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# PREPARATION AND PROPERTIES OF METHYL(CYCLOPENTADIENYL)THALLIUM DERIVATIVES

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## SUMMARY

The preparation of the compound $CH_3(C_5H_5)TlX$ [where $X=OCOCH_3$, $OCOC_2H_5$, $OCO\text{-i-}C_3H_7$, tropolonate and 4-isopropyltropolonate] is described and their chemical behaviors as well as their PMR and IR spectra are discussed.

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## INTRODUCTION

Cyclopentadienyl derivatives containing the Group IIIa elements ($B^{1,2}$, $Al^{3-5}$, $Ga^{5}$, $In^{6-8}$ and $Tl^{8-13}$) have been described in the literature.

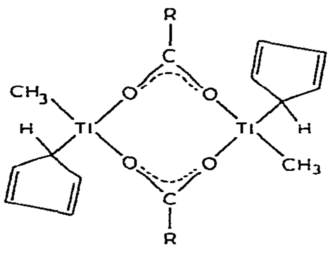
The nature of the metal–cyclopentadienyl bonding has been discussed in a few cases[8-13]. This study was undertaken to examine spectroscopically and chemically the thallium–cyclopentadienyl bond for a series of methyl(cyclopentadienyl)thallium derivatives, which are similar in some respects to the methyl(allyl)thallium compounds previously reported[14].

## DISCUSSION

Methyl(cyclopentadienyl)thallium carboxylates were easily prepared by the reaction of monomethylthallium carboxylates with tri-n-butyl(cyclopentadienyl)tin prepared *in situ* from tri-n-butyltin chloride with cyclopentadienylthallium(I). These carboxylates decompose on exposure to air.

In the infrared spectra of the methyl(cyclopentadienyl)thallium derivatives, multiple bands in the olefinic C–H stretching region were observed both in solution and in the solid state, suggesting the existence of a $\sigma$-bonded diene-type cyclopentadienyl group. This conclusion is supported by the presence of a medium band near 315 $cm^{-1}$, tentatively assigned to the thallium carbon stretching due to the $TlC_5H_5$ moiety (Table 2). Also the $J(Tl-CH_3)$ values obtained for $CH_3(C_5H_5)TlX$ (Table 3) are reasonable for a covalent $Tl-C_5H_5$ bond, as can be seen by referring to the $J(Tl-CH_3)$ values of $CH_3(R)TlOCO\text{-i-}C_3H_7$ with a covalent bonded $CH_3-Tl-R$ group ($R=C_2H_5$, $CH_2{=}CHCH_2$, $CH_3$, $CH_2{=}CH$ and $C_6H_5$) (Table 4).

The structure of the carboxylate derivatives could be written as shown in Fig. 1 because of the results of molecular weight measurement (Table 1) and the characteristic absorption bands due to the bridging carboxylate group[15] (Table 2).



$R = CH_3, C_2H_5$ and $i\text{-}C_3H_7$

Fig. 1.

A doublet arising from the thallium–proton couplings for all five cyclopentadienyl protons (Table 3) can be reconciled by assuming that the thallium atom has an equal probability of being attached to every carbon atom of the cyclopentadienyl ring, which would result from rapid intramolecular rotation* of the $C_5H_5$ group on the thallium atom. The rate of this intramolecular rotation could not be slowed down sufficiently to observe the patterns for nonequivalent cyclopentadienyl protons even at −72° in $CD_3OD$ and −45° in $CDCl_3$.

In $CD_3OD$ significant broadening of the ring proton resonances of $CH_3(C_5H_5)TlOCO\text{-}i\text{-}C_3H_7$ occurred with a rise of temperature from 5° to 20°. On cooling they sharpened again. This fact seems to show the existence of an intermolecular migration of the $C_5H_5$ group at an elevated temperature. However we were unsuccessful in verifying this possibility because all of these cyclopentadienyl compounds are thermally unstable at higher temperatures.

The reactions of $CH_3(C_5H_5)TlOCO\text{-}i\text{-}C_3H_7$ with $Cl^-$ and $B(C_6H_5)_4^-$, which have been found to react in a particular way with monoalkylthallium compounds, gave the reductive decomposition product, TlCl, and the phenylated product, $CH_3(C_6H_5)TlB(C_6H_5)_4$, respectively. The reaction with $SSCN(CH_3)_2^-$ and oxine in excess** gave $CH_3TlY_2$ [$Y = SSCN(CH_3)_2$ and oxinate]. In Table 4, it is clear that $CH_3(R)TlOCO\text{-}i\text{-}C_3H_7$ ($R = C_2H_5, CH_2{=}CHCH_2, CH_3, CH_2{=}CH$ and $C_6H_5$), with $J(Tl\text{-}CH_3)$ values comparable to that of $(CH_3)_2TlOCO\text{-}i\text{-}C_3H_7$, gave reaction products maintaining the $CH_3\text{-}Tl\text{-}R$ moiety. Although the $J(Tl\text{-}CH_3)$ value of $CH_3(C_5H_5)TlOCO\text{-}i\text{-}C_3H_7$ is very close to that of $CH_3(C_6H_5)TlOCO\text{-}i\text{-}C_3H_7$, the reactions of the former compound with $Cl^-$ and $B(C_6H_5)_4^-$ are found to be similar to those of monomethylthallium carboxylates. This facile cleavage of the thallium–cyclopentadienyl bond may be associated with the fluxional behavior between the thallium atom and the $C_5H_5$ group.

## EXPERIMENTAL

All manipulations were carried out under a nitrogen atmosphere.

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* It was reported concerning the intramolecular rearrangements of cyclopentadienylmercury[26,27] and tin[28,29].

** With equimolar oxine a mixed chelate $CH_3Tl(OCO\text{-}i\text{-}C_3H_7)Ox$ was the product (see experimental part).

### *Preparations of methyl(cyclopentadienyl)thallium derivatives*

#### $CH_3(C_5H_5)TlOCO\text{-}i\text{-}C_3H_7$

A benzene solution (20 ml) of $(n\text{-}C_4H_9)_3SnCl$ (1.54 ml; 6 mmol) was added to $TlC_5H_5$[10] (1.6 g; 6 mmol). The reaction mixture was stirred for 30 min at room temperature. Then $CH_3Tl(OCO\text{-}i\text{-}C_3H_7)_2$[15] (2.01 g; 5.1 mmol) in $CH_2Cl_2$ (30 ml) was added dropwise over 10 min and stirring was continued for 30 min. The reaction mixture was evaporated to dryness under reduced pressure and washed with n-hexane (200 ml) to remove $(n\text{-}C_4H_9)_3SnOCO\text{-}i\text{-}C_3H_7$. The residue was dissolved in $CH_2Cl_2$ (30 ml). To the filtrate, n-hexane (30 ml) was added and the mixture was concentrated under reduced pressure to yield white fluffy crystals of this compound (1.59 g; 84%). Methyl(cyclopentadienyl)thallium acetate and propionate* were prepared in benzene-THF in a manner similar to that described above. All of the carboxylates shown in Table 1 became dark in a few hours when exposed to air.

They did not decompose in several months in a sealed tube. They are soluble in methanol, ethanol, $CHCl_3$ and $CH_2Cl_2$ but decompose in polar solvents such as DMSO, HMPA and pyridine.

When maleic anhydride (0.66 g) in dry benzene (10 ml) was mixed with $CH_3(C_5H_5)TlOCO\text{-}i\text{-}C_3H_7$ (0.25 g) in $CH_2Cl_2$ (5 ml), a white precipitate was obtained. After filtration, the precipitate was washed with benzene (15 ml) and dried in vacuum to give 0.19 g (m.p. 140–141°) of a product. Its elemental analysis is in agreement with that of the 1/1 adduct. (Found: C, 35.70; H, 3.38. $C_{14}H_{17}O_5Tl$ calcd.: C, 35.80; H, 3.65%.) However, its structure has not been well characterized because of its limited solubility.

TABLE 1

PROPERTIES OF METHYL(CYCLOPENTADIENYL)THALLIUM DERIVATIVES $CH_3(C_5H_5)TlX$

| X | M.p. (dec.) (°C) | Analysis: found (calcd.) (%) | | Mol. wt.[b] | |
|---|---|---|---|---|---|
| | | C | H | Found (calcd.) | Concn. (wt.%) |
| $OCOCH_3$ | 119–121 | 27.83<br>(27.97) | 3.13<br>(3.23) | 661<br>(344) | 0.82 |
| $OCOC_2H_5$ | >100[a] | 29.65<br>(30.23) | 3.54<br>(3.60) | 693<br>(356) | 0.91 |
| $OCO\text{-}i\text{-}C_3H_7$ | >120[a] | 32.32<br>(32.32) | 4.50<br>(4.07) | 650<br>720<br>(371) | 0.42<br>1.20 |
| Tropolonate | >125[a] | 38.11<br>(38.50) | 3.13<br>(3.23) | | |
| 4-Isopropyltropolonate | 117–118 | 42.64<br>(42.93) | 4.03<br>(4.23) | 539<br>(448) | 0.27 |

[a] Gradually darkens above this temperature. [b] Measured in chloroform solution at 37° using a Hitachi Perkin–Elmer 115 Vapor Pressure Osmometer.

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* The new compound, $CH_3Tl(OCOC_2H_5)_2$, was prepared from the reaction of $CH_3TlO$ and $C_2H_5COOH$. M.p. 102–104°. (Found: C, 22.37; H, 3.67. $C_7H_{13}O_4Tl$ calcd.: C, 23.00; H, 3.58%.)

### *$CH_3(C_5H_5)TlC_{10}H_{11}O_2$, ($C_{10}H_{11}O_2$=4-isopropyltropolonate)*

A solution of 4-isopropyltropolone (0.12 g; 0.75 mmol) in $CH_2Cl_2$ was added dropwise to $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ (0.28 g; 0.75 mmol) in $CH_2Cl_2$ (5 ml) at room temperature. The yellow solution obtained was concentrated to 1 ml under reduced pressure, and after addition of n-hexane (20 ml), the mixture was allowed to stand overnight in a refrigerator. A yellow precipitate resulted, which was recrystallized from $CH_2Cl_2$/n-hexane to give this compound (0.11 g; 34%).

### *$CH_3(C_5H_5)TlC_7H_5O_2$, ($C_7H_5O_2$=tropolonate)*

Methyl(cyclopentadienyl)thallium tropolonate was obtained as yellow crystals which precipitated gradually from a methanol solution of tropolone (0.12 g; 1 mmol) and $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ (0.37 g; 1 mmol). The yield was 0.2 g (51%). This compound is very air stable and insoluble in most organic solvents.

The properties of these compounds are summarized in Table 1.

### *Reaction of methyl(cyclopentadienyl)thallium carboxylates*

*With $NaB(C_6H_5)_4$.* To an aqueous solution (10 ml) of $NaB(C_6H_5)_4$ (0.3 g) was added $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ (0.06 g) and the mixture was stirred for 30 min. The white amorphous precipitate was recrystallized from acetone to give 0.05 g of $CH_3(C_6H_5)TlB(C_6H_5)_4$[16].

*With aqueous HCl.* Into a methanol solution of $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ was added aqueous HCl. Thallous chloride was precipitated immediately (almost quantitatively).

*With $KSSCN(CH_3)_2$.* To a methanol solution of $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ was added $KSSCN(CH_3)_2$ (equimol.) in the same solvent. A pale yellow precipitate was obtained immediately. It was identified as $CH_3Tl[SSCN(CH_3)_2]_2$[17] by its melting point and IR spectrum. By adding an additional equimolar quantity of $KSSCN(CH_3)_2$, an almost quantitative yield of this compound was obtained.

*With oxine.* $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ and oxine (1/1 mole ratio) were dissolved in $CDCl_3$, and the NMR spectrum was measured immediately. The peaks due to $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ were not observed, but new peaks appeared at 7.07 and 3.54 ppm, attributed to cyclopentadiene (lit.[18]: 7.10 and 3.58 ppm in $CCl_4$), and at 8.28 ppm ($J$ 860 Hz) due to a monomethylthallium species. $CH_3Tl(OCO\text{-i-}C_3H_7)Ox$ was isolated by the following experiment. A methanol solution (5 ml) of oxine (0.06 g; 0.4 mmol) was added to $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ (0.15 g; 0.4 mmol) in the same solvent (5 ml). The yellow solution was evaporated under reduced pressure to give a yellow precipitate, which was recrystallized from benzene/petroleum ether. The IR spectrum and the sharp melting point (118–119°) of the yellow crystalline compound obtained (0.09 g) are quite different from those of $CH_3Tl(OCO\text{-i-}C_3H_7)_2$[15] and $CH_3TlOx_2$[15]. Also by elemental analysis the yellow crystalline compound was confirmed to be $CH_3Tl(OCO\text{-i-}C_3H_7)Ox$*. (Found: C, 37.45; H, 3.68; N, 3.10. $C_{14}H_{16}O_3NTl$ calcd.: C, 37.41; H, 3.58; N, 3.11%.) The same compound was also isolated by mixing $CH_3Tl(OCO\text{-i-}C_3H_7)_2$ and $CH_3TlOx_2$ in $CH_2Cl_2$. $CH_3$-

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* However, in solution it is not certain whether the peak at 8.28 ppm, $J$ 860 Hz is due to the methyl protons of $CH_3Tl(OCO\text{-i-}C_3H_7)Ox$ or those in the rapid ligand exchange equilibrium:

$$2\,CH_3Tl(OCO\text{-i-}C_3H_7)Ox \rightleftarrows CH_3Tl(OCO\text{-i-}C_3H_7)_2 + CH_3TlOx_2$$

$TlOx_2$ was obtained when a methanol solution of $CH_3(C_5H_5)TlOCO\text{-i-}C_3H_7$ was treated with an excess of oxine.

*Infrared spectra*

The infrared spectra were obtained using a Hitachi Model 225 spectrophotometer equipped with gratings. Spectra were measured in nujol and hexachlorobuta-

TABLE 2

RELEVANT INFRARED FREQUENCIES (in $cm^{-1}$) FOR $CH_3(C_5H_5)TlX$ IN NUJOL AND HEXACHLOROBUTADIENE MULLS

| X=OCO-i-$C_3H_7$[a] | X=$OCOCH_3$ | X=$OCOC_2H_5$ | X=Tropolonate | X=4-Isopropyl-tropolonate | Assignments[b] |
|---|---|---|---|---|---|
| 3105 (sh) | 3111 w | 3115 m | 3109 w | 3105 (sh) | ν(C–H) |
| 3092 w | 3100 w | 3103 m | 3096 w | 3090 w | |
| 3077 (sh) | 3080 (sh) | 3082 w | 3085 w | 3075 w | |
| 3069 w | 3068 w | 3070 (sh) | 3065 w | | |
| 3061 w | 3056 w | 3060 m | 3052 w | 3055 w | |
| | | 2978 (sh) | 3019 m | 3012 w | |
| 2970 (sh) | 2968 w | 2965 m | | 2960 m | |
| 2965 m | | 2930 m | | | |
| 2930 m | 2932 m | 2915 m | 2921 m | 2920 m | |
| 2865 w | | 2872 m | | 2865 w | |
| 1520 vs | 1530 s | 1525 s | 1592 vs | 1584 vs | $\nu_{asym}$(COO) or ν(C=O) |
| 1422 vs | 1420 s | 1425 s | | | $\nu_{sym}$(COO) |
| 1025 m | 1021 m | 1020 s | 1026 m | 1020 m | δ[C(5)H] |
| 995 m | 990 m | 988 m | 989 m | 993 w | δ[C(5)H] |
| 822 m | 820 w | 818 m | 821 w | 819 w | ring def. |
| 776 s | 785 s | 780 s | 771 s | 771 s | ρTl–$CH_3$ |
| 752 vs | 752 s | 748 s | 754 s | 751 s | π(C–H) |
| 648 s | 648 s | 648 s | 645 s | 646 m | δ(C–H) |
| 508 m | 513 m | 507 m | 505 m | 500 m | ν(Tl–$CH_3$) |
| 313 m[c] | 318 m | 316 m[d] | 313 m | 315 m | ν[Tl–C(5)] |

The IR spectrum of this compound in $CHCl_3$ (5 wt.%) was almost identical with that in the solid state. [b] ν, Stretching; δ, in-plane bending; π, out-of-plane bending; ρ, rocking. [c] Additional bands; 359 w, 355 (sh), 274 w $cm^{-1}$. [d] Additional bands; 292 m, 280 (sh) $cm^{-1}$.

TABLE 3

NMR PARAMETERS FOR $CH_3(C_5H_5)TlX$

| X | Solvent | Temp. (°C) | J(Tl–$CH_3$)[a] | J(Tl–$C_5H_5$)[a] | τ($CH_3$)[b] | τ($C_5H_5$)[b] |
|---|---|---|---|---|---|---|
| $OCOCH_3$ | $CDCl_3$ | 20 | 451 | 219 | 8.74 | 3.89 |
| $OCOC_2H_5$ | $CDCl_3$ | 20 | 454 | 220 | 8.73 | 3.90 |
| OCO-i-$C_3H_7$ | $CDCl_3$ | 20 | 456 | 217 | 8.72 | 3.90 |
| | $CDCl_3$ | −40 | 456 | 217 | 8.72 | 3.91 |
| | $CD_3OD$ | 12 | 491 | 225 | 8.83 | 3.99 |
| | $CD_3OD$ | −72 | 492 | 210 | 8.90[c] | 4.00[c] |
| 4-Isopropyl-tropolonate | $CDCl_3$ | 20 | 445 | 216 | 8.58 | 3.92 |

[a] The separation of $J(^{205}Tl\text{–}CH_3)$ and $J(^{203}Tl\text{–}CH_3)$ (in Hz) can not be observed. [b] Internal standard tetramethylsilane (10 ppm). [c] Very broad.

TABLE 4

$J(\text{Tl-CH}_3)$ VALUES (AT 20°) FOR $CH_3(R)TlX$ AND REACTION PRODUCTS WITH $Cl^-$, $B(C_6H_5)_4^-$ AND $SSCN(CH_3)_2^-$

| R | X | Solvent | $J(\text{Tl-CH}_3)$ (Hz) | Reagents | | |
|---|---|---|---|---|---|---|
| | | | | $Cl^-$ | $B(C_6H_5)_4^-$ | $SSCN(CH_3)_2^-$ (=Dtc) |
| $C_2H_5$ | OCO-i-Pr[a] | $CDCl_3$ | 331[b] | $CH_3(C_2H_5)TlCl$[c] | $CH_3(C_2H_5)TlB(C_6H_5)_4$[d] | $CH_3(C_2H_5)TlDtc$[b] |
| $CH_2{=}CHCH_2$ | OCO-i-Pr | $CDCl_3$ | 365[e] | $CH_3(CH_2{=}CHCH_2)TlCl$[e] | $CH_3(CH_2{=}CHCH_2)TlB(C_6H_5)_4$[f] | $CH_3(CH_2{=}CHCH_2)TlDtc$[e] |
| $CH_3$ | OCO-i-Pr | $CDCl_3$ | 377[g] | $(CH_3)_2TlCl$[g] | $(CH_3)_2TlB(C_6H_5)_4$[h] | $(CH_3)_2TlDtc$[i] |
| $CH_2{=}CH$ | OCO-i-Pr | $CDCl_3$ | 412[g] | $CH_3(CH_2{=}CH)TlCl$[j] | $CH_3(CH_2{=}CH)TlB(C_6H_5)_4$[k] | $CH_3(CH_2{=}CH)TlDtc$[l] |
| $C_6H_5$ | OCO-i-Pr | $CDCl_3$ | 426[g] | $CH_3(C_6H_5)TlCl$[c] | $CH_3(C_6H_5)TlB(C_6H_5)_4$[m] | $CH_3(C_6H_5)TlDtc$[n] |
| $C_5H_5$ | OCO-i-Pr | $CDCl_3$ | 456 | TlCl | $CH_3(C_6H_5)TlB(C_6H_5)_4$ | $CH_3Tl(Dtc)_2$ |
| $C_6H_5C{\equiv}C$ | OAc[o] | $D_2O$ | 672[m] | $CH_3(C_6H_5C{\equiv}C)TlCl$[m] | $CH_3(C_6H_5C{\equiv}C)TlB(C_6H_5)$[m] | $CH_3Tl(Dtc)_2$[n] |
| CN | OAc | $D_2O$ | 828[m] | TlCl[g] | $CH_3(C_6H_5)TlB(C_6H_5)_4$[m] | $CH_3Tl(Dtc)_2$[p] |
| | $(OCO\text{-}i\text{-}Pr)_2$ | $CHCl_3$ | 902[m] | TlCl[q] | $CH_3(C_6H_5)TlB(C_6H_5)_4$[m] | $CH_3Tl(Dtc)_2$[r] |

[a] OCO-i-Pr = OCO-i-$C_3H_7$ [b] See ref. 20. [c] See ref. 21. [d] >230° (Dec.). Found (Calcd.); C, 57.25 (57.12); H, 4.84 (4.97)%. [e] See ref. 14. [f] >210° (Dec.). Found (Calcd.); C, 57.30 (58.01); H, 4.68 (4.87)%. [g] R. Okawara *et al.* unpublished data. [h] Also can be isolated from $(CH_3)_2TlOH$ with $NaB(C_6H_5)_4$.[23] [i] Also can be obtained from $(CH_3)_2TlCl$ with NaDtc[24]. [j] See ref. 22. [k] >220° (Dec.). Found (Calcd.); C, 57.26 (57.33); H, 4.69 (4.63)%. [l] M.p. 97–98°. Found (Calcd.); C, 19.70 (19.65); H, 3.16 (3.30); N, 3.60 (3.82)%. [m] See ref. 16. [n] M.p. 127–128°. Found (Calcd.); C, 29.07 (29.38); H, 3.39 (3.45); N, 3.30 (3.43)%. [o] OAc = $OCOCH_3$. [p] See ref. 25. [q] See ref. 15. [r] See ref. 17.

diene mulls and in chloroform solution (5 wt. %). The relevant frequencies and probable assignments, which were made by referring to the spectrum of $(C_5H_5)_2Hg$[19], are given in Table 2.

### *NMR spectra*

The NMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer at 60 MHz and a Varian 3H-100 spectrometer at 100 MHz, and the results are shown in Table 3. In Table 4 are summarized the relation of the $J(Tl-CH_3)$ values of the representative unsymmetrical methyl(organo)thallium compounds and the reaction products of these with $Cl^-$, $B(C_6H_5)_4^-$ and $SSCN(CH_3)_2^-$.

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