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CYCLOPENTADIENYLCYCLOOCTATETRAENETITANIUM

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SUMMARY

The complex $C_5H_5TiC_8H_8$ was prepared by reaction of $K_2C_8H_8$ with either $C_5H_5TiCl_3$, $(C_5H_5)_2TiCl_2$, or a mixture of $TiCl_4$ and C_5H_5Na in tetrahydrofuran or toluene. The new compound is thermally stable, but it is sensitive to oxygen. There is one unpaired electron per molecule. The infrared spectrum shows the C_5H_5 group and probably also the C_8H_8 group to be π-bonded to the metal. The mass spectrum has been studied and a partial fragmentation scheme is given.

INTRODUCTION

Complexes of cyclooctatetraene with transition metals of Groups IV and V were not known until recently. In 1966 Breil and Wilke[1] reported the synthesis of the complexes $Ti(C_8H_8)_2$, $Ti_2(C_8H_8)_3$ and $V(C_8H_8)_2$. This paper describes the synthesis and some properties of cyclopentadienylcyclooctatetraenetitanium, $C_5H_5TiC_8H_8$. The compound is sensitive to oxygen, but it is thermally stable and can be stored at room temperature in an inert atmosphere.

EXPERIMENTAL

General

All experiments were carried out in an atmosphere of purified argon[2]. Solvents were purified by conventional methods; they were freed from oxygen by repeated degassing and saturating with argon. Tetrahydrofuran was distilled from $LiAlH_4$ under argon. $K_2C_8H_8$ was prepared by reaction of cyclooctatetraene with a slight excess of finely divided potassium in tetrahydrofuran. After filtration the reaction mixture was cooled at −15°; the mother liquor was removed and the crystals were freed from tetrahydrofuran *in vacuo*. The other starting materials were prepared according to published procedures[3,4]. Elementary analyses of C and H were carried out at the Microanalytical Department of this laboratory under the supervision of Mr. W. M. Hazenberg; titanium was analyzed under the supervision of Drs. B. P. Knol.

Preparation starting from $C_5H_5TiCl_3$

$K_2C_8H_8$ (2.42 g, 13.3 mmole) was added to a solution of $C_5H_5TiCl_3$ (1.94 g, 8.8 mmole) in 150 ml of tetrahydrofuran. After addition of 4.4 mmole of $K_2C_8H_8$ the reaction mixture became violet; during the addition of the remaining $K_2C_8H_8$ the mixture gradually turned green. The reaction mixture was refluxed for about 15 min and the solvent was removed *in vacuo*. The residue was sublimed at 120°/0.1 mm; dark green crystals separated. The yield of $C_5H_5TiC_8H_8$ was 0.736 g (3.7 mmole, 42%). Upon heating the crystals under argon in a sealed glass capillary the compound decomposed at about 160° without melting. (Found: C, 71.73, 71.88; H, 5.84, 5.71; Ti, 21.86, 22.01. $C_{13}H_{13}Ti$ calcd.: C, 71.90; H, 6.04; Ti, 22.06%.)

Preparation starting from $(C_5H_5)_2TiCl_2$

$K_2C_8H_8$ (479 mg, 2.6 mmole) was added to a solution of $(C_5H_5)_2TiCl_2$ (622 mg, 2.5 mmole) in 30 ml of tetrahydrofuran. The reaction mixture was refluxed for a few minutes and the solvent was removed *in vacuo*. The residue was extracted with 25 ml of boiling toluene. After evaporation of the solvent the residue was sublimed as described above; the yield of $C_5H_5TiC_8H_8$ was 120 mg (0.55 mmole, 22%).

Preparation starting from $TiCl_4$

To a solution of $TiCl_4$ (803 mg, 5.2 mmole) in 35 ml of toluene were added C_5H_5Na (430 mg, 5.2 mmole) and $K_2C_8H_8$ (1429 mg, 7.8 mmole). The reaction mixture was refluxed for 1 h. After filtration the green solution was cooled at −15°. Green crystals of $C_5H_5TiC_8H_8$ separated. The yield was 680 mg (3.1 mmole, 60%).

Spectra

The mass spectrum of $C_5H_5TiC_8H_8$ was recorded by Mrs. I. Rozema-Meijer by means of an AEI MS 9 instrument. Peaks with relative intensities higher than 10% of that of the parent ion $C_{13}H_{13}Ti^+$ are listed in Table 1; 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 the peaks corresponding to ^{48}Ti are included in Table 1. Metastable peaks were observed at *m/e* = 168.1, 66.9 and 58.8.

Infrared spectra were measured by Drs. F. W. Siegert by means of a HITACHI EPI-G spectrophotometer; the samples were embedded in discs of KBr, that had been degassed as described previously[5]. The spectrum of $C_5H_5TiC_8H_8$ is given in Fig. 1a; for comparison the spectrum of $C_5H_5TiCl_3$ is given in Fig. 1b.

The magnetic susceptibility of $C_5H_5TiC_8H_8$ between 90° K and 300° K was

TABLE 1

MASS SPECTRUM OF $C_5H_5TiC_8H_8$

m/e	Rel. abundance	Ion	*m/e*	Rel. abundance	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	$C_{13}H_{13}Ti^{2+}$	52	14	$C_4H_4^+$, $C_8H_8^{2+}$
104	91	$C_8H_8^+$	51	23	$C_4H_3^+$
95.5	20	$C_{11}H_{11}Ti^{2+}$	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	$C_3H_2Ti^+$	28	14	$C_2H_4^+$

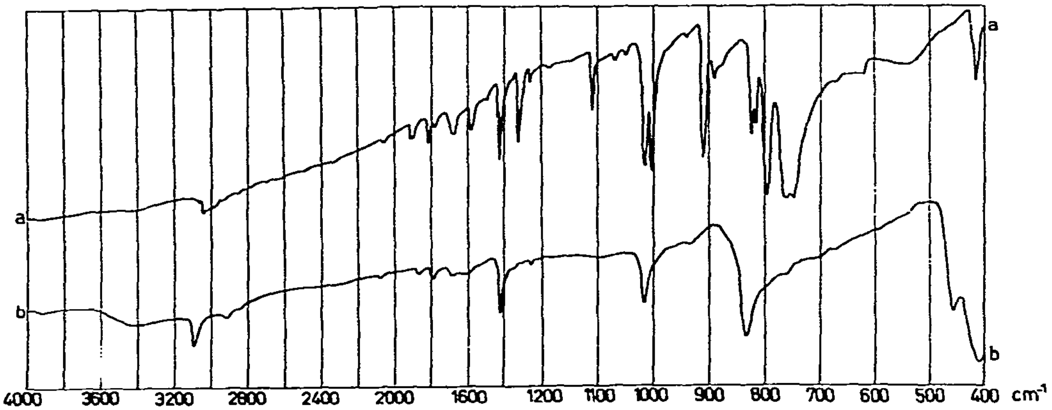


Fig. 1. Infrared spectra of (a) $C_5H_5TiC_8H_8$ and (b) $C_5H_5TiCl_3$ in KBr discs.

determined by Miss A.H.C. Bruining by the Faraday method. In the whole temperature range μ_{eff} was 1.60 ± 0.01 B.M. (corrected for induced diamagnetism) corresponding to one unpaired electron (calculated for spin only: $\mu_{eff} = 1.73$ B.M.).

DISCUSSION

The chemical analyses, the mass spectrum and the magnetic properties of the new compound are in agreement with the formula $C_5H_5TiC_8H_8$.

The infrared spectrum of the compound (Fig. 1a) indicates that the cyclopentadienyl group is π-bonded to the metal; the normal vibrations of π-cyclopentadienyl ligands are observed in the usual ranges[6] (*cf.* Fig. 1a and 1b). The other infrared absorption bands are presumably due to the cyclooctatetraene ligand.

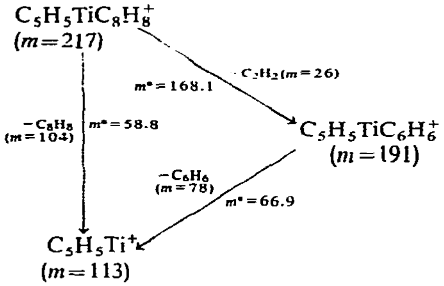
The absence of absorptions in the range 1600–1650 cm^{-1} indicates that no localized C=C bonds are present in the molecule; it seems probable therefore, that the cyclooctatetraene ligand is also π-bonded to the metal. Apart from this, the infrared spectrum of $C_5H_5TiC_8H_8$ differs from the spectra reported for other cyclooctatetraene complexes of transition metals, and we do not wish to speculate at present on the conformation of the cyclooctatetraene ligand. It is hoped, that X-ray analysis will give the necessary information.

The mass spectrum of $C_5H_5TiC_8H_8$ (Table 1) shows the main fragmentation products to be $C_5H_5Ti^+$ and $C_8H_8^+$, indicating, that the C_8H_8 ligand is lost more readily than the C_5H_5 group. All the fragmentation products consistent with the presence of a π-C_5H_5M group in the molecule[7] are observed. Mass-spectrographic data of complexes containing a C_8H_8M group are not numerous, but the main fragmentation products arising from $U(C_8H_8)_2$[8] are consistent with our data.

The occurrence of the fragments $C_{11}H_{11}Ti^+$ and $C_{11}H_{11}Ti^{2+}$ indicates that fragmentation of $C_{13}H_{13}Ti^+$ partly occurs by elimination of acetylene; this is in agreement with the observation of a metastable peak at $m/e = 168.1$ (calcd. $m/e = 168.1$ for ^{48}Ti) in the mass spectrum. The fragment $C_{11}H_{11}Ti^+$ loses C_6H_6 to give $C_5H_5Ti^+$, as is shown by the metastable peak at $m/e = 66.9$ (calcd. $m/e = 66.9$); this indicates that the fragment $C_{11}H_{11}Ti^+$ is to be regarded as $C_5H_5TiC_6H_6^+$ and that the acetylene group was eliminated from the cyclooctatetraene ligand. Direct fragmentation of

SCHEME 1

PARTIAL FRAGMENTATION SCHEME OF $C_5H_5TiC_8H_8$; ONLY SPECIES WITH ^{48}Ti ARE GIVEN



$C_5H_5TiC_8H_8^+$ to $C_5H_5Ti^+$ also occurs, as is shown by the observation of a metastable peak at $m/e = 58.8$ (calcd. $m/e = 58.8$). A partial fragmentation scheme is presented in Scheme 1.

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REFERENCES

1 H. Breil and G. Wilke, *Angew. Chem.*, 78 (1966) 20.
2 H. J. de Liefde Meijer, M. J. Janssen and G. J. M. van der Kerk, *Studies in the Organic Chemistry of Vanadium*, Inst. for Org. Chem. T.N.O., Utrecht, 1963.
3 C. Sloan and W. A. Barber, *J. Amer. Chem. Soc.*, 81 (1959) 1364.
4 G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, 76 (1954) 4281.
5 H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, 8 (1967) 115.
6 H. P. Fritz and H. Keller, *Chem. Ber.*, 95 (1962) 158.
7 R. B. King, *J. Amer. Chem. Soc.*, 90 (1968) 1417.
8 A. Streitwieser Jr. and U. Müller-Westerhoff, *J. Amer. Chem. Soc.*, 90 (1968) 7364.