Section

General Considerations. The ^1H NMR spectra were recorded on a JEOL PS-100 and JEOL JNM-27S spectrometer operating at 100 and 270 MHz, respectively. Chemical shifts of ^1H 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, m = multiplet, c = complex, br = broad), coupling constant (Hz), relative intensity, and interpretation. IR spectra were measured on a Hitachi 215 or Hitachi 270-50 infrared spectrometer. Melting points were determined in open capillaries on a Mitamura Riken Kogyo melting point apparatus and are uncorrected.

Materials. Crown ethers, 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6),[15] 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane (1,10-DTC),[16] 1,7-dithia-4,10,13,16-tetracyclooctadecane (1,7-DTC),[17] 1,4-dithia-7,10,13,16-tetraoxacyclooctadecane (1,4-DTC),[17]

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[10] The enhancement of the ortho ($H_{2'}$) or meta ($H_{5'}$) proton intensity was measured upon irradiating the OCH_3 protons.

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and 1-thia-4,7,10,13,16-pentaoxacyclooctadecane (MTC)[17] were prepared by literature methods. Phenols, alkylbenzenes, and solvents except for acetonitrile were used without further purification. Acetonitrile was dried over P_2O_5 and was purified by distillation.

[Phenylthallium(III)(18-crown-6)] Diperchlorate (1a). 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 (**1a**) (6.70 g, 9.0 mmol, 90% yield), mp 181 °C dec. ^{1}H NMR (CD_3CN): δ 3.67 (s, 24 H, 18-crown-6), 7.49 (dd, J_{TlH} = 1173 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.66 (dt, J_{TlH} = 494 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.65 (dt, J_{TlH} = 166 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 6.12 (s, 2 H, H_2O). IR (Nujol): ν(OH) 3400 (s), ν(C–O–C and ClO_4) 1085 (s) cm^{-1}. Anal. Calcd for $(C_{18}H_{29}Cl_2O_{14}Tl)H_2O$: C, 28.35; H, 4.10. Found: C, 28.21; H, 4.26.

[Phenylthallium(III)(MTC)] Diperchlorate (1b) 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 and were purified by an addition of 100 mL of diethyl ether to an acetonitrile (5 mL) solution of the solids, affording colorless [phenylthallium(III)(MTC)] diperchlorate (**1b**) (5.33 g, 7.0 mmol, 70% yield), mp 178–179 °C dec. ^{1}H NMR (CD_3CN): δ 4.02 (dt, J_{TlH} = 290 Hz, 4 H, SCH_2), 3.72–3.91 (c, 16 H, OCH_2CH_2O), 4.35 (dt, J_{TlH} = 23 Hz, 4 H, SCH_2CH_2), 7.59 (dd, J_{TlH} = 994 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.65 (dt J_{TlH} = 424 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.60 (dt, J_{TlH} = 153 Hz, J_{HH} = 8.0 Hz, 1 H, H_4). IR (Nujol): ν(C–O–C and ClO_4) 1075 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{29}Cl_2O_{13}ST1$: C, 28.42; H, 3.84. Found: C, 28.50; H, 3.83.

[Phenylthallium(III)(1,4-DTC)] Diperchlorate (1c), a colorless solid, mp 166 °C dec, was obtained (6.21 g, 8.0 mmol, 80% yield). ^{1}H NMR (CD_3CN): δ 3.72 (br d, J_{TlH} = 170 Hz, 8 H, SCH_2), 3.75 (s, 8 H, OCH_2CH_2O), 4.01 (br d, J_{TlH} = 15 Hz, 8 H, SCH_2CH_2), 7.61 (dd, J_{TlH} = 965 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.65 (dt, J_{TlH} = 403 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.59 (dt, J_{TlH} = 149 Hz, J_{HH} = 8.0 Hz, 1 H, H_4). IR (Nujol): ν(C–O–C and ClO_4) 1060–1080 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{29}Cl_2O_{12}S_2Tl$: C, 27.83; H, 3.76. Found: C, 28.16; H, 3.75.

[Phenylthallium(III)(1,7-DTC)] Diperchlorate (1d), a pale yellow solid, mp 148 °C dec, was obtained (5.44 g, 7.0 mmol, 70% yield). ^{1}H NMR (CD_3CN): δ 3.40 (br d, J_{TlH} = 54 Hz, 8 H, SCH_2), 3.56 (br t, J_{HH} = 4 Hz, 4 H, $SCH_2CH_2OCH_2CH_2S$), 3.8–3.9 (m, 8 H, OCH_2CH_2O), 4.0 (br d, J_{HH} = 4 Hz, 4 H, SCH_2CH_2O), 7.56 (dd, J_{TlH} = 1008 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.59 (dt, J_{TlH} = 419 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.53 (dt, J_{TlH} = 160 Hz, J_{HH} = 8.0 Hz, 1 H, H_4). IR (Nujol): ν(C–O–C and ClO_4) 1060–1080 (s) cm^{-1}. Anal. Calcd for $(C_{18}H_{29}Cl_2O_{12}S_2Tl)_3CH_3CN$: C, 28.36; H, 3.83; N, 0.59. Found: C, 28.30; H, 3.83; N, 0.40.

[Phenylthallium(III)(1,10-DTC)] Diperchlorate (1e), a colorless solid, mp 195–196 °C dec, was obtained (6.21 g, 8.0 mmol, 80% yield). ^{1}H NMR (CD_3CN): δ 3.72 (br d, J_{TlH} = 170 Hz, 8 H, SCH_2), 3.75 (m, 8 H, OCH_2CH_2O), 4.01 (br d, J_{TlH} = 15 Hz, 8 H, SCH_2CH_2), 7.74 (dd, J_{TlH} = 987 Hz, J_{HH} = 7.0 Hz, 2 H H_2), 7.72 (dt, J_{TlH} = 432 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.69 (dt, J_{TlH} = 156 Hz, J_{HH} = 8.0 Hz, 1 H, H_4). IR (Nujol): ν(C–O–C and ClO_4) 1060–1080 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{29}Cl_2O_{12}S_2Tl$: C, 27.83; H, 3.76. Found: C, 28.04; H, 3.76.

Reactions of 1a–e with Phenol in NMR Tubes. Complexes **1a–e** (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}H NMR spectrum.

[Phenyl(4′-hydroxyphenyl)thallium(III)(18-crown-6)] Perchlorate (2). In a typical procedure, the complex **1a** (1.49 g, 2.00 mmol) was dissolved in 3 mL of acetonitrile in a test tube (18 mm i.d. × 180 mm length). An acetonitrile (2 mL) solution of phenol (0.755 g, 8.02 mmol) was added into the solution of **1a**. 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 colorless [phenyl(4′-hydroxyphenyl)-thallium(18-crown-6) perchlorate (**2**) (1.43 g, 1.94 mmol, 97% yield), mp 207 °C dec. ^{1}H NMR (CD_3CN): δ 3.66 (s, 24 H, 18-crown-6), 7.74 (dd, J_{TlH} = 447 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.56 (dt, J_{TlH} = 140 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.39 (dt, J_{TlH} = 51 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.50 (dd, J_{TlH} = 436 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{2'}$) 7.04 (dd, J_{TlH} = 111 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{3'}$). IR (Nujol): ν(OH) 3360 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{34}ClO_{11}Tl$: C, 38.99; H, 4.77. Found: C, 39.02; H, 4.66.

[Phenyl(3′-methyl-4′-hydroxyphenyl)thallium(III)(18-crown-6)] Perchlorate (3), a colorless solid, mp 190 °C dec, was obtained (1.28 g, 1.70 mmol, 85% yield). ^{1}H NMR (CD_3CN): δ 2.37 (d, J_{TlH} = 22 Hz, 3 H, CH_3) 3.57 (s, 24 H, 18-crown-6), 7.73 (dd, J_{TlH} = 445 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.53 (dt, J_{TlH} = 140 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.36 (dt, J_{TlH} = 50 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.41 (d, J_{TlH} = 444 Hz, 1 H, $H_{2'}$), 6.99 (dd, J_{TlH} = 124 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{5'}$), 7.34 (dd, J_{TlH} = 436 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{6'}$). IR (Nujol): ν(OH) 3400 (s) cm^{-1}. Anal. Calcd for $(C_{25}H_{36}ClO_{11}Tl)_2CH_2Cl_2$: C, 38.53; H, 4.69. Found: C, 38.84; H, 4.79.

[Phenyl(2′-methyl-4′-hydroxyphenyl)thallium(III)(18-crown-6)] Perchlorate (4), a colorless solid, mp 195 °C dec, was obtained (0.35 g, 0.46 mmol, 23% yield) by the reaction of **1a** with 2-methylphenol for 7 days and by the same purification as described above. ^{1}H NMR (CD_3CN): δ 2.32 (d, J_{TlH} = 26 Hz, 3 H, CH_3), 3.66 (s, 24 H, 18-crown-6), 7.78 (dd, J_{TlH} = 480 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.53 (dt, J_{TlH} = 157 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.37 (dt, J_{TlH} = 59 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.19 (d, J_{TlH} = 158 Hz, 1 H, $H_{3'}$), 6.93 (dd, J_{TlH} = 152 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{5'}$), 7.53 (dd, J_{TlH} = 471 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{6'}$). IR (Nujol): ν(OH) 3400 (s) cm^{-1}. Anal. Calcd for $(C_{25}H_{36}ClO_{11}Tl)_2CH_2Cl_2$: C, 38.53; H, 4.69. Found: C, 38.38; H, 4.72.

[Phenyl(3′,5′-dimethyl-4′-hydroxyphenyl)thallium(III)-(18-crown-6)] Perchlorate (5), a colorless solid, mp 190 °C dec, was obtained (1.30 g, 1.70 mmol, 85% yield). ^{1}H NMR (CD_3CN): δ 2.25 (d, J_{TlH} = 22 Hz, 6 H, CH_3), 3.56 (s, 24 H, 18-crown-6), 6.26 (s, 1 H, OH), 7.68 (dd, J_{TlH} = 442 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.54 (dt, J_{TlH} = 138 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.39 (dt, J_{TlH} = 54 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.25 (d, J_{TlH} = 450 Hz, 2 H, $H_{2'}$). IR (Nujol): ν(OH) 3420 (s) cm^{-1}. Anal. Calcd for $C_{26}H_{38}ClO_{11}Tl$: C, 40.75; H, 5.00. Found: C, 40.60; H, 5.06.

[Phenyl(4′-hydroxy-3′-methoxyphenyl)thallium(III)(18-crown-6)] Perchlorate (6a) and [Phenyl(3′-hydroxy-4′-methoxyphenyl)thallium(III)(18-crown-6)] Perchlorate (6b), a colorless solid, mp 188 °C dec, was obtained (1.32 g, 1.72 mmol, 86% yield) as a mixture (**6a**/**6b** = 3/1). This mixture could not be separated by column chromatography. The ratio of **6a**/**6b** was determined by a comparison of the intensity ratio of $H_{2'}$ in **6a** and **6b**. **6a**: ^{1}H NMR (CD_3CN) δ 3.60 (s, 24 H, 18-crown-6), 3.90 (s, 3 H, OCH_3), 7.75 (dd, J_{TlH} = 453 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.35 (d, J_{TlH} = 484 Hz, 1 H, $H_{2'}$), 7.20 (dd, J_{TlH} = 451 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{6'}$). The chemical shifts of H_3, H_4, and $H_{5'}$ could not be determined because these signals overlapped with other signals. **6b**: ^{1}H NMR (CD_3CN) δ 3.60 (s, 24 H, 18-crown-6), 3.90 (s, 3 H, OCH_3), 7.80 (dd, J_{TlH} = 453 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.26 (d, J_{TlH} = 466 Hz, 1 H, $H_{2'}$), 7.20 (dd, J_{TlH} = 451 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{6'}$). The chemical shifts H_3, H_4, and $H_{5'}$ could not be determined because these signals overlapped with other signals. IR (Nujol): ν(OH) 3390 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{36}ClO_{12}Tl$: C, 39.08; H, 4.72. Found: C, 38.59; H, 4.77.

[Phenyl(2′-hydroxy-4′-methoxyphenyl)thallium(18-crown-6)] Perchlorate (7). 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. × 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 pure colorless [phenyl(2′-hydroxy-4′-methoxyphenyl)thallium(III)(18-crown-6)] perchlorate (7), mp >235 °C (0.200 g, 0.26 mmol, 13% yield). ^1H NMR (CD_3CN): δ 3.60 (s, 24 H, 18-crown-6), 7.83 (dd, J_{TlH} = 486 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.59 (dt, J_{TlH} = 158 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.38 (dt, J_{TlH} = 64 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 6.61 (d, J_{TlH} = 194 Hz, 1 H, $H_{3'}$), 7.02 (dd, J_{TlH} = 144 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{5'}$), 7.58 (dd, J_{TlH} = 460 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{6'}$). IR (Nujol): ν(OH) 3390 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{36}ClO_{12}Tl$: C, 39.08; H, 4.72. Found: C, 38.91; H, 4.81.

[Phenyl(3′,4′-dihydroxyphenyl)thallium(III)(18-crown-6)] Perchlorate (8), a colorless solid, mp 212 °C dec, was obtained (0.39 g, 0.52 mmol, 26% yield). ^1H NMR (CD_3CN): δ 3.59 (s, 24 H, 18-crown-6), 6.85 (s, 2 H, OH), 7.69 (dd, J_{TlH} = 448 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.64 (dt, J_{TlH} = 135 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.36 (dt, J_{TlH} = 68 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.22 (d, J_{TlH} = 474 Hz, 1 H, $H_{2'}$), 7.01 (d, J_{TlH} = 151 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{5'}$), 7.08 (dd, J_{TlH} = 443 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{6'}$). IR (Nujol: ν(OH) 3370 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{34}ClO_{12}Tl$: C, 38.21; H, 4.54. Found: C, 38.33; H, 4.62.

[Phenyl(2′,4′-dihydroxyphenyl)thallium(III)(18-crown-6)] Perchlorate (9), a colorless solid, mp 230 °C dec, was obtained (0.66 g, 0.88 mmol, 44% yield) by the reaction of **1a** with resorcinol for 7 days and by the same purification as described above. ^1H NMR (CD_3CN): 3.66 (s, 24 H, 18-crown-6), 7.69 (dd, J_{TlH} = 481 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.48 (dt, J_{TlH} = 156 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 6.47 (d, J_{TlH} = 197 Hz, 1 H, $H_{3'}$), 6.92 (dd, J_{TlH} = 146 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{5'}$), 7.43 (dd, J_{TlH} = 464 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{6'}$). The chemical shift of H_4 could not be determined because the signal overlapped with other signals. IR (Nujol): ν(OH) 3310 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{34}ClO_{12}Tl$: C, 38.21; H, 4.54. Found: C, 38.01; H, 4.63.

[Phenyl(3′-*tert*-butyl-4′-hydroxyphenyl)thallium(III)-(18-crown-6)] Perchlorate (10), a colorless solid, mp >235 °C dec, was obtained (1.34 g, 1.68 mmol, 84% yield). ^1H NMR (CD_3CN): δ 1.41 (s, 9 H, $C(CH_3)_3$), 3.60 (s, 24 H, 18-crown-6), 7.79 (dd, J_{TlH} = 447 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.57 (dt, J_{TlH} = 137 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.44 (dt, J_{TlH} = 57 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.62 (dd, J_{TlH} = 465 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{2'}$), 7.01 (dd, J_{TlH} = 133 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{5'}$), 7.32 (d, J_{TlH} = 434 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{6'}$). IR (Nujol): ν(OH) 3270 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{42}ClO_{11}Tl$: C, 42.33; H, 5.33. Found: C, 42.54; H, 5.38.

[Phenyl(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)thallium-(III)(18-crown-6)] Perchlorate (11), a colorless solid, mp 173–174 °C dec, was obtained (1.62 g, 1.90 mmol, 95% yield). ^1H NMR (CD_3CN): δ 1.47 (s, 18 H, $C(CH_3)_3$), 3.57 (s, 24 H, 18-crown-6), 7.73 (dd, J_{TlH} = 441 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.57 (dt, J_{TlH} = 137 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.38 (dt, J_{TlH} = 59 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.68 (d, J_{TlH} = 480 Hz, 2 H, $H_{2'}$). IR (Nujol): ν(OH) 3550 (s) cm^{-1}. Anal. Calcd for $(C_{32}H_{50}ClO_{11}Tl)H_2O$: C, 44.25; H, 6.03. Found: C, 44.35; H, 5.92.

[Phenyl(2′,3′,4′-trihydroxyphenyl)thallium(III)(18-crown-6)] Perchlorate (12a) and [Phenyl(3′,4′,5′-trihydroxyphenyl)thallium(III)(18-crown-6)] Perchlorate (12b). The reaction of **1a** 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 was produced. This oil was purified through a silica gel column chromatography (eluent CH_3CN/CH_2Cl_2 = 1/2, 20 mm i.d. × 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 [phenyl(2′,3′,4′-trihydroxyphenyl)-thallium(III)(18-crown-6)] perchlorate (**12a**) and [phenyl(3,4,5-trihydroxyphenyl)thallium(III)(18-crown-6)] perchlorate (**12b**) as a mixture (**12a**/**12b** = 1/1), mp 173–175 °C dec, (0.408 g, 0.52 mmol, 26% yield). **12a**: ^1H NMR (CD_3CN) δ 3.57 (s, 24 H, 18-crown-6), 7.73 (dd, J_{TlH} = 450 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.09 (dd, J_{TlH} = 150 Hz, J_{HH} = 8.0 Hz, 1 H, $H_{5'}$), 7.10 (d, J_{TlH} = 441 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{6'}$). The chemical shifts of H_3 and H_4 could not be determined because these signals overlapped with other signals. **12b**: ^1H NMR (CD_3CN) δ 3.57 (s, 24 H, 18-crown-6), 7.73 (dd, J_{TlH} = 450 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.24 (d, J_{TlH} = 471 Hz, 2 H, $H_{2'}$). The chemical shift of H_3 and H_4 could not be determined because these signals overlapped with other signals. IR (Nujol): ν(OH) 3400 (s) cm^{-1}. Anal. Calcd for $(C_{24}H_{34}ClO_{13}Tl)_2(C_2H_5)_2O$: C, 38.68; H, 4.87. Found: C, 38.29; H, 4.59.

Attempted Reactions of 1a with Alkylbenzenes. The complex **1a** (0.074 g, 0.1 mmol) was dissolved in 0.3 mL of acetonitrile in an NMR tube. Into the solution of **1a** 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 ^1H 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 a 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 the NMR tube (5 mm o.d.) was transferred 0.5 mL (0.1 mmol of $PhTl(ClO_4)_2$) 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 ^1H NMR spectroscopy.