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THERMAL DECOMPOSITION OF ARYL- AND BENZYL-DICYCLOPENTADIENYLTITANIUM(III) COMPOUNDS AND THEIR DINITROGEN COMPLEXES

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Summary

The compounds Cp_2TiR and their dinitrogen complexes $(Cp_2TiR)_2N_2$ (R = benzyl, aryl) were investigated by differential thermal analysis and analysis of the products of thermolysis. The following stability sequences were found: for Cp_2TiR: $R = C_6H_5 \approx m\text{-}CH_3C_6H_4 \approx p\text{-}CH_3C_6H_4 < CH_2C_6H_5 < o\text{-}CH_3C_6H_4 \approx C_6F_5 < 2,6\text{-}(CH_3)_2C_6H_3 \approx 2,4,6\text{-}(CH_3)_3C_6H_2$; for $(Cp_2TiR)_2N_2$: $R = o\text{-}CH_3C_6H_4 < C_6F_5 < CH_2C_6H_5 < C_6H_5 \approx m\text{-}CH_3C_6H_4 \approx p\text{-}CH_3C_6H_4$.

The complexes $(Cp_2TiR)_2N_2$ lose the complexed N_2 molecule with formation of Cp_2TiR. The compounds Cp_2TiR ($R = C_6F_5$ being an exception) decompose on heating with formation of RH (essentially quantitative) and a Ti-containing residue of complex nature. The Cp_2Ti structure is lost. Experiments using deuterated ligands and solvents show the thermal decomposition to be intermolecular in aromatic solutions. An explanation of the observed variation of the thermal stabilities of the compounds Cp_2TiR and $(Cp_2TiR)_2N_2$ is given.

Introduction

The compounds Cp_2TiR and their dinitrogen complexes $(Cp_2TiR)_2N_2$ (R = aryl, benzyl) show a remarkable variation in thermal stability [1, 2]. In order to understand these variations, we studied the thermal behaviour of the compounds in detail by differential thermal analysis (DTA) and by investigating the products of thermolysis.

Experimental

The experiments were performed under Ar or N_2 or in vacuum using Schlenk-type glassware [1, 2]. Thermograms were recorded with a low-temperature DTA apparatus [3]. The compounds Cp_2TiR and $(Cp_2TiR)_2N_2$ were prepared as described before [1, 2]; Cp_2TiCl_2-d_{10} was prepared according to Martin [4], other deuterated starting materials and solvents were obtained commercially (Merck). Samples (about 20 mg) were sealed in evacuated (0.1 mmHg) glass ampoules and heated at 2–3°/min. The temperature effect, ΔT, was plotted vs. the temperature, T, of the sample-holder block. The observed effects were reproducible to within 2°. Thermal decomposition of the compounds was also studied by heating samples (mmole scale, 10 ml solvent) at a fixed temperature in vacuum (only for solid compounds) or under Ar or N_2. The volatile components of the reaction mixture were condensed in a cold trap and analyzed by GLC and IR and/or mass spectrometry. The non-volatile residue was also examined (IR, reaction with HCl or Br_2 [1, 2]).

Results

Differential thermal analysis

The solid compounds Cp_2TiR (R = C_6H_5, o-$CH_3C_6H_4$, 2, 6-$(CH_3)_2C_6H_3$, 2, 4, 6-$(CH_3)_3C_6H_2$, C_6F_5, $CH_2C_6H_5$) and $(Cp_2TiR)_2N_2$ (R = C_6H_5, m-$CH_3C_6H_4$, p-$CH_3C_6H_4$, C_6F_5, $CH_2C_6H_5$) were studied by DTA. With the exception of the compounds with $R = C_6F_5$ simple thermograms were obtained. For most compounds only a single exothermic peak is observed. The compounds Cp_2TiR with R = o-$CH_3C_6H_4$, 2, 4, 6-$(CH_3)_3C_6H_2$, 2, 6-$(CH_3)_2C_6H_3$ show an endothermic effect at 69, 78 and 181°, respectively, in addition to the exothermal peak at higher temperatures. These effects are reversible and due to melting of the compounds. The compounds Cp_2TiR with R = m-$CH_3C_6H_4$, or p-$CH_3C_6H_4$ could not be obtained in sufficiently pure form to permit reliable DTA measurements; in toluene solution they show the same thermal stability as $Cp_2TiC_6H_5$. $Cp_2TiC_6F_5$ gives a complex thermogram showing a succession of exothermal effects above 100°. The corresponding dinitrogen complex $(Cp_2TiC_6F_5)_2N_2$ shows an endothermic effect at 20° due to loss of nitrogen; above 100° the thermogram is the same as that recorded for $Cp_2TiC_6F_5$. In Fig. 1 the thermogram of

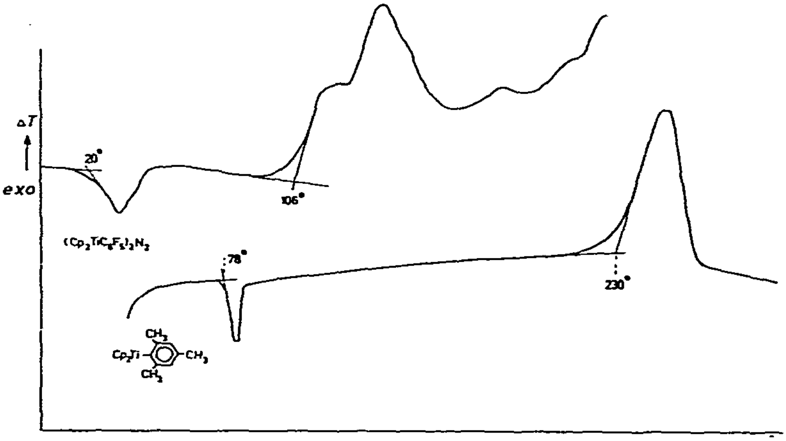

Fig. 1. Thermograms of $(Cp_2TiC_6F_5)_2N_2$ and $Cp_2Ti[2,4,6$-$(CH_3)_3C_6H_2]$.

TABLE 1

DATA EFFECTS DETERMINED FOR Cp_2TiR AND $(Cp_2TiR)_2N_2$

R	Cp_2TiR effect (°C)		$(Cp_2TiR)_2N_2$ effect (°C)
C_6H_5		29 (*exo*)	67 (*exo*)
o-$CH_3C_6H_4$	69 (*endo*)	95 (*exo*)	$< -20^{b}$
m-$CH_3C_6H_4$	*a*	*a*	66 (*exo*)
p-$CH_3C_6H_4$	*a*	*a*	70 (*exo*)
2, 6-$(CH_3)_2C_6H_2$	181 (*endo*)	228 (*exo*)	*c*
2, 4, 6-$(CH_3)_3C_6H_2$	78 (*endo*)	230 (*exo*)	*c*
C_6F_5		106 (*exo*)	20 (*endo*)
$CH_2C_6H_5$		43 (*exo*)	52 (*exo*)

[a] Not determined. [b] No reliable DTA curve obtained. [c] Complexes could not be synthesized [2].

$(Cp_2TiC_6F_5)_2N_2$ is given together with that of $Cp_2Ti[2,4,6\text{-}(CH_3)_3C_6H_2]$, an example of the more simple thermograms. The interpolated transition temperatures are listed in Table 1.

Thermolysis of the solid compounds Cp_2TiR and $(Cp_2TiR)_2N_2$

The exothermal effects in the thermograms of Cp_2TiR are associated with fast decomposition. At temperatures slightly below the start of the peaks noticeable decomposition occurred within 1 h. Thus, when $Cp_2TiC_6H_5$ was kept at 10° for 1 h in vacuum, benzene (31% of the phenyl groups) was found in the cold trap. Treatment of the residue with Br_2(in n-pentane, at −78°) produced Cp_2TiBr_2 (63%) and C_6H_5Br (61%) together with some green polymeric material, in which the Cp_2Ti structure was not present. Evidently about one third of the original $Cp_2TiC_6H_5$ had decomposed.

When heated at or above the temperatures of the exothermal effects (Table 1), fast decomposition started and was always complete within 1 h. For the compounds Cp_2TiR (except for R = C_6H_5) essentially quantitative formation of RH was found. Traces of higher boiling materials were also present, but the amounts were too small to allow identification. The yield of RH did not depend on the atmosphere (vacuum, N_2 or Ar) applied during the thermolysis.

The complexes $(Cp_2TiR)_2N_2$ were investigated in a similar way. Here the exothermal effect also indicated a fast thermal decomposition. The products were very like those obtained for the compounds Cp_2TiR. Quantitative formation of RH was found. The complexed nitrogen was almost quantitatively liberated as nitrogen gas. The residue was very much the same as obtained for the nitrogen-free compounds thermolyzed under nitrogen. In a typical experiment $(Cp_2TiC_6H_5)_2N_2$ was heated at 80° in a vessel equipped with a gas burette. Nitrogen evolution set in immediately. After 1 h of heating, the amount of N_2 evolved was measured (found: 0.9 mole N_2 per mole of complex). The amount of benzene produced was 85%.

The endothermic effect observed in the thermogram of $(Cp_2TiC_6F_5)_2N_2$ at 20° was due to the liberation of the complexed nitrogen. Heating the complex at room temperature for 1 h produced $Cp_2TiC_6F_5$ and about 0.9 mole N_2 per mole of $(Cp_2TiC_6F_5)_2N_2$.

Table 2 gives the yields of RH obtained under various conditions. The dia-

TABLE 2

YIELDS OF RH, OBTAINED AFTER THERMOLYSIS OF THE COMPOUNDS Cp_2TiR AND $(Cp_2TiR)_2N_2$

R	Cp_2TiR experimental conditions	RH(%)	$(Cp_2TiR)_2N_2$ experimental conditions	RH(%)
C_6H_5	1 h, 10°, vacuum	31[a]	1 h, 80°, vacuum	88
	1 h, 25°, vacuum	83	1 h, 150°, N_2	85
	50 h, 20°, toluene, N_2	95		
o-$CH_3C_6H_4$	1 h, 70°, vacuum	26[a]		
	1 h, 95°, vacuum	90		
	1 h, 110°, N_2	90		
	25 h, 80°, benzene, N_2	88		
m-$CH_3C_6H_4$	1 h, 80°, benzene, N_2	101	1 h, 80°, vacuum	91
			1 h, 80°, N_2	95
p-$CH_3C_6H_4$	60 h, 20°, benzene, N_2	99	1 h, 80°, vacuum	98
	100 h, 20°, THF, N_2	75	1 h, 80°, N_2	67
2,6-$(CH_3)_2C_6H_3$	1 h, 180°, Ar	14[a]		
	1 h, 230°, Ar	83		
	1 h, 240°, N_2	93		
2,4,6-$(CH_3)_3C_6H_2$	1 h, 85°, vacuum	3[a]		
	1 h, 190°, vacuum	13[a]		
	1 h, 240°, Ar	88		
C_6F_5	1 h, 130—160°, vacuum	Trace		
$CH_2C_6H_5$	1 h, 45°, vacuum	97	1 h, 55°, N_2	92
	20 h, 20°, benzene, N_2	92		

[a] After treatment of the residues with HCl or Br_2, equimolar amounts of RH and Cp_2TiCl_2 or RBr and Cp_2TiBr_2 were found. This indicates the presence of a corresponding amount of starting material intact [1]. The total of groups R obtained was more than 90% of groups R in the original sample.

magnetic residues obtained after thermal decomposition are virtually insoluble in n-pentane and ether and only partially soluble in benzene or toluene; they probably consist of a mixture of related compounds*. The exact composition and structure of these products could not be established, but a structural relation with so-called "stable" titanocene $[Cp(C_5H_4)TiH]_2$ [5] is evident from the spectroscopic and chemical properties of the residues. IR spectra show the presence of π-bonded Cp groups (bands at 3100, 1430, 1125, 1010, 800 - 790 cm^{-1}) [6]. A band at 1050-1060 cm^{-1} which is observed in all spectra is also found for $[Cp(C_5H_4)TiH]_2$ [5] and $[Cp(C_5H_4)TiCl]$ [5, 7] and is thought to be characteristic of the C_5H_4 group. Upon reaction of the residues with HCl in ether, H_2 was evolved and brown-purple mixtures were formed. A purple compound was isolated and identified as $[Cp(C_5H_4)TiCl]_2$ by IR and UV-visible spectroscopy [5, 7]. Reaction with HCl in excess completely converted the residues into a green insoluble, apparently polymeric, product. No red Cp_2TiCl_2 was obtained, demonstrating the loss of the Cp_2Ti structure. The IR spectrum of the green material was identical with that of $[Cp(C_5H_4)TiCl_2]_n$ the final product of the reaction of $[Cp(C_5H_4)TiCl]_2$ with HCl in excess [7].

$Cp_2TiC_6F_5$ decomposed in a different way. Only traces of C_6F_5H and un-

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* In experiments carried out under N_2, the residues contained some nitrogen in a reduced form (up to 0.2 N per Ti); this will be reported in detail in a forthcoming paper.

TABLE 3

THERMAL DECOMPOSITION OF $(Cp_2TiR)_2N_2$ USING DEUTERATED COMPLEXES AND SOLVENTS

Complex	Experimental conditions	Composition of RH
$(Cp_2TiC_6D_5)_2N_2$	1 h, 80°, vacuum	C_6D_5H
$(Cp_2TiC_6H_5)_2N_2$	1 h, 80°, toluene-d_8, N_2	C_6H_6
$(Cp_2TiC_6H_5)_2N_2$ $+ Cp_2TiC_6D_5\text{-}d_{10})_2N_2$	1 h, 80°, toluene, N_2	C_6H_6, C_6H_5D, C_6D_5H, C_6D_6
$[Cp_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$	50 h, 20°, benzene-d_6, N_2	$CH_3C_6H_5$
$[Cp_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$	100 h, 20°, THF-d_8, -N_2	$CH_3C_6H_5$, $CH_3C_6H_4D$

known higher boiling products were found after thermolysis of the compound at 130 - 160° in vacuum. A yellow compound sublimed into the cold part of the reaction vessel; it was identified (mass and IR spectra) as $Cp_2Ti(F)C_6F_5$ [8].

Thermal decomposition of the compounds Cp_2TiR in solution

At room temperature the dinitrogen complexes dissolve in benzene or toluene according to eqn. 1 (ref. 2). Therefore the study of the thermal decomposition of these complexes in solution was not possible.

$$(Cp_2TiR)_2N_2 \rightarrow 2Cp_2TiR + N_2 \qquad (1)$$

The products of thermolysis of Cp_2TiR in aromatic solvents were the same as found for the solid compounds. Quantitative formation of RH was established (Table 2). The Ti-containing products obtained after removing the solvent in vacuum proved to be the same as the residues of the solid compounds (for experiments performed under N_2 (see footnote on page 244).

Experiments with deuterated ligands and solvents

A number of thermolysis experiments were performed using compounds with deuterated cyclopentadienyl groups, group R or deuterated solvents in order to elucidate the mechanism of the thermal decomposition. The product RH was investigated by mass spectrometry. The experimental conditions and compositions of RH are summarized in Table 3.

Discussion

The results show that the thermal stability of the two series of compounds strongly depends on the nature of group R. In particular, methyl substituents on the *ortho* position of the phenyl group R have a very marked effect. In the series of the compounds Cp_2TiR the stability sequence is: $R = C_6H_5 \approx m\text{-}CH_3C_6H_4 \approx p\text{-}CH_3C_6H_4 < CH_2C_6H_5 < o\text{-}CH_3C_6H_4 \approx C_6F_5 < 2,6(CH_3)_2\text{-}C_6H_3 \approx 2,4,6\text{-}(CH_3)_3C_6H_2$ (Table 1). Our failure to prepare compounds Cp_2TiR with R = alkyl [1] indicates that these compounds would probably be less stable than those discussed. Here maximum stability is found for the phenyl compounds with both *ortho* positions substituted by methyl groups.

In the series of the compounds $(Cp_2TiR)_2N_2$ the stability sequence is: $R = o\text{-}CH_3C_6H_4 < C_6F_5 < CH_2C_6H_5 < m\text{-}CH_3C_6H_4 \approx p\text{-}CH_3C_6H_4 \approx C_6H_5$

(Table 1). Taking into account the fact that for R = 2, 6-$(CH_3)_2C_6H_3$ and 2, 4, 6-$(CH_3)_3C_6H_2$ the dinitrogen complexes were not formed, the stability sequence is seen to be the opposite of that observed for Cp_2TiR, the minimum stability being shown by the phenyl compounds with both *ortho* positions substituted by methyl groups.

In both series the compounds with R = C_6F_5 occupy an intermediate position. The complex thermogram of $Cp_2TiC_6F_5$ shows that the initial decomposition at about 100° is followed by a series of exothermic reactions. The main product, $Cp_2Ti(F)C_6F_5$, is probably formed by an intermolecular fluorine transfer from a pentafluorophenyl group to a titanium atom. This carbon-to-metal migration of fluorine is characteristic for other fluorocarbon—metal bonds and is also observed in the thermal decomposition of $Cp_2Ti(C_6F_5)_2$ [8]. However, $Cp_2TiC_6F_5$ cannot be satisfactorily compared with the other Cp_2TiR compounds since its decomposition evidently takes a different route.

From the investigations of the compounds Cp_2TiR under various conditions it is clear that their decomposition proceeds according to eqn. 2. The exact

$$Cp_2TiR \rightarrow \text{"}C_{10}H_9Ti\text{"} + RH \qquad (2)$$

composition of the titanium containing residue "$C_{10}H_9Ti$" is not yet clear. Chemical and physical evidence suggest that it is a mixture of related compounds, in which both Cp and C_5H_4 groups are present, but no Cp_2Ti entity. The presence of C_5H_4 groups may be responsible for the complex nature of the product. C_5H_4 groups are known to act as bridging groups, being π-bonded to one metal atom and simultaneously σ-bonded to another. Such C_5H_4-bridges are found in $[Cp(C_5H_4)TiAl(C_2H_5)_2]_2$ [9, 10] and in niobocene $[Cp(C_5H_4)NbH]_2$ [10] and may also be present in "stable" titanocene $[Cp(C_5H_4)TiH]_2$ and the chloride $[Cp(C_5H_4)TiCl]_2$ [5]. This special property of a C_5H_4 group may lead to dimeric structures but also more highly associated and even polymeric structures.

The thermal behaviour of the complexes $(Cp_2TiR)_2N_2$ with R = o-$CH_3C_6H_4$, C_6F_5 and the DTA curve of the latter indicate that the N_2 complexes decompose endothermally [2] according to eqn. 3. The solid dinitrogen complexes with

$$(Cp_2TiR)_2N_2 \rightarrow 2Cp_2TiR + N_2 \qquad (3)$$

R = C_6H_5, p-$CH_3C_6H_4$, m-$CH_3C_6H_4$ and $CH_2C_6H_5$ decompose at temperatures at which the products Cp_2TiR are highly unstable and immediately decompose further with formation of "$C_{10}H_9Ti$" and RH, and the overall decomposition reaction is exothermic. In aromatic solvents (benzene, toluene) the dinitrogen complexes lose nitrogen at room temperature [2], and a study of the thermal decomposition in solvents is essentially a study of Cp_2TiR compounds.

The thermolysis experiments, particularly those using deuterated ligands and solvents (Table 3) permit some conclusions concerning the mechanism of the thermal decomposition. In aromatic solvents and in the solid state the hydrogen atom for the formation of RH is supplied by the cyclopentadienyl ligands. The thermolysis of an equimolar mixture of $(Cp_2TiC_6H_5)_2N_2$ and $(Cp_2TiC_6D_5)_2N_2$ (Table 3) indicates that the decomposition proceeds via an intermolecular reaction. This reaction may be bimolecular, but more complicated routes are also possible. A free-radical decomposition is rejected, because no

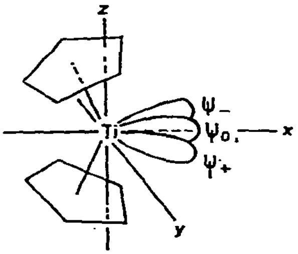

Fig. 2. Ballhausen and Bahl's bonding model.

radical coupling products R—R, not hydrogen abstractions from the solvent were observed*.

Ballhausen and Dahl's picture of the bonding in metallocene derivatives with non-parallel rings [11] (Fig. 2) allows a discussion of the supposed decomposition mechanism and the relative stabilities of the compounds studied. For the compounds Cp_2TiR, R is bonded via one of the hybrid orbitals Ψ_+, Ψ_0, Ψ_-, and an odd electron is accommodated in another orbital (Cp_2TiR has 15 electrons in the valence shell of the metal). One orbital is empty and the compounds are expected to display Lewis acid character (i.e. to be able to form complexes with donor molecules) or to behave as electrophilic agents. In this concept the thermal decomposition of the compounds Cp_2TiR may be explained by the electrophilic attack of a Cp_2TiR molecule on a cyclopentadienyl group of another molecule. The second step is the formation of RH and the bridging $Ti—C_5H_4—Ti$ structure. The next phase may be an intramolecular reaction producing $[Cp(C_5H_4)Ti]_2$ or more likely, a reaction with a third Cp_2TiR molecule leading to more complicated oligomers or polymers containing C_5H_4 groups bridging Ti atoms (Fig. 3). In this scheme a cyclopentadienyl group is metallated by titanium. Metallation of cyclopentadienyl ligands by other metals (Na, Li, Hg) is known for ferrocene and for some other organotransition metal compounds [12], but has not yet been reported for titanium compounds.

The stabilization of Cp_2TiR by *ortho* substituents in the aryl group R is believed to be purely a steric effect. The effective blocking of the empty orbital by an *ortho* methyl group will result in a decrease in reactivity of the molecule and thus an enhanced thermal stability. It is unlikely that the stabilizing effect

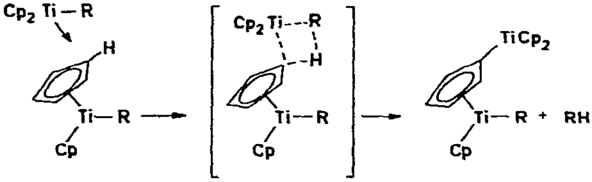

Fig. 3. Suggested decomposition scheme for Cp_2TiR compounds.

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*In THF-d_8 (Table 3), RD was found together with RH, indicating participation of the solvent. Apparently the thermal decomposition in coordinating solvents is more complex, and free-radical formation may be of importance.

of *ortho* substituents is of an electronic nature. The inductive effects of *ortho* substituents will be about the same as those of *para* substituents; in the latter case no stabilization of Cp_2TiR is observed. In the dinitrogen complexes the N_2 molecule presumably coordinates via Ψ_+, R is bound via Ψ_-, and the odd electron is placed in Ψ_0. The N_2 molecule is simultaneously complexed to another molecule of Cp_2TiR giving the complex $(Cp_2TiR)_2N_2$ [2]. The complexed N_2 ligand occupies the reaction site active in thermal decomposition and stabilizes the Cp_2TiR entity. Similar stabilization of the compounds Cp_2TiR may be expected on coordination with other donor molecules or solvents like THF. Since both the electrophilic properties of Cp_2TiR (responsible for thermal decomposition) and the acceptor properties depend on the nature of R, it is understandable that the stability sequence of the complexes $(Cp_2TiR)_2N_2$ is the reverse of that of Cp_2TiR. The stability of the dinitrogen complexes with $R = C_6F_5$, $o\text{-}CH_3C_6H_4$ and the non-existence of complexes with $R = 2,6\text{-}(CH_3)_2\text{-}C_6H_3$ or $2,4,6\text{-}(CH_3)_3C_6H_2$ is obviously related with the steric hindrance exerted by the *ortho* fluorine or methyl groups.

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