

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

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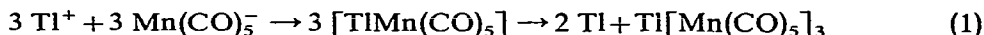
(Received December 1st, 1971)

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 solution¹. The presence of the last trace of acetonitrile in the thallium(III) chloride, which is prepared by chlorination of thallium(I) chloride in acetonitrile², 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, $\text{TIMn}(\text{CO})_5^{**}$. Instead, the disproportionation reaction, (1),



occurred instantly at room temperature in aqueous solution leading to the formation of the thallium(III) complex, $\text{Tl}[\text{Mn}(\text{CO})_5]_3$, 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 $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_3\text{Tl}$ from $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoTl}$ has previously been observed by King⁷ 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 described¹.

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** Similar unsuccessful attempts have been made to prepare $\text{TIMn}(\text{CO})_5$ in various non-aqueous solvents⁶.

Preparation of tris(pentacarbonylmanganese)thallium

Solid $\text{NaMn}(\text{CO})_5$ was prepared by sodium amalgam reduction of $\text{Mn}_2(\text{CO})_{10}$ 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 spectra¹. The black residue analysed as thallium metal.

ACKNOWLEDGEMENTS

We are grateful to Prof. J. M. Burlitch for communication of his unpublished results and to the British Council for an award (to A.T.T.H.).

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