

## COMMENTS ON THE CLAIMED NOVEL COMPOUND CYCLOHEPTATRIENYL THALLIUM(III) DICHLORIDE

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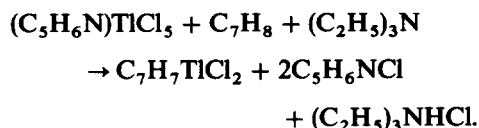
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**Abstract**—Reaction of pyridinium pentachlorothallate(III) with cycloheptatriene and triethylamine in dichloromethane yielded the pyridine adduct  $(C_5H_6N)TlCl_4 \cdot C_5H_5N$  and not the novel complex originally claimed. Cycloheptatriene does not interact at all with the metal under the experimental conditions.

Cycloheptatriene forms well-known complexes of the  $C_7H_7^+$  ligand when a hydride has been abstracted from the parent hydrocarbon. The ligand formally is a six-electron donor akin to  $C_5H_5^-$  and  $C_6H_6$ . Similarly, a formal seven-electron donor function is obtained if a hydrogen atom is abstracted (e.g. by using Pt).<sup>1,2</sup> A third ligating function has been claimed for cycloheptatriene: namely that of acting as  $C_7H_7^-$  after proton abstraction from the parent. This was proposed on the basis of a number of reactions reported with various transition metal chlorides such as  $TaCl_5$  and  $WOCl_4$  in refluxing benzene, when hydrogen chloride was evolved.<sup>3,4</sup>

An extension of this function to Main Group compounds of Sn(IV), Pb(IV) and Tl(III) was also claimed, although only the thallium reaction has apparently been published.<sup>5</sup> The reaction involved the interaction of pyridinium pentachlorothallate(III) with the hydrocarbon in dichloromethane, using triethylamine as a proton abstractor:



On the basis of the reported IR spectral frequencies, a  $\pi$ -bonding function for the  $C_7$  ligand was suggested. This seemed unusual because cyclic hydrocarbon derivatives of Group III metals do not generally form well-defined  $\pi$ -bonded complexes in the same manner as transition metals. For example,

the species  $C_5H_5MR_2$  ( $M = Al, Ga$  or  $In$ ;  $R = CH_3, C_2H_5$ ) appear to form a series in which the  $C_5$  ring is not bonded in a  $\eta^5$  manner.<sup>6</sup> Likewise none of the rings in tris(cyclopentadienyl) indium can be classified as  $\pi$ -bonded in the 'sandwich' manner.<sup>7</sup> While the large Tl(III) cation probably could accommodate a  $\pi$ -bonded planar ring, it seemed more likely that the marked stability of di-organothallium(III) compounds would tend to force a product to that stoichiometry or, alternatively, sufficient electron density would be donated to the metal to cause its facile reduction to the +I state.<sup>8</sup>

Of further interest to us was the reactivity of the chlorothallate reagent. Leaving aside for the moment the confusion over whether the authors' description of the use of the pentachlorothallate really meant that reagent,<sup>9</sup> it appeared to be a possibility that one mole equivalent of the amine added to  $(C_5H_6N)_2TlCl_5$  could form a donor-acceptor complex as was found with dimethylsulfoxide.<sup>10</sup> In addition, unless the product was exceptionally stable, it seemed unlikely that cycloheptatriene ( $pK_a \sim 30^{11}$ ) would be deprotonated by the amine under the mild reaction conditions reported. In view of the novel nature of the reported compound, we have reinvestigated the stated synthetic procedure, using both  $(C_5H_6N)_2TlCl_5$  and  $(C_5H_6N)TlCl_4$  as starting materials.

### EXPERIMENTAL

Pyridinium salts of  $TlCl_5^{2-}$  and  $TlCl_4^-$  were prepared from  $Tl_2O_3$  as described previously<sup>9,12</sup> and triethylamine and cycloheptatriene of good commercial quality were purified according to the directions given by Perrin *et al.*<sup>13</sup> Reactions were

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Table 1. Microanalytical results<sup>a</sup>

Sample	% C	% H	% N	% Cl	Product
A	23.5 (23.8)	2.3 (2.2)	5.6 (5.5)	27.9 (28.1)	(C <sub>5</sub> H <sub>6</sub> N)TiCl <sub>4</sub> · C <sub>5</sub> H <sub>5</sub> N
B	28.3 (29.0)	2.8 (2.8)	6.7 (6.8)	29.1 (28.5)	(C <sub>5</sub> H <sub>6</sub> N) <sub>2</sub> TiCl <sub>3</sub> · C <sub>5</sub> H <sub>5</sub> N
C	18.5 (18.6)	1.9 (1.9)		32.6 (33.0)	(C <sub>5</sub> H <sub>6</sub> N) <sub>3</sub> Ti <sub>2</sub> Cl <sub>9</sub>
D	12.5 (14.1)	1.3 (1.4)		33.9 (33.3)	(C <sub>5</sub> H <sub>6</sub> N)TiCl <sub>4</sub>

<sup>a</sup>Microanalyses were performed by AMDEL, Melbourne or by Malissa and Reuter, Engelskirchen, F.R.G. Values in parentheses are those calculated for the product suggested.

performed in a N<sub>2</sub>-filled glovebox and manipulations were performed using appropriate vacuum line procedures when necessary.

The reaction described by Kumar and Sharma<sup>5</sup> was performed with both possible chlorothallate starting materials as described below.

(i) *Using* (C<sub>5</sub>H<sub>6</sub>N)<sub>2</sub>TiCl<sub>5</sub>. Equimolar quantities (10 mmol) of pyridinium pentachlorothallate (5.4 g), cycloheptatriene (0.92 g) and triethylamine (1.0 g) were mixed in CH<sub>2</sub>Cl<sub>2</sub> (350 cm<sup>3</sup>) and left to stand for ½ h at 18°C in a glovebox. A slight turbidity was observed and was removed by filtration through a G4 frit. This operation caused some white crystals, m.p. 151°C, to precipitate in the filtrate. Once these had been removed, the remainder of the filtrate was concentrated on a vacuum line and yielded two more crops of the same material, m.p. 151°C. Microanalysis: sample A (Table 1).

(ii) *Using* (C<sub>5</sub>H<sub>6</sub>N)TiCl<sub>4</sub>. The above procedure was repeated with equimolar quantities (2 mmol) of (C<sub>5</sub>H<sub>6</sub>N)TiCl<sub>4</sub> (1.0 g), triethylamine and cycloheptatriene. After 1 h, a slightly cloudy orange solution was obtained which was filtered to remove the very fine suspension. Part of the resulting solution was concentrated on a rotary evaporator (under a N<sub>2</sub> bleed), while the remainder was concentrated on a hot-water bath in the air. Both methods yielded a brown-orange oil, but operations in air result in the oil decomposing faster as evidenced by its progressive darkening.

The oil obtained from the rotary evaporator was examined by <sup>13</sup>C NMR spectroscopy (JEOL JNM-PS-100 PFT instrument operating at 25 MHz; ~600 pulses, 2.5 s repetition time; CDCl<sub>3</sub> solution) (Table 2).

The potential for triethylamine and cycloheptatriene to react separately with each of the chlorothallate reagents was examined as described below.

#### Reactions with triethylamine

(i) *Pyridinium pentachlorothallate*(III). To a solution of (C<sub>5</sub>H<sub>6</sub>N)<sub>2</sub>TiCl<sub>5</sub> (2 g, 4 mmol) in 200 cm<sup>3</sup> CH<sub>2</sub>Cl<sub>2</sub> was added an equimolar amount of

triethylamine (0.51 cm<sup>3</sup>). The mixture was allowed to stand for 1 h after which the cloudiness was removed using filter aid and the resulting clear solution was concentrated on a vacuum line. The white solid which separated on concentrating the solution had a m.p. 144–145°C. Microanalysis: sample B (Table 1).

(ii) *Pyridinium tetrachlorothallate*(III). A similar reaction was performed using (C<sub>5</sub>H<sub>6</sub>N)TiCl<sub>4</sub> (1.0 g, 2.3 mmol) and triethylamine (0.35 cm<sup>3</sup>). The slightly cloudy orange solution obtained after ~1½ h was filtered and separated into two portions. One of these was evaporated quickly on a vacuum line and the oil so obtained was redissolved in CDCl<sub>3</sub> for a <sup>13</sup>C NMR spectrum. The remainder was concentrated on a hot water bath and also yielded an oil from which thallium(I) chloride precipitated over some hours.

#### Reactions with cycloheptatriene

(i) *Pyridinium pentachlorothallate*(III). To a solution of (C<sub>5</sub>H<sub>6</sub>N)<sub>2</sub>TiCl<sub>5</sub> (1.92 g, 3.5 mmol) in 300 cm<sup>3</sup>, was added cycloheptatriene (0.37 cm<sup>3</sup>) and the mixture allowed to stand for ~1 h after which it was concentrated on a vacuum line to yield a white solid, m.p. 130°C. Microanalysis: sample C (Table 1).

(ii) *Pyridinium tetrachlorothallate*(III). In a similar reaction, (C<sub>5</sub>H<sub>6</sub>N)TiCl<sub>4</sub> (1.0 g, 2.3 mmol) was mixed with cycloheptatriene (0.25 cm<sup>3</sup>) in CH<sub>2</sub>Cl<sub>2</sub> (300 cm<sup>3</sup>). The very fine white solid which developed over ~4 h was removed by filtration and the filtrate was concentrated on a vacuum line to yield a crystalline material. Microanalysis: sample D (Table 1).

## RESULTS

Microanalytical data obtained on the precipitated products are given in Table 1, while the <sup>13</sup>C NMR spectra obtained on the oily products are presented in Table 2. Samples A and B appear to be chlorothallate-pyridine adducts and their IR spectral data are given in Table 3.

Table 2.  $^{13}\text{C}$  NMR spectra in  $\text{CDCl}_3$ 

Sample	Chemical shift (ppm)	Peak height (%)	Assignment
$(\text{C}_5\text{H}_6\text{N})\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{N} + \text{C}_7\text{H}_8$ (orange-brown oil—fresh sample)	29.67	13.24	C7
	120.74	14.42	C1
	126.50	11.75	C2
	130.87	17.05	C3
	124.13	19.19	pyH <sup>+</sup>
	136.93	19.72	
	144.13	30.54	
	9.10	42.94	$(\text{C}_2\text{H}_5)_3\text{N}$
	46.78	85.86	
$(\text{C}_5\text{H}_6\text{N})\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{N}$ (orange-brown oil—fresh sample)	124.07	11.75	pyH <sup>+</sup>
	136.67	17.36	
	149.25	29.07	
	9.28	37.48	$(\text{C}_2\text{H}_5)_3\text{N}$
	46.66	109.50 O/F	
Triethylamine (distilled)	11.71	41.54	
	46.35	100.82 O/F	
Cycloheptatriene (distilled)	27.97 (28.8) <sup>a</sup>	181.16	C7
	120.74 (123.3)	46.24	C1
	126.50 (129.8)	53.90	C2
	130.92 (134.1)	57.03	C3
Reference compounds			
$(\text{C}_3\text{H}_5)_3\text{M}(\text{C}_7\text{H}_7)$ (M = Cr, Mo, Ti or Zr) <sup>b</sup>	80–90		One peak, seven equiv. C atoms
$\eta^6\text{-C}_7\text{H}_8$ in $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)^b$	23.48		C7
	24.17		C7
	57.61		C1
	58.15		C6
	99.47		C3
	100.22		C4
	101.73		C2
	102.27		C5

<sup>a</sup>Values in parentheses are taken from Ref. 17.<sup>b</sup>Values obtained from Ref. 18.

## DISCUSSION

It is quite clear from the results obtained here that an 85% yield of a red-brown compound with formula  $\text{C}_7\text{H}_7\text{TiCl}_2$  was not obtained under the conditions described by Kumar and Sharma.<sup>5</sup> From the pentachlorothallate(III) starting material, the colorless product obtained analyzed well for the adduct  $(\text{C}_5\text{H}_6\text{N})\text{TiCl}_4 \cdot \text{C}_5\text{H}_5\text{N}$  and this formulation was supported by the IR spectrum which displayed vibrations characteristic of coordinated pyridine<sup>14</sup> in addition to those of the pyridinium ion (Table 3). Evidence for interaction of the metal with cycloheptatriene was not forthcoming. Using the tetrachlorothallate(III) instead, an orange oil could be isolated, but this was unstable at room temperature and decomposed within 5 h. The  $^{13}\text{C}$  NMR spectrum obtained while the sample was still

fresh showed that those peaks which were due to cycloheptatriene were virtually unchanged from those of the pure hydrocarbon (Table 2). Certainly, they bore no resemblance to those spectra which have been reported for authentic  $\eta^7\text{-C}_7\text{H}_7$  or even for  $\eta^6\text{-C}_7\text{H}_8$  complexes, in which considerable shifts are observed for the various C resonances.

In the absence of the amine, cycloheptatriene also did not interact with the thallium center. Its addition to a solution of  $(\text{C}_5\text{H}_6\text{N})_2\text{TiCl}_3$  caused  $(\text{C}_5\text{H}_6\text{N})_3\text{Ti}_2\text{Cl}_9$  to separate. It appears that the hydrocarbon merely changes the properties of the solvent, so as to shift the chlorothallate equilibrium in favor of the rather stable enneachloride. With  $(\text{C}_5\text{H}_6\text{N})\text{TiCl}_4$ , somewhat impure starting material was the only solid product obtained.

Any orange colors which were observed appeared to arise from oxidation of the amine by  $(\text{C}_5\text{H}_6\text{N})\text{TiCl}_4$ . Highly colored materials have been

Table 3. IR spectra of chlorothallate-pyridine adducts (KBr pellets)

Compound	$C_3H_5N^+$ Ion	Assignments	
		Coordinated $C_3H_5N$	$\nu(Tl-Cl)$
$(C_3H_5N)_2TlCl_5 \cdot C_3H_5N$	3340–2600 w, br; 1635 m; 1607 m; 1595 m; 1532 s; 1488 s; 1385 w; 1365 sh; 1325 w; 1260 sh; 1241 w; 1198 m; 1164 m; 1050 sh; 1040 sh; 740 s; 610 s; 610 s; 674 s; 389 w	1446 s; 1350 w; 1208 m; 1152 w; 1060 m; 1032 m; 1010 m; 865 w, br; 755 m; 698 s; 631 m; 417 m	295 s, 235 s
$(C_3H_5N)TlCl_4 \cdot C_3H_5N$	1040 m; 1607 not well resolved; 560 w, br		260 (sh), 230 s
$Mn(C_3H_5N)_2Cl_2^a$		1442, 1362, 1223, 1152, 1076, 1005, 691, 625, 417	

<sup>a</sup>From Ref. 4.

recognized from such reactions for many years, but these have not been investigated further.<sup>8</sup> There was a small ( $\sim 2.5$  ppm) downfield shift for the  $C_1$  atom of the amine when the reaction occurred. This change in the NMR spectrum was, however, very much larger than was observed for any of the carbon atoms of the cycloheptatriene.

It is evident, then, that the major role of the amine in the reaction mixture is to remove a proton from the pyridinium cation rather than from the cycloheptatriene, which thus remains unreacted. Free pyridine is thereby released and is able to form an adduct with one of the chlorothallate species in solution. Such proton transfer behavior is quite consistent with the relative acidities of the species involved: cycloheptatriene, being an exceptionally weak acid, while triethylamine ( $K_b = 5.6 \times 10^{-4}$ ) is a stronger base than pyridine ( $K_b = 2.3 \times 10^{-9}$ ).<sup>15</sup>

Consequently, we remain unconvinced of the  $\pi$ -cycloheptatrienyl thallium(III) dichloride reported by Kumar and Sharma and are left querying whether some essential experimental details were omitted from their paper. We have had cause to complain before about what appeared to be unreliable analytical procedures employed by this group<sup>9,16</sup> but in this instance in which there appears to be no resemblance at all to the product claimed, the standard of the work appears to be very disappointing.

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