Journal of Organometallic Chemistry, 84 (1975) 247—253

DERIVATIVES OF CYCLOOCTATETRAENECYCLOPENTADIENYLTITANIUM CONTAINING SUBSTITUENTS IN THE FIVE-MEMBERED RING

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(Received July 15th, 1974)

Summary

The syntheses of some substituted cyclooctatetraenecyclopentadienyltitanium compounds are described, viz: $(h^8\text{-}C_8H_8)(h^5\text{-}R)Ti$ with R = $C_5H_4CH_3$, $C_5H_4C(CH_3)_3$, $C_5H_4Si(CH_3)_3$, indenyl (= Ind) and fluorenyl (= Flu). The compounds have been prepared by reaction of $[(h^8\text{-}C_8H_8)TiCl{\cdot}THF]_2$ with RNa in ether solution. The paramagnetic compounds are thermally stable to ca. 350°, but they are sensitive to air and water. The IR spectra and dipole moments of the compounds are given. The mass spectra of the complexes $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)Ti$, $(h^8\text{-}C_8H_8)(h^5\text{-}Ind)Ti$ and $(h^8\text{-}C_8H_8)(h^5\text{-}Flu)Ti$ indicate weakening of the $Ti{-}h^5R$ bond-strength in this sequence.

Introduction

Our studies on the preparation of titanium complexes containing a $h^8\text{-}C_8H_8$ ligand led to the isolation of the compounds $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)Ti$ [1, 2], $(h^8\text{-}C_8H_8)(h^4\text{-}C_4Ph_4)Ti$ [3], $(h^8\text{-}C_8H_8)(h^3\text{-}allyl)Ti$ [4], $[(h^8\text{-}C_8H_8)TiCl{\cdot}THF]_2$ [5] and $[(h^8\text{-}C_8H_8)TiCl]_4$ [5]. The present paper describes the synthesis and some properties of five-ring substituted complexes $(h^8\text{-}C_8H_8)(h^5\text{-}R)Ti$ with R = $C_5H_4CH_3$, $C_5H_4C(CH_3)_3$, $C_5H_4Si(CH_3)_3$, indenyl and fluorenyl.

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods; before use they were freed from oxygen by repeated degassing and saturating with nitrogen. Commercial $TiCl_3$ and cyclooctatetraene were used without purification. Elementary analyses of C and H were carried out at the Microanalytical Department of this University under the supervision of Mr. W.M. Hazenberg; Ti was analyzed in our laboratory under the supervision of Mr. A.F. Hamminga.

TABLE 1

ANALYTICAL DATA, YIELDS AND DECOMPOSITION TEMPERATURES FOR THE COMPLEXES $(h^8\text{-}C_8H_8)(h^5\text{-}R)Ti$

R	Analysis found (calcd.) (%)			Yield (%)	Dec. temp (°C)
	C	H	Ti		
$C_5H_4CH_3$	72.46	6.56	20.91	60	355
(green)	72.60	6.71	20.90		
	(72.73)	(6.48)	(20.74)		
$C_5H_4C(CH_3)_3$	74.88	7.93	17.63	61	364
(green)	75.00	7.98	17.43		
	(74.72)	(7.75)	(17.53)		
$C_5H_4Si(CH_3)_3$	66.08	7.23	16.56	63	360
(green)	66.13	7.27	16.47		
	(66.42)	(7.32)	(16.56)		
Indenyl	76.26	5.87	17.61	77	367
(green)	76.58	5.82	17.64		
	(76.41)	(5.66)	(17.93)		
Fluorenyl	79.51	5.55	14.96	63	336
(red)	79.70	5.57	14.97		
	(79.50)	(5.40)	(15.10)		

Preparation of $(h^8\text{-}C_8H_8)(h^5\text{-}R)Ti$

The compounds were prepared by reaction of $[(h^8\text{-}C_8H_8)TiCl\cdot THF]_2$ with RNa (RLi for the fluorenyl compound) in ether solution at room temperature.

To a well-stirred suspension of $[(h^8\text{-}C_8H_8)TiCl\cdot THF]_2$ in ether one equivalent of RNa was added. The reaction mixture was stirred for 3 h. The solvent was removed under reduced pressure. The compounds were isolated by crystallization from pentane (R = $C_5H_4C(CH_3)_3$) or toluene (R = Ind, Flu) or by sublimation after extraction with pentane (R = $C_5H_4CH_3$, $C_5H_4Si(CH_3)_3$). The yields, analytical data and decomposition temperatures are summarized in Table 1. Dipole moment measurements were performed at 20° ± 0.1°C in benzene solution with a WTW dipole meter (type DM 01). Dipole moment data were calculated using the formula given by Guggenheim [6]. The dipole moments given in Table 2 are not corrected for the polarizabilities of the compounds; due to

TABLE 2

DIPOLE MOMENTS (IN D) AND MAGNETIC SUSCEPTIBILITIES (IN BM) FOR THE COMPLEXES $(h^8\text{-}C_8H_8)(h^5\text{-}R)Ti$

R	Dipole moment	μ_{eff}
C_5H_5	1.2 ± 0.1	1.60
$C_5H_4C(CH_3)_3$	1.6	
$C_5H_4Si(CH_3)_3$	1.4	1.65
Indenyl	1.4	1.63
Fluorenyl	1.4	1.60

TABLE 3

MASS SPECTRUM OF $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)Ti$

m/e	Rel. int.	Ion	*m/e*	Rel. int.	Ion
217	100	$C_{13}H_{13}Ti^+$	78	49	$C_6H_6^+$
191	17	$C_{11}H_{11}Ti^+$	73	14	C_2HTi^+
150	11	$C_8H_6Ti^+$	66	17	$C_5H_6^+$
113	74	$C_5H_5Ti^+$	65	14	$C_5H_5^+$
108.5	11	$C_{13}H_{13}Ti^{++}$	52	14	$C_4H_4^+$, $C_8H_8^{++}$
104	91	$C_8H_8^+$	51	23	$C_4H_3^+$
95.5	20	$C_{11}H_{11}Ti^{++}$	50	14	$C_4H_2^+$
91	11	$C_7H_7^+$	48	14	Ti^+
87	20	$C_3H_3Ti^+$	39	17	$C_3H_3^+$
86	14	$C_3H_2Ti^+$			

Metastable peaks:

168.1 $C_{13}H_{13}Ti^+ \xrightarrow{-C_2H_2} C_{11}H_{11}Ti^+$

66.9 $C_{11}H_{11}Ti^+ \xrightarrow{-C_6H_6} C_5H_5Ti^+$, $C_5H_5Ti^+ \xrightarrow{-C_2H_2} C_3H_3Ti^+$

58.8 $C_{13}H_{13}Ti^+ \xrightarrow{-C_8H_8} C_5H_5Ti^+$

TABLE 4

MASS SPECTRUM OF $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_4CH_3)Ti$

m/e	Rel. int.	Ion	*m/e*	Rel. int.	Ion
231	100	$C_{14}H_{15}Ti^+$	113	26	$C_5H_5Ti^+$
229	37	$C_{14}H_{13}Ti^+$	104	14	$C_8H_8^+$
217	21	$C_{13}H_{13}Ti^+$	103	10	$C_8H_7^+$
215	10	$C_{13}H_{11}Ti^+$	102.5	12	$C_{12}H_{13}Ti^{++}$
205	9	$C_{12}H_{13}Ti^+$	87	7	$C_3H_3Ti^+$
203	8	$C_{12}H_{11}Ti^+$	79	11	$C_6H_7^+$
191	7	$C_{11}H_{11}Ti^+$	78	15	$C_6H_6^+$
150	13	$C_8H_6Ti^+$	77	9	$C_6H_5^+$
128	7	$C_6H_8Ti^+$	73	10	C_2HTi^+
127	51	$C_6H_7Ti^+$	48	12	Ti^+
126	21	$C_6H_6Ti^+$	39	7	$C_3H_3^+$

Metastable peaks:

202.0 $C_{14}H_{15}Ti^+ \xrightarrow{-CH_3} C_{13}H_{12}Ti^+$

181.9 $C_{14}H_{15}Ti^+ \xrightarrow{-C_2H_2} C_{12}H_{13}Ti^+$

168.1 $C_{13}H_{13}Ti^+ \xrightarrow{-C_2H_2} C_{11}H_{11}Ti^+$

157.9 $C_{14}H_{15}Ti^+ \xrightarrow{-C_3H_4} C_{11}H_{11}Ti^+$

66.9 $C_{11}H_{11}Ti^+ \xrightarrow{-C_6H_6} C_5H_5Ti^+$; $C_5H_5Ti^+ \xrightarrow{-C_2H_2} C_3H_3Ti^+$

58.8 $C_{13}H_{13}Ti^+ \xrightarrow{-C_8H_8} C_5H_5Ti^+$

the strong absorption of the compounds in the visible range it is not possible to derive their polarizabilities from refractive indices [7].

The magnetic susceptibilities of some of the compounds between 90 K and 300 K were determined by the Faraday method. The susceptibilities given in Table 2 are corrected for diamagnetism; they correspond to one unpaired electron per molecule (calculated for spin only: μ_{eff} = 1.73 BM).

The IR spectra of the compounds (Fig. 1) were recorded using an EPI-G spectrophotometer. The samples were examined as mulls in hexachlorobutadiene or Voltalef 3 S oil (4000-1200 cm^{-1}) and Nujol (1200-400 cm^{-1}) between KBr discs.

The mass spectra (Tables 3-8) were run on an AEI MS 9 mass spectrometer. Operating conditions: energy 70 eV; resolution 1000; accelerating voltage 8 kV; inlet temperature ca. 130°. The samples were introduced directly into the ion source using a metal probe. No ions were observed with *m/e* larger than the parent ion. The groups of peaks assigned to Ti containing ions showed the normal isotopic distribution of titanium; only peaks corresponding to ^{48}Ti are

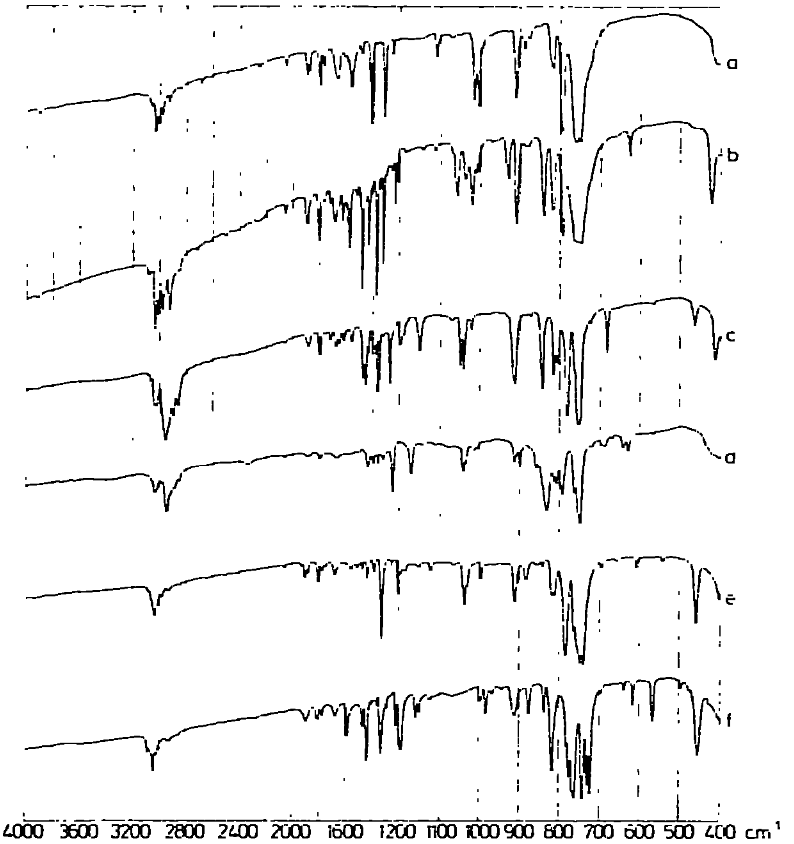

Fig. 1. Infrared spectra of. (a) $C_8H_8TiC_5H_5$, (b) $C_8H_8TiC_5H_4CH_3$, (c) $C_8H_8TiC_5H_4C(CH_3)_3$, (d) $C_8H_8TiC_5H_4Si(CH_3)_3$, (e) C_8H_8TiInd and (f) C_8H_8TiFlu. Spectra (c) and (d) were recorded in Voltalef 3 S oil (4000-1300 cm^{-1})

TABLE 5

MASS SPECTRUM OF (h^8-C_8H_8)(h^5-$C_5H_4C(CH_3)_3$)Ti

m/e	Rel. int.	Ion	*m/e*	Rel. int.	Ion
273	100	$C_{17}H_{21}Ti^+$	137	2	$C_7H_5Ti^+$
257	29	$C_{16}H_{17}Ti^+$	129	3	$C_6H_9Ti^+$: $C_{16}H_{18}Ti^{++}$
215	5	$C_{13}H_{11}Ti^+$	115	5	$C_9H_7^+$
153	6	$C_8H_9Ti^+$	114	6	$C_9H_6^+$
152	7	$C_8H_8Ti^+$	113	3	$C_5H_5Ti^+$
151	5	$C_8H_7Ti^+$	104	6	$C_8H_8^+$
150	8	$C_8H_6Ti^+$	78	4	$C_6H_6^+$
138	4	$C_7H_6Ti^+$			

Metastable peak·

243.8 $C_{17}H_{21}Ti^+ \xrightarrow{-CH_3} C_{16}H_{18}Ti^+$

listed in the Tables. The relative intensities are uncorrected. Metastable peaks observed in the spectra are included in the Tables.

Results and discussion

The reaction of $[(h^8\text{-}C_8H_8)TiCl\cdot THF]_2$ with RNa (R = C_5H_5, $C_5H_4CH_3$, $C_5H_4C(CH_3)_3$, $C_5H_4Si(CH_3)_3$, indenyl or fluorenyl) in ether gives the complexes (h^8-C_8H_8)(h^5-R)Ti. The compounds are thermally stable. Differential thermal analysis (heating rate 4°/min) (Table 1), shows that the compounds decompose at ca. 350°. The complexes are sensitive to air and water.

The mass spectra of the compounds (h^8-C_8H_8)(h^5-C_5H_5)Ti, (h^5-C_8H_8)(h^5-Ind)Ti and (h^8-C_8H_8)(h^5-Flu)Ti show, that the ratio $I(C_8H_8Ti^+)/I(h^5\text{-}RTi^+)$ increases in the order given. This indicates that the strength of the bond between titanium and the pentahapto ligand decreases in the same order, in agreement with data given

TABLE 6

MASS SPECTRUM OF (h^8-C_8H_8)(h^5-$C_5H_4Si(CH_3)_3$)Ti

m/e	Rel. int.	Ion	*m/e*	Rel. int.	Ion
289	100	$C_{16}H_{21}SiTi^+$	150	10	$C_8H_6Ti^+$
215	14	$C_{13}H_{11}Ti^+$	140	7	$C_5H_4SiTi^+$
185	4	$C_8H_{13}SiTi^+$	126	6	$C_6H_6Ti^+$
183	12	$C_8H_{11}SiTi^+$	124	4	$C_6H_4Ti^+$
181	11	$C_8H_9SiTi^+$	113	14	$C_5H_5Ti^+$
168	8	$C_7H_8SiTi^+$	104	6	$C_8H_8^+$
165	8	$C_7H_5SiTi^+$	78	11	$C_6H_6^+$
153	14	$C_8H_9Ti^+$	73	8	$C_3H_9Si^+$
152	7	$C_8H_8Ti^+$	48	8	Ti^+

TABLE 7

MASS SPECTRUM OF $(h^8\text{-}C_8H_8)(h^5\text{-indenyl})Ti$

m/e	Rel. int.	Ion	*m/e*	Rel. int.	Ion
267	100	$C_{17}H_{15}Ti^+$	116	50	$C_9H_8^+$
241	5	$C_{15}H_{13}Ti^+$	115	41	$C_9H_7^+$
163	54	$C_9H_7Ti^+$	113	12	$C_5H_5Ti^+$
161	21	$C_9H_5Ti^+$	104	5	$C_8H_8^+$
152	9	$C_8H_8Ti^+$	91	16	$C_7H_7^+$
150	16	$C_8H_6Ti^+$	48	5	Ti^+
137	14	$C_7H_5Ti^+$			

Metastable peaks:

217.5 $C_{17}H_{15}Ti^+ \xrightarrow{-C_2H_2} C_{15}H_{13}Ti^+$

115.1 $C_9H_7Ti^+ \xrightarrow{-C_2H_2} C_7H_5Ti^+$

by King [8] and Samuel [9]. The IR spectra of the complexes give evidence for the presence of a $h^8\text{-}C_8H_8$ ligand in the molecules; the absorption bands of the $h^8\text{-}C_8H_8$ group are observed at the usual wave numbers [1-5]. The other absorptions are due to the substituted five-membered ring. The influence of the substituents on the frequencies of the $h^8\text{-}C_8H_8$ ligand are very small. The magnetic measurements indicate that the complexes have one unpaired electron per molecule. This is in agreement with the presence of a $h^8\text{-}C_8H_8$ and a h^5-R ligand in the molecule of $(h^8\text{-}C_8H_8)(h^5\text{-R})Ti$ giving the titanium atom a 17-electron configuration.

TABLE 8

MASS SPECTRUM OF $(h^8\text{-}C_8H_8)(h^5\text{-fluorenyl})Ti$

m/e	Rel. int.	Ion	*m/e*	Rel. int.	Ion
317	100	$C_{21}H_{17}Ti^+$	124	3	$C_6H_4Ti^+$
213	14	$C_{13}H_9Ti^+$	113	8	$C_5H_5Ti^+$
211	11	$C_{13}H_7Ti^+$	104	18	$C_8H_8^+$
166	33	$C_{13}H_{10}^+$	103	10	$C_8H_7^+$
165	34	$C_{13}H_9^+$	91	5	$C_7H_7^+$
158.5	5	$C_{21}H_{17}Ti^{++}$	82.5	6	$C_{13}H_9^{++}$
152	27	$C_8H_8Ti^+$	78	10	$C_6H_6^+$
150	13	$C_8H_6Ti^+$	48	3	Ti^+
126	4	$C_6H_6Ti^+$			

Metastable peak:

267.1 $C_{21}H_{17}Ti^+ \xrightarrow{-C_2H_2} C_{19}H_{15}Ti^+$

Acknowledgements

The authors are much indebted to Prof. Dr. F. Jellinek and Dr. H.J. de Liefde Meijer for their stimulating interest and to Mr. A. Kiewiet for recording the mass spectra. This investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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