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CYCLOOCTATETRAENE(TETRAPHENYLCYCLOBUTADIENE)-TITANIUM

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SUMMARY

The compound $C_8H_8TiC_4(C_6H_5)_4$ has been prepared by reaction of $TiCl_3$ and i-C_3H_7MgBr in ether in the presence of cyclooctatetraene and diphenylacetylene. The green compound is diamagnetic and stable in the air in the solid state. IR, NMR and mass spectra show the presence of a π-bonded tetraphenylcyclobutadiene and a π-bonded cyclooctatetraene ligand in the complex. A by-product in the synthesis is hexaphenylbenzene.

INTRODUCTION

Complexes of cyclooctatetraene with transition metals of Groups IV and V have been known for some years. Breil and Wilke[1] described the synthesis of the complexes $(C_8H_8)_3Ti_2$ and $(C_8H_8)_2M$ with M = Ti, V, and the compounds with M = Zr, Nb have also been prepared[2]. Lehmkuhl and Mehler[3] reported the electrochemical synthesis of the compounds $[C_8H_8TiCl]_2$ and $C_8H_8TiCl{\cdot}THF$. In previous papers we described the sandwich compound $C_8H_8TiC_5H_5$[4] and the π-1-methylallyl complex $C_8H_8TiC_3H_4CH_3$[5]. We now report the synthesis and some properties of cyclooctatetraene(tetraphenylcyclobutadiene)titanium. This compound, which probably has a sandwich structure, is the first cyclobutadiene derivative of titanium.

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 $TiCl_3$ (Stauffer), cyclooctatetraene (EGA) and diphenylacetylene (EGA) were used without purification. 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 $C_8H_8TiC_4(C_6H_5)_4$

$TiCl_3$ (3.20 g, 20.7 mmoles) and i-C_3H_7MgBr (62 mmoles in 80 ml of ether) were added successively to a cooled (−78°) solution of diphenylacetylene (6.90 g, 38.7 mmoles) and cyclooctatetraene (2.1 g, 20 mmoles) in 150 ml of ether. The mixture was stirred and allowed to warm slowly to room temperature. The solvent was removed by distillation and the residue was dried at 80°/0.1 mmHg for 8 h. The resulting reddish-brown material was extracted with toluene. The green toluene solution was evaporated until dry. Toluene (25 ml) was added, the green solution was filtered and cooled to −78°. n-Pentane (100 ml) was distilled onto the toluene solution. Flocculent green material separated. After removal of the solvents the material was washed twice with 25 ml of n-pentane and dried *in vacuo*. Repeated recrystallization from hot n-heptane gave the pure compound. The residue isolated from the resulting heptane proved to be mainly hexaphenylbenzene. The yield of $C_8H_8TiC_4(C_6H_5)_4$ was 1.20 g (2.36 mmoles, 11.4%).

(Found: C, 85.34, 85.51; H, 5.62, 5.76; Ti, 9.49, 9.31. $C_{36}H_{28}Ti$ calcd.: C, 85.03; H, 5.55; Ti, 9.42%). The compound is thermally stable up to 300°.

Spectra

The mass spectrum was recorded on an AEI MS 9 mass spectrometer. Operating conditions: energy: 70 eV; resolution: 1000; accelerating voltage: 8 kV; inlet temperature: 200 °. The sample was introduced directly into the ion source using a

SCHEME 1

PARTIAL FRAGMENTATION SCHEME OF h^8-C_8H_8Ti-h^4-$C_4(C_6H_5)_4$

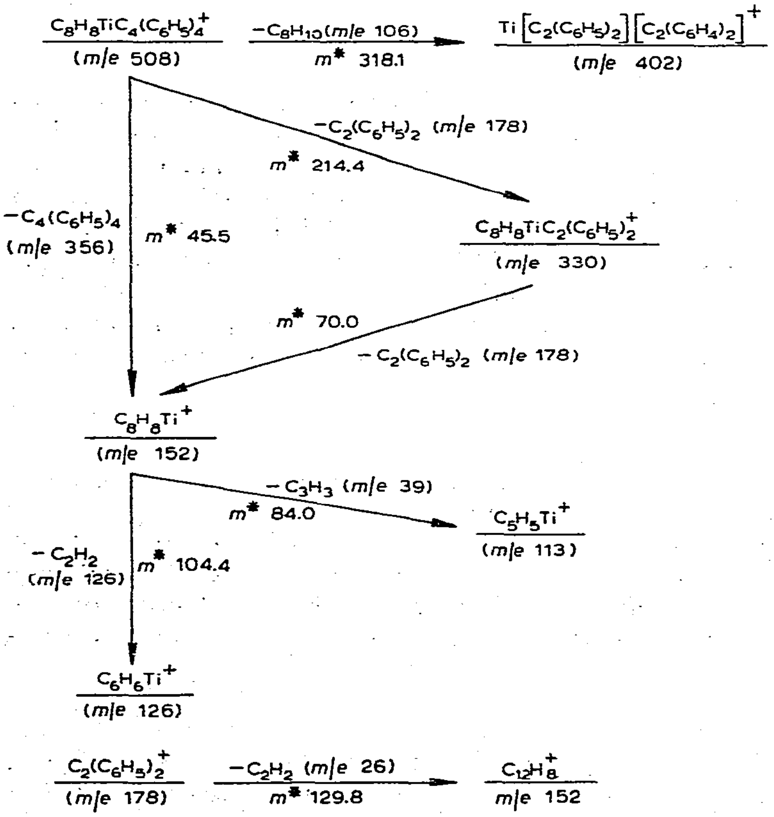


TABLE 1

MASS SPECTRUM OF h^8-C_8H_8Ti-h^4-$C_4(C_6H_5)_4$

Only ions with ^{48}Ti are listed.
Metastable peaks (m^*): 318.1, 214.4, 129.8, 104.4, 84.0, 70.0, 45.5.

m/e	*Rel. abundance*	*Ion*
508	100.0	$C_8H_8TiC_{28}H_{20}^+$
402	1.0	$C_{28}H_{18}Ti^+$
356	0.7	$C_{28}H_{20}^+$
330	1.1	$C_8H_8TiC_{14}H_{10}^+$
254	2.3	$C_8H_8TiC_{28}H_{20}^{2+}$
224	2.2	$C_{14}H_8Ti^+$
178	10.7	$C_{14}H_{10}^+$
152	66.7	$C_8H_8Ti^+$
126	4.0	$C_6H_6Ti^+$
124	4.3	$C_6H_4Ti^+$
113	3.0	$C_5H_5Ti^+$
98	1.4	$C_4H_2Ti^+$
78	0.6	$C_6H_6^+$
73	0.9	C_2HTi^+
65	0.7	$C_5H_5^+$
48	3.0	Ti^+

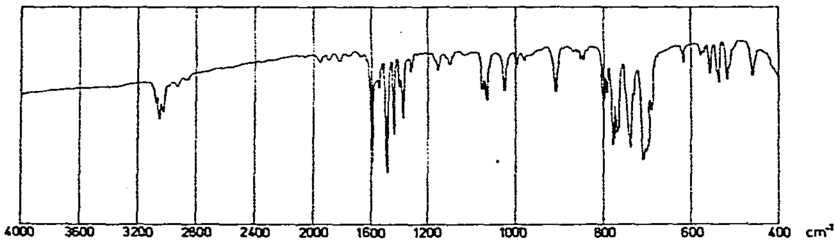


Fig. 1. IR spectrum of h^8-C_8H_8Ti-h^4-$C_4(C_6H_5)_4$.

metal probe. The data are summarized in Table 1. A partial fragmentation scheme is given in Scheme 1. No peaks 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 Ti; only peaks corresponding to ^{48}Ti are listed in Table 1. The metastable peaks in the spectrum are included in Table 1.

The IR spectrum (Fig. 1) was recorded on a Hitachi EPI G spectrophotometer. The samples were examined as mulls in hexachlorobutadiene (4000–1200 cm^{-1}) and Nujol (1200–400 cm^{-1}) between KBr discs.

The NMR spectrum in $CDCl_3$ solution (40°) was recorded with a Varian A 60 high-resolution instrument. It shows two signals: a singlet at τ 3.4 ppm and a multiplet at τ 2.65–2.90 ppm; their intensities are in the ratio of 8 to 20; the chemical shifts are given relative to TMS (τ 10 ppm) which was used as internal standard.

DISCUSSION

The reaction of $TiCl_3$ and i-C_3H_7MgBr in ether in the presence of cyclooctatetraene and diphenylacetylene (tolane) gives a green diamagnetic titanium complex together with a considerable amount of hexaphenylbenzene (at least 20% based on the initial amount of tolane). The complex is thermally stable up to 300°, and in the solid state it is stable in air at room temperature. The elemental analysis and the mass spectrum (parent peak at m/e 508) indicate that the molecular formula is $C_{36}H_{28}Ti$.

The presence of a planar h^8-C_8H_8 ligand in the compound was established by the following three observations:

(*i*) The singlet signal of 8 protons in the NMR spectrum at τ 3.4 ppm showing the equivalence of the protons of the C_8H_8 group;

(*ii*) The absorptions in the IR spectrum at about 3040, 1440, 1320, 910 and 740 cm^{-1}, which are also found in the spectra of the titanium compounds containing a planar C_8H_8 group, *viz.* h^8-C_8H_8Ti-h^5-C_5H_5[4,6] and h^8-C_8H_8Ti-h^4-1,2,3,4-C_8H_8[1,7];

(*iii*) The presence in the mass spectrum of the ion $C_8H_8Ti^+$ in a high intensity and the degradation pattern of this ion (Scheme 1), which agrees with the fragmentation pattern of the $C_8H_8Ti^+$ ion arising from the h^8-C_8H_8Ti compounds mentioned.

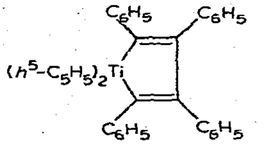
The presence of a tetraphenylcyclobutadiene ligand was shown by the following observations:

(*i*) The mass spectrum of the compound shows a degradation of the parent ion, $C_{36}H_{28}Ti^+$, by elimination of the fragment $C_2(C_6H_5)_2$ giving the ion $C_8H_8TiC_2(C_6H_5)_2{}^+$, which in turn loses another fragment $C_2(C_6H_5)_2$ to give the ion $C_8H_8Ti^+$. This two-step fragmentation route seems to be characteristic for tetraphenylcyclobutadiene ligands π-bonded to a metal. King and Efraty[8] observed a similar degradation pattern in the mass spectra of tetraphenylcyclobutadiene complexes of iron and cobalt, *viz.* h^5-C_5H_5Co-h^4-$C_4(C_6H_5)_4$, C_9H_7Co-h^4-$C_4(C_6H_5)_4$ and h^4-$C_4(C_6H_5)_4$-$Fe(CO)_3$. Also the observed one-step degradation of the parent ion by elimination of the $C_4(C_6H_5)_4$ fragment supports the presence of a cyclobutadiene ligand in the molecule.

(*ii*) The τ-value of the unresolved multiplet signal (τ 2.65–2.90 ppm) in the NMR spectrum due to the 20 phenyl protons are found in the same range as those of similar tetraphenylcyclobutadiene complexes, for instance h^5-C_5H_5Co-h^4-$C_4(C_6H_5)_4$ (τ 2.32–2.83 ppm)[9].

(*iii*) The presence of a medium to strong absorption band in the IR spectrum at about 1370 cm^{-1}. This absorption is also observed in spectra of the tetraphenylcyclobutadiene complexes h^4-$C_4(C_6H_5)_4NiBr_2$ and h^4-$C_4(C_6H_5)_4PdCl_2$. According to Fritz[10] this band is characteristic for the presence of a π bonded cyclobutadiene group.

In view of the evidence presented above it seems reasonable to regard $C_{36}H_{28}Ti$ as a sandwich complex, *viz.* h^8-C_8H_8Ti-h^4-$C_4(C_6H_5)_4$. Assuming the eight electrons of the cyclooctatetraene group and the four electrons of the tetraphenylcyclobutadiene group all to be involved in bonding the metal atom would achieve a 16 electron configuration which is compatible with the observed diamagnetism of the compound. In



the metal atom also has a 16 electron configuration. The $C_4(C_6H_5)_4$ ligand is not present as a cyclobutadiene ring. A tetraphenylcyclobutadiene configuration would cause steric hindrance between this ring and the two h^5-C_5H_5 ligands[11-14]. This steric hindrance does not occur in the new compound.

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REFERENCES

1 H. Breil and G. Wilke, *Angew. Chem.*, 78 (1966) 20.
2 H. O. van Oven and H. J. de Liefde Meijer, unpublished results.
3 H. Lehmkuhl and K. Mehler, *J. Organometal. Chem.*, 25 (1970) C44.
4 H. O. van Oven and H. J. de Liefde Meijer, *J. Organometal. Chem.*, 19 (1969) 373.
5 H. O. van Oven, H. K. Hofstee and H. J. de Liefde Meijer, *J. Organometal. Chem.*, 42 (1972) 404.
6 P. A. Kroon and R. B. Helmholdt, *J. Organometal. Chem.*, 25 (1970) 451.
7 H. Dietrich and M. Soltwisch, *Angew. Chem., Int. Ed. Engl.*, 8 (1969) 765.
8 R. B. King and A. Efraty, *Org. Mass. Spectrom.*, 3 (1970) 1233.
9 M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, 35 (1970) 3888.
10 H. P. Fritz, *Z. Naturforsch. B*, 16 (1961) 415.
11 K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jap.*, 39 (1966) 1178.
12 M. E. Vol'pin, V. A. Dubovitskii, O. V. Nogina and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, 151 (1963) 1100.
13 V. O. Reikhsfeld and K. L. Makovetskii, *Russ. Chem. Rev.*, 35 (1966) 510.
14 F. W. Siegert, Thesis, (1970), The University, Groningen, The Netherlands.