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# REDUCTIVE THALLIUM–CARBON BOND CLEAVAGE IN MONOARYLTHALLIUM(III) CROWN ETHER COMPLEXES

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## Summary

Photolysis and thermolysis of a crown ether-stabilized phenyl(iodo)thallium(III) complex gave good yields of iodobenzene, at least partly through a phenyl radical intermediate. Reduction of a *p*-tolyl(hydroxo)thallium(III)-crown ether complex with $P(OMe)_3$, ascorbic acid or *N*-benzyl-1,4-dihydronicotinamide gave toluene, but not the di-*p*-tolylthallium(III) species, which was formed in considerable amount in the corresponding reduction of a crown-free *p*-tolylthallium(III) cation.

## Introduction

Decomposition upon reduction of monoorganothallium(III) compounds induced by the action of reductants or nucleophiles has received attention from both synthetic and environmental chemical points of view [1–3]. One of the crucial steps in the decomposition is apparently the access of donor group(s) contained in these reagents to the thallium and/or the thallium-bound carbon atom, typical examples including coordinative interaction of reductants with $RTl^{III}$ cations in the case of hydrodethallation [3a,b,c,], or intermolecular metal-alkyl-metal bridging in the reductive disproportionation [2,3a]. Crown ethers complexed to monoorganothallium(III) cations may be expected, through generation of the restricted coordination site *, to alter both the ease and the course of such reductive decomposition. This expectation was realized in successful isolation of a reasonably stable phenyl(iodo)thallium(III)-crown ether complex [5], while in the absence of the crown ethers $ArTl^{III}$ cations generally undergo rapid reaction with iodide ion to give ArI, a process which is of synthetic value [1]. We describe here thermal and photolytic decomposition of such a crown ether-stabilized iodide complex (**1**) as well as its

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* Diorganothallium(III) cations have been shown to form extremely rigid crown ether complexes, with the six oxygen atoms being located approximately on the equatorial plane and the two organic groups at the axial sites [4].

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analogs (**2**–**4**). Also reported is the unique behavior of another crown ether complex (**5**) in terms of its decomposition upon reduction, as compared to that of crown-free $p$-MeC$_6$H$_4$Tl(OAc)$_2$ (**6**).

[$p$-RC$_6$H$_4$(X)Tl(L)]picrate

(**1**, R = H, X = I;
**2**, R = H, X = Br;
**3**, R = H, X = Cl;
**4**, R = H, X = SPh;
**5**, R = Me, X = OH.
L = dibenzo-18-crown-6)

## Results and discussion

In contrast to extremely rapid decomposition of PhTl(OAc)$_2$ by the action of NaI in methanol or $H_2O$ at room temperature, the complex isolated (**1**) was found to be stable when kept in acetonitrile at room temperature for longer periods. However, it formed PhI almost quantitatively when heated at 100°C for 12 h in the same solvent (eq. 1). Also, irradiation of this solution in an evacuated pyrex tube with a mercury lamp at room temperature gave PhI as well as benzene (79% conversion after 5 h; PhI/PhH 82/18). In contrast, the bromide and the chloride analogs **2** and **3** were much more reluctant to undergo the analogous thermolysis and photolysis reactions; for example, irradiation of these complexes under the same conditions gave only very small amounts of benzene, but formation of PhBr or PhCl could not be detected.

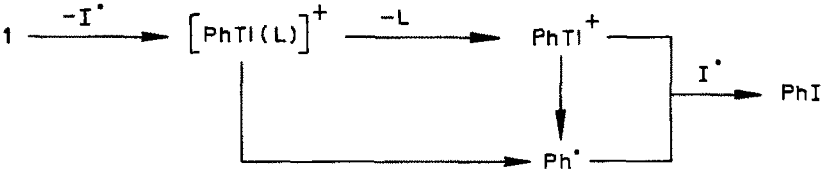
$$\mathbf{1} \rightarrow \text{PhI} + [\text{Tl(L)}]\text{picrate} \tag{1}$$

Phenyl radical was trapped as the spin adduct PhN(O$^\cdot$)C$_6$HMe$_4$ [6], as was confirmed by ESR spectra, when a mixture of **1** and nitrosodurene in MeCN/PhH was heated at 60°C. On the other hand, the same spin adduct was not observed in mixtures containing nitrosodurene and **2**, **3** or PhTl(OAc)$_2$. Photolysis of **1** in oxygen-saturated acetonitrile reduced, though not to a large extent, the total yield (50%) of PhI and benzene with almost identical product ratio. Photolysis of **1** in tetrahydrofuran afforded a higher amount of benzene (57%) than PhI (24%), possibly due to facile hydrogen abstraction from the solvent by phenyl radical.

It was found previously [4a,5] that dissociation of the organothallium(III) cations from the crown ethers in the complexes of type **1**–**3** as well as their dimethylthallium(III) analogs is extremely slow at room temperature. Therefore, it seems highly unlikely that the photoreaction of **1** (eq. 1) begins with decomplexation from the crown ether of the Ph(I)Tl$^+$ moiety or PhTl$^{2+}$ and I$^-$ ions, followed by rapid coupling of the phenyl and iodo groups outside the crown ether cavity. However, this possibility is not completely ruled out in the case of thermolysis at 100°C.

We assume that behind the differences in reactivity of **1** and **2** or **3** is the difference in the redox potential of I$^-$ and Br$^-$ or Cl$^-$ ions. Since it is expected that intramolecular charge transfer or electron transfer from the coordinated halide ligand to the thallium(III) ion occurs more easily in the iodide than in the bromide or the chloride complexes, the initial step of the reaction of eq. 1 would be thermally or photochemically induced, intramolecular electron transfer from $I^-$ to $PhTl^{2+}$ ions, even though we failed to obtain evidence for iodo radical intermediates *. Such an electron transfer process would then have led to facile Tl–C bond homolysis [3] of a $PhTl^+$ moiety that may or may not have left the crown ether cavity (see Scheme 1). It is also possible that the iodo radical attacked the $PhTl^+$ moiety to afford PhI after the decomplexation of this cation. In view of the incomplete decrease in the yield of product in the reaction carried out under oxygen, the reaction pathways described above may have occurred mostly in the solvent cage.

SCHEME 1



Complex **5** reacted with $P(OMe)_3$, ascorbic acid (AH) and *N*-benzyl-1,4-dihydronicotinamide (BNAH) in methanol to give toluene and the thallium(I) complex (eq. 2).

$$\mathbf{5} \xrightarrow{[\text{red.}]} MeC_6H_5 + [Tl(L)]\text{picrate} \tag{2}$$

In the absence of reductants, **5** was fairly stable under these reaction conditions. The reductants were converted to $PO(OMe)_3$, dehydroascorbic acid and *N*-benzyl-3-carbamoylpyridinium cation, respectively, as was the case in the corresponding reactions of $RTl(OAc)_2$ (R = alkyl, aryl) previously reported [3a,b,c]. As expected from the protecting effect of the crown ether on the attack of the reductant, the reaction process of eq. 2 was considerably slower than that of the reaction between crown-free $(p\text{-}MeC_6H_4)Tl(OAc)_2$ (**6**) and the respective reductant. The exclusive formation of toluene in eq. 2 is noteworthy because in the reaction of **6** not only toluene but also $(p\text{-}MeC_6H_4)_2TlOAc$ (**7**) in amounts comparable to or somewhat higher than that of toluene was formed (see Experimental).

Reductant-induced disproportionation of $RMX_n$ to $R_2MX_{n-1}$ and $MX_{n-1}$ (M = Hg, $n = 1$; M = Tl, $n = 2$) generally proceeds [7] through either (A) an initial spontaneous disproportionation equilibrium (eq. 3) followed by rapid reductive quenching of $MX_{n+1}$, or (B) direct reductant-$RMX_n$ interaction which activates

$$2\,RMX_n \rightleftharpoons R_2MX_{n-1} + MX_{n+1} \tag{3}$$

the M–C bond toward attack of electrophiles (e.g. $RMX_n$ in the case of the disproportionation) or toward homolysis. The M–C bond homolysis would be followed by coupling of alkyl radical with $RMX_n$ or $RMX_{n-1}$, accomplishing the disproportionation. In any case, it is expected that both these disproportionation pathways (A and B) are inhibited by rigid complexation of the crown ether with the thallium atom, and this was indeed the case as shown in eq. 2.

Disproportionation of $RTl(OAc)_2$ induced by $P(OMe)_3$ was initially proposed [2]

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* A similarly facile photolysis of the thiolate complex **4** (5 h irradiation; $Ph_2S$, 25%; $Ph_2S_2$, 8%; PhH, 66%) may also be ascribed to a high electron-transfer tendency of the $SPh^-$ ion.

to proceed through path A shown above. We later pointed out [3a] that the more probable course is path B. In doing so we made one assumption that remained to be evidenced, that is, the reducing ability of $P(OMe)_3$ ought to be high enough to reduce the $RTl^{2+}$ ion, a less favorable electron acceptor than the purely inorganic $Tl^{3+}$ ion. The reaction of eq. 2 involving $P(OMe)_3$ may thus be regarded as an example to demonstrate such an ability of this reductant.

## Experimental

The method of preparation for **1**–**5** is essentially the same as that for the perchlorate analogs [5], and has been described elsewhere [8]. The reaction products were analyzed by GLC (Hitachi 163 Gas chromatograph). The reactions were also monitored by $^1H$ NMR spectroscopy (JEOL JNM-PS-100) using deuterated methanol or acetonitrile as reaction solvents. By this method the formation of a $Tl^I$-crown ether complex and di-*p*-tolylthallium(III) species was also confirmed where their proton resonances were compared with those of authentic samples.

Photodecomposition of **1** (0.2 mmol) in MeCN (20 $cm^3$) in an evacuated pyrex glass tube (after three freeze-thaw cycles) was carried out using a 300 W high pressure mercury lamp with the water-cooled reaction tube kept in touch with a lamp jacket. After 5 h of irradiation, the tube was opened and the reaction mixture was examined by GLC (SE-30, 1 m × 3 mm for PhI; PEG-1000, 2 m × 3 mm for PhH) to show formation of 65% of PhI and 14% of PhH. A trace of biphenyl was also detected (SE-30). Photolysis of **1** in THF was performed similarly. A sample for thermolysis of **1** in MeCN was prepared in a manner essentially the same as that for the photolysis shown above. The reaction tube was immersed in a boiling water bath for 12 h. The subsequent procedure was the same as that described above. Photolysis of **1** was also carried out in MeCN through which oxygen gas had been bubbled for 20 min prior to the irradiation.

Photodecomposition of **2** and **3** in degassed MeCN was carried out similarly to give 12% and a trace of benzene, respectively, after 5 h of irradiation. The formation of PhBr or PhCl was not confirmed within the GLC detection limit (SE-30). Photolysis of **4** was carried out similarly to give $Ph_2S$ (25%), $Ph_2S_2$ (8%) (SE-30), and PhH (66%).

The reduction of **5** is typified by the following procedure. To a MeOH solution (5 $cm^3$) of **5** (40 mg; 0.044 mmol) was added under nitrogen 11 mg (0.089 mmol) of $P(OMe)_3$. The solution was allowed to stand at room temperature for 24 h. GLC analysis (PEG-1000 and SE-30) showed the formation of 95% of toluene and of $PO(OMe)_3$. The reaction of $p$-$MeC_6H_4Tl(OAc)_2$ (**6**) with $P(OMe)_3$ to give a ca. 1/1 mixture of toluene and $(p\text{-}MeC_6H_4)_2TlOAc$ (**7**) was described before [3a]. In a similar way, the reaction of **5** (0.1 mmol) with AH (0.6 mmol) or BNAH (0.3 mmol) in $CD_3OD$ (1.5 $cm^3$) at room temperature for 24 h gave toluene in 48 or 45% yield, respectively. A trace of bitolyl was also formed in each case. $^1H$ NMR analysis indicated that the balance of these products was accounted for mostly by the starting material **5**, but any resonances ascribable to di-*p*-tolylthallium(III) species could not be observed. The corresponding reaction of **6** at room temperature for 6 h gave toluene and **7** in 11 and 44% yield with AH, or 36 and 14% yield with BNAH.

ESR spin trapping experiments were carried out in a manner essentially the same as those described previously [3c].

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