Journal of Organometallic Chemistry, 59 (1973) 259–266

METHYL SUBSTITUTED DERIVATIVES OF CYCLOPENTADIENYL(CYCLOHEPTATRIENYL)TITANIUM

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(Received January 20th, 1973)

SUMMARY

The mono- and dimethyl substituted complexes $(h^5\text{-}C_5H_4R)(h^7\text{-}C_7H_6R)Ti$ ($R=H$ or CH_3) have been prepared by reaction of $(h^5\text{-}C_5H_4R)TiCl_3$ with $i\text{-}C_3H_7MgBr$ in ether in the presence of an excess of C_7H_7R. The blue, diamagnetic compounds are stable up to at least 300°, but sensitive to air and water. The IR and NMR spectra of the compounds are given. The mass spectra indicate that substantial proportions of the compounds rearrange to ions of dibenzenetitanium derivatives upon electron impact.

INTRODUCTION

Müller and Göser[1] observed in the mass spectrum of $(h^5\text{-}C_5H_5)(h^7\text{-}C_7H_7)V$ a degradation of the ion $C_{12}H_{12}V^+$ into benzene and the ion $C_6H_6V^+$, and they suggested that the dibenzenevanadium ion plays a role in the fragmentation process. A similar type of degradation was found in the mass spectra of the ring-substituted compounds $(h^5\text{-}C_5H_5)(h^7\text{-}C_7H_6R)V$. ($R=CH_3$, C_6H_5, CN)[2]. Rettig and coworkers[3] studied the mass spectrum of the partly deuterated compound $(h^5\text{-}C_5D_5)(h^7\text{-}C_7H_7)V$. They propose an intramolecular rearrangement to dibenzenevanadium species following electron impact and suggest a pathway for the transfer of the CH fragment from the seven-membered to the five-membered ring.

Elimination of benzene was also observed in our study of the mass spectrum of the corresponding titanium compound $(h^5\text{-}C_5H_5)(h^7\text{-}C_7H_7)Ti$[4]. Since thermal decomposition of the latter occurs only at a much higher temperature than that in the mass spectrometer, we discarded the possibility that the changes in ring size occur with the uncharged molecule.

This paper describes the synthesis and some properties of a number of mono- and dimethyl substituted compounds, $(h^5\text{-}C_5H_4R)(h^7\text{-}C_7H_6R)Ti$ ($R=H$, CH_3). The mass spectra show that degradation of the parent ions follows the same route as had been found for the unsubstituted titanium and vanadium compounds. The results are best explained by assuming a transfer of CH or CCH_3 fragments after electron impact resulting in rearrangement to dibenzenetitanium species. Investigations of other ring-substituted sandwich compounds are in progress.

TABLE 1

ANALYTICAL DATA OF THE COMPOUNDS (h^5-C_5H_4R)(h^7-C_7H_6R)Ti(R=H, CH_3).

Starting materials (C_5H_4R)$TiCl_3$, C_7H_7R'	*Compound* (C_5H_4R)(C_7H_6R')Ti	*Found (calcd.) (%)*			*Yield* (%)
		C	*H*	*Ti*	
R=R'=H		70.64 70.86 (70.61)	5.72 5.94 (5.93)	23.46 23.47 (23.47)	40
R=CH_3, R'=H		71.79 71.86 (71.57)	6.64 6.59 (6.47)	22.02 22.03 (21.96)	25
R=H, R'=CH_3		71.65 71.88 (71.57)	6.88 6.52 (6.47)	22.06 21.93 (21.96)	25
R=R'=CH_3		72.35 72.28 (72.42)	7.09 7.29 (6.95)	20.26 20.53 (20.63)	10

TABLE 2

MASS SPECTRUM OF $C_5H_5TiC_7H_7$

m/e	*Rel. intensity*	*Ion*	*m/e*	*Rel. intensity*	*Ion*
204	100	$C_{12}H_{12}Ti^+$	87	8	$C_3H_3Ti^+$
178	2	$C_{10}H_{10}Ti^+$	86	6	$C_3H_2Ti^+$
176	1	$C_{10}H_8Ti^+$	85	4	C_3HTi^+
152	2	$C_8H_8Ti^+$	78	2	$C_6H_6{}^+$
150	2	$C_8H_6Ti^+$	74	3	$C_2H_2Ti^+$
138	2	$C_7H_6Ti^+$	73	7	C_2HTi^+
137	2	$C_7H_5Ti^+$	66	2	$C_5H_6{}^+$
126	73	$C_6H_6Ti^+$	65	2	$C_5H_5{}^+$
124	15	$C_6H_4Ti^+$	63	1	$C_6H_6Ti^{2+}$
113	15	$C_5H_5Ti^+$	48	33	Ti^+
102	9	$C_{12}H_{12}Ti^{2+}$	39	2	$C_3H_3{}^+$
100	1	$C_4H_4Ti^+$			
99	2	$C_4H_3Ti^+$			
98	4	$C_4H_2Ti^+$			
91	2	$C_7H_7{}^+$			

*Metastable peaks m**
77.8, 67.0, 18.3

TABLE 3

MASS SPECTRUM OF $C_5H_4CH_3TiC_7H_7$

m/e	*Rel. intensity*	*Ion*	*m/e*	*Rel. intensity*	*Ion*
218	100	$C_{13}H_{14}Ti^+$	91	7	$C_7H_7^+$
204	8	$C_{12}H_{12}Ti^+$	87	5	$C_3H_3Ti^+$
190	1	$C_{11}H_{10}Ti^+$	86	6	$C_3H_2Ti^+$
163	1	$C_9H_7Ti^+$	85	4	C_3HTi^+
150	2	$C_8H_6Ti^+$	79	4	$C_6H_7^+$
140	41	$C_7H_8Ti^+$	78	4	$C_6H_6^+$
138	22	$C_7H_6Ti^+$	73	6	C_2HTi^+
126	41	$C_6H_6Ti^+$	65	2	$C_5H_5^+$
124	6	$C_6H_4Ti^+$	48	31	Ti^+
113	11	$C_5H_5Ti^+$	39	5	$C_3H_3^+$
109	7	$C_{13}H_{14}Ti^{2+}$			
92	3	$C_7H_8^+$			

*Metastable peaks m** 89.9, 72.8

EXPERIMENTAL

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods and freed from oxygen by repeated degassing and saturation with nitrogen. Commercial cycloheptatriene (EGA) was used without purification. (h^5-C_5H_5)$TiCl_3$[5] and methylcycloheptatriene[6] were prepared according to published procedures. (h^5-$C_5H_4CH_3$)$TiCl_3$ was prepared from $C_5H_4CH_3Na$[7] and an excess of $TiCl_4$ in boiling xylene. Elementary analyses of C and H were carried out at the Microanalytical Department of this University under supervision of Mr. W.M. Hazenberg. Ti was analyzed in our laboratory by Mr. A. Meetsma.

Synthesis of (h^5-C_5H_4R)(h^7-C_7H_6R)Ti

The synthesis of the compounds was carried out as described for the unsubstituted complex[4]; the products were purified by sublimation at ca. 120°/0.1 mm Hg or by recrystallization from n-pentane. Yields and analytical data are summarized in Table 1. Differential thermal analysis showed the compounds to be thermally stable up to at least 300°.

SPECTRA

The mass spectra were run on an AEI MS 9 mass spectrometer. The spectra of the methyl-substituted complexes and the unsubstituted compound are collected in Tables 2–5.

Operating conditions: energy 70 eV; resolution 1000; accelerating voltage 8 kV. The samples were introduced directly into the ion source using a metal probe. The inlet temperatures were ca. 140°, which is considerably lower than the decomposition temperatures of the compounds. Therefore, ions arising from thermal decomposition products will not be present in the mass spectra. No ions were observed with *m/e* larger than the parent ions. The groups of peaks assigned to titanium containing ions showed the normal isotopic distribution of Ti, and only peaks corresponding to ^{48}Ti are listed in Tables 2–5. The relative intensities are uncorrected. The metastable peaks observed in the spectra are included in the Tables and fragmentation schemes are shown in Scheme 1.

The IR spectra of the compounds (Fig. 1) were recorded using a Hitachi EPI-G spectrophotometer. The samples were examined as mulls in hexachlorobutadiene (4000–1200 cm^{-1}) or in Nujol (1200–400 cm^{-1}) between KBr discs.

The NMR spectra of the compounds in C_6D_6 solution (40°) were recorded with a Varian A 60 high-resolution instrument. The results are summarized in Table 6. The chemical shifts are given relative to TMS (τ 10 ppm) which was used as internal standard

RESULTS AND DISCUSSION

In a previous paper we described the compound (h^5-C_5H_5)(h^7-C_7H_7)Ti[4] assuming a sandwich-type structure similar to (h^5-C_5H_5)(h^7-C_7H_7)V[8]. This result has recently been confirmed by X-ray analysis[9]. We assume the ring-substituted compounds to have analogous sandwich structures. Their IR spectra (Fig. 1) show

TABLE 4

MASS SPECTRUM OF $C_5H_5TiC_7H_6CH_3$

m/e	*Rel. intensity*	*Ion*	*m/e*	*Rel. intensity*	*Ion*
218	100	$C_{13}H_{14}Ti^+$	104	2	$C_8H_8^+$
204	1	$C_{12}H_{12}Ti^+$	91	3	$C_7H_7^+$
202	1	$C_{12}H_{10}Ti^+$	87	8	$C_3H_3Ti^+$
190	11	$C_{11}H_{10}Ti^+$	86	5	$C_3H_2Ti^+$
178	2	$C_{10}H_{10}Ti^+$	85	4	C_3HTi^+
164	1	$C_9H_8Ti^+$	78	2	$C_6H_6^+$
163	1	$C_9H_7Ti^+$	73	6	C_2HTi^+
152	1	$C_8H_8Ti^+$	66	2	$C_5H_6^+$
150	4	$C_8H_6Ti^+$	65	2	$C_5H_5^+$
140	50	$C_7H_8Ti^+$	48	16	Ti^+
138	21	$C_7H_6Ti^+$	39	3	$C_3H_3^+$
126	30	$C_6H_6Ti^+$			
124	5	$C_6H_4Ti^+$			
113	22	$C_5H_5Ti^+$			
109	7	$C_{13}H_{14}Ti^{2+}$			

*Metastable peaks m**
165.6, 89.9, 72.8

TABLE 5

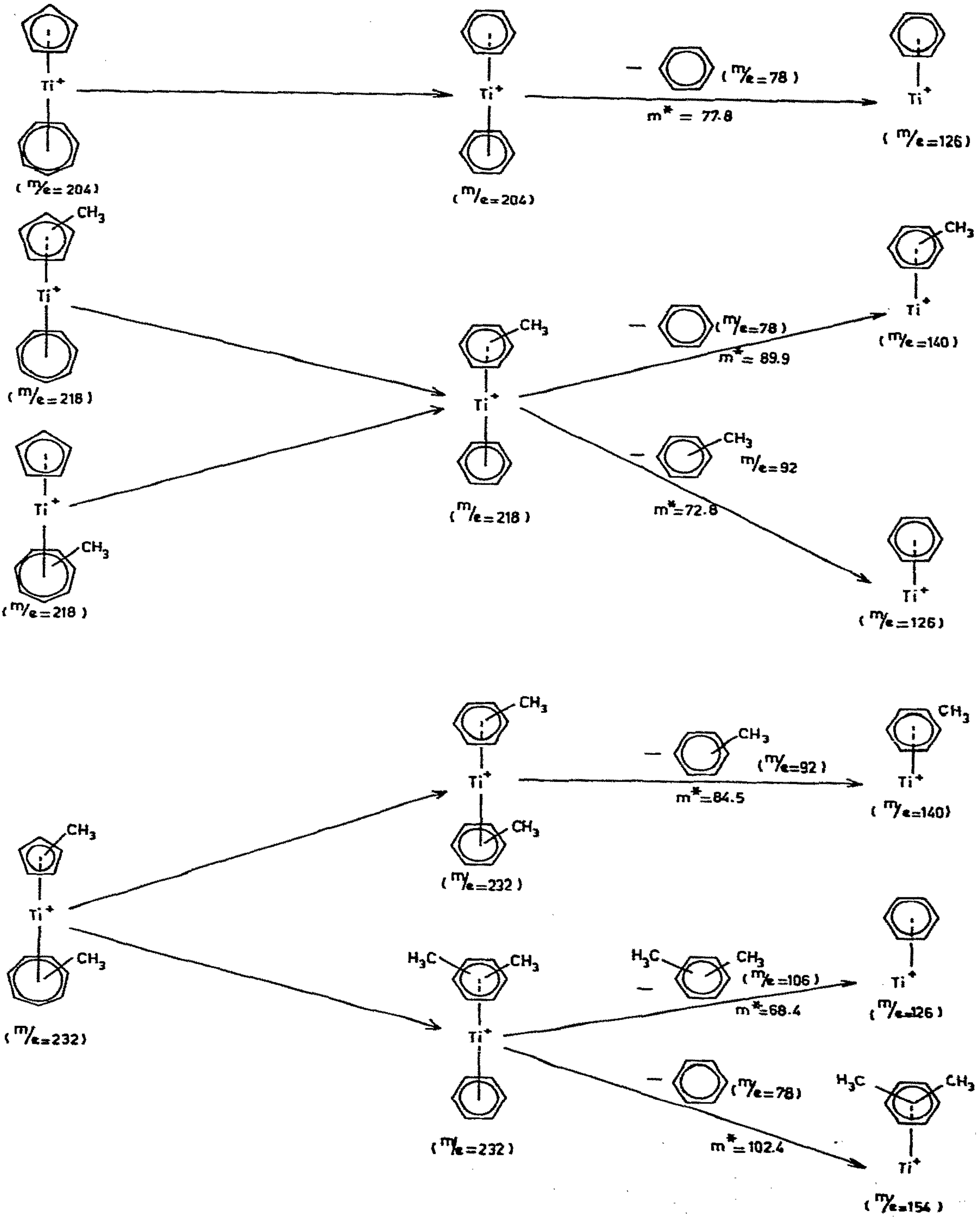
MASS SPECTRUM OF $C_5H_4CH_3TiC_7H_6CH_3$

m/e	*Rel. intensity*	*Ion*	*m/e*	*Rel. intensity*	*Ion*
232	100	$C_{14}H_{16}Ti^+$	99	4	$C_4H_3Ti^+$
218	3	$C_{13}H_{14}Ti^+$	98	4	$C_4H_2Ti^+$
204	3	$C_{12}H_{12}Ti^+$	92	5	$C_7H_8^+$
165	2	$C_9H_9Ti^+$	91	18	$C_7H_7^+$
163	1	$C_9H_7Ti^+$	87	4	$C_3H_3Ti^+$
154	8	$C_8H_{10}Ti^+$	86	4	$C_3H_2Ti^+$
152	9	$C_8H_8Ti^+$	79	23	$C_6H_7^+$
150	6	$C_8H_6Ti^+$	78	28	$C_6H_6^+$
140	46	$C_7H_8Ti^+$	77	24	$C_6H_5^+$
139	11	$C_7H_7Ti^+$	73	6	C_2HTi^+
138	20	$C_7H_6Ti^+$	65	5	$C_5H_5^+$
126	36	$C_6H_6Ti^+$	63	5	$C_5H_3^+$
116	17	$C_{14}H_{16}Ti^{2+}$	52	9	$C_4H_4^+$
115	5	$C_5H_7Ti^+$	51	15	$C_4H_3^+$
113	7	$C_5H_5Ti^+$	50	7	$C_4H_2^+$
106	15	$C_8H_{10}^+$	48	14	Ti^+
105	100	$C_8H_9^+$	39	10	$C_3H_3^+$
104	46	$C_8H_8^+$			
103	36	$C_8H_7^+$			
102	5	$C_8H_6^+$			

*Metastable peaks m**
179.4, 102.2, 84.5, 68.4

that the absorption bands of the unsubstituted rings are hardly changed whereas those of the substituted rings are. The NMR spectra (Table 6) show, that the protons of the unsubstituted rings are equivalent as are the methyl protons. The protons of the substituted rings give rise to multiplets centered at nearly the same τ-values as those of the unsubstituted rings.

Scheme 1. Partial fragmentation schemes of the compounds $(C_5H_4R)Ti(C_7H_6R)(R=H, CH_3)$.



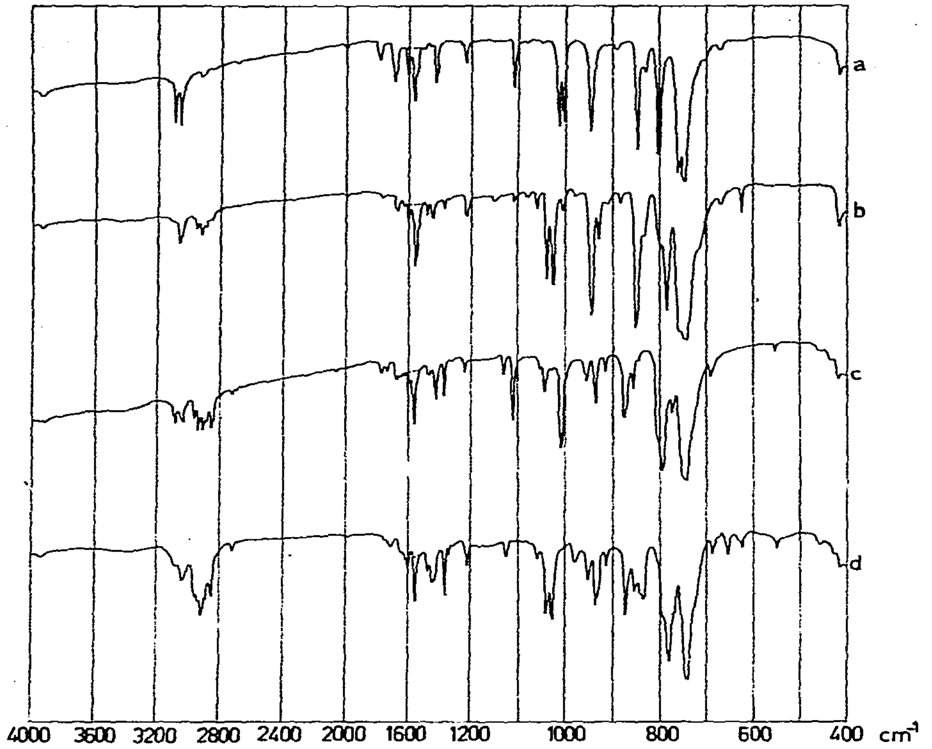


Fig. 1. IR spectra of: (a) $(h^5\text{-}C_5H_5)(h^7\text{-}C_7H_7)Ti$, (b) $(h^5\text{-}C_5H_4CH_3)(h^7\text{-}C_7H_7)Ti$, (c) $(h^5\text{-}C_5H_5)(h^7\text{-}C_7H_6CH_3)Ti$, (d) $(h^5\text{-}C_5H_4CH_3)(h^7\text{-}C_7H_6CH_3)Ti$ in hexachlorobutadiene (4000–1200 cm^{-1}) and Nujol (1200–400 cm^{-1}).

TABLE 6

PROTON NMR DATA OF THE COMPOUNDS $C_5H_4RTiC_7H_6R'$[a]

R	*R'*	*C₅*	*C₇*	*CH₃(C₅)*	*CH₃(C₇)*
H	H	5.03 s[b](5)[c]	4.53 s(7)		
CH_3	H	5.10 m (4)	4.54 s(7)	8.19 s(3)	
H	CH_3	5.04 s(5)	4.57 m(6)		7.48 s(3)
CH_3	CH_3	5.12 m(4)	4.62 m(6)	8.21 s(3)	7.48 s(3)

[a] C_6D_6 solution (40°) TMS internal standard. τ 10 ppm. [b] Multiplicity, s = singlet, m = multiplet. [c] Relative intensities between brackets.

The most interesting feature in the mass spectrum of the compound $(h^5\text{-}C_5H_5)$-$(h^7\text{-}C_7H_7)Ti$ is the degradation of the ion $C_{12}H_{12}Ti^+$ via the elimination of benzene giving the ion $C_6H_6Ti^+$. In the mass spectra of the compounds $(h^5\text{-}C_5H_4R)(h^7\text{-}C_7H_6R)Ti$ (R = H, CH_3) the same phenomenon is observed.

In the spectra of both monosubstituted compounds, the ions $C_{13}H_{14}Ti^+$ appear to break down via two routes (Scheme 1). In the first route the ions lose benzene to give the ion $C_6H_5CH_3Ti^+$; in the second toluene is eliminated giving the ion

$C_6H_6Ti^+$. Obviously, substantial amounts of the original materials are converted to the same ion and this is consistent with the view that the monosubstituted complexes rearrange to the benzene–titanium–toluene ion, $(h^6\text{-}C_6H_6)(h^6\text{-}C_6H_5CH_3)Ti^+$ by transfer of a CH or CCH_3 fragment from the seven to the five-membered ring.

A similar rearrangement is found in the mass spectrum of the dimethyl-substituted compound $(h^5\text{-}C_5H_4CH_3)(h^7\text{-}C_7H_6CH_3)Ti$. Two rearrangements are now possible: migration of a CH-fragment from the seven- to the five-membered ring will give the symmetrical ditoluenetitanium ion, $(h^6\text{-}C_6H_5CH_3)_2Ti^+$; migration of a CCH_3-fragment will give the asymmetrical benzene–titanium–xylene ion, $(h^6\text{-}C_6H_6)[h^6\text{-}C_6H_4(CH_3)_2]Ti^+$. Indeed the mass spectrum provides evidence for the existence of both these rearranged ions (Scheme 1). Degradation of the ion $(h^6\text{-}C_6H_5CH_3)_2Ti^+$ occurs via the elimination of toluene giving the ion $h^6\text{-}C_6H_5CH_3Ti^+$. The ion $(h^6\text{-}C_6H_6)[h^6\text{-}C_6H_4(CH_3)_2]Ti^+$ appears to break down via two pathways: in the first, xylene is eliminated to give the ion $h^6\text{-}C_6H_6Ti^+$, in the other the ion breaks down via the elimination of benzene to give the ion $[h^6\text{-}C_6H_4(CH_3)_2]Ti^+$.

These data strongly suggest that the rearrangements described above are analogous to that of $(h^5\text{-}C_5H_5)(h^7\text{-}C_7H_7)V$, the ion $(h^5\text{-}C_5H_5)(h^7\text{-}C_7H_7)Ti^+$ rearranging to $(h^6\text{-}C_6H_6)_2Ti^+$ and the $C_6H_6Ti^+$ ions arising exclusively from fragmentation of $(h^6\text{-}C_6H_6)_2Ti^+$.

In the mass spectra of compounds containing a methyl substituent in the seven-membered ring, elimination of a C_2H_4 fragment from the parent ions $C_{13}H_{14}Ti^+$ and $C_{14}H_{16}Ti^+$ was also observed, yielding the ions $C_{11}H_{10}Ti^+$ and $C_{12}H_{12}Ti^+$ respectively. It is likely, that the seven-membered ring breaks down. This type of degradation was not observed in the spectra of the compounds with unsubstituted C_7H_7 rings. In all probability the methylcycloheptatrienyl ring is degraded, before the parent ions rearrange to dibenzenetitanium ions.

$$\underset{(m/e\ 218)}{C_5H_5TiC_7H_6CH_3^+} \xrightarrow[m^*\ 165.5]{-C_2H_4\ (m/e\ 28)} \underset{(m/e\ 190)}{C_5H_5TiC_6H_5^+}$$

$$\underset{(m/e\ 232)}{C_5H_4CH_3TiC_7H_6CH_3^+} \xrightarrow[m^*\ 179.4]{-C_2H_4\ (m/e\ 28)} \underset{(m/e\ 204)}{C_5H_4CH_3TiC_6H_5^+}$$

In the mass spectra of the unsubstituted cyclopentadienyl ring compounds degradation of the ion $h^5\text{-}C_5H_5Ti^+$ occurs via the elimination of a C_2H_2-fragment giving the ion $C_3H_3Ti^+$

$$\underset{(m/e\ 113)}{C_5H_5Ti^+} \xrightarrow[m^*\ 67.0]{-C_2H_2\ (m/e\ 26)} \underset{(m/e\ 87)}{C_3H_3Ti^+}$$

These mass spectra show that the titanium compounds partly follow a fragmentation route in which species containing a $h^5\text{-}C_5H_5$ or a $h^7\text{-}C_7H_7$ ligand are produced, while a substantial amount of the material introduced rearranges on electron impact to dibenzenetitanium ions, before degradation occurs.

ACKNOWLEDGEMENTS

We are much indebted to Prof. Dr. F. Jellinek and Dr. H. J. de Liefde Meijer for their stimulating interest. We thank Mr. A. Kiewiet for recording the mass and NMR spectra and Drs. W. G. Visser for his assistance in the synthesis of $(h^5\text{-}C_5H_4CH_3)(h^7\text{-}C_7H_7)Ti$.

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