

CYCLOHEPTATRIENYL CYCLOHEPTADIENYL TITANIUM

H. O. VAN OVEN AND H. J. DE LIEFDE MELJER

Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Bloemsingel 10, Groningen (The Netherlands)

(Received March 9th, 1971)

SUMMARY

The complex $C_7H_7TiC_7H_9$ has been prepared by treatment of $TiCl_3$ with $i-C_3H_7MgBr$ in ether in the presence of an excess of cycloheptatriene. The diamagnetic compound is sensitive to oxygen and water; the NMR spectrum indicates, that the C_7H_7 ligand is a planar cycloheptatrienyl ring and the C_7H_9 ligand a cycloheptadienyl ring. The infrared and mass spectra are given.

INTRODUCTION

A number of compounds containing a planar cycloheptatrienyl ring are known, for instance $C_5H_5MC_7H_7$ ($M = Ti^1, Zr^2, V^3, Nb^2, Cr^4$). Some compounds containing a cycloheptadienyl ring have also been reported, for instance the iron complex $[(C_7H_9)Fe(CO)_3]^+[BF_4]^-$ ⁵, the cobalt complexes $R_4C_4CoC_7H_8Y$ ($R = \text{phenyl, tolyl}$; $Y = H, OH, OCH_3$)⁶, and the rhodium and iridium complexes $[M(C_5Me_5)(C_7H_9)^+][PF_6]^-$ ⁷. However, organometallic compounds containing both a cycloheptatrienyl and a cycloheptadienyl ring have not been reported previously. This paper describes the synthesis of the first compound of this type, *viz.* $C_7H_7TiC_7H_9$, and some of its properties. Investigations concerning analogous compounds of other transition metals are being undertaken.

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. Cycloheptatriene (EGA) and $TiCl_3$ (Alfa Inorganics) 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 at our laboratory under supervision of Drs. B. P. Knol.

Synthesis of $C_7H_7TiC_7H_9$

A solution of C_7H_8 (127 mmoles) in 70 ml of ether was cooled to -78° . Subsequently $TiCl_3$ (6.60 g, 43 mmoles) and $i-C_3H_7MgBr$ (138 ml of a 0.98 M solution in ether) was added. The mixture was stirred and allowed to warm slowly to room temperature. After refluxing for about 15 min the solvent was removed under reduced

TABLE 1

MASS SPECTRUM OF $C_7H_7TiC_7H_9$
Only species with ^{48}Ti are listed.

<i>m/e</i>	Rel. abundance	Ion
232	20.8	$C_{14}H_{16}Ti^+$
230	10.0	$C_{14}H_{14}Ti^+$
204	4.8	$C_{12}H_{12}Ti^+$
152	10.4	$C_8H_8Ti^+$
140	16.7	$C_7H_8Ti^+$
139	12.5	$C_7H_7Ti^+$
138	11.3	$C_7H_6Ti^+$
126	14.2	$C_6H_6Ti^+$
113	15.4	$C_5H_5Ti^+$
94	13.8	$C_7H_{10}^+$
93	26.7	$C_7H_9^+$
92	26.3	$C_7H_8^+$
91	100.0	$C_7H_7^+$
87	10.0	$C_3H_3Ti^+$
79	31.7	$C_6H_7^+$
78	16.7	$C_6H_6^+$
77	29.2	$C_6H_5^+$
66	10.8	$C_5H_6^+$
65	31.7	$C_5H_5^+$
63	10.0	$CH_3Ti^+, C_5H_3^+$
51	10.8	$H_3Ti^+, C_4H_3^+$
48	25.0	Ti^+
41	11.7	$C_3H_5^+$
39	31.7	$C_3H_3^+$

TABLE 2

PROTON NMR DATA OF SOME CYCLOHEPTADIENYL LIGANDS

Compound	Chemical shifts (τ) and multiplicity ^b					Coupling constants (Hz)	
	H _a	H _b	H _c	H _d	H _e	J _{ab}	J _{bc}
$C_7H_7TiC_7H_9$ ^{a,c}	5.69	4.31	~5.0	~8.1	~8.9	8.1	10.8
$[C_7H_9Fe(CO)_3]^+$ ^d	tt	dd	m	m	m		
	3.03	4.81	~5.15	~7.4	~8.2	6.5	9.9
$R_4C_4CoC_7H_9$ ^f	t ^e	dd	br	m	m		
	4.2	5.2	6.0	7.5	8.5		
$[(Me_5C_5)Rh(C_7H_9)]^+[PF_6]^-$ ^g	i	m	m	m	m		
	3.52	4.55	5.41		7.5-8.5	6.2	8.6
$C_7H_9^-$ anion ^h	t	dd	m	m			
	6.86	4.33	6.49	7.47		7.8	9.4
	tt	i	m	m			

^a C_6D_6 solvent, temp. 40°, TMS internal standard ($\tau = 10$ ppm). ^b s: singlet; d: doublet; dd: double doublet; t: triplet; tt: triplet of triplets; m: multiplet; br: broad. ^c $\tau(3,1) = 4.65$; $J_{bc} = 2.8$ Hz. ^d Ref. 3. ^e Unsym. triplet. ^f Ref. 6. ^g Ref. 7. ^h Ref. 9; $J_{ac} = 1.2$ Hz. ⁱ Four lines.

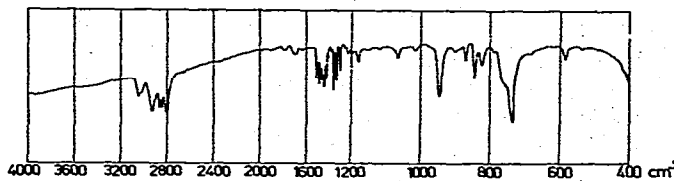
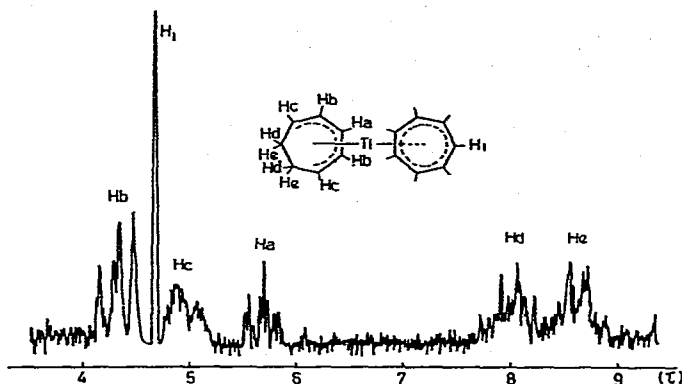


Fig. 1. IR spectrum of $C_7H_7TiC_7H_9$ in hexachlorobutadiene ($4000-1200\text{ cm}^{-1}$) and nujol ($1200-400\text{ cm}^{-1}$).



pressure; the black residue was extracted with pentane. On cooling the extract at -78° green crystals separated. The crystals were washed twice with cold pentane and dried *in vacuo*. Recrystallization from pentane gave the pure product. The yield of $C_7H_7TiC_7H_9$ was 3.30 g (14 mmoles, 30%). (Found: C, 72.40, 72.89; H, 7.19, 7.05; Ti, 19.95, 19.98. $C_{14}H_{16}Ti$ calcd.: C, 72.42; H, 6.95; Ti, 20.63%.)

Spectra

The mass spectrum of $C_7H_7TiC_7H_9$ was recorded by Mrs. I. Rozema-Meijer with an AEI MS 9 instrument; the data are summarized in Table 1. 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 IR spectrum (Fig. 1) was measured with a Hitachi EPI-G spectrophotometer.

The NMR spectrum of $C_7H_7TiC_7H_9$ (Fig. 2) in C_6D_6 solution (40°) was measured by Drs. S. Reiffers with a Varian A 60 high-resolution instrument. The chemical shifts, given in Table 2, are relative to TMS ($\tau = 10$ ppm), which was used as an internal standard.

DISCUSSION

The reaction of $TiCl_3$ and $i-C_3H_7MgBr$ in ether in the presence of an excess of cycloheptatriene gives a green, diamagnetic titanium complex. The compound is thermally stable but sensitive to oxygen and water, both in solution and in the solid state. No reaction with N_2 or H_2 was observed. The elemental analyses and the mass spectrum (parent peak at $m/e = 232$) indicate, that the molecular formula is $C_{14}H_{16}Ti$:

i.e. the complex probably contains two seven-membered carbon rings. Indeed the fragmentation products, present in the mass spectrum, are as expected for this type of sandwich compounds. Information concerning the distribution of the hydrogen atoms over the carbon rings can be obtained from the IR spectrum and the NMR spectrum. The IR spectrum, in particular the absorptions at about 850 and 950 cm^{-1} , indicate that one of the ligands is a cycloheptatrienyl group, C_7H_7 , since the same absorptions are found in the IR spectra of the complexes $\text{C}_5\text{H}_5\text{MC}_7\text{H}_7$ ($\text{M} = \text{Ti, Zr, V, Nb}$). Moreover, the seven-proton signal in the NMR spectrum at $\tau = 4.65$ ppm, which is also found in the NMR spectrum of $\text{C}_5\text{H}_5\text{TiC}_7\text{H}_7$ ($\tau = 4.53$), confirms the presence of the cycloheptatrienyl ring.

The other NMR signals, *viz.*: the double doublet at τ 4.31 (relative intensity 2), the multiplet at $\tau \sim 5.0$ (2), the triplet of triplets at τ 5.69 (1) and the multiplets centered at $\tau \sim 8.1$ (2) and at $\tau \sim 8.9$ (2), must then arise from the other seven-membered ring, C_7H_9 . The observed chemical shifts, intensities, multiplicities and coupling constants are similar to those, found in other cycloheptadienyl-transition metal complexes (Table 2), except for the chemical shift of the H_a proton, which is observed at an unusually high field in $\text{C}_7\text{H}_7\text{TiC}_7\text{H}_9$; in this respect the spectrum of the cycloheptadienyl ligand of our complex resembles the spectrum of the free C_7H_9^- anion.

Assuming the seven π -electrons of the C_7H_7 ring and the five π -electrons of the C_7H_9 ring all to be involved in bonding with the metal, one would have a 16-electron configuration, which is compatible with the magnetic and spectroscopic observations and the chemical behaviour of the complex. It seems reasonable, therefore, to regard $\text{C}_7\text{H}_7\text{TiC}_7\text{H}_9$ as *heptahaptocycloheptatrienyl-pentahaptocycloheptadienyltitanium**.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Dr. F. Jellinek for his stimulating interest and Miss A. Beuker for her skilful experimental assistance.

REFERENCES

- 1 H. O. VAN OVEN AND H. J. DE LIEFDE MEIJER, *J. Organometal. Chem.*, 23 (1970) 159.
- 2 H. O. VAN OVEN AND H. J. DE LIEFDE MEIJER, unpublished results.
- 3 R. B. KING AND F. G. A. STONE, *J. Amer. Chem. Soc.*, 81 (1959) 5263.
- 4 E. O. FISCHER AND S. BREITSCHAFT, *Angew. Chem.*, 75 (1963) 94; R. B. KING AND M. B. BISNETTE, *Tetrahedron Lett.*, (1963) 1137; R. B. KING AND M. B. BISNETTE, *Inorg. Chem.*, 3 (1964) 785.
- 5 H. J. DAUBEN AND D. J. BERTELLI, *J. Amer. Chem. Soc.*, 83 (1961) 497.
- 6 A. EFRATY AND P. M. MAITLIS, *J. Amer. Chem. Soc.*, 89 (1967) 3744.
- 7 K. MOSELEY, J. W. KANG AND P. M. MAITLIS, *J. Chem. Soc. A*, (1970) 2875.
- 8 A. DAVISON, W. MCFARLANE, L. PRATT AND G. WILKINSON, *J. Chem. Soc.*, (1962) 4821.
- 9 H. KLOOSTERZIEL AND J. A. A. VAN DRUNEN, *Recl. Trav. Chim. Pays-Bas*, 88 (1969) 1084. *cf.* R. B. BATES, W. H. DEINES, D. A. MCCOMBS AND D. E. POTTER, *J. Amer. Chem. Soc.*, 91 (1969) 4608.
- 10 F. A. COTTON, *J. Amer. Chem. Soc.*, 90 (1968) 6230.

* For an explanation of the nomenclature see ref. 10.