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A CONVENIENT SYNTHESIS OF TRIS(PENTACARBONYLMANGANESE)-THALLIUM(III)

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SUMMARY

Tris(pentacarbonylmanganese)thallium(III) is isolated in nearly quantitative yield from the reaction of thallium(I) salts with sodium pentacarbonylmanganate in aqueous solution.

Tris(pentacarbonylmanganese)thallium(III) has been prepared in yields up to 45% by the metathetical reaction between anhydrous thallium(III) chloride and sodium pentacarbonylmanganate(–I) in tetrahydrofuran solution[1]. The presence of the last trace of acetonitrile in the thallium(III) chloride, which is prepared by chlorination of thallium(I) chloride in acetonitrile[2], often leads to difficulty in separating the product from the reaction mixture.

During the course of an investigation on the nature of transition metal–Group IIIB metal bonds[1,3–5], we treated thallium(I) salts with sodium pentacarbonylmanganate in an attempt to obtain the thallium(I) complex, $TlMn(CO)_5$**. Instead, the disproportionation reaction, (1),

$$3\,Tl^+ + 3\,Mn(CO)_5^- \rightarrow 3\,[TlMn(CO)_5] \rightarrow 2\,Tl + Tl[Mn(CO)_5]_3 \qquad (1)$$

occurred instantly at room temperature in aqueous solution leading to the formation of the thallium(III) complex, $Tl[Mn(CO)_5]_3$, in almost quantitative yield.

The driving force in this reaction appears to be the large difference in stability of the thallium(I) and -(III) complexes. The formation of $[\pi\text{-}C_5H_5(CO)_3Mo]_3Tl$ from $\pi\text{-}C_5H_5(CO)_3MoTl$ has previously been observed by King[7] although in this case, the thallium(III) complex was isolated only in 10% yield.

EXPERIMENTAL

All manipulations were performed under an atmosphere of nitrogen and solvents were degassed before use. The characterisation of the complex has been described[1].

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** Similar unsuccessful attempts have been made to prepare $TlMn(CO)_5$ in various non-aqueous solvents[6].

Preparation of tris(pentacarbonylmanganese)thallium

Solid $NaMn(CO)_5$ was prepared by sodium amalgam reduction of $Mn_2(CO)_{10}$ in tetrahydrofuran followed by evaporation of the solvent. The off-white solid was dissolved in a little water and the solution was filtered into an aqueous solution containing an equivalent of $TlNO_3$. The mixture immediately turned black, and the voluminous precipitate produced was filtered off, washed well with water and briefly dried (1–2 h) *in vacuo* over phosphoric oxide. Extraction of the black solid with acetone gave a deep red solution, from which the product was isolated by concentrating, filtering and cooling. The thallium(III) complex, obtained in yields $>95\%$, was identified by elemental analysis and by its infrared and mass spectra[1]. The black residue analysed as thallium metal.

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