

## PREPARATION AND SOME REACTIONS OF TRIS(POLYCHLOROPHENYL)-THALLIUM(III) COMPOUNDS

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### Summary

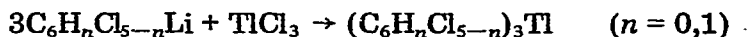
Fairly stable tris(polychlorophenyl)thallium(III)  $R_3Tl$  (I,  $R = C_6Cl_5$ ; II,  $R = 2,3,5,6-C_6HCl_4$ ) have been prepared from thallic chloride and the corresponding chlorophenyllithium. I and II react with some amines forming 1/1 complexes. II reacts with  $M(\pi-C_3H_5)ClL$  ( $M = Pd$  or  $Pt$ ,  $L = PPh_3$  or pyridine) to give a novel type of complexes  $M(\pi-C_3H_5)(C_6HCl_4)L$ .  $Au(C_6HCl_4)(PPh_3)$  can be isolated similarly from II and  $AuCl(PPh_3)$ .

### Introduction

The metal-carbon bond in various chlorine- or fluorine-substituted phenyl-metal compounds has been known [1] to be stable thermally and kinetically. As far as the corresponding compounds of the type  $R_3Tl$  are concerned, the preparations of  $(C_6F_5)_3Tl$  [2] and  $(p-HC_6F_4)_3Tl$  [3] have been reported. We describe here the preparation of air-stable tris(polychlorophenyl)thallium(III) compounds and their potential utility as a convenient arylating reagent.

### Results and discussion

$(C_6Cl_5)_3Tl$  (I) and  $(2,3,5,6-C_6HCl_4)_3Tl$  (II) were prepared from thallium chloride and the corresponding chlorophenyllithium according to the following equation:



In contrast to the usual  $R_3Tl$  ( $R = CH_3$ ,  $C_2H_5$  or  $C_6H_5$ ), which are known to be highly air sensitive and readily hydrolyzable [4,5], I and II show high resistance to hydrolysis and do not decompose in air. Further, they were recovered unchanged on heating at  $200^\circ C$  for 2 h in the solid state or in refluxing xylene for 2 h. II is monomeric in chloroform solution, but I is too insoluble for a molecular weight determination by osmometry.

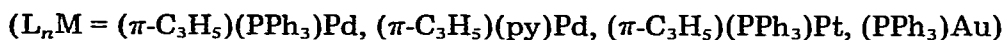
TABLE 1  
 PROPERTIES OF POLYCHLOROPHENYLTHALLIUM(III) COMPOUNDS

Compound <sup>a</sup>		M.p.(°C)	Analysis found (calcd.)(%)		
			C	H	N
R <sup>1</sup> <sub>3</sub> Tl	I	280	22.66 (22.70)		
R <sup>1</sup> <sub>3</sub> Tl(py) <sub>2</sub>		285	30.25 (30.28)	0.69 (0.91)	2.59 (2.52)
R <sup>1</sup> <sub>3</sub> Tl(γ-picoline)		220	27.95 (27.57)	0.45 (0.68)	1.70 (1.34)
R <sup>1</sup> <sub>3</sub> Tl(β-picoline)		210	27.90 (27.57)	0.42 (0.68)	1.65 (1.34)
R <sup>1</sup> <sub>3</sub> Tl(TMED)		145	26.71 (26.98)	1.51 (1.51)	2.89 (2.62)
R <sup>1</sup> <sub>2</sub> TlCl		314	19.37 (19.52)		
R <sup>2</sup> <sub>3</sub> Tl <sup>b</sup>	II	209	25.39 (25.46)	0.32 (0.36)	
R <sup>2</sup> <sub>3</sub> Tl(py) <sup>b</sup>		208	29.60 (29.76)	0.76 (0.89)	1.48 (1.51)
R <sup>2</sup> <sub>3</sub> Tl(β-picoline)		205	30.70 (30.60)	1.08 (1.08)	1.60 (1.49)
R <sup>2</sup> <sub>2</sub> TlCl		325	21.53 (21.53)	0.32 (0.30)	

<sup>a</sup> R<sup>1</sup> = C<sub>6</sub>Cl<sub>5</sub>, R<sup>2</sup> = 2,3,5,6-C<sub>6</sub>HCl<sub>4</sub>. <sup>b</sup> Molecular weights determined in chloroform at 25°C, II: found 852, calcd. 849, R<sup>2</sup><sub>3</sub>Tl(py): found 830, calcd. 928.

Like other Group III triorganometallic compounds, I and II reacted with some amines forming 1/1 adducts except for (C<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>Tl(py)<sub>2</sub>. In the pyridine adducts the presence of nitrogen—thallium bonding in the solid state is shown from their IR spectra in Nujol mull; the pyridine ring vibrations in these compounds are observed at higher frequencies than those in free pyridine [6]\*. All the amine adducts completely lost the amines when heated at 100°C in vacuo. The observed molecular weight of (2,3,5,6-C<sub>6</sub>HCl<sub>4</sub>)<sub>3</sub>Tl(py) in chloroform suggests a slight dissociation of pyridine (Table 1).

II reacted with metal halide in chloroform, dichloromethane or benzene to give the corresponding tetrachlorophenylmetallic compounds in good yield as shown below.



The poor solubility of I precluded a similar treatment with L<sub>n</sub>MCl. As would be expected, all the tetrachlorophenylmetal compounds obtained in this way are stable in air and can be readily isolated except for Pd(π-C<sub>3</sub>H<sub>5</sub>)(C<sub>6</sub>HCl<sub>4</sub>)(py). The palladium and platinum complexes are particularly interesting in that these are the first π-allyl-palladium(II) or -platinum(II) complexes containing a stable metal—carbon σ-bond\*\* as well. It is also notable that in the <sup>1</sup>H NMR spectra

\* The pyridine ring vibrations of (C<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>Tl(py)<sub>2</sub> and (C<sub>6</sub>HCl<sub>4</sub>)<sub>3</sub>Tl(py) are located at 411, 419, 635 and 421, 632 cm<sup>-1</sup>, respectively while they are observed at 405, 602 cm<sup>-1</sup> in free pyridine.

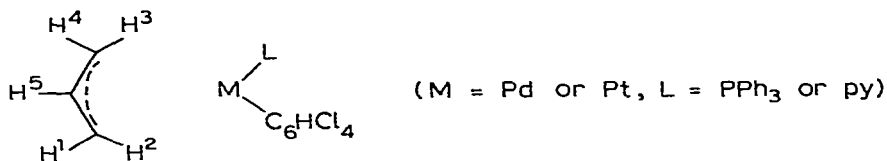
\*\* Analogous nickel compounds, Ni(π-allyl)(C<sub>6</sub>Cl<sub>5</sub>)(PPhMe<sub>2</sub>) have been prepared recently [13].

TABLE 2

<sup>1</sup>H NMR DATA<sup>a</sup> FOR ALLYLIC COMPLEXES OF PALLADIUM(II) AND PLATINUM(II) AT 23°C IN CDCl<sub>3</sub>

Compound	H(1)	H(2)	H(3)	H(4)	H(5)
Pd( $\pi$ -C <sub>3</sub> H <sub>5</sub> )(C <sub>6</sub> HCl <sub>4</sub> )(PPh <sub>3</sub> )	4.13t J(5) = 6 J(P) = 6	3.14dd J(5) = 13 J(P) = 9	2.70d J(5) = 13	3.80d J(5) = 7	5.45m
Pd( $\pi$ -C <sub>3</sub> H <sub>5</sub> )(C <sub>6</sub> HCl <sub>4</sub> )(py)	3.26d J(5) = 7	2.56d J(5) = 12	2.56d J(5) = 12	3.26d J(5) = 7	5.58m
Pt( $\pi$ -C <sub>3</sub> H <sub>5</sub> )(C <sub>6</sub> HCl <sub>4</sub> )(PPh <sub>3</sub> )	3.96t J(5) = 6 J(P) = 6	3.16dd J(5) = 13 J(P) = 10 J(Pt) = 56	2.84d J(5) = 13 J(Pt) = 40	4.19d J(5) = 7	5.32m

<sup>a</sup> Chemical shifts  $\delta$  in ppm, coupling constants in Hz, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, J(X) = coupling constants with proton numbered X, J(P) = coupling constants with <sup>31</sup>P, J(Pt) = coupling constants with <sup>195</sup>Pt.



(Table 2) of Pd( $\pi$ -C<sub>3</sub>H<sub>5</sub>)(C<sub>6</sub>HCl<sub>4</sub>)(PPh<sub>3</sub>) the allylic proton resonances did not show any sign of fluxionality even at 80°C or in the presence of added phosphines, in marked contrast to the non-rigid character of Pd( $\pi$ -C<sub>3</sub>H<sub>5</sub>)Cl(PPh<sub>3</sub>) [7-8]. These facts may be partly attributed to the inability of the tetrachlorophenyl group to form a bridging intermediate and/or to the bulkiness of the tetrachlorophenyl group which suppresses attack by phosphines to form a penta-coordinated transition state [7]. On account of its thermal instability, attempts to isolate Pd( $\pi$ -C<sub>3</sub>H<sub>5</sub>)(C<sub>6</sub>HCl<sub>4</sub>)(py) were unsuccessful, although its existence in solution was clearly confirmed by <sup>1</sup>H NMR spectroscopy (Table 2). Unlike the phosphine analog, Pd( $\pi$ -C<sub>3</sub>H<sub>5</sub>)(C<sub>6</sub>HCl<sub>4</sub>)(py) undergoes ligand exchange, resulting in the equivalence between H(1) and H(4), H(2) and H(3) in the allyl group in the <sup>1</sup>H NMR spectrum\*.

It is believed that the use of II for the preparation of various polychlorophenylmetal compounds through the reactions with the appropriate halides will prove to be of practical value because (C<sub>6</sub>HCl<sub>4</sub>)<sub>2</sub>TiCl formed is sparingly soluble in common solvents such as benzene or chloroform and therefore easily removed out of the reaction mixture.

## Experimental

Molecular weights were determined using a Mechrolab vapor pressure osmometer Model 302. Infrared spectra were run on a Hitachi 225 spectrophotometer.

\* Note added in proof. A careful reexamination of the <sup>1</sup>H NMR spectrum of the reaction mixture from II and Pd( $\pi$ -C<sub>3</sub>H<sub>5</sub>)Cl(py) has revealed the existence of additional peaks at  $\delta$  3.88 (J(5) 8) and 3.18 (J(5) 13) which are located very close to the resonances due to unreacted  $\pi$ -allyl complex. Those new resonances, together with the resonances shown in Table 2, may well be interpreted as arising from a rigid structure of Pd( $\pi$ -C<sub>3</sub>H<sub>5</sub>)(C<sub>6</sub>HCl<sub>4</sub>)(py).

Proton NMR spectra were recorded on a Japan Electron Optics JNM-PS-100 spectrometer with tetramethylsilane as internal standard. Analytical data and molecular weights are summarized in Table 1. Literature methods were used to prepare the complexes  $\text{Pd}(\pi\text{-C}_3\text{H}_5)\text{Cl}(\text{PPh}_3)$  [7],  $\text{Pd}(\pi\text{-C}_3\text{H}_5)\text{Cl}(\text{py})$  [9],  $\text{Pt}(\pi\text{-C}_3\text{H}_5)\text{Cl}(\text{PPh}_3)$  [10] and  $\text{AuCl}(\text{PPh}_3)$  [11]. Thallic chloride was obtained by chlorination of thallic chloride, followed by dehydration with anhydrous  $\text{CuSO}_4$ .

*Preparation of tris(pentachlorophenyl)thallium(III) (I)*

$\text{TlCl}_3$  (2.1 g, 6.8 mmol) in diethyl ether (25 ml) was added dropwise under nitrogen atmosphere at  $-70^\circ\text{C}$  to a solution of pentachlorophenyllithium [12] which was obtained from hexachlorobenzene (5.7 g, 20 mmol) in diethyl ether (400 ml) and an equivalent amount of commercial n-butyllithium in n-hexane at  $-10^\circ\text{C}$ . Rapid stirring at this temperature was continued for 1 h. The reaction mixture then was allowed to warm to room temperature and stirred overnight.  $\text{LiCl}$  which precipitated was extracted with two 100 ml portions of saturated aqueous ammonium chloride. The ether layer was evaporated to dryness. Yellow powders thus obtained were recrystallized from hot benzene to give I (4 g) as a white powder. A small amount of bis(pentachlorophenyl)thallium(III) chloride (0.2 g) was obtained as the benzene-insoluble product.

*Preparation of tris(2,3,5,6-tetrachlorophenyl)thallium(III) (II)*

From  $\text{TlCl}_3$  (7.6 g, 24.5 mmol) and 2,3,5,6-tetrachlorophenyllithium which was prepared from 1,2,4,5-tetrachlorobenzene (25 g, 116 mmol) and equimolar amounts of n-butyllithium in ether (1000 ml) and tetrahydrofuran (350 ml) at  $-40^\circ\text{C}$ , colorless crystals of II (6.3 g) and  $(2,3,5,6\text{-C}_6\text{HCl}_4)_2\text{TlCl}$  (0.3 g) were obtained in a manner similar to that described above. Crystallization of I and II from their amine solutions gave amine adducts in quantitative yields.

*Transarylation reactions of II*

*(i) with chloro( $\pi$ -allyl)(triphenylphosphine)palladium(II) and chloro( $\pi$ -allyl)-(triphenylphosphine)platinum(II)*

A solution of II (716 mg) in 8 ml of benzene was added to a solution of  $\text{Pd}(\pi\text{-C}_3\text{H}_5)\text{Cl}(\text{PPh}_3)$  (375 mg) in 5 ml of dichloromethane. After 24 h,  $(2,3,5,6\text{-C}_6\text{HCl}_4)_2\text{TlCl}$  which precipitated was filtered and the solid products obtained by vacuum evaporation of the filtrate were recrystallized from benzene/methanol to give  $\text{Pd}(\pi\text{-C}_3\text{H}_5)(2,3,5,6\text{-C}_6\text{HCl}_4)(\text{PPh}_3)$  (210 mg) as colorless crystals, m.p.  $118^\circ\text{C}$ . (Found: C, 51.90; H, 3.32.  $\text{C}_{27}\text{H}_{21}\text{Cl}_4\text{PPd}$  calcd.: C, 51.90; H, 3.39%.)

Colorless crystals of  $\text{Pt}(\pi\text{-C}_3\text{H}_5)(2,3,5,6\text{-C}_6\text{HCl}_4)(\text{PPh}_3)$  (275 mg) were obtained in a similar manner from II (549 mg) and  $\text{Pt}(\pi\text{-C}_3\text{H}_5)\text{Cl}(\text{PPh}_3)$  (349 mg), m.p.  $180^\circ\text{C}$ . (Found: C, 45.74; H, 3.05.  $\text{C}_{27}\text{H}_{21}\text{Cl}_4\text{PPt}$  calcd.: C, 45.46; H, 2.97%.)

*(ii) with chloro( $\pi$ -allyl)(pyridine)palladium(II)*

II (26 mg) and  $\text{Pd}(\pi\text{-C}_3\text{H}_5)\text{Cl}(\text{py})$  (85 mg) were dissolved in 0.5 ml of  $\text{CDCl}_3$ .  $(\text{C}_6\text{HCl}_4)_2\text{TlCl}$  precipitated immediately. In the  $^1\text{H}$  NMR spectrum of the filtrate the allylic proton resonances of  $\text{Pd}(\pi\text{-C}_3\text{H}_5)\text{Cl}(\text{py})$  had decreased and new resonances assignable to  $\text{Pd}(\pi\text{-C}_3\text{H}_5)(2,3,5,6\text{-C}_6\text{HCl}_4)(\text{py})$  were observed (Table 2).

*(iii) with triphenylphosphinegold(I) chloride*

Colorless crystals of  $(2,3,5,6\text{-C}_6\text{HCl}_4)\text{Au}(\text{PPh}_3)$  (102 mg) were obtained in a manner similar to that described above from II (169 mg) and  $\text{ClAu}(\text{PPh}_3)$  (98 mg) in 1.5 ml of chloroform. Recrystallization from benzene/methanol gave the product, m.p.  $134^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.68 ~ 7.40 (15H,  $\text{PPh}_3$ ), 7.32 (3H,  $\text{C}_6\text{H}_6$ ), 7.22 (1H,  $\text{C}_6\text{HCl}_4$ ). (Found: C, 45.44; H, 2.70.  $\text{C}_{24}\text{H}_{16}\text{Cl}_4\text{PAu} \cdot 1/2\text{C}_6\text{H}_6$  calcd.: C, 45.47; H, 2.70%.)

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