Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CYCLOPENTADIENYLCYCLOHEPTATRIENYLTITANIUM

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(Received January 10th, 1970)

SUMMARY

The complex $C_5H_5TiC_7H_7$ was prepared by reaction of $C_5H_5TiCl_3$ and i-C_3H_7MgBr in ether in the presence of an excess of C_7H_8; during the reaction nitrogen was temporarily absorbed. The new compound is thermally stable, but it is sensitive to moisture. The compound is diamagnetic; the NMR spectrum indicates that it has a sandwich structure, probably analogous to that of $C_5H_5VC_7H_7$ and the visible and infrared absorption spectra and the mass spectrum are similar to those of the latter.

INTRODUCTION

Few sandwich compounds containing a cycloheptatrienyl ring are known. King and Stone[1] described the synthesis of $C_5H_5VC_7H_7$ and the analogous compound of chromium was reported by Fischer and Breitschaft[2]. In a previous paper[3] we described the compound $C_5H_5TiC_8H_8$, and we now report the synthesis of the complex $C_5H_5TiC_7H_7$, which seems to have a sandwich structure analogous to that of $C_5H_5VC_7H_7$.

EXPERIMENTAL

All experiments were carried out in an atmosphere of purified nitrogen[4]. Solvents were purified by conventional methods and freed from oxygen by repeated degassing and saturation with nitrogen. $C_5H_5TiCl_3$[5] and $C_5H_5VC_7H_7$[1] were prepared according to published procedures. Cycloheptatriene (Aldrich) was used without further purification. Elementary analyses of C and H were carried out at the Microanalytical Department of this University under supervision of Mr. W. M. Hazenberg; titanium was analyzed at our laboratory under supervision of Drs. B. P. Knol. D.T.A. measurements were performed by Drs. J. C. Wildervanck.

Synthesis of $C_5H_5TiC_7H_7$

A solution of $C_5H_5TiCl_3$ (4.04 g, 18.4 mmoles) and C_7H_8 (6.2 g, 68 mmoles) in ether was cooled to −78° and 70 ml of a 0.81 *M* solution of i-C_3H_7MgBr in ether were added during 3 h. The colour of the mixture changed from yellow to reddish-brown. After stirring for another hour at −78°, the mixture was allowed to warm slowly to room temperature. At about −60° the colour rapidly changed to black as nitrogen was absorbed; the nitrogen absorption continued in the temperature interval between −60° and 0°, but at about 10° gas evolution set in and the colour gradually changed to green. After stirring for 12 h at room temperature the solvent was removed *in vacuo*, and the residue was washed with two portions of 100 ml of pentane. The resulting olive-coloured residue was sublimed at 125°/1 mm to give beautiful sky-blue crystals. The yield of $C_5H_5TiC_7H_7$ was 1.26 g (6.2 mmoles, 33%). (Found: C, 70.64, 70.86; H, 5.72, 5.94; Ti, 23.46, 23.47. $C_{12}H_{12}Ti$ calcd.: C, 70.61; H, 5.93; Ti, 23.47%.)

Spectra

Mass spectra of $C_5H_5TiC_7H_7$ and $C_5H_5VC_7H_7$ were recorded by Mrs. I. Rozema-Meijer with an AEI MS 9 instrument; they are given in Table 1a and 1b respectively. All peaks with relative intensities higher than 10% of that of the parent ion, $C_{12}H_{12}M^+$, are included; no peaks were observed above the value of *m/e* of the parent ion. The groups of peaks, assigned to Ti containing ions, showed the normal isotopic distribution of Ti; only peaks corresponding to ^{48}Ti are listed in Table 1a. The metastable peaks observed in the two spectra are included in Table 1.

TABLE 1

(*a*). MASS SPECTRUM OF $C_5H_5TiC_7H_7$ (*b*). MASS SPECTRUM OF $C_5H_5VC_7H_7$

Only species with ^{48}Ti are listed.

m/e	Rel. abundance[a]	Ion	*m/e*	Rel. abundance[a]	Ion
204	100	$C_{12}H_{12}Ti^+$	207	100	$C_{12}H_{12}V^+$
178	2.2	$C_{10}H_{10}Ti^+$	181	1.7	$C_{10}H_{10}V^+$
139	0.7	$C_7H_7Ti^+$	142	1.0	$C_7H_7V^+$
126	76.9	$C_6H_6Ti^+$	129	26.3	$C_6H_6V^+$
113	15.4	$C_5H_5Ti^+$	116	26.3	$C_5H_5V^+$
102	9.6	$C_{12}H_{12}Ti^{++}$	103.5	1.8	$C_{12}H_{12}V^{++}$
91	2.3	$C_7H_7^+$	91	1.0	$C_7H_7^+$; $C_3H_4V^+$
87	9.2	$C_3H_3Ti^+$	90	7.9	$C_3H_3V^+$
78	2.4	$C_6H_6^+$	78	0.8	$C_6H_6^+$; $C_2H_3V^+$
73	7.3	C_2HTi^+	76	5.5	C_2HV^+
66	2.2	$C_5H_6^+$	66	0.3	$C_5H_6^+$
65	2.1	$C_5H_5^+$	65	1.2	$C_5H_5^+$
48	34.6	Ti^+	51	44.7	V^+
39	2.3	$C_3H_3^+$	39	2.0	$C_3H_3^+$
28	19.2	$C_2H_4^+$	28	0.9	$C_2H_4^+$
26	1.4	$C_2H_2^+$	26	0.3	$C_2H_2^+$
Metastable peaks (*m**)			*Metastable peaks* (*m**)		
77.8			158.3		
67.0			80.4		
18.3			69.8		
			65.0		
			20.2		

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[a] All peaks with relative intensities higher than 10% of the parent ion are included.

IR spectra were measured by Miss A. W. Rensema with a Hitachi EPI-G spectrophotometer. The samples were embedded in discs of KBr, degassed as described previously[6]. The spectra of $C_5H_5TiC_7H_7$ and $C_5H_5VC_7H_7$ are shown in Fig. 1a and 1b respectively.

The visible absorption spectra were recorded by Miss A. W. Rensema with a Unicam SP 800 spectrophotometer. The spectra each show one maximum in cyclohexane: at λ 695 mμ for $C_5H_5TiC_7H_7$ and at λ 564 mμ for $C_5H_5VC_7H_7$.

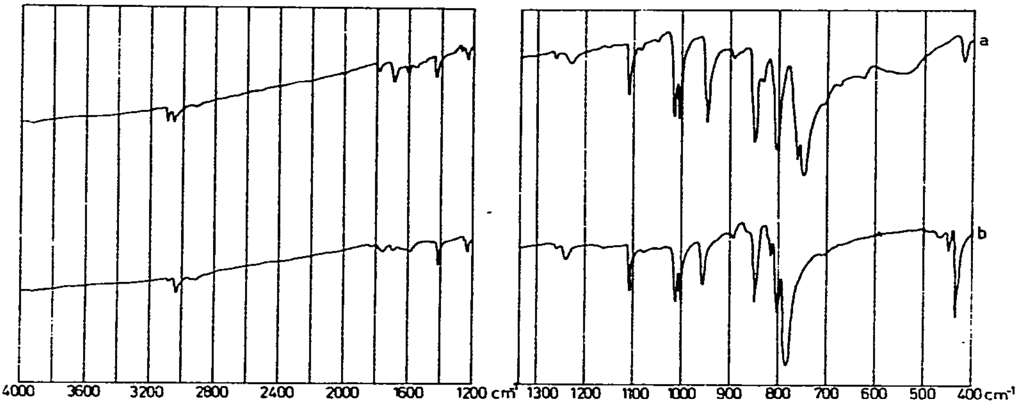

Fig. 1. Infrared spectra of (a) $C_5H_5TiC_7H_7$ and (b) $C_5H_5VC_7H_7$ in KBr discs.

Magnetic measurements were carried out by Miss A. H. C. Bruining; $C_5H_5TiC_7H_7$ was found to be diamagnetic; $C_5H_5VC_7H_7$ is paramagnetic and has one unpaired electron per molecule[1].

The NMR spectrum of $C_5H_5TiC_7H_7$ in C_6D_6 solution (40°) was measured by Mrs. I. Rozema-Meijer with a Varian A 60 high-resolution instrument. It shows two singlet signals at τ values of 4.53 and 5.03 ppm respectively; their intensities are in the ratio of 7 to 5. The chemical shifts are given relative to TMS ($\tau = 10$ ppm) as internal standard.

RESULTS AND DISCUSSION

The chemical analyses, mass spectrum, and magnetic properties of the new compound are consistent with the formula $C_5H_5TiC_7H_7$. The NMR spectrum indicates that the seven protons of the cycloheptatrienyl ring are equivalent, as are the five cyclopentadienyl protons. This shows the rings to be planar so that $C_5H_5TiC_7H_7$ probably has a structure like that of $C_5H_5VC_7H_7$, with the two rings planar and parallel[7]. Further evidence for the similarity of the structures of the titanium and vanadium compounds is provided by their IR and mass spectra. The IR spectrum of $C_5H_5TiC_7H_7$ (Fig. 1a) is very similar to the spectrum of $C_5H_5VC_7H_7$ (Fig. 1b). The cyclopentadienyl groups are π-bonded to the metal the normal vibrations of π-cyclopentadienyl ligands appearing in the usual ranges. The other absorption bands must be due to the cycloheptatrienyl ligand.

The mass spectra of $C_5H_5TiC_7H_7$ and $C_5H_5VC_7H_7$ (Table 1a and 1b resp.) show the expected analogies. Apart from the difference in the value of *m/e* of titanium and vanadium containing species, the fragmentation products are the same in the two spectra and only the relative intensities differ. The main fragmentation products are $C_6H_6M^+$, $C_5H_5M^+$, $C_3H_3M^+$, M^+, and for the titanium compound also $C_2H_4^+$. All the fragmentation products consistent with the presence of a π-C_5H_5 group in the molecule are observed. The occurrence of the fragment $C_6H_6M^+$ is noteworthy, the more so as this ion arises from the parent ion, $C_{12}H_{12}M^+$, by elimination of benzene. This is shown by metastable peaks in the two spectra: at *m/e* 77.8 (calcd.: *m/e* 77.8) for M=Ti and at *m/e* 80.4 (calcd.: *m/e* 80.4) for M=V. Fragmentation of $C_6H_6M^+$ then partly occurs by elimination of another molecule of benzene as indicated by the appearance of a metastable peak at *m/e* 18.3 (calcd.: *m/e* 18.3) and at *m/e* 20.2 (calcd.: *m/e* 20.2) for the Ti and V compound respectively.

The presence of the fragments $C_6H_6M^+$and $C_6H_6^+$ implies the formation of benzene-containing fragments from the parent ion. Ring expansion and contraction reactions are known, for example, for some chromium compounds[8-10]. In our case, however, there are no indications that the changes in ring size occur with the uncharged molecule. Differential thermal analysis measurements on the two compounds show that heat effects occur only at a much higher temperature than the temperature at which the mass spectra were recorded (130°). Moreover, no visible change was observed when the compounds were heated to 200° in a sealed glass capillary.

Fragmentation of the parent ion of the vanadium compound, $C_{12}H_{12}V^+$, partly occurs by elimination of acetylene, as is shown by a metastable peak at *m/e* 158.3 (calcd.: *m/e* 158.3). A metastable peak consistent with the elimination of C_7H_7 from $C_{12}H_{12}V^+$ is observed at *m/e* 65.0 (calcd.: *m/e* 65.0). Finally in both spectra a metastable peak is found, arising from the elimination of acetylene from the fragment $C_5H_5M^+$; for $C_5H_5Ti^+$ at *m/e* 67.0 (calcd.: *m/e* 67.0) and for $C_5H_5V^+$ at *m/e* 69.8 (calcd.: *m/e* 69.8). A partial fragmentation scheme is presented in Scheme 1.

SCHEME 1

(*a*). PARTIAL FRAGMENTATION SCHEME OF $C_5H_5TiC_7H_7$

Only species with ^{48}Ti are included.

$$\underset{(m=204)}{C_{12}H_{12}Ti^+} \xrightarrow[m^*=77.8]{-C_6H_6\ (m=78)} \underset{(m=126)}{C_6H_6Ti^+} \xrightarrow[m^*=18.3]{-C_6H_6\ (m=78)} \underset{(m=48)}{Ti^+}$$

(*b*). PARTIAL FRAGMENTATION SCHEME OF $C_5H_5VC_7H_7$

$$\begin{tikzcd}
 & \underset{(m=129)}{C_6H_6V^+} \arrow[r, "-C_6H_6\ (m=78)", "m^*=20.2"'] & \underset{(m=51)}{V^+} \\
\underset{(m=207)}{C_{12}H_{12}V^+} \arrow[ur, "-C_6H_6\ (m=78)", "m^*=80.4"'] \arrow[r, "-C_2H_2\ (m=26)", "m^*=158.3"'] \arrow[dr, "-C_7H_7\ (m=91)", "m^*=65.0"'] & \underset{(m=181)}{C_{10}H_{10}V^+} & \\
 & \underset{(m=116)}{C_5H_5V^+} \arrow[r, "-C_2H_2\ (m=26)", "m^*=69.8"'] & \underset{(m=90)}{C_3H_3V^+}
\end{tikzcd}$$

$C_5H_5TiC_7H_7$ shows a high thermal stability. No decomposition was observed when the compound was heated in a sealed glass capillary up to 320°; at this temperature the compound sublimed.

The absorption of nitrogen, observed during the preparation of $C_5H_5TiC_7H_7$, is not unusual in reaction mixtures containing titanium compounds and reducing agents for instance Grignard reagents. Since the well-known observation of Vol'pin and Shur[11] this type of reaction has received considerable attention, and many reaction mixtures containing titanium in a low valence state, have been found to absorb molecular nitrogen at normal temperature and pressure[12].

ACKNOWLEDGEMENTS

The authors wish to thank Professor Dr. F. Jellinek for his stimulating interest and Dr. J. Weringa for his valuable advices concerning the mass spectra.

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