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# THERMAL STUDY OF SOME TRANSITION METAL COMPLEXES OF MESITYLENE

W. LUDWIG and W. SEIDEL
Department of Chemistry, Friedrich Schiller University, Jena, GDR

## ABSTRACT

Several bis-, tris- and tetramesityls - mesityles fixed with second ligands and salt-like mesityl transition-metal complexes of Zn, Hg, (Mg, Al), Ti, V, Cr, Mo and Fe - are characterized by thermal methods and the decomposition products identified by gas chromatography. The decomposition takes mainly place by homolytic splitting of mesitylene. A correlation between the temperatures of decomposition and the bond energies becomes evident. Depending on donor-strength, second ligands stabilize the mesityl complexes only to a certain extent. On the contrary, the salt-like compounds show a higher thermal stability compared with the simple metal mesityls.

## INTRODUCTION

The mesityl group (2,4,6- $(CH_3)$-$C_6H_2$) belongs to the ligands with $\sigma$-bonds which render more difficulty to an internal decomposition of organo transition-metal compounds (1). Recently a series of interesting new complex compounds have become accessible (2-7), which gives new possibilities for the synthesis of organo transition-metal compounds. Statements concerning the stability of mesityl complexes have been exclusively derived from the reactivity in solution. Thermal investigations of the solid compounds may therefore be considered as an essential completion to these results.

## METHODS

The compounds, sensitive to air, were removed under inert conditions in thin-walled glass-ampoules, closed under slight vacuum and thermally characterized in an earlier described apparatus (8) with a heating rate of 5 $K \cdot min^{-1}$. Independent, also under inert conditions, the masschange in dependence on the temperature was measured by an electromagnetic compensated thermobalance (9) with masses of 20 mg and a heating rate of 5 $K \cdot min^{-1}$. The decomposition products were identified by gas chromatography.

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## RESULTS AND DISCUSSION

### The thermal behaviour of two-coordinated mesityl complexes

The DTA-curves of the dimesityl compounds of Zn, Hg, Mg and Fe are shown in Fig.1. Zn·mes$_2$ melts undecomposed at 195 °C and is sublimable in vacuum at this temperature. At 300 °C a beginning thermal decomposition becomes evident, finally finished at 360 °C by separation of metallic zinc besides compounds containing less amounts of hydrogen. Almost only mesitylene was found as decomposition product. Hg·mes$_2$ shows a lower melting point at 178 °C and a beginning of decomposition above 300 °C. In these gradual differences the common gradation of the bond energies (Zn-C) (Hg-C) was visible. Mg.mes$_2$ also posseses a good thermal stability, with melting at 154 °C and the splitting of one mole mesitylene at 175 °C. No dimesitylene was found in the decomposition products and no evidence of metallic magnesium. Therefore a different mechanism of decomposition must be supposed than in the case of Zn.mes$_2$. A combination of some structure units may be accepted for the "Mg·mes". Fe·mes$_2$ is thermally stable up to 120 °C. Above this temperature it decomposes in an exothermic reaction by splitting to give mesitylene predominantly besides smaller amounts of xylene and toluene.

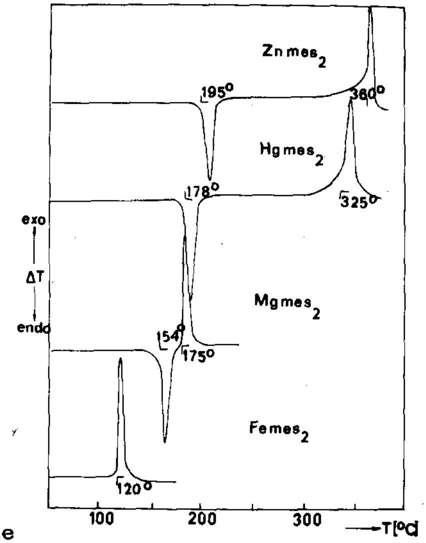

Fig.1

### Thermal stabilities of four-coordinated mesityl complexes

With regard to the chemical and thermal behaviour the tetramesityls of Ti, V, Cr and Mo act similarly, visible in the DTA-curves of Fig.2. The thermal decomposition of Ti·mes$_4$ takes place at 160 °C without preceding melting. The behaviour of V·mes$_4$ is analogous to an elimination of the ligands at 152 °C.

As expected, in consequence of the decreasing power of the metal-carbon bonds in the same oxidization state from Ti to Cr, the thermal splitting of Cr·mes$_4$ was found in an exothermic step at the lower temperature of 110 °C. In all cases smaller amounts of

m-xylene appeared as reaction products besides mainly mesitylene and in traces dimesitylene.
The highest thermal stability shows the Mo·mes$_4$ with decomposition at 276 °C. Almost only mesitylene was eliminated. The increasing bond energies of the metal-carbon bond with increasing atom number from Cr to Mo was hereby confirmed. The high thermal stability of the Mo·mes$_4$ is therefore an expression of the high bond energies of the Mo-C-bonds.

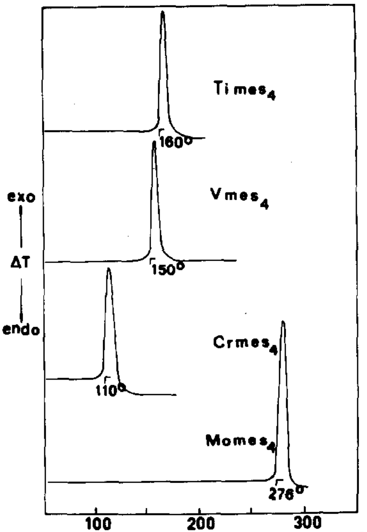

Fig. 2

## Influence of fixed second ligands on thermal stability of metal-mesityles

As shown in the TG- and DTA-curves of V·mes$_3$·1.25 THF in Fig. 3 the species V·mes$_3$ is not stable. The second ligand was split and immediately after this the homolytic splitting of mesitylene followed. Therefore the stability of V·mes$_3$ is connected with the existence of second ligands. As shown in the same figure, a different thermal stability becomes evident for the isostructural mesityl compound Al·mes$_3$·THF. After the decomposition of THF at 133 °C and following melting at 160 °C the Al·mes$_3$ is stable up to 320 °C. In this case the THF as second ligand is of no influence on the thermal stability of the Al·mes$_3$. This also becomes evident by the curve with dotted lines of Al·mes$_3$ without solvent, which results from heating in vacuum at 150 °C.

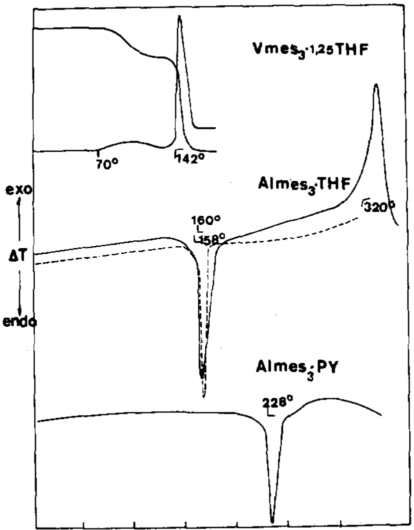

Fig. 3

The introduction of stronger donor ligands, for instance pyridine, is however, of significant influence as seen by the higher melting point of 228 °C.

## Thermal behaviour of salt-like mesityl complexes

As a consequence of the influence of polar bonds in the case of salt-like mesityl complexes, the DTA-curves of Fig.4 showed for the Li(V.mes$_4$)·THF and K(V·mes$_4$) decomposition temperatures of 160 °C and 204 °C, a significant higher stability than for the V·mes$_4$. The differences between the Li- and K-salts may be related to the different anionic polarization.

A difference in the thermal behaviour of Li(Cr·mes$_4$). THF was visible. The decomposition of THF is followed by two exothermic processes at 86 °C and 110 °C. This different behaviour, in contrast to the corresponding Li(V·mes$_4$)·THF, may be interpreted in terms of the electronic configuration of the central atoms. The course of the exothermic reaction at 86 °C is to explain in this way as a redox- or disproportion reaction, followed by the homolytic splitting of the Cr·mes$_4$ formed at 110 °C.

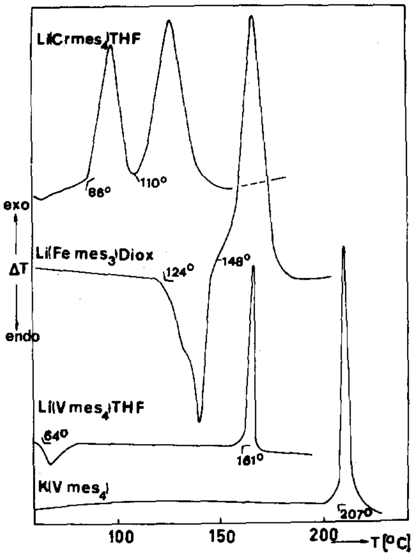

Fig.4

In the same way Li(Fe·mes$_4$)·dx with a decomposition temperature at 148 °C proved more stable in contrast to the Fe·mes$_2$.

Besides THF and dioxan, preferably mesitylene and less amounts of m-xylene, toluene and dimesitylene as organic products were found.

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