CHEMISTRY LETTERS, pp. 941-942, 1982.

PREPARATION OF MONOPHENYLTHALLIUM(III)DIBENZO-18-CROWN-6 COMPLEXES WITH A SOFT LIGAND: $[C_6H_5Tl(DBC)X]ClO_4$

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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 δ(Tl-SH) was observed at 1.15 ppm with ^2J(Tl-SH) = 405 Hz in CH_2Cl_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 Tl-S bond also are limited to the compounds with chelate ligands[4-6] and the compounds with a thioalkyl 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 Tl-I or Tl-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 CH_2Cl_2 and slightly soluble in CH_3OH. They are stable in the air and to heat to their melting points. The IR spectrum of **3c** in CH_2Cl_2 solution shows a strong and sharp band of S-H stretching frequency at 2570 cm^{-1}. The S-H proton

$$C_6H_5TlO + HClO_4 + DBC \xrightarrow[\text{r.t.}]{\text{THF}} [C_6H_5Tl(DBC)OH]ClO_4 \cdot H_2O \quad \mathbf{1}$$

$$\mathbf{1} + HClO_4 + [Na(15\text{-}C\text{-}5)]I \xrightarrow[\text{r.t.}]{CH_3CN} [C_6H_5Tl(DBC)I]ClO_4 \quad \mathbf{2}$$

$$\mathbf{1} + HSR \xrightarrow[\text{r.t. or } -30\,°C]{CH_3CN} [C_6H_5Tl(DBC)SR]ClO_4$$

$R= CH_3C(O)$, **3a**; C_2H_5, **3b**

$$\mathbf{3a} \xrightarrow[\text{r.t.}]{CF_3COOH} [C_6H_5Tl(DBC)SH]ClO_4 \quad \mathbf{3c}$$

resonance of **3c** was observed at $\delta = 1.15$ in the same solvent and was splitted by spin-spin coupling with the thallium nucleus (^2J(Tl-SH)= 405 Hz). This signal was observed also in CF_3COOH (δ= 0.76, ^2J(Tl-SH)= 396 Hz), but disappeared in a mixed solvent of CH_2Cl_2 and CH_3OD. **3b** is stable at 80°C for 3 day in CD_3CN solution. It was also stable in the presence of excess amount of $C_6H_5CH_2SH$ for a few day at room temperature in CD_3CN solution, but decomposition to Tl(I) ion and a ligand substitution reaction giving $[C_6H_5Tl(DBC)SCH_2C_6H_5]ClO_4$ occurred simultaneously with a low rate. A demetallation reaction of **2** occurred slowly in pyridine.

$$\mathbf{2} \xrightarrow[\text{r.t. 3 week}]{\text{py}} [C_6H_5Tl(py)_nI]ClO_4 \; (\mathbf{4}) + DBC$$

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.

(Recieved April 23, 1982)