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Mass Spectrometry of Organometallics. I. Titanium Cyclopentadieny Complexes[*1]

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The possibility of mass spectral analysis of less volatile and air sensitive organometallic compunds has been studied with an electron-impact, Muttauch-type mass spectrograph. Several organotitanium compounds, $(C_5H_5)_2Ti$, $(C_5H_5)_2Ti$-methylacetylene complex, $(C_5H_5)_2Ti$-allylchloride and $(C_5H_5)_2TiCl_2$-$AlEt_2Cl$ complex, have been subjected to mass spectral analysis, and the parent ion has been detected for each compound. The $(C_5H_5)_2Ti$-methylacetylene complex gave a parent ion of $(C_5H_5)_2Ti(C_3H_4)_2^+$; NMR and IR suggested the structure as a five-membered cyclic diene complex of $(C_5H_5)_2Ti$. The $(C_5H_5)_2Ti$-allylchloride gave a parent ion of $(C_5H_5)_2Ti(C_3H_5)^+$ which proves the existence of allyl complex of $(C_5H_5)_2Ti$. The $(C_5H_5)_2TiCl_2$-$AlEt_2Cl$ complex gave a parent ion of $(C_5H_5)_2TiCl_2AlEtCl^+$ which is in agreement with the composition reported in the literature.

There has been considerable interest in mass spectra of organometallics of transition metals in recent years. It has been felt that the mass spectral study should shed direct light on the composition of the organometallic catalysts. Although a variety of the organo transition metal compounds have been subjected to mass spectral analysis, these compounds, in most cases, are either stable to air and moisture or sufficiently volatile to use the conventional reservior inlet system. Relatively few studies on the mass spectral analysis of organometallic compounds which are less volatile and sensitive to air and moisture have been reported in the literature. The work described in this report resulted from our interest in learning whether less volatile, air sensitive organotitanium compounds would be detected by a mass spectrograph.

Experimental

The mass spectra were determined with a Japan Electron Optics Lab. double-focusing mass spectrograph (JMS-01SG). Since the compounds were not sufficiently volatile to use the conventional reservior inlet system, samples were introduced directly into the ion source from a glass tube. In the cases of the compounds which were sensitive to air and moistrue, all operations were carried out under argon or nitrogen atmosphere and samples were introduced as dilute solutions. The solvents were removed in the pre-evacuation chamber of the direct sample inlet system. Ions were formed by the electron bombardment with 75 V electrons and were accelerated at 6000 V. Ions were detected by the Ilford Q2 photographic plate. Perfluorokerosene was used as an internal reference.

Bis(cyclopentadienyl)titaniumdichloride was obtained from Arapahoe Chem. Co. and used without further purification. Bis(cyclopentadienyl)titanium was prepared by the reduction of bis(cyclopentadienyl)titaniumdichloride with sodium amalgam according to the direction of Shikata.1)

A 10 m*l* portion of benzene solution (0.075 mol/*l*) of bis(cyclopentadienyl)titanium was stirred under methylacetylene atmosphere at 50°C for 2 hr. The solution turned immediately from green to reddish one. The excess methylacetylene was removed under reduced pressure and the complex was subjected to IR, NMR and mass spectral analysis.

Bis(cyclopentadienyl)titanium solution was also treated with allylchloride in the molar ratio of 1 : 2; the color of the solution turned from green to red. The reaction mixture was subjected to mass spectral analysis.

Bis(cyclopentadienyl)titanium dichloride-diethylaluminumchloride complex was obtained by the reaction of these two reagents at 50°C in the Al/Ti ratio of 4. The solvent (*n*-heptane) was removed under reduced pressure (4 mmHg) at 20°C and the complex was subjected to mass spectral analysis.

Results and Discussion

Bis(cyclopentadienyl)titaniumdichloride. Inasmuch as the usual organotitanium compounds are very sensitive to air and moisture, initial experiments were carried out with the air stable bis(cyclopentadienyl)titaniumdichloride to see the possibility of accurate mass determination. As may be seen in Table 1, nine lines were observed at *m/e* 246—254, the region of which corresponds to the molecular ion of bis(cyclopentadienyl)titaniumdichloride. Since titanium, chlorine and carbon atoms have five, two and two appreciable isotopes respectively, forty masses might be written in combination with these isotopes. It is impossible, however, to distinguish the masses which

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[*1] This report was presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

1) K. Shikata, K. Nishino and K. Azuma, *Kogyo Kagaku Zasshi*, (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **68**, 490 (1965).

TABLE 1. MOLECULAR IONS OF $(C_5H_5)_2TiCl_2$

m/e	Found		Calculated				
	RI*	Mass	Mass	Isotope assign.			RA**
				Ti,	Cl,	Cl	
246	m	245.966	245.969	(46,	35,	35)	10.9
247	m	246.965	246.968	(47,	35,	35)	10.2
248	vs	247.965	247.964	(48,	35,	35)	100
249	m	248.968	248.965	(47,	35,	37)	6.8
			248.964	(49,	35,	35)	7.5
250	s	249.961	249.961	(48,	35,	37)	66.6
			249.961	(50,	35,	35)	7.5
251	m	250.966	250.961	(49,	35,	37)	5.0
252	m	251.965	251.958	(48,	37,	37)	11.1
253	w	252.965	252.958	(49,	37,	37)	0.8
254	w	253.950	253.955	(50,	37,	37)	0.8

* RI: relative intensity, judged by the degree of blackening of the photographic plate.
** RA: relative abundance, calculated from the natural abundance of isotopes.

belong to the same m/e value, *e.g.* $^{48}Ti^{35}Cl_2C_{10}H_{10}$ (247.964 m. u.), $^{47}Ti^{35}Cl_2{}^{13}CC_9H_{10}$ (247.971 m.u.), $^{46}Ti^{35}Cl^{37}ClC_{10}H_{10}$ (247.966 m.u.), *etc.* Among these, only the principal masses with their assignments for isotopes are listed in Table 1. From the agreement between the experimental data and the calculated ones, the nine lines can be reasonably assigned to the molecular ion of bis(cyclopentadienyl)titaniumdichloride. The limit of error in determining of these masses can be drawn within 0.009 m.u. In the present work, ions were detected only by the photographic plate and no attempt was made to achieve quantitative fragmentation patterns (pattern coefficients); the object instead was to determine accurate masses of the parent ions.

Bis(cyclopentadienyl)titanium and Its Complexes. The mass spectra of cyclopentadienyl complexes of several transition metals have been reported.[2] The mass spectral data on bis(cyclopentadienyl)titanium, however, has not been reported, whereas it has been well known that bis(cyclopentadienyl)titanium can be prepared by sodium amalgam reduction of bis(cyclopentadienyl)titaniumdichloride[1] or by the decomposition of bis(cyclopentadienyl)dimethyltitanium with hydrogen.[3] Difficulty in introducing the bis(cyclopentadienyl)titanium into a mass spectrograph because of its sensitivity to air and moisture appears to be responsible, in part, for the paucity of data on bis(cyclopentadienyl)titanium. Then, in this work, a dilute solution of bis(cyclopentadienyl)titanium was handled under nitrogen atmosphere. Solvent was removed in the pre-evacuation chamber of the direct sample inlet system and the bis(cyclopentadienyl)titanium was introduced directly into the ion source. Table 2 represents the mass spectrum of bis(cyclopentadienyl)titanium thus analyzed. The molecular ion was detected concerning to five isotopes of titanium. Various

TABLE 2. MASS SPECTRUM OF $(C_5H_5)_2Ti$

Ion	$(Mass)_{found}$	IR	$(Mass)_{calcd}$	
$Ti(C_5H_5)_2^+$	176.027	s	176.031	(^{46}Ti)
	177.032	s	177.030	(^{47}Ti)
	178.024	vs	178.026	(^{48}Ti)
	179.028	s	179.026	(^{49}Ti)
	180.028	s	180.023	(^{50}Ti)
$TiC_9H_8^+$	164.002	vw	164.011	
$TiC_8H_8^+$	152.001	m	152.011	
$TiC_7H_8^+$	140.000	vw	140.011	
$TiC_6H_6^+$	126.001	w	125.995	
$TiC_6H_5^+$	124.991	w	124.987	
$TiC_5H_5^+$	112.985	vs	112.987	
$TiC_5H_4^+$	111.991	s	111.980	
$TiC_4H_3^+$	98.962	w	98.971	
$TiC_3H_3^+$	86.965	m	86.971	
$TiC_3H_2^+$	85.958	m	85.964	
$TiC_2H_2^+$	73.956	w	73.964	
TiC_2H^+	72.955	m	72.956	
$(C_5H_5)_4Ti_2O^+$	372.041	w	372.047	
$(C_5H_5)_2TiOH^+$	195.035	m	195.029	
$(C_5H_5)_2TiO^+$	194.027	vw	194.021	
$C_5H_5TiOH^+$	129.991	s	129.989	
$C_5H_5TiO^+$	128.985	s	128.981	

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[2] a) L. Friedman, A. P. Irsa and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955). b) J. Müller and L. D'Or, *J. Organometal. Chem.*, **10**, 313 (1967). c) A. F. Reid, J. S. Shannon, J. M. Swan and P. C. Wailes, *Austral. J. Chem.*, **18**, 173 (1965). d) M. I. Bruce, *Inorg. Nucl. Chem. Letters*, **3**, 157 (1967). e) A. N. Nesmeyanov, V. A. Duboritskii, O. V. Nogina and V. N. Bochkarev, *Dokl. Akad. Nauk SSSR*, **165**, 125 (1965). f) E. Schmacher and R. Taubenest, *Helv. Chim. Acta*, **49**, 1447 (1966). g) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **69**, 3198 (1965). h) R. G. Denning and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **88**, 4619 (1966). i) R. B. King, *ibid.*, **88**, 2075 (1966).

[3] K. Clauss and H. Bestian, *Ann.*, **654**, 8 (1962).

fragment ions were also detected. The assingments of these ions are somewhat uncertain, however, by the fact that the isotope lines which belong to the same *m/e*, *e. g.* $^{48}TiC_6H_6^+$ and $^{49}TiC_6H_5^+$, *etc.* could not be distinguished, since the spectrum was determined at resolution of 12000. The assignment was done by the qualitative relative intensities. Under these conditions, the accuracy of determination somewhat diminished because of broadening of the lines; a probable limit of error can be taken as 0.012 m.u.

Ions which could be taken as support for the existence of bis(cyclopentadienyl)titanium dimer have never been detected; bis(cyclopentadienyl)titanium appears to vaporize as a monomer. On the other hand, several oxygen-containing ions which might come from the reaction of bis(cyclopentadienyl)titanium with air and moisture were detected at *m/e* of 129, 130, 194, 195 and 372. From these ions, it appears to be reasonable to conclude that oxygen-containing compounds such as $(C_5H_5)_2$-TiO, $(C_5H_5)_2TiOH$ and $(C_5H_5)_4Ti_2O$ existed in the sample; it is noteworthy that oxygen-containing bis(cyclopentadienyl)titanium dimer exists in the vapor phase.

When the benzene solution of bis(cyclopentadienyl)titanium was treated with methylacetylene at 50°C, the color of the solution turned green to reddish. Mass spectral analysis of this solution gave a line at 258.092 m.u., which can be assigned to $(C_5H_5)_2Ti(C_3H_4)_2^+$ (258.089 m.u.). Infrared spectra of bis(cyclopentadienyl)titanium and its methylacetylene complex are shown in Fig. 1. The complex exhibited absorption bands at 1580 and 1410 cm^{-1} which are characteristic of a conjugated diene system, and did not exhibit any absorption bands at 2100—2260 cm^{-1} which corresponds to a carbon-carbon triple bond. It can, therefore, be concluded that the two molecules of methylacetylene bond to bis(cyclopentadienyl)titanium as a conjugated diene. The 60 Mc NMR spectrum of the complex exhibited rather broad signals at δ(benzene) = 335 cps and δ(benzene) = 354 cps.

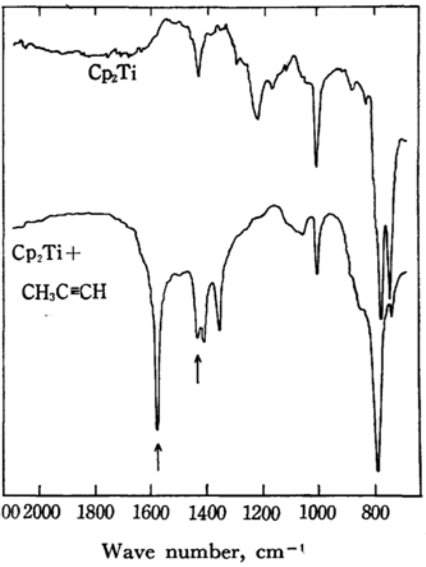
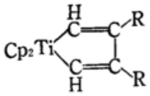
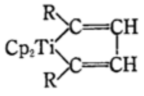


Fig. 1. Infrared spectra of $(C_5H_5)_2Ti$ and $(C_5H_5)_2Ti$-methylacetylene complex.

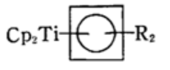
Vol'pin and his co-workers⁴⁾ studied the complex of bis(cyclopentadienyl)titanium with phenylacetylene and assumed the structures of I and II. Sonogashira and Hagihara⁵⁾ also investigated this complex by means of NMR, IR and electronic absorption spectra and supported the structure I.



Ia



Ib



II

The present work supports the structure I and NMR (60 Mc) signals at δ(benzene) = 335 cps and δ(benzene) = 354 cps can be assigned to the methyl groups of Ia and Ib. The fact that $C_6H_8^+$ which is expected from structure II was not detected in the mass spectrum may support the structure I rather than the structure II.

In connection with the cyclic diene complex, a reaction mixture of bis(cyclopentadienyl)titanium with allylchloride was subjected to mass spectral analysis to see the possibility of the formation of allyl complex of bis(cyclopentadienyl)titanium. The results are presented in Table 3. As may be seen in Table 3, the predominant product of the reaction was bis(cyclopentadienyl)titaniumdichloride. A line was, however, observed at 219.062 m.u. which can be taken as a support of the formation of allyl complex of bis(cyclopentadienyl)titanium. Besides the titanium-containing ions, $C_6H_{10}^+$ was also observed.

TABLE 3. MASS SPECTRAL ANALYSIS OF $(C_5H_5)_2Ti$-ALLYLCHLORIDE

m/e	RI	Ion	(Mass)$_{found}$	(Mass)$_{calcd}$
219	w	$(C_5H_5)_2TiC_3H_5^+$	219.062	219.065
248	vs	$(C_5H_5)_2TiCl_2^+$	247.962	247.964
82	m	$C_6H_{10}^+$	82.081	82.078

Bis(cyclopentadienyl)titaniumdichloride-diethylaluminumchloride Complex. While the complex of bis(cyclopentadienyl)titaniumdichloride with diethylaluminumchloride was investigated in

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4) M. E. Vol'pin, V. A. Dubovitskii, O. V. Nogina and D. N. Kursanov, *Dokl. Akad. Nauk SSSR,* **151**, 1100 (1963).

5) K. Sonogashira and N. Hagihara, This Bulletin, **39**, 1178 (1966).

TABLE 4. MASS SPECTRAL ANALYSIS OF $(C_5H_5)_2TiCl_2$-$AlEt_2Cl$

Ion	Found		Calculated				
	Mass	RI	Mass	Isotope assign.			
				Ti,	Cl,	Cl,	C
$(C_5H_5)_2TiCl_2AlClEt^+$	338.950	m	338.953	(48,	35,	35,	12)
	339.953	vw	339.956	(48,	35,	35,	13)
	340.950	m	340.950	(48,	35,	37,	12)
	341.954	vw	341.954	(48,	35,	37,	13)
$(C_5H_5)_2TiCl_2AlCl^+$	307.915	vw	307.919	(46,	35,	35,	12)
	308.915	vw	308.918	(47,	35,	35,	12)
	309.910	s	309.916 309.914	(46, (48,	35, 35,	37, 35,	12) 12)
	310.906	w	310.915 310.917 310.915	(47, (48, (49,	35, 35, 35,	37, 35, 35,	12) 13) 12)
	311.906	s	311.913 311.911	(46, (48,	37, 35,	37, 37,	12) 12)
	312.905	w	312.912 312.914 312.911	(47, (48, (49,	37, 35, 35,	37, 37, 37,	12) 13) 12)
	313.908	m	313.908 313.908	(48, (50,	37, 35,	37, 37,	12) 12)
$(C_5H_5)_2TiCl_2AlEt^+$	303.981	w	303.985	(48,	35,	35,	12)
$(C_5H_5)_2TiEt^+$	207.070	w	207.065	(48,	—,	—,	12)
$TiEt^+$	96.981	w	96.987	(48,	—,	—,	12)

detail by Natta and Mazzanti,⁶⁾ the mass spectral data on this complex has never been reported. Then, the mass spectral analysis was carried out in the same manner as described for bis(cyclopentadienyl)titanium. The lines observed in the highest mass region was *m/e* 339—342, which are shown in Fig. 2. These ions can be assigned to $(C_5H_5)_2TiCl_2$-$AlEtCl^+$ and its isotopic ions, as may be seen in the first four entries of Table 4. Besides $(C_5H_5)_2TiCl_2$-$AlEtCl^+$, a weak line was observed at 333.019m.u. which corresponds to $(C_5H_5)_2TiCl_2AlEt_2^+$. This is not, however, conclusive in establishing proof for the existence of the complex in the form of $(C_5H_5)_2TiCl_2AlEt_2$, because diethylaluminumchloride unfortunately gives a line at 333.021 m.u.*2 Although it is not clear whether the line at 333.019 m.u. is due to the existence of $(C_5H_5)_2TiCl_2AlEt_2^+$ or whether the diethyaluminumchloride also plays a part, it is more likely that the complex is predominantly in the form of $(C_5H_5)_2TiCl_2AlEtCl$, because the line at *m/e* 339 is much more intense than that at *m/e* 333 as may be seen in Fig. 2. This composition of the complex agrees with that reported by Natta and Mazzanti.⁶⁾ Fragment ions of the complex are also included in Table 4. The only observable fragment ions are $(C_5H_5)_2$-$TiCl_2AlCl^+$ and $(C_5H_5)_2TiCl_2AlEt^+$, which correspond to (P-Et) and (P-Cl), respectively.*3 Absence of other fragment ions which contain both titanium and aluminum appears to suggest the weakness of chlorine-bridged titanium-aluminum cluster.

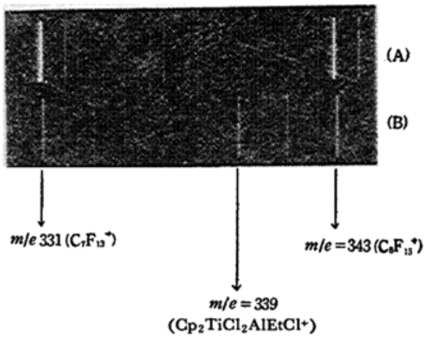

Fig. 2. Partial spectrum of $(C_5H_5)_2TiCl_2AlEtCl^+$.
(A) Perfluorokerosene
(B) Perfluorokerosene + complex

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6) G. Natta and G. Mazzanti, *Tetrahedron*, **8**, 86 (1960).

*2 Diethylaluminumchloride gives a variety of oxygen-containing ions at *m/e* 150—400; Preprints for the 21st Annual Meeting of the Chemical Society of Japan (Osaka, 1968), III, p. 1959.

*3 $(C_5H_5)_2TiEt^+$ and $TiEt^+$ would not be the fragment ions of the complex but come from an ethyltitanium compound produced presumably by the exchange reaction between $(C_5H_5)_2TiCl_2$ and $AlEt_2Cl$.