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DERIVATIVES OF CYCLOHEPTATRIENYLCYCLOPENTADIENYLTITANIUM

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Summary

The syntheses of the ring-substituted sandwich complexes $(h^7\text{-}C_7H_7)(h^5\text{-}R)Ti$ (R = $C_5H_4C(CH_3)_3$, $C_5H_4Si(CH_3)_3$, indenyl), $(h^7\text{-}C_7H_6C_6H_5)(h^5\text{-}C_5H_5)Ti$ and of the compound $(h^7\text{-}C_9H_9)(h^5\text{-}C_5H_5)Ti$ are described. The IR, NMR and mass spectra of the compounds are discussed.

Introduction

Our studies on Ti complexes containing an $h^7\text{-}C_7H_7$ ligand led to the isolation of the compounds $(h^7\text{-}C_7H_6R)(h^5\text{-}C_5H_4R)Ti$ (R = H, CH_3) [1-3] and $(h^7\text{-}C_7H_7)(h^5\text{-}C_7H_9)Ti$ [4]. The present paper describes the synthesis and some properties of the ring-substituted complexes $(h^7\text{-}C_7H_7)(h^5\text{-}R)Ti$ (R = $C_5H_4C(CH_3)_3$, $C_5H_4Si(CH_3)_3$, indenyl (= Ind)), $(h^7\text{-}C_7H_6C_6H_5)(h^5\text{-}C_5H_5)Ti$ and of the compound $(h^7\text{-}C_9H_9)(h^5\text{-}C_5H_5)Ti$.

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods and freed from oxygen before use by repeated degassing and saturating with nitrogen. Cycloheptatriene, indene, $TiCl_4$ and $(CH_3)_3MCl$ (M = C, Si, Ge, Sn) were used without purification. The compounds C_7H_7R [5,6] (R = 7-C_6H_5, 3-OCH_3, 7-CN), $(C_5H_5)TiCl_3$ [7], $(C_5H_5)TiCl_2$ [8], $(C_5H_5)M(CH_3)_3$ (M = C, Si, Ge, Sn) [9], $Na[C_5H_4M(CH_3)_3]$ (M = C, Si) [10], bicyclo[6.1.0]nonatriene (C_9H_{10}) [11] and lithium cyclononatetraenide (C_9H_9Li) [11,12] were prepared according to published procedures. The com-

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pounds $Na[C_5H_4M(CH_3)_3]$ could not be obtained for M = Ge, Sn. The compounds $(h^5\text{-R})TiCl_3$ (R = $C_5H_4C(CH_3)_3$, $C_5H_4Si(CH_3)_3$, Ind) were prepared by reaction of the appropriate sodium salt with a threefold excess of $TiCl_4$ in boiling xylene. They were isolated by sublimation and purified by recrystallization from pentane. Elemental analyses were carried out at the Analytical Department of this University under the supervision of Mr. A.F. Hamminga.

Mass spectra were run on an AEI MS9 mass spectrometer. Operating conditions: energy 70 eV; resolution 1000; accelerating voltage 8 kV; inlet temperature ca. 140°C. The samples were introduced directly into the ion source using a metal probe. Only peaks corresponding to ^{48}Ti are listed in the Tables.

NMR spectra were recorded on a Varian A-60 high resolution instrument. TMS was used as internal standard, except for the Si-containing compounds, where C_6H_6 was used as a reference.

IR spectra were recorded on a Hitachi EPI-G spectrophotometer. The samples were examined as mulls in hexachlorobutadiene (4000-1300 cm^{-1}) and Nujol (1300-400 cm^{-1}). The IR spectrum of the compound $(h^7\text{-}C_9H_9)(h^5\text{-}C_5H_5)$-Ti could only be recorded in Nujol, since decomposition occurred in hexachlorobutadiene.

Synthesis of the compounds $(h^7\text{-}C_7H_7)(h^5\text{-R})Ti$ *and* $(h^7\text{-}C_7H_6R')(h^5\text{-}C_5H_5)Ti$

The reactions were carried out as described for the synthesis of the methyl substituted compounds [2]. Purification was achieved by extraction with pentane, followed by recrystallization from this solvent and sublimation at ca. 120°C/0.1 mm Hg. Analytical data, yields and colours are summarized in Table 1.

Our attempts at syntheses of the compounds with R′ = CN, OCH_3 were not successful: for R′ = CN the starting material $(C_5H_5)TiCl_3$ was recovered and for R′ = OCH_3 only a small amount of $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_5)Ti$ was isolated.

(continued on p. 53)

TABLE 1

ANALYTICAL DATA, YIELDS AND COLOURS OF SOME SANDWICH COMPOUNDS

Compound	Found (calcd.) (%)				Yield (%)	Colour
	C	H	Si	Ti		
$(C_7H_7)(C_5H_4C(CH_3)_3)Ti$	73.90	7.85		18.37	10	blue
	73.70	7.72		18.31		
	(73.85)	(7.75)		(18.40)		
$(C_7H_7)(C_5H_4Si(CH_3)_3)Ti$	65.88	7.43	10.04	17.24	10	blue
	65.86	7.49	10.03	17.10		
	(65.21)	(7.29)	(10.17)	(17.33)		
$(C_7H_7)(Ind)Ti$	74.94	5.82		18.80	4	green
	74.88	5.81		18.59		
	(75.60)	(5.55)		(18.85)		
$(C_7H_6C_6H_5)(C_5H_5)Ti$	77.05	5.59		16.84	18	green
	76.98	5.91		16.79		
	(77.15)	(5.76)		(17.09)		
$(C_9H_9)(C_5H_5)Ti$	73.59	6.40		20.13	13	green
	73.26	6.36		20.34		
	(73.06)	(6.13)		(20.81)		

TABLE 2

^{1}H NMR DATA OF THE COMPOUNDS $(h^7\text{-}C_7H_7)(h^5\text{-}R)Ti$ AND $(h^7\text{-}C_7H_6R')(h^5\text{-}C_5H_5)Ti^{a,b}$

Compound	Solvent	δ C(7)-ring	δ C(5)-ring	δ substituent
R = $C_5H_4C(CH_3)_3$	C_6D_6	5.47 s (7)	4.93 m (4)	1.03 s (9)
R = $C_5H_4Si(CH_3)_3$	C_6D_6	5.48 s (7)	5.15 m (4)	0.16 s (9)
R = Ind	C_6D_6	5.27 s (7)	5.12 d (2)	6.72 m (2)
			5.32 t (1)	7.18 m^c
R' = C_6H_5	C_6D_6	5.95 m (2)	4.94 s (5)	7.65 m (2)
		5.50 m (4)		7.25 m (3)
	CS_2	6.06 m (2)	5.10 s (5)	7.92 m (2)
		5.77 m (4)		7.47 m (3)

[a] Multiplicity: s = singlet, d doublet, t triplet, m multiplet. [b] Relative intensities between brackets. [c] Integration not reliable due to overlap with the signal of benzene.

TABLE 3

MASS SPECTRUM OF $(h^7\text{-}C_7H_7)(h^5\text{-}Ind)Ti$

m/e	Rel. int. (%)	Ion	*m/e*	Rel. int. (%)	Ion
254	100	$C_{16}H_{14}Ti^+$	126	19	$C_6H_6Ti^+$
176	31	$C_{10}H_8Ti^+$	124	8	$C_6H_4Ti^+$
174	21	$C_{10}H_6Ti^+$	116	7	$C_9H_8{}^+$
163	8	$C_9H_7Ti^+$	115	7	$C_9H_7{}^+$
161	6	$C_9H_5Ti^+$	113	9	$C_5H_5Ti^+$
139	5	$C_7H_7Ti^+$	91	12	$C_7H_7{}^+$
137	9	$C_7H_5Ti^+$	48	32	Ti^+

Metastable peaks:

122 $C_{16}H_{14}Ti^+ \rightarrow C_{10}H_8Ti^+$

62 $C_{16}H_{14}Ti^+ \rightarrow C_6H_6Ti^+$

TABLE 4

MASS SPECTRUM OF $(h^7\text{-}C_7H_6C_6H_5)(h^5\text{-}C_5H_5)Ti$

m/e	Rel. int. (%)	Ion	*m/e*	Rel. int. (%)	Ion
280	100	$C_{18}H_{16}Ti^+$	113	12	$C_5H_5Ti^+$
202	27	$C_{12}H_{10}Ti^+$	98	2	$C_4H_2Ti^+$
200	21	$C_{12}H_8Ti^+$	91	1	$C_7H_7{}^+$
178	2	$C_{10}H_{10}Ti^+$	87	4	$C_3H_3Ti^+$
174	5	$C_{10}H_6Ti^+$	86	2	$C_3H_2Ti^+$
168	6	$C_9H_{12}Ti^+$	85	2	C_3HTi^+
167	8	$C_9H_{11}Ti^+$	78	1	$C_6H_6{}^+$
165	3	$C_9H_9Ti^+$	73	3	C_2HTi^+
163	2	$C_9H_7Ti^+$	66	3	$C_5H_6{}^+$
161	2	$C_9H_5Ti^+$	65	13	$C_5H_5{}^+$
154	3	$C_8H_{10}Ti^+$	63	2	$C_5H_3{}^+$
153	2	$C_8H_9Ti^+$	51	2	$C_4H_3{}^+$
152	3	$C_8H_8Ti^+$	50	2	$C_4H_2{}^+$
150	3	$C_8H_6Ti^+$	48	11	Ti^+
140	2	$C_{18}H_{16}Ti^{++}$	40	2	$C_3H_4{}^+$
126	10	$C_6H_6Ti^+$	39	4	$C_3H_3{}^+$
124	7	$C_6H_4Ti^+$			

Metastable peaks:

198	$C_{12}H_{10}Ti^+ \rightarrow C_{12}H_8Ti^+$	76	$C_{12}H_{10}Ti^+ \rightarrow C_6H_4Ti^+$
146	$C_{18}H_{16}Ti^+ \rightarrow C_{12}H_{10}Ti^+$	56	$C_{18}H_{16}Ti^+ \rightarrow C_6H_6Ti^+$

TABLE 5

MASS SPECTRUM OF $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_4C(CH_3)_3)Ti$

m/e	Rel. int. (%)	Ion	*m/e*	Rel. int. (%)	Ion
260	100	$C_{16}H_{20}Ti^+$	130	5	$C_{16}H_{20}Ti^{++}$
245	38	$C_{15}H_{17}Ti^+$	126	19	$C_6H_6Ti^+$
241	7	$C_{15}H_{13}Ti^+$	122.5	7	$C_{15}H_{17}Ti^{++}$
218	3	$C_{13}H_{14}Ti^+$	113	17	$C_5H_5Ti^+$
217	9	$C_{13}H_{13}Ti^+$	108.5	2	$C_{13}H_{13}Ti^{++}$
215	3	$C_{13}H_{11}Ti^+$	99	3	$C_4H_3Ti^+$
204	3	$C_{12}H_{12}Ti^+$	98	3	$C_4H_2Ti^+$
202	3	$C_{12}H_{10}Ti^+$	91	15	$C_7H_7^+$
191	2	$C_{11}H_{11}Ti^+$	87	9	$C_3H_3Ti^+$
178	2	$C_{10}H_{10}Ti^+$	86	6	$C_3H_2Ti^+$
176	2	$C_{10}H_8Ti^+$	85	3	C_3HTi^+
166	13	$C_9H_{10}Ti^+$	78	2	$C_6H_6^+$
163	13	$C_9H_7Ti^+$	73	5	C_2HTi^+
153	18	$C_8H_9Ti^+$	65	5	$C_5H_5^+$
151	14	$C_8H_7Ti^+$	48	12	Ti^+
150	19	$C_8H_6Ti^+$	41	4	$C_3H_5^+$
139	20	$C_7H_7Ti^+$	39	3	$C_3H_3^+$
137	26	$C_7H_5Ti^+$			

Metastable peaks:

231	$C_{16}H_{20}Ti^+ \rightarrow C_{15}H_{17}Ti^+$	96	$C_{15}H_{17}Ti^+ \rightarrow C_8H_9Ti^+$
192	$C_{15}H_{13}Ti^+ \rightarrow C_{13}H_{11}Ti^+$ $C_{15}H_{17}Ti^+ \rightarrow C_{13}H_{13}Ti^+$	90	$C_{13}H_{13}Ti^+ \rightarrow C_7H_7Ti^+$
181	$C_{16}H_{20}Ti^+ \rightarrow C_{13}H_{13}Ti^+$	78	$C_{12}H_{12}Ti^+ \rightarrow C_6H_6Ti^+$
106	$C_{16}H_{20}Ti^+ \rightarrow C_9H_{10}Ti^+$ $C_{13}H_{11}Ti^+ \rightarrow C_8H_7Ti^+$		

TABLE 6

MASS SPECTRUM OF $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_4Si(CH_3)_3)Ti$

m/e	Rel. int. (%)	Ion	*m/e*	Rel. int. (%)	Ion
276	100	$SiC_{15}H_{20}Ti^+$	130.5	10	$SiC_{14}H_{17}Ti^{++}$
261	9	$SiC_{14}H_{17}Ti^+$	126	9	$C_6H_6Ti^+$
257	1	$SiC_{14}H_{13}Ti^+$	118	1	$SiC_3H_6Ti^+$
234	2	$SiC_{12}H_{14}Ti^+$	116.5	1	$SiC_{12}H_{13}Ti^{++}$
233	2	$SiC_{12}H_{13}Ti^+$	113	4	$C_5H_5Ti^+$
215	1	$C_{13}H_{11}Ti^+$	92	2	$SiC_5H_4^+$
204	8	$C_{12}H_{12}Ti^+$	91	6	$C_7H_7^+$
		$SiC_{10}H_8Ti^+$	87	2	$C_3H_3Ti^+$
202	1	$C_{12}H_{10}Ti^+$	86	2	$C_3H_2Ti^+$
196	8	$SiC_9H_{12}Ti^+$	85	1	C_3HTi^+
194	2	$SiC_9H_{10}Ti^+$	78	2	$C_6H_6^+$
192	2	$SiC_9H_8Ti^+$	73	9	C_2HTi^+
180	2	$SiC_8H_8Ti^+$			$SiC_3H_9^+$
178	2	$C_{10}H_{10}Ti^+$	66	1	$SiC_3H_2^+$
		$SiC_8H_6Ti^+$	65	2	$C_5H_5^+$
168	3	$SiC_7H_8Ti^+$	48	5	Ti^+
166	3	$C_9H_{10}Ti^+$	45	1	$SiCH_5^+$
		$SiC_7H_6Ti^+$	44	2	$SiCH_4^+$
165	2	$SiC_7H_5Ti^+$	43	1	$SiCH_3^+$
153	3	$C_8H_9Ti^+$			
		$SiC_6H_5Ti^+$	40	4	SiC^+
140	3	$SiC_5H_4Ti^+$			$C_3H_4^+$
139	1	$C_7H_7Ti^+$	39	2	$C_3H_3^+$
138	3	$SiC_{15}H_{20}Ti^{++}$			
137	1	$C_7H_5Ti^+$			

Metastable peaks:

247	$SiC_{15}H_{20}Ti^+ \rightarrow SiC_{14}H_{17}Ti^+$	142	$SiC_9H_{10}Ti^+ \rightarrow SiC_7H_6Ti^+$
212	$SiC_{14}H_{17}Ti^+ \rightarrow SiC_{12}H_{15}Ti^+$	78	$C_{12}H_{12}Ti^+ \rightarrow C_6H_6Ti^+$
192	$SiC_9H_{12}Ti^+ \rightarrow SiC_9H_{10}Ti^+$		

Synthesis of the compound $(h^7\text{-}C_9H_9)(h^5\text{-}C_5H_5)Ti$

To a well-stirred suspension of $(C_5H_5)TiCl_3$ (1.98 g, 9.0 mmol) in 50 ml of THF, a solution of C_9H_9Li (26 mmol) in 20 ml of THF was slowly added at —20°C. During the addition of C_9H_9Li the colour of the reaction mixture changed to green. After stirring for three hours at room temperature, the solvent was removed under reduced pressure. The compound was purified by recrystallization from pentane. Analytical data and yields are given in Table 1.

The compound $(h^7\text{-}C_9H_9)(h^5\text{-}C_5H_5)Ti$ was also prepared by reaction of $(C_5H_5)TiCl_2$ with 2 equivalents of C_9H_9Li. Attempted synthesis by reaction of $(C_5H_5)TiCl_3$ with 3 equivalents of i-C_3H_7MgBr in the presence of C_9H_{10} failed; the products obtained from the reaction mixture could not be identified.

Results and discussion

In a previous paper we described the compound $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_5)Ti$ [1]. The proposed sandwich structure of the compound has been confirmed by X-ray analysis [3]. The properties of the ring-substituted compounds $(h^7\text{-}C_7H_7)(h^5\text{-}R)Ti$ and $(h^7\text{-}C_7H_6C_6H_5)(h^5\text{-}C_5H_5)Ti$ indicate that they have analogous structures. Their IR spectra (Fig. 1b-e) show that the absorption bands of the unsubstituted rings are hardly changed whereas those of the substituted rings are. The NMR spectra (Table 2) show that the protons of the unsubstituted rings are equivalent as are the methyl protons of the $(CH_3)_3C$— and $(CH_3)_3Si$— groups. The protons of the substituted rings give rise to multiplets and the protons of the five-membered ring of $(h^7\text{-}C_7H_7)(h^5\text{-}Ind)Ti$ to a doublet and a triplet, as expected.

The mass spectra of the compounds $(h^7\text{-}C_7H_6R)(h^5\text{-}C_5H_4R)Ti$ ($R = H, CH_3$) indicate that substantial proportions of the compounds rearrange to ions of dibenzenetitanium derivatives upon electron impact [2]. This rearrangement occurs by transfer of a CH or CR fragment from the seven- to the five-membered ring. A similar rearrangement is observed in the mass spectra of the complexes $(h^7\text{-}C_7H_7)(h^5\text{-}Ind)Ti$ (Table 3) and $(h^5\text{-}C_7H_6C_6H_5)(h^5\text{-}C_5H_5)Ti$ (Table 4). Migration of a CH fragment from the seven- to the five-membered ring of the indenyl group in $(h^7\text{-}C_7H_7)(h^5\text{-}Ind)Ti^+$ gives the benzene—naphthalene—titanium ion, $(C_6H_6)(C_{10}H_8)Ti^+$. This ion appears to break down either by loss of a benzene fragment to give the naphthalene—titanium ion, $(C_{10}H_8)Ti^+$, or by loss of a naphthalene fragment giving the benzene—titanium ion, $(C_6H_6)Ti^+$.

The mass spectrum of the compound $(h^7\text{-}C_7H_6C_6H_5)(h^5\text{-}C_5H_5)Ti$ shows the benzene—diphenyl—titanium ion $(C_6H_6)(C_6H_5)_2Ti^+$, formed by migration of either a CH or a CC_6H_5 fragment from the seven- to the five-membered ring. This ion breaks down either by loss of benzene to give the diphenyl—titanium ion, $(C_6H_5)_2Ti^+$, or by loss of a diphenyl group resulting in the benzene—titanium ion, $(C_6H_6)Ti^+$. A similar rearrangement could not be established with certainty in the mass spectra of the complexes $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_4R)Ti$ ($R = C(CH_3)_3$, $Si(CH_3)_3$) (Table 5 and 6). The ions $(C_6H_5R)Ti^+$ and $C_6H_5R^+$ are not observed in these spectra. The presence of the ion $C_{12}H_{12}Ti^+$ in both spectra and the break-down of this ion by loss of C_6H_6 to give the ion $(C_6H_6)Ti^+$ indicate that a CH group migrates from the seven- to the five-membered ring. However, it is not clear whether this occurs in the parent ions or in fragmentation products like

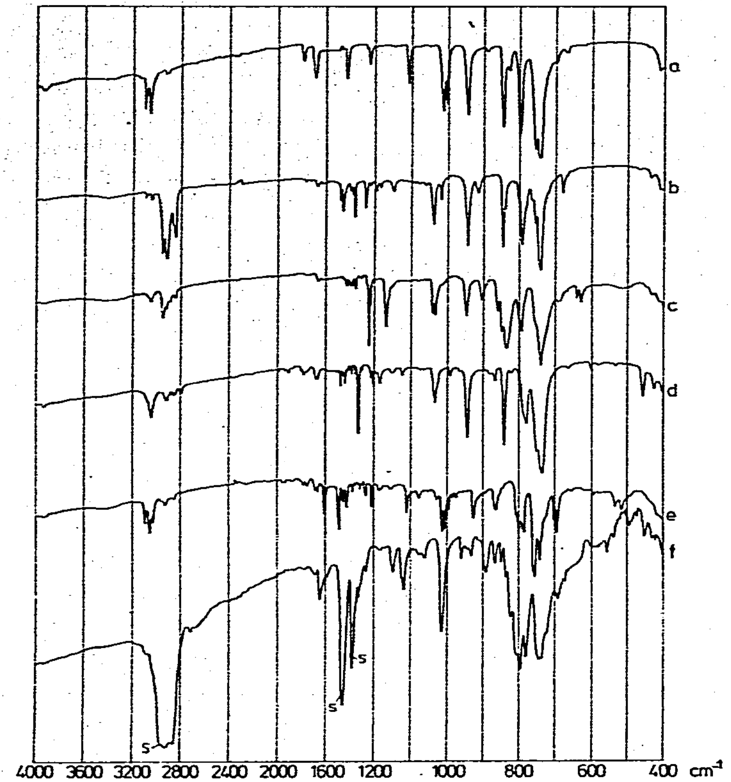

Fig. 1. Infrared spectra of (a) $C_7H_7TiC_5H_5$, (b) $C_7H_7TiC_5H_4C(CH_3)_3$, (c) $C_7H_7TiC_5H_4Si(CH_3)_3$, (d) C_7H_7TiInd and (e) $C_7H_6C_6H_5TiC_5H_5$ in hexachlorobutadiene (4000-1300 cm^{-1}) and Nujol (1300-400 cm^{-1}) and of (f) $C_9H_9TiC_5H_5$ in Nujol (4000-400 cm^{-1}).

$(C_7H_7)(C_5H_5)Ti^+$, which arise from the parent ions by the loss of the substituent in the five-membered ring. In view of the mass spectra of the complexes $(h^5\text{-}C_5H_4R)TiCl_3$ (R = $C(CH_3)_3$, $Si(CH_3)_3$) and the mass spectral data of the complex $[C_6H_5Si(CH_3)_3]_2Cr$ [13], the latter possibility seems to be the more likely.

By reaction of $(C_5H_5)TiCl_3$ or $(C_5H_5)TiCl_2$ with 3 or 2 equivalents of C_9H_9Li, respectively, a green diamagnetic compound was obtained which is very reactive, particularly in solution. Elemental and mass-spectral analyses indicate that the molecular formula of the compound is $C_{14}H_{14}Ti$.

The IR spectrum of the compound shows the C_5H_5 ring absorptions in the usual range (Fig. 1f). At ca. 1640 cm^{-1} a medium to strong absorption band is found, indicating the presence of a localized C=C bonding in the molecule. Further, the spectrum strongly resembles that of a sandwich compound containing a substituent in the C_7H_7 ring [2].

The NMR spectrum of the compound shows a singlet at δ 4.6 ppm with relative intensity of 5 due to the protons of the C_5H_5 ring. At δ 4.8 ppm a doublet (J = 1.2 Hz) with an intensity of 2 is found. This signal probably belongs to the protons of a non-coordinated double bond. At somewhat lower field (ca. 5.0-6.6 ppm) a number of resonances with total intensity of 7 are found.

The mass spectrum of the compound (Table 7) shows that the parent ion,

TABLE 7

MASS SPECTRUM OF $(h^7\text{-}C_9H_9)(h^5\text{-}C_5H_5)Ti$

m/e	Rel. int. (%)	Ion	m/e	Rel. int. (%)	Ion
230	100	$C_{14}H_{14}Ti^+$	117	10	$C_9H_9^+$
215	5	$C_{13}H_{11}Ti^+$	113	50	$C_5H_5Ti^+$
204	40	$C_{12}H_{12}Ti^+$	102	4	$C_8H_6^+$
178	10	$C_{10}H_{10}Ti^+$	91	6	$C_7H_7^+$
163	9	$C_9H_7Ti^+$	87	12	$C_3H_3Ti^+$
152	34	$C_8H_8Ti^+$	78	4	$C_6H_6^+$
137	5	$C_7H_7Ti^+$	48	11	Ti^+
126	16	$C_6H_6Ti^+$			

Metastable peaks:

181	$C_{14}H_{14}Ti^+ \rightarrow C_{12}H_{12}Ti^+$	84	$C_8H_8Ti^+ \rightarrow C_5H_5Ti^+$
155	$C_{12}H_{12}Ti^+ \rightarrow C_{10}H_{10}Ti^+$	78	$C_{12}H_{12}Ti^+ \rightarrow C_6H_6Ti^+$

$C_{14}H_{14}Ti^+$, breaks down by elimination of C_2H_2, giving the ion $C_{12}H_{12}Ti^+$. The fragmentation of this ion occurs via two routes. In the first route C_2H_2 is again eliminated, giving the ion $C_{10}H_{10}Ti^+$ which probably breaks down by successive elimination of C_2H_2 and C_3H_3, resulting in the ion $C_5H_5Ti^+$. In the second, more interesting, route a rearrangement of the ion $C_{12}H_{12}Ti^+$ to the ion $(C_6H_6)_2Ti^+$ occurs, which ion breaks down by elimination of C_6H_6 to give the ion $(C_6H_6)Ti^+$. As has been seen, such a rearrangement is characteristic for $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_5)Ti$ and derivatives suggesting that the C_9H_9 group acts as a *heptahapto* cyclononatetraenyl ligand.

From the combined evidence it may be concluded that $C_{14}H_{14}Ti$ is a sandwich compound, $(h^7\text{-}C_9H_9)(h^5\text{-}C_5H_5)Ti$. Only 7 of the 9 π-electrons of the C_9H_9 ring are involved in bonding to Ti, resulting in a 16-electron configuration for the metal, which is compatible with the observed diamagnetism of the compound.

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