PREPARATION OF MONOPHENYLTHALLIUM(III)DIBENZO-18-CROWN-6 COMPLEXES WITH A SOFT LIGAND: [C6H5T1(DBC)X]ClO4

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Monophenylthallium(III) complexes with a Tl-I or Tl-SR bond were prepared in the presence of dibenzo-18-crown-6. These complexes are stable in the air and to heat to their melting points. In the hydrogen sulfide complex, ν (S-H) band was found at 2570 cm⁻¹ and $\boldsymbol{\delta}$ (Tl-SH) was observed at 1.15 ppm with $^{2}J(TI-SH) = 405$ Hz in $CH_{2}Cl_{2}$ solution.

Generally monophenylthallium(III) compounds are unstable in the presence of soft ligands such as I and decompose to thallium(I) ion.¹⁾ Therefore, monophenylthallium(III) compounds with Tl-I bond are very few.^{2,3)} Monophenylthallium(III) compounds with TI-S bond also are limited to the compounds with chelate ligands $^{4-6}$ and the compounds with a thicalkyl or hydrogen sulfide group were not reported. One of reasons of unstability of the monophenylthallium(III) compounds is that two soft ligands can coordinate to the thallium atom at suitable positions simultaneously. It was reported that crown ethers form stable complexes with dimethylthallium(III) ion, 7,8) in which a linear C-Tl-C moiety is perpendicularly fixed in the plane formed by six oxygen atoms. These complexex are inert to demetallation.⁷⁾ In monophenylthallium (III) dibenzo-18-crown-6 complexes, therefore, only one soft ligand can coordinate to the thallium atom and isolation of the stable complexes with a TI-I or TI-SR bond may be expected.

Monophenylthallium(III)dibenzo-18-crown-6 complexes with a soft ligand were prepared by the procedures shown below.⁹⁾ The complexes are soluble in CH_3CN or CH₂Cl₂ and slightly soluble in CH₃OH. They are stable in the air and to heat to their melting points. The IR spectrum of 3c in CH2Cl2 solution shows a strong and sharp band of S-H stretching frequency at 2570 cm 1. The S-H proton

$$C_{6}H_{5}TIO + HClo_{4} + DBC \xrightarrow{THF} [C_{6}H_{5}TI(DBC)OH]Clo_{4} \cdot H_{2}O$$

$$\frac{1}{r} + HClo_{4} + [Na(15-C-5)]I \xrightarrow{CH_{3}CN} [C_{6}H_{5}TI(DBC)I]Clo_{4}$$

$$\frac{1}{r} + HSR \xrightarrow{CH_{3}CN} [C_{6}H_{5}TI(DBC)SR]Clo_{4}$$

$$R = CH_{3}C(O), 3a; C_{2}H_{5}, 3b$$

$$\frac{3a}{r} \xrightarrow{CF_{3}COOH} [C_{6}H_{5}TI(DBC)SH]Clo_{4}$$

$$R = CH_{3}C(O), 3a; C_{2}H_{5}, 3b$$

$$\frac{3a}{r} \xrightarrow{CF_{3}COOH} [C_{6}H_{5}TI(DBC)SH]Clo_{4}$$

$$R = CH_{3}C(O), 3a; C_{2}H_{5}, 3b$$

resonance of 3c was observed at $\delta = 1.15$ in the same solvent and was splitted by spin-spin coupling with the thallium nucleus $({}^{2}J(TI-SH) = 405 \text{ Hz})$. This signal was observed also in CF₃COOH ($\delta = 0.76$, ${}^{2}J(TI-SH) = 396 \text{ Hz}$), but disappeared in a mixed solvent of CH₂Cl₂ and CH₃OD. 3b is stable at 80°C for 3 day in CD₃CN solution. It was also stable in the presence of excess amount of C₆H₅CH₂SH for a few day at room temperature in CD₃CN solution, but decomposition to Tl(I) ion and a ligand substitution reaction giving [C₆H₅Tl(DBC)SCH₂C₆H₅]ClO₄ occurred simultaneously with a low rate. A demetallation reaction of 2 occurred slowly in pyridine.

$$\frac{2}{r.t. 3 \text{ week}} \begin{bmatrix} C_6 H_5 T1(py)_n I \end{bmatrix} Clo_4 + DBC$$

The presence of monophenyl(iodo)thallium(III) species, 4, in this solvent was deduced from the detection of the phenyl proton signals splitted by spin-spin coupling with the thallium nucleus.

References

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- 9. Elemental analyses of all complexes agree to the calculated values within 0.3%. 1 % yield 90, mp 132 - 140°C. 2 % yield 75, mp 234- 236°C. 3a % yield 73, mp 200 - 201°C. 3b % yield 81, mp 248 - 252°C. 3c % yield 78, mp 146 - 152°C.

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