Journal of Organometallic Chemistry, 82 (1974) C25—C26

Preliminary communication

STEPWISE ELIMINATION OF METHANE IN THE REACTION OF DIMETHYLINDIUM(III) COMPOUNDS WITH DIBASIC ACIDS

J.J. HABEEB and D.G. TUCK*

Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4 (Canada)

(Received October 7th, 1974)

Summary

The reaction between acetato(dimethyl)indium(III) and toluene-3,4-dithiol (H_2TDT) involves elimination of either one or two moles of methane, depending on experimental conditions; the unusual intermediate $[CH_3In(OAc)(HTDT)]_2$ has been identified. The stepwise elimination reaction appears to be common to other dimethylindium(III) species.

The reaction of the trialkyl compounds of Group III (R_3M) with molecules containing an acidic hydrogen (R'H) typically involves the formation of R_2MR' and RH [1]. The preparation of dialkylindium(III) compounds R_2InX by the reaction of R_3In and HX is a well-established procedure based on such alkane elimination [2]. In an earlier paper [3], we reported that trimethylindium reacts in an analogous fashion with the dibasic toluene-3,4-dithiol (H_2TDT), eliminating two moles of methane to form methyl(toluene-3,4-dithiolato)indium(III).

We have now found that a number of dimethylindium(III) species also react with excess toluene-3,4-dithiol, and that in these systems the reaction may lead to the formation of either one or two moles of methane, depending on the experimental (and in particular on the solvent). The reaction is easily followed by measuring the volume of gas evolved; elemental analysis confirms the reaction scheme proposed.

$$\begin{tikzcd}
(CH_3)_2In(OAc) + H_2TDT \arrow[rr, "EtOH", "-CH_4"'] \arrow[dr, "\begin{array}{c}DMSO\\-2CH_4\end{array}"'] & & CH_3In(OAc)(HTDT) \arrow[dl, "\begin{array}{c}DMSO\\-CH_4\end{array}"] \\
& In(OAc)(TDT) &
\end{tikzcd}$$

SCHEME 1

In the system investigated in the greatest detail thus far, involving H_2TDT and acetato(dimethyl)indium(III), reaction scheme 1 applies. In each case, the evolution of gas is complete at room temperature in approximately 20 mins.

The vibrational and ^1H NMR spectra of $CH_3In(OAc)(HTDT)$ confirm the presence of CH_3 bonded to indium in this very unusual compound, in which a potentially reactive methyl group and an acidic hydrogen atom are present in the same molecule. Molecular weight determinations in ethanol show that the species in solution is $[CH_3In(OAc)(HTDT)]_2$. Analogy with the known crystal structure of $(CH_3)_2In(OAc)$ itself [4], and with the properties of some of its recently investigated adducts [5] suggests that the dimerisation involves acetate bridging. The stabilisation of the structure, in terms of the blocking of the methyl—hydrogen reaction, probably depends on hydrogen bonding between the thiol group and an oxygen atom of an acetato ligand.

The room temperature reaction of H_2TDT with $(CH_3)_2In(TFAC)$ (TFAC = 1,1,1-trifluoro-2,4-pentanedionato anion) and $(CH_3)_2In(C_4H_3N \cdot CHO)$ ($C_4H_3N \cdot CHO$ = 2-pyrrolealdehyde anion) with H_2TDT in ethanol also stops after elimination of one mole of methane. Similarly, we find that the reaction between $(CH_3)_2In$-(OAc) and the dibasic compounds 1,2-ethanedithiol, 1,3-propanedithiol, salicylic acid, and phthalic acid in either ethanol or dimethyl sulphoxide involves only one methyl group of the starting material. These reactions are appreciably slower than that with H_2TDT, requiring approximately 24 h to go to completion in the case of phthalic acid.

The stepwise elimination reaction then appears to be of some generality in these systems, and raises important questions about the controlling factors in the stabilisation of the intermediates involved, the role of the solvent, and the energetics of the reactions.

Acknowledgement

This work was supported in part by an Operating Grant from the National Research Council of Canada.

References

1 G.E. Coates and K. Wade, Organometallic Compounds, Vol. 1, 3rd ed., Methuen, London, 1967, pp. 192 et seq.
2 H.C. Clark and A.L. Pickard, J. Organometal. Chem., 8 (1966) 427.
3 A.F. Berniaz and D.G. Tuck, J. Organometal. Chem., 46 (1972) 243.
4 F.W.B. Einstein, M.M. Gilbert and D.G. Tuck, J. Chem. Soc. Dalton, (1973) 248.
5 J.J. Habeeb and D.G. Tuck, Can. J Chem., in press.