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Boekel, C.P.; Teuben, J.H.; Liefde Meijer, H.J. de

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# THERMAL DECOMPOSITION OF ARYLDICYCLOPENTADIENYLMETAL COMPLEXES OF NIOBIUM AND VANADIUM

C.P. Boekel, J.H. Teuben and H.J. de Liefde Meijer.

Laboratorium voor Anorganische Chemie,
Rijksuniversiteit, Zernikelaan, Groningen,
The Netherlands.

Analogous aryldicyclopentadienylmetal complexes of titanium, niobium and vanadium show appreciable differences in thermal stability.
Investigations were undertaken to elucidate the mechanisms of the decomposition reactions. The results show that the decomposition routes cannot be covered by one reaction scheme.
The thermal decomposition of $Cp_2TiR$ (1) and $Cp_2TiR_2$ (2) has already been described in some detail.
We now report on the thermal decomposition of $Cp_2VR$ and $Cp_2NbR_2$ complexes.

The niobocene diaryls ($Cp_2NbR_2$) show an appreciable higher thermal stability than the titanium analogues (2).
In the solid state and in aromatic and aliphatic hydrocarbon solvents the compounds decompose with quantitative formation of R-H and a Nb-containing residue which has lost the $Cp_2Nb$ structure.
Experiments with deuterated compounds and solvents showed that decomposition proceeds with an intramolecular abstraction of hydrogen atoms from cyclopentadienylrings, which is in contrast to the corresponding titanium complexes where the main route proceeds via the abstraction of hydrogen from aryl groups with formation of an intermediate benzynetitanium complex (2).

Aryldicyclopentadienylvanadium compounds and $Cp_2TiR_2$ are of comparable thermal stability.

The stability sequence of the vanadocene aryls (DTA) is

R = phenyl = m-tolyl = p-tolyl < o-tolyl < 2,6 - xylyl < perfluorophenyl.

In the solid state and in hydrocarbon solution the compounds (except for R = $C_6f_5$) decompose with formation of R-H, $Cp_2V$ and a vanadocene derivative with R substituted in one of the cyclopentadienyl rings, $Cp(C_5H_4-R)V$.

This derivative was identified by elemental analysis, IR, MS and by magnetic measurements; reaction with HCl/ether gave the expected vanadocenemonochloride:

$2\ Cp(C_5H_4-R)V + 2\ HCl \rightarrow 2\ Cp(C_5H_4-R)VCl + H_2$.

The decomposition reaction which was studied by experiments with compounds with deuterated aryl and cyclopentadienyl ligands will also be discussed.

References:

1. J.H. Teuben, J. Organometal. Chem. 69 (1974) 241.

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