Journal of Organometallic Chemistry, 131 (1977) C5—C6
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Preliminary communication

NOVEL ANIONIC ORGANOTHALLIUM(III) COMPLEXES

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(Received February 22nd, 1977)

Summary

The novel organothallium(III) anions $[Tl(C_6F_5)_4]^-$, $[Tl(C_6F_5)_2(C_6Cl_5)_2]^-$, $[Tl(C_6F_5)_3Cl]^-$ and $[\{Tl(C_6F_5)_2Cl\}_2Cl]^-$ have been prepared, and isolated as the tetraalkylammonium salts.

The only previously described anionic tetraalkyl- or tetraaryl-thallium(III) complex $[TlMe_4]^-$, isolated in form of its lithium salt [1], is unstable in daylight and atmospheric moisture. The organothallium(III) anions of different types [2—5] $[TlRX_3]^-$, $[TlR_2X_2]^-$, $[TlR_3X]^-$, $[TlRX_4]^-$, $[TlR_2X_3]^-$, $[(TlR_3)_2X]^-$ and $[TlR_2B_{10}H_{12}]^-$ are poorly represented, and for $R = C_6F_5$ only compounds [3] of the $[Tl(C_6F_5)_2X_2]^-$ type (X = Cl, Br, I or SCN) are known.

We now report the synthesis of novel anionic organothallium(III) complexes containing the anions $[Tl(C_6F_5)_4]^-$, $[Tl(C_6F_5)_2(C_6Cl_5)_2]^-$, $[Tl(C_6F_5)_3Cl]^-$ and $[\{Tl(C_6F_5)_2Cl\}_2Cl]^-$, which have been isolated as the respective tetraalkylammonium salts.

The tetraalkylammonium tetrakis(pentafluorophenyl)thalliate(III) can be made by the reaction of an ether solution of LiC_6F_5 with $(C_6F_5)_2TlBr$, $R_4N[TlX_4]$, or $TlCl_3$ and, if necessary, subsequent addition of R_4NBr, as shown in eqns. 1—3.

$$(C_6F_5)_2TlBr + LiC_6F_5 \xrightarrow{+R_4NBr} R_4N[Tl(C_6F_5)_4] \quad (1)$$

$$R_4N[TlX_4] + LiC_6F_5 \longrightarrow R_4N[Tl(C_6F_5)_4] \quad (2)$$

$$TlCl_3 + LiC_6F_5 \xrightarrow{+R_4NBr} R_4N[Tl(C_6F_5)_4] \quad (3)$$

The reactions were carried out at −78°C under dry nitrogen. The stirred solutions were allowed to warm to room temperature. Then R_4NBr was added, and though insoluble in ether it dissolved immediately. Evaporation gave solids which were recrystallized from dichloromethane/hexane. The yields are about 70, 70 and 90% for processes 1, 2 and 3, respectively.

On the other hand, if $(C_6F_5)_2TlBr$ is added to a stirred ether solution of

TABLE I

PROPERTIES OF ANIONIC ORGANOTHALLIUM(III) COMPLEXES

		M.p. (°C)	Λ_M (ohm^{-1} cm^2 mol^{-1})	ν(Tl—Cl)
I	$(n\text{-}Bu_4N)[Tl(C_6F_5)_4]$	127 (dec.)	99	—
II	$(Et_4N)[Tl(C_6F_5)_4]$	132 (dec.)	117	—
III	$(n\text{-}Bu_4N)[Tl(C_6F_5)_2(C_6Cl_5)_2]$	142 (dec.)	85	—
IV	$(n\text{-}Bu_4N)[Tl(C_6F_5)_3Cl]$	83	97	251
V	$(n\text{-}Bu_4N)[\{Tl(C_6F_5)_2Cl\}_2Cl]$	152	114	255

LiC_6Cl_5 at −15°C in dry nitrogen, subsequent addition of $n\text{-}Bu_4NBr$ gives $n\text{-}Bu_4N[Tl(C_6F_5)_2(C_6Cl_5)_2]$ which can readily be isolated (eq. 4). This is one of

$$(C_6F_5)_2TlBr + 2\ LiC_6Cl_5 \xrightarrow{n\text{-}Bu_4NBr} n\text{-}Bu_4N[Tl(C_6F_5)_2(C_6Cl_5)_2] \qquad (4)$$

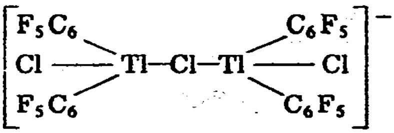
the few compounds which contain both a C_6F_5 and a C_6Cl_5 group (the other are $Ni(C_6F_5)(C_6Cl_5)(PPh_2Me)_2$ [6] and $Pd(C_6F_5)(C_6Cl_5)(PEt_3)_2$ [7]), and it is the sole example of a complex containing two ligands of each type.

When $n\text{-}Bu_4N[Tl(C_6F_5)_4]$ is treated with $TlCl_3$ at room temperature (in ether with 40 h stirring) white crystals of $n\text{-}Bu_4N[\{Tl(C_6F_5)_2Cl\}_2Cl]$ separate. Filtration followed by evaporation of the filtrate leaves an oil and addition of $n\text{-}Bu_2O$ gives white crystals of $n\text{-}Bu_4N[Tl(C_6F_5)_3Cl]$.

The anion $[Tl(C_6F_5)_4]^-$ is not capable of oxidizing gold(I) complexes; thus $Et_4N[Tl(C_6F_5)_4]$ reacts with $ClAuPPh_3$ to give $C_6F_5AuPPh_3$ and $Et_4N[Tl(C_6F_5)_2Cl_2]$.

All the complexes gave satisfactory elemental analyses (C, H, N and Tl). Table 1 lists their melting points, conductivities, and the values of ν(Tl—Cl). The conductivities in acetone are those expected for 1/1 electrolytes. The complexes are stable in daylight and atmospheric moisture at room temperature.

Complexes IV and V show vibrations in the 400—200 cm^{-1} region which point to the presence of terminal Tl—Cl bonds [3]. Though complex V very probably has a dinuclear structure, we could not detect the vibration due to ν(Tl—Cl—Tl) which must be beyond the range of our spectrophotometer (Perkin—Elmer 577, 4000—200 cm^{-1}).



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