

## THALLIUM

## ANNUAL SURVEY COVERING THE YEAR 1975

Hideo Kurosawa

Department of Applied Chemistry, Osaka University, Suita, Osaka (JAPAN)

This survey will deal with 1) reviews, 2) synthesis, structure and spectroscopy of organothallium(III) compounds, 3) compounds containing thallium-metal bonds, 4) reactions of organothallium(III) compounds and 5) thallium(I) compounds.

1. Reviews

Walther and Albert have reviewed compounds containing both thallium-non-transition and -transition element bonds (1). A closely related article on organometallic complexes containing bonds between Group IIIb and transition metals also appeared (2). Reactions of organothallium compounds have been surveyed by Lee (3), and reviews on X-ray diffraction studies of the molecular structure of Group IIIb metal compounds (4) and organobimetallic compounds as intermediates in transmetalation between organometallic compounds and Hg metal (5) included topics on organothallium compounds of related interest.

2. Synthesis, Structure and Spectroscopy of Organothallium(III) Compounds

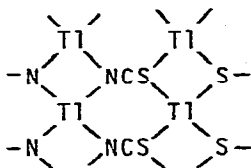
Chow and Britton have determined the crystal structures of dimethylthallium cyanide, azide, thiocyanate and cyanate (6). The cyanide, azide and monoclinic thiocyanate have distorted sodium chloride structures similar to those of the dimethylthallium halides (see Z. Naturforsch., 29b (1974) 193). In the thiocyanate, the different ends of the thiocyanate ion are accommodated

---

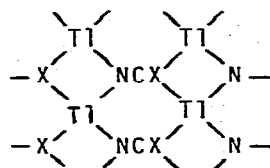
Thallium, Annual Survey covering the year 1974 see J. Organometal. Chem., 98 (1976) 467-493.

References p. 145

by alternate  $TlN_4$  and  $TlS_4$  groups as in I (methyl groups are excluded). In the orthorhombic thiocyanate and cyanate, infinite layers of  $Me_2TlX$  pack together in a different way such that the thallium atoms are all equivalent in a  $TlN_2S_2$  or  $TlN_2O_2$  group as in II. The trigonal cyanate has a quite different structure with recognizable  $[Me_2TlNCO]_2$  groups (III) which are held together through  $Tl-O$  bonds to form a three-dimensional polymer. The  $C-Tl-C$  angle was found to be  $166^\circ$  in the two forms of the cyanate and  $180-177^\circ$  in

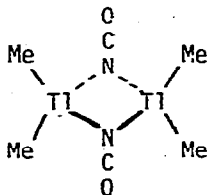


I

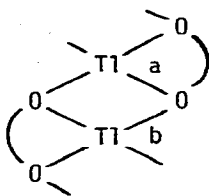


II (X = S or O)

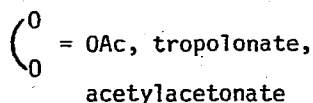
the other compounds. The structures of three dimethylthallium chelate compounds (IV) also were determined (7). In all of these, monomeric units are held together by further  $Tl-O$  bonds to form infinite linear polymers, with sixfold coordination around each thallium atom as shown in IV.



III



IV



The  $C-Tl-C$  angle varied from  $166.9^\circ$  (tropolonate) through  $170.0^\circ$  (acetylacetonate) to  $171.8^\circ$  (acetate). Steric crowding between two methyl groups on adjacent acetylacetonate rings produced somewhat longer  $Tl-O$  bond (b), and a partial resolution of the structure of the dibenzoylmethanide derivative suggested the association of only two monomeric units, possibly due to steric

hindrance between phenyl groups. The same authors further studied the structures of dimethylthallium tricyanomethide and dicyanamide (Fig. 1 and 2) (8). In both compounds the thallium atom is octahedrally coordinated with an almost linear C-Tl-C unit and four equatorial nitrogen atoms.

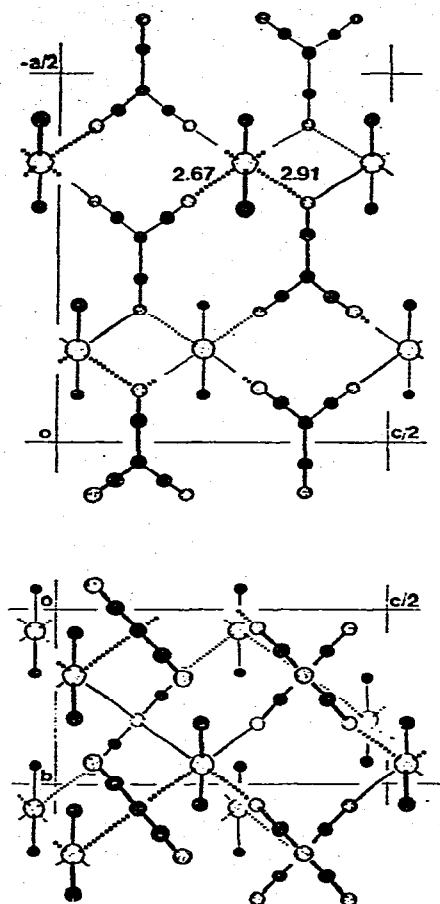


Fig. 1.

The structure of dimethylthallium tricyanomethide. Top: view along *b*. Bottom: view along *a*. [Reproduced from *Acta Cryst.*, B31 (1975) 1934]

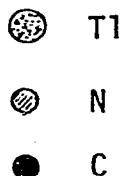
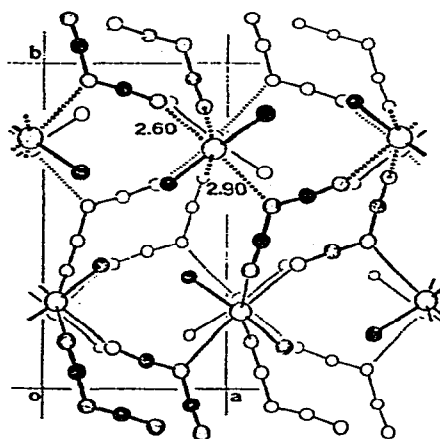
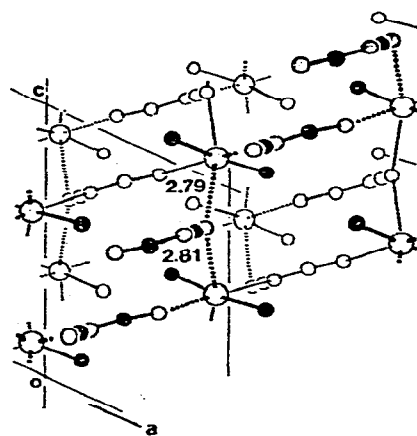
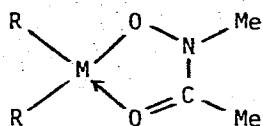


Fig. 2.

The structure of dimethylthallium dicyanamide. Top: view along *b*. Bottom: view along *c*. [Reproduced from *Acta Cryst.*, B31 (1975) 1934]

A thermally stable tetraorganothallate,  $\text{Me}_3\text{Tl}^+\text{CH}_2\text{PMe}_3^-$  has been prepared, together with its gallium and indium analogs, from  $\text{Me}_3\text{M}$  (M= Tl, Ga, In) and  $\text{Me}_3\text{PCH}_2$  (9).  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for these compounds were reported and discussed. The reaction of  $\text{MeC(O)N(Me)OH}$  with  $\text{R}_3\text{M}$  (R= Me, Et; M= Tl, Ga, In) yielded monomeric dialkylmetal hydroxamates, V (10). The IR, Raman and  $^1\text{H}$  NMR spectra were recorded and discussed.



V (M= Tl, Ga, In)

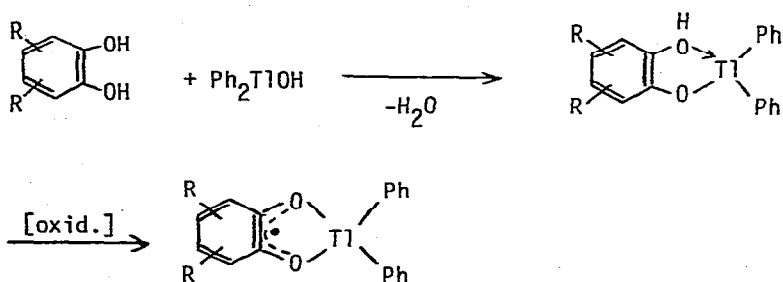
Some new tris- and bis(polychlorophenyl)thallium compounds,  $\text{R}_3\text{Tl}$  and  $\text{R}_2\text{TlCl}$  (R=  $\text{C}_6\text{Cl}_5$ ,  $\text{p-HC}_6\text{Cl}_4$ ) and their mono or bis pyridine adducts were prepared using the corresponding polychlorophenyllithium compounds (11).  $(\text{p-HC}_6\text{Cl}_4)_3\text{Tl}$  was a particularly useful transaryllating reagents; its reactions with appropriate transition metal halide complexes gave novel  $\text{M}(\pi\text{-C}_3\text{H}_5)(\text{HC}_6\text{Cl}_4)(\text{PPh}_3)$  (M= Pt, Pd) and  $\text{Au}(\text{HC}_6\text{Cl}_4)(\text{PPh}_3)$ . Some bis(polyfluorophenyl)thallium acetates,  $\text{R}_2\text{TlOAc}$  (R=  $\text{C}_6\text{F}_5$ ,  $\text{p-HC}_6\text{F}_4$ ,  $\text{m-HC}_6\text{F}_4$ ), were prepared by  $\text{SO}_2$  elimination from the appropriate lithium polyfluorobenzenesulfonates and thallium(III) acetate under mild conditions (12). Owing to reduction of the thallium salt by liberated  $\text{SO}_2$ , good yields required the stoichiometry  $2 \text{LiO}_2\text{SR} : 3 \text{TlX}_3$ .

The reaction of  $\text{CpFeC}_5\text{H}_4\text{Li}$  with  $\text{TlCl}$  followed by addition of  $\text{CpFeC}_5\text{H}_4\text{I}$  gave  $(\text{CpFeC}_5\text{H}_4)_3\text{Tl}$ , hydrolysis of which produced  $[(\text{CpFeC}_5\text{H}_4)_2\text{Tl}]_2\text{O}$  and ferrocene (13). Similarly,  $\text{CpFeC}_5\text{H}_4\text{Li}$ ,  $\text{TlCl}$  and  $\text{BuI}$  gave  $(\text{CpFeC}_5\text{H}_4)_2\text{TlBu}$ , whose hydrolysis resulted in formation of  $[(\text{CpFeC}_5\text{H}_4)(\text{Bu})\text{Tl}]_2\text{O}$ . Diarylthallium nitrates and nitrites,  $\text{R}_2\text{TlX}$  (R= Ph, o, m and p-toly; X=  $\text{NO}_3$  and  $\text{NO}_2$ ), were prepared by the reaction of  $\text{R}_2\text{TlCl}$  with  $\text{NaNO}_3$  and  $\text{NaNO}_2$  (14). Reaction of decaborane(14) with  $\text{Me}_3\text{Tl}$  afforded  $[\text{Me}_2\text{Tl}][\text{B}_{10}\text{H}_{13}]$  and  $[\text{Me}_2\text{Tl}][\text{B}_{10}\text{H}_{12}\text{TlMe}_2]$  (15). The latter was suggested to have one thallium

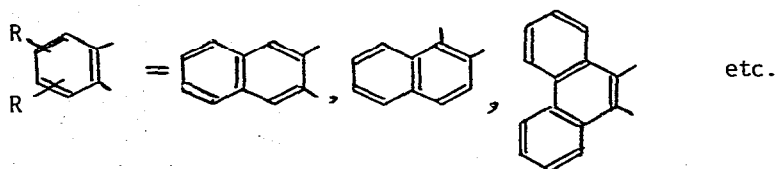
atom coordinated to the dodecahydro-nido-decaborate(2-) anion on the basis of analytical, conductivity, IR and  $^1\text{H}$  NMR spectral data.  $[\text{Ph}_3\text{MeP}][\text{B}_{10}\text{H}_{12}\text{TlMe}_2]$  and  $[\text{Ph}_3\text{MeP}][\text{B}_{10}\text{H}_{12}\text{HgMe}]$  were obtained on treatment of  $[\text{Me}_2\text{Tl}][\text{B}_{10}\text{H}_{12}\text{TlMe}_2]$  with  $[\text{Ph}_3\text{MeP}]\text{Br}$  and  $\text{MeHgCl}$ . Fluorene was metalated with sodium and treated with dipyridinium thallium pentachloride to give difluorenylthallium chloride (16). This compound was treated with  $\text{NaBH}_4$  to produce difluorenylthallium borohydride and with  $\text{NaH}$  it gave difluorenylthallium hydride.

Stegmann *et al.* reported the formation of stable paramagnetic diphenylthallium complexes of semiquinone and semidione from  $\text{Ph}_2\text{TlOH}$  and 43 different catechols, pyrogallols and 1,2-diketones in various solvents (17), e.g. as in Scheme 1. Pyrogallols further gave 1 : 2 complexes as shown in VI. Based on the observed dependence of the thallium coupling and the g-factor in the ESR

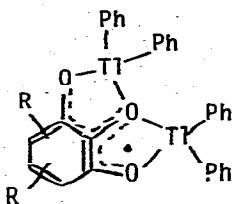
Scheme 1



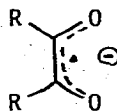
$\text{R} = 3, 4$  and/or  $5$ -alkyl (alkyl = Me, *i*-Pr, *t*-Bu,  $\text{CMe}_2\text{CH}_2\text{CMe}_3$ ,  $\text{CPh}_3$ ),  
 $3$  or  $4$ - $\text{COOR}'$  ( $\text{R}' = \text{Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, TlPh}_2$ ),  
 $3$  or  $4$ -OH,  $3$ -OMe,  $4$ -CHO,  $3, 4, 5$  and/or  $6$ -X ( $\text{X} = \text{Cl, Br}$ )



spectra on the nature of ligands, solvents and temperatures, the authors assumed that the radicals obtained are ion pairs in which a diphenylthallium cation interacts with the semiquinone or semidione (VII) anion radicals.



VI R = 4, 5 and/or 6-COOR'  
(R' = Me, Et, TlPh<sub>2</sub>),  
4-COMe, 5-CONH<sub>2</sub>



VII R<sub>2</sub> = Ph, Me; Ph<sub>2</sub>; (2-furyl)<sub>2</sub>  
etc.

Solvent effects on  $J(\text{M}-\text{CH}_3)$ , methyl chemical shifts and UV spectral data of dimethylthallium oxinate as well as of some dimethyllead compounds have been studied (18). Changes in  $J(\text{M}-\text{CH}_3)$  values were interpreted in terms of changes in the mean singlet-triplet excitation energy involved in the Fermi contact term. The changes in  $^7\text{Li}$  chemical shift in the "ate" complexes of  $\text{Li}[\text{MMe}_4]$  (M = Tl, B, Al, Ga) in diethyl ether, THF and DME have been discussed in terms of solvation of the lithium ion and ion pair formation (19). Different ways of assigning  $^{13}\text{C}$  NMR data of arylthallium(III) compounds in earlier reports by two research groups (Kitching *et al.*, *J. Organometal. Chem.*, 70 (1974) 339 and Ernst, *J. Organometal. Chem.*, 82 (1974) 319) were reexamined by the former group (20). On the basis of the data from *p*-tolylthallium ditrifluoroacetate containing one deuterium atom at the ortho position, these authors confirmed that the assignment by Ernst concerning  $J(\text{Tl}-\text{C}_{\text{ortho}})$  and  $J(\text{Tl}-\text{C}_{\text{meta}})$  was correct. Variable-temperature  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$  NMR and  $^1\text{H}-\{^{205}\text{Tl}\}$  INDOR spectra of dimeric dimethylthallium ethoxide provided evidence of chemical exchange (21). The thallium-thallium coupling constants and thallium chemical shifts were measured for the ethoxide, dimethylthallium

dimethylamide and some other related thallium compounds. The  $^1\text{H}$  NMR spectra of the dimethylthallium ion has been studied in both anionic and cationic detergent nematic phases (22). The spectra were analyzed to derive the values of inter- and intramethyl proton-proton dipolar coupling and the intermethyl scalar coupling constants. The degree of orientation of the dimethylthallium cation is much higher in the anionic nematic phase than in the cationic phase. Though not directly concerned with organothallium compounds, another important spectroscopic study appeared in which variable-temperature  $^1\text{H}$  or  $^{19}\text{F}$  NMR spectra of  $\text{Tl}(\text{OAc})_3$  in methanol- $d_4$  or of  $\text{Tl}(\text{OCCF}_3)_3$  in THF revealed that Tl-H or Tl-F couplings can be observed at low temperatures ( $< -65^\circ$ ) due to a slower ligand exchange process (23).

### 3. Compounds Containing Thallium-Metal Bonds

A detailed report on the stability of Tl(I) derivatives of transition metal carbonyl anions was given by Pedersen and Robinson (24). Thus, the reaction of  $\text{Tl}[\text{Co}(\text{CO})_4]$  with a variety of Lewis bases in non-coordinating solvents gave either  $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]$  (eq. 1) or  $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$  (eq. 2), depending on the basicity of  $\text{Co}(\text{CO})_3\text{L}^-$ . The former compounds could be isolated with those L which give a  $\text{pK}_a$  of  $\text{HCo}(\text{CO})_3\text{L}$  less than 5 ( $\text{L} = \text{P}(\text{OPh})_3, \text{P}(\text{OC}_6\text{H}_4\text{Cl-p})_3$ ),



while the latter predominated when the  $\text{pK}_a$  of  $\text{HCo}(\text{CO})_3\text{L}$  is greater than 7 (e.g.  $\text{L} = \text{AsPh}_3, \text{SbPh}_3, \text{P}(\text{n-Bu})_3$ ). Metastable Tl(I) compounds could be isolated or at least detected in solution for those  $\text{Co}(\text{CO})_3\text{L}^-$  ligands which lie in between the above two classes of anions (e.g.  $\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{P}(\text{OCH}_2)_3\text{CEt}$ ). The same authors further prepared a series of Tl(I) derivatives of other transition metal carbonyl anions (25). The stability of these compounds was shown again to depend on the base strength of the anion as well as on its

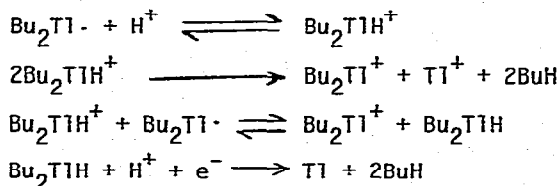
steric bulk. Stable complexes thus formed, either through metathetical reactions between  $TlNO_3$  and metal carbonyl anions or ligand substitution, included  $TlR$  where  $R = Fe(CO)_3NO$ ,  $Fe(CO)_2(NO)P(OC_6H_4Cl-p)_3$ ,  $Fe(CO)_4R'$  ( $R' = CH_2CN$ ,  $COPh$ ,  $CN$ ),  $Fe(CO)_3L(SnPh_3)$  ( $L = CO$ ,  $P(OC_6H_4Cl-p)_3$ ,  $PPh_3$ ,  $P(n-Bu)_3$ ),  $V(CO)_6$  and  $CrCp(CO)_3$ . The stability of  $TlFe(CO)_3L(SnPh_3)$  in particular was attributed to the large size of the anions which prevents the formation of the corresponding  $Tl(III)$  derivatives according to eq. 2.

Exposure of  $Tl[Co(CO)_4]$  to  $^{60}Co$   $\gamma$ -rays at  $77^\circ K$  resulted in a complex ESR spectrum in which the high field component of the doublet expected for a  $Tl(II)$  center could be detected together with sets of lines due to the  $[Co(CO)_4]^{2-}$  (26). At room temperature the only ESR signal detected corresponded to a species having the properties expected for the  $[Co(CO)_4(O_2)]$ .

#### 4. Reactions of Organothallium(III) Compounds

Substituted diphenylthallium chlorides,  $(XC_6H_4)_2TlCl$  ( $X = p-Ome$ ,  $p-Me$ ,  $m-Me$ ,  $H$ ,  $p-Cl$ ,  $p-MeCOO$ ) have been prepared and polarographic and chronopotentiometric studies of these compounds indicated that  $[ArTlHgAr]^+$  are intermediates in the transmetalation reaction between  $Ar_2Tl^+$  and mercury metal to give  $Ar_2Hg$  (27). Another polarographic study of dibutylthallium(III) cation over various pH ranges has suggested that other than transmetalation with mercury or further reduction of a species  $Bu_2Tl\cdot$  produced electrolytically, the reaction with  $H^+$  to form  $Bu_2TlH^+$  also plays some role particularly at the lower pH (28) as shown in Scheme 2.

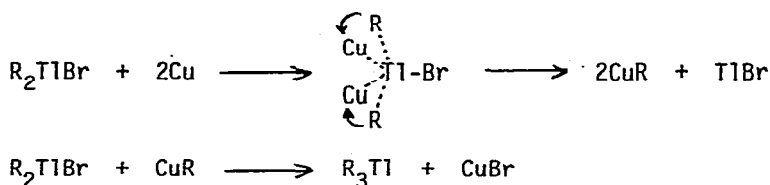
Scheme 2



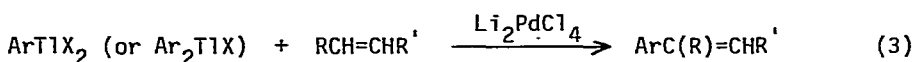


Uson *et al.* reexamined the reaction of  $(C_6F_5)_2TlBr$  with  $PdCl_2L_2$  ( $L = PR_3, AsR_3$ ) (Chem. Commun., (1969) 421) to find that the reported preparation of  $Pd(C_6F_5)_2Cl_2(PPh_3)_2$  could not be repeated (29). Instead, mixtures of  $Pd_2(C_6F_5)_2Cl_2L_2$  and  $Pd(C_6F_5)ClL_2$  were obtained. Reactions of bis(polyfluorophenyl)thallium bromides,  $R_2TlBr$  ( $R = C_6F_5, p-HC_6F_4, m-HC_6F_4, 3,5-H_2C_6F_3$ ), and  $(C_6F_5)_2TlOH$  with copper powder in boiling 1,4-dioxane or diethyl ether gave the corresponding trisorganothallium compounds (30, 31).  $R_2TlBr$  ( $R = o-HC_6F_4, 3,6-H_2C_6F_3, Ph$ ) failed to undergo a similar reaction. A possible reaction path for such symmetrization is shown in Scheme 3.

Scheme 3



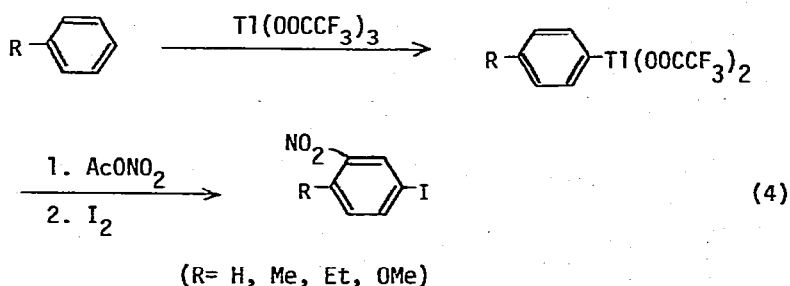
Several aryl- and diarylthallium(III) compounds were treated with olefins in the presence of  $Li_2PdCl_4$ , either in equimolar quantity or using only catalytic quantities of the Pd(II) complex with added  $CuCl_2$ , to give aryl-substituted olefins (32) as shown in eq. 3.



( $Ar = Ph, p\text{-tolyl, mesityl}$ ;  $R = H, Ph$ ;  $R' = CO_2Me, H$ ;  $X = O_2CCF_3, OAc, Cl, CN$ )

A wide range of arylthallium ditrifluoroacetates reacted with diborane in THF to give, after hydrolysis, good yields of the corresponding arylboronic acids (33). Oxidation of such reaction mixtures gave phenols in good yield. The aryl groups in the  $ArTl(OOCCF_3)_2$  thus studied include  $Ph, p\text{-tolyl, mesityl, } p\text{-EtC}_6H_4, 3,4\text{-Me}_2C_6H_3, 2,4\text{-Me}_2C_6H_3$  and  $2,5\text{-Me}_2C_6H_3$ . Some  $Ar_2TlOOCCF_3$  ( $Ar = Ph, o, m, p\text{-tolyl, } 3,4\text{-Me}_2C_6H_3, m\text{-ClC}_6H_4, m\text{-MeOC}_6H_4, \alpha, \beta\text{-naphthyl, 2-dibenzofuryl}$ )

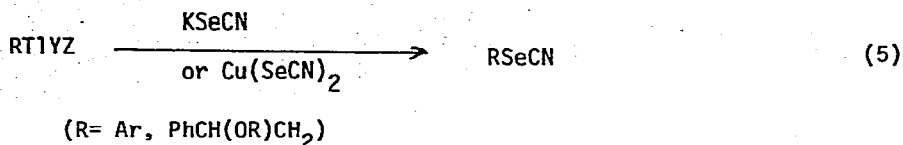
prepared either by heating arylthallium ditrifluoroacetates in acetone or by the Grignard method were shown to be useful, versatile intermediates for the synthesis of unsymmetrical biphenyls (by irradiation in benzene), aryl iodides (by heating with iodine in chloroform) and phenols (by reaction with  $\text{Pb}(\text{OAc})_4\text{-PPh}_3$  in  $\text{CF}_3\text{COOH}$  followed by alkaline hydrolysis of the resulting aryl trifluoroacetates) (34). In other study of application of arylthallium compounds in organic synthesis, Taylor *et al.* reported a convenient, high-yield synthesis of nitroaryl iodides through nitration of  $\text{ArTl}(\text{OCCF}_3)_2$  with acetyl nitrate, followed by treatment of the resulting nitroarylthallium intermediates with iodine in chloroform (35) as shown in eq. 4. Other than the products



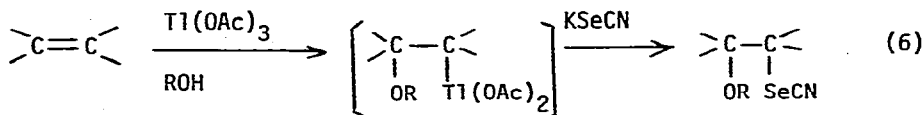
shown in eq. 4, nitroiodomesitylene, 4-nitro-6-iodo-*m*-xylene, 4-nitro-4'-iodobiphenyl and 2-nitro-4'-iodobiphenyl were obtained from mesitylene, *m*-xylene and biphenyl. A method of selectively nitrating aromatic substrates has also been reported in which nitrogen dioxide displaces a thallium(III) substituent in arylthallium(III) compounds obtained by thallation of toluene, ethylbenzene or other alkylbenzenes, anisol, biphenyl and halobenzenes (36). The scope and limitations in this method were discussed briefly.

Uemura and co-workers extended their study of halodethallation of organothallium(III) compounds to a method of preparing aryl and alkyl selenocyanates (37). Thus,  $\text{ArTlYZ}$  (Ar= Ph, *p*-tolyl, 3,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*- and *m*-ClC<sub>6</sub>H<sub>4</sub>; Y,Z= OAc, OCCF<sub>3</sub>, ClO<sub>4</sub>, NO<sub>3</sub>, OH) reacted with

$\text{KSeCN/CuSO}_4 \cdot 5\text{H}_2\text{O}$  or  $\text{Cu}(\text{SeCN})_2$  in dioxane to give aryl selenocyanates in good yields (eq. 5). Alkoxythallates of styrene underwent similar reactions.

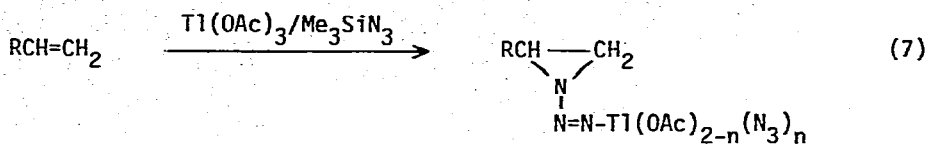


These authors further described oxyselenocyanation of 1-octene, 1-hexene, *o*-allylphenol, ethyl vinyl ether, vinyl acetate and 1,3-butadiene in a manner similar to eq. 5 except that an intermediate oxythallated adduct need not be isolated as shown in eq. 6.

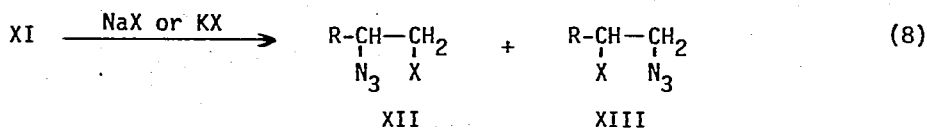


A research group in Canada extended mechanistic studies of the decomposition of oxythallated adducts of olefins (Can. J. Chem., 52 (1974) 2677) (38). Analysis of products and kinetic data of the decomposition of  $\text{Me}_2\text{C}(\text{OX})\text{CH}_2\text{Tl}(\text{OAc})_2$  (X= H, Me, Et) under acidic conditions led the authors to confirm that  $\text{Me}_2\text{C}(\text{OX})\text{CH}_2\text{Tl}^{2+}$  is the principal reactive species and migration of the OX group plays an important role during cleavage of the Tl-C bond. The comparative study of the oxidation of 1-octene by Pb(IV), Tl(III) and Hg(II) acetates in methanol (J. Chem. Soc. Perkin I, (1974) 1929) was extended to the reaction in other solvents including acetic acid and trifluoroacetic acid (39). The general rules developed for the methanol system are applicable to these solvents. Comparison was also made of oxidation of trans-4-octene where the major products from Tl(III) acetate include two isomeric allyl acetates, VIII and IX, and the diacetate X as shown in Schema 4 and 5. The predominance of





XI

(R = PhCH<sub>2</sub>, C<sub>5</sub>H<sub>11</sub>, t-Bu, MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>; n = 1, 2)

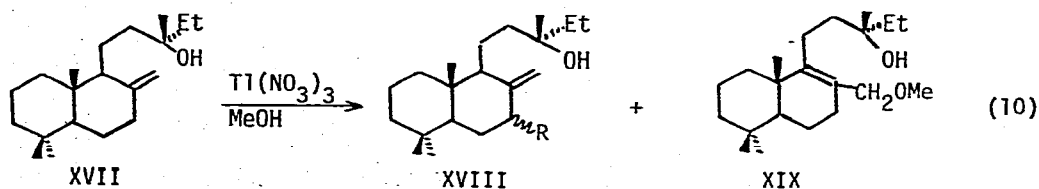
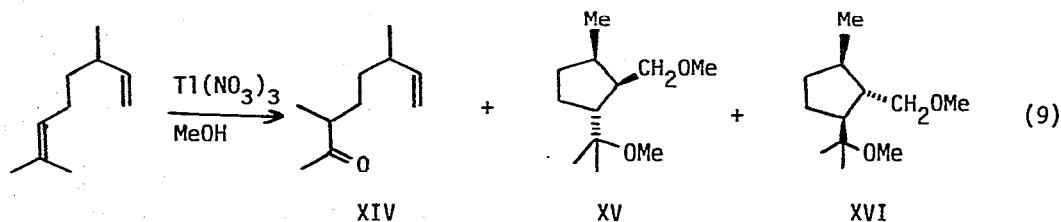
XII

XIII

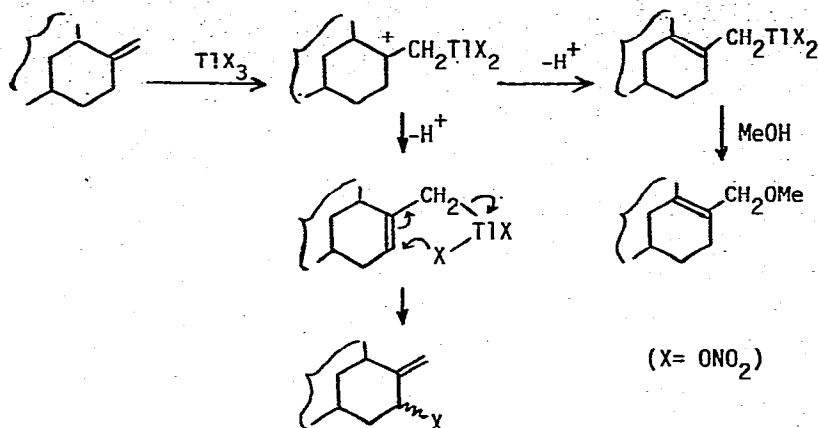
(X = F, Cl, Br, I, NCS)

methylenecyclohexane,  $\beta$ -pinene and cyclohexene have also been investigated.

Oxidation with  $\text{Tl}(\text{NO}_3)_3$  in methanol of 3,7-dimethylocta-1,6-diene afforded the ketone XIV and two isomeric cyclopentane derivatives, XV and XVI, as shown in eq. 9 (42). Oxidation of XVII with  $\text{Tl}(\text{NO}_3)_3$  in methanol gave XVIII (R =  $\alpha$ -ONO<sub>2</sub>,  $\alpha$ -OH,  $\beta$ -OMe) and XIX, but no ring-enlarged ketones as shown in eq. 10 (43). A similar result was obtained with 2-methylene-8,13-epoxylabdane. A possible route to the observed products is shown in Scheme 6. In a related work, Ochiai and Fujita obtained the allylic nitrates XX and XXI from oxidation

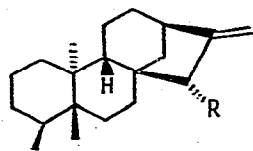


Scheme 6

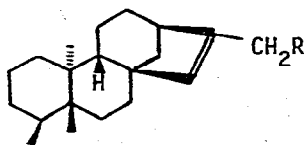


of ent-16-kaurene XXII and ent-15-kaurene XXIII with  $Ti(NO_3)_3$  (44).

Structures have been assigned to seven minor products obtained from treatment of methyl ent-trachyloban-19-oate with  $Ti(OAc)_3$  (45) (see also Can. J. Chem., 51 (1973) 4167). The synthesis of natural isoflavones through oxidative rearrangement of chalcones by  $Ti(NO_3)_3$  was reported (46).

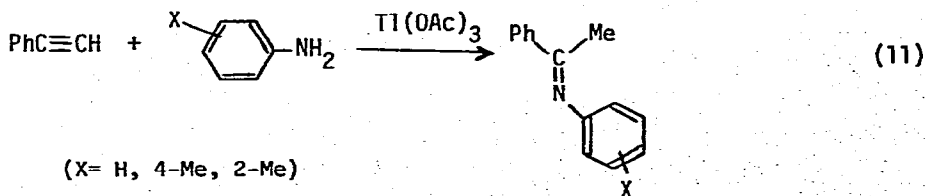
XX R = ONO<sub>2</sub>

XXII R = H

XXI R = ONO<sub>2</sub>

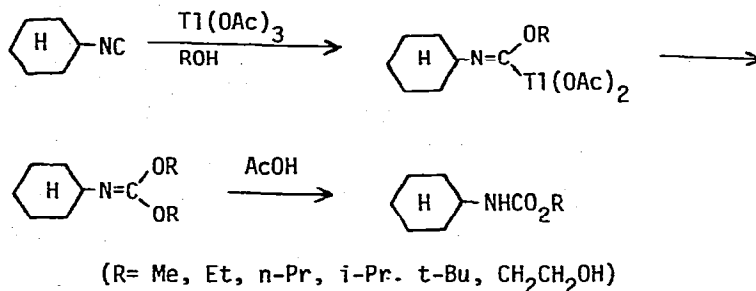
XXIII R = H

The reaction of phenylacetylene with  $Ti(OAc)_3/ArNH_2$  in dioxane or THF afforded the imines in good yields (47) as in eq. 11. In these reactions,



$\text{Tl}(\text{OAc})_3$  used could be recovered quantitatively. Oxidation of cyclohexyl isocyanide with  $\text{Tl}(\text{OAc})_3$ ,  $\text{Hg}(\text{OAc})_2$  and  $\text{Pb}(\text{OAc})_4$  in benzene/ $\text{AcOH}$  gave cyclohexyl isocyanate, possibly through acetoxymetalation (48).  $\text{Tl}(\text{OAc})_3$  also oxidized the isocyanide into carbamates in various alcohols as shown in Scheme 7.

Scheme 7



### 5. Thallium(I) Compounds

The thermal expansion of  $\text{C}_5\text{H}_5\text{Tl}$  was determined at 78–295° K by using X-ray powder diffractometry (49). Expansion is very anisotropic;  $\alpha_1 = 125 \pm 12$ ,  $\alpha_2 = 97 \pm 5$ ,  $\alpha_3 = 0 \pm 4$  (all in  $10^{-6} \text{ K}^{-1}$ ). Directions and ratio of the two greatest expansion coefficients,  $\alpha_1$  and  $\alpha_2$ , were explained by considering the shortest distances,  $\text{Tl}^+ - \text{Tl}^+$ , in the ionic structure.  $\text{C}_5\text{H}_5\text{Tl}$  was used in the reaction with  $\text{R}_2\text{PCl}$  or  $\text{RPCl}_2$  (R = Ph, Me) to prepare  $\text{C}_5\text{H}_5\text{PR}_2$  or  $(\text{C}_5\text{H}_5)_2\text{PR}$  (50). Cyclopentadienylthallium with one carbon position labeled at a concentration greater than 90 atom %  $^{13}\text{C}$  was prepared using  $\text{C}_4^{13}\text{CH}_6$  (51). A new method of preparing such labeled cyclopentadiene was also presented.

### References

1. B. Walther and H. Albert, Z. Chem., 15 (1975) 293.
2. A. T. T. Hsieh, Inorg. Chim. Acta, 14 (1975) 87.

3. A. G. Lee, *Organometal. React.*, 5 (1975) 1.
4. M. B. Hursthouse, *Mol. Struct. Diffr. Methods*, 2 (1974) 429; *Chem. Abstr.*, 83 (1975) 19098.
5. O. A. Reutov and K. P. Butin, *J. Organometal. Chem.*, 99 (1975) 171.
6. Y. M. Chow and D. Britton, *Acta Cryst.*, B31 (1975) 1922.
7. Y. M. Chow and D. Britton, *Acta Cryst.*, B31 (1975) 1929.
8. Y. M. Chow and D. Britton, *Acta Cryst.*, B31 (1975) 1934.
9. H. Schmidbauer, H. J. Füller and F. H. Köhler, *J. Organometal. Chem.*, 99 (1975) 353.
10. H.-U. Schwering and J. Weidlein, *J. Organometal. Chem.*, 99 (1975) 223.
11. S. Numata, H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, 102 (1975) 259.
12. G. B. Deacon and I. K. Johnson, *J. Fluorine Chem.*, 6 (1975) 437; *Chem. Abstr.*, 83 (1975) 206359.
13. A. N. Nesmeyanov, D. A. Lemenovskii and E. G. Perevalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1975) 1667; *Chem. Abstr.*, 83 (1975) 179186.
14. T. N. Srivastava and K. K. Bajpai, *J. Indian Chem. Soc.*, 52 (1975) 549; *Chem. Abstr.*, 83 (1975) 206357.
15. N. N. Greenwood, B. S. Thomas and D. W. Waite, *J. Chem. Soc. Dalton*, (1975) 299.
16. N. Kumar and R. K. Sharma, *J. Chin. Chem. Soc.*, 21 (1974) 271; *Chem. Abstr.*, 82 (1975) 98034.
17. H. B. Stegmann, K. B. Ulmschneider and K. Scheffler, *J. Organometal. Chem.*, 101 (1975) 145.
18. M. Aritomi and Y. Kawasaki, *J. Organometal. Chem.*, 90 (1975) 185.
19. R. J. Hogan, P. A. Sherr, A. T. Weibel and J. P. Oliver, *J. Organometal. Chem.*, 85 (1975) 265.
20. W. Kitching, C. J. Moore, D. Doddrell and W. Adcock, *J. Organometal. Chem.*, 94 (1975) 469.
21. G. M. Sheldrick and J. P. Yesinowski, *J. Chem. Soc. Dalton*, (1975) 870.



22. Y. Lee and L. W. Reeves, *Can. J. Chem.*, 53 (1975) 162.
23. R. J. Abraham, G. E. Hawkes and K. M. Smith, *Tetrahedron Lett.*, (1975) 1999.
24. S. E. Pedersen and W. R. Robinson, *Inorg. Chem.*, 10 (1975) 2360.
25. S. E. Pedersen and W. R. Robinson, *Inorg. Chem.*, 10 (1975) 2365.
26. M. C. R. Symons and D. N. Zimmerman, *J. Chem. Soc. Dalton*, (1975) 2545.
27. K. P. Butin, V. V. Strelets, I. F. Gunkin, I. P. Beletskaya and O. A. Reutov, *J. Organometal. Chem.*, 85 (1975) 123.
28. T. Murayama and K. Kikuchi, *Bull. Chem. Soc. Japan*, 48 (1975) 1357.
29. R. Uson, P. Royo, J. Fornies and F. Martinez, *J. Organometal. Chem.*, 90 (1975) 367.
30. G. B. Deacon and D. G. Vince, *Aust. J. Chem.*, 28 (1975) 1931.
31. G. B. Deacon and D. G. Vince, *J. Fluorine Chem.*, 5 (1975) 87; *Chem. Abstr.*, 82 (1975) 86315.
32. T. Spencer and F. G. Thorpe, *J. Organometal. Chem.*, 99 (1975) C8.
33. S. W. Breuer, G. M. Pickles, J. C. Podesta and F. G. Thorpe, *Chem. Commun.*, (1975) 36.
34. E. C. Taylor, H. W. Atland and A. McKillop, *J. Org. Chem.*, 40 (1975) 2351.
35. E. C. Taylor, H. W. Atland and A. McKillop, *J. Org. Chem.*, 40 (1975) 3441.
36. B. Davies and C. B. Thomas, *J. Chem. Soc. Perkin I*, (1975) 65.
37. S. Uemura, A. Toshimitsu, M. Okano and K. Ichikawa, *Bull. Chem. Soc. Japan*, 48 (1975) 1925.
38. C. Beaudry and M. Zador, *J. Organometal. Chem.*, 102 (1975) 265.
39. A. Lethbridge, R. O. C. Norman, C. B. Thomas and W. J. E. Parr, *J. Chem. Soc. Perkin I*, (1975) 231.
40. A. Lethbridge, R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. Perkin I*, (1975) 2465.
41. E. Maxa, E. Zbiral, G. Schulz and E. Haslinger, *Justus Liebigs Ann. Chem.*, (1975) 1705.
42. F. J. McQuillin and D. G. Parker, *J. Chem. Soc. Perkin I*, (1975) 2092.

43. P. K. Grant, H. T. L. Liao and K. S. Low, *Aust. J. Chem.*, 28 (1975) 903.
44. M. Ochiai and E. Fujita, *Chem. Commun.*, (1975) 967.
45. H. M. Campbell, P. A. Gunn, A. J. McAlees and R. McCrindle, *Can. J. Chem.*, 53 (1975) 20.
46. S. Antus, L. Farkas, Z. Kardos-Balogh and M. N<sup>o</sup>gr<sup>a</sup>di, *Chem. Ber.*, 108 (1975) 3883.
47. J. Barluenga and F. Aznar, *Synthesis*, (1975) 704.
48. S. Tanaka, H. Kido, S. Uemura and M. Okano, *Bull. Chem. Soc. Japan*, 48 (1975) 3415.
49. J. F. Berar, G. Calvarin, C. Pommier and D. Weigel, *J. Appl. Cryst.*, 8, pt. 3 (1975) 386; *Chem. Abstr.*, 83 (1975) 511985.
50. F. Mathey and J. P. Lampin, *Tetrahedron*, 31 (1975) 2685.
51. S. D. Larsen, P. J. Vergamini and T. W. Whaley, *J. Labelled Compounds*, 11 (1975) 325; *Chem. Abstr.*, 84 (1976) 44238.