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A NEW ORGANOMETALLIC COMPOUND OF TITANIUM: INDENYLCYCLOOCTATETRAENYLTITANIUM(III)

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Summary

The synthesis of a new organotitanium compound, $C_9H_7TiC_8H_8$, is described. The compound is green, thermally stable, but very sensitive to water and oxygen. The infrared spectrum indicates that the $C_9H_7^-$ and $C_8H_8^{2-}$ groups are π-bonded to the metal. During the preparation, titanium(IV) is reduced to titanium(III).

Introduction

A number of organotitanium compounds involving π-bonding are known [1-5]. In 1969, Van Oven and de Liefde Meijer [6] reported the synthesis and some interesting properties of cyclopentadienylcyclooctatetraenyltitanium, $C_5H_5TiC_8H_8$. From its infrared spectrum, it was concluded that the five-membered ring is π-bonded to the metal. The experimental data are less clear for the cyclooctatetraenyl anion, but Kroon and Helmholdt [7] showed by X-ray diffraction that $C_8H_8^{2-}$ is also π-bonded to the metal. This paper describes the synthesis and some properties of indenylcyclooctatetraenyltitanium, $C_9H_7TiC_8H_8$.

Experimental

General

All experiments were carried out in glove boxes under purified argon. Solvents were purified by conventional methods [6]. $K_2C_8H_8$ and NaC_9H_7 were prepared as previously described [8,9].

To a solution of 10 mmol of $TiCl_4$ in 100 ml of benzene or toluene, $K_2C_8H_8$ (15 mmol) and NaC_9H_7 (10 mmol) were added simultaneously. The mixture was stirred and refluxed overnight. After filtration, the green solution was evaporated under vacuum. The residue was extracted with benzene for 12 h. After partial

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evaporation of the solvent and cooling, green crystals of $C_9H_7TiC_8H_8$ were obtained in 50-60% yield. Mol. wt. found: (mass spectrometry) 267, calcd.: Ti, 17.93; found: Ti, 17.9%. The product can be sublimed at 130°C under 10^{-4} Torr.

Spectra

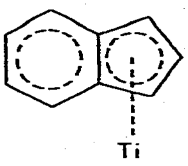
The infrared spectrum was recorded on solid samples, in KBr, KI or CsI pellets, with a Perkin—Elmer Model 125 (4000-400 cm^{-1}) a Beckman model IR 12 (400-200 cm^{-1}), or a Cameca instrument (200-100 cm^{-1}). The visible and the near infrared spectra in THF solution were recorded with a Cary 17 spectrophotometer.

It was not possible to obtain the Raman spectrum of $C_9H_7TiC_8H_8$ since the solid sublimed on exposure to the laser (Ar or He-Ne) beam.

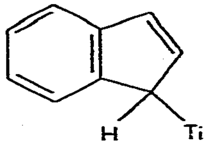
Results and discussion

The chemical analysis, the mass spectrum and the magnetic properties [10] of the new compound are consistent with the formula $C_9H_7TiC_8H_8$. The infrared spectrum is given in Table 1 (Fig. 1) and compared with those of some related compounds.

For the indenyl group, we have two possible structures; the C_5 ring is π-bonded with a C_s symmetry or it is σ-bonded with total loss of symmetry:



C_S symmetry



σ-bonded

For the cyclooctatetraenyl ring, we have also two possibilities: the $C_8H_8^{2-}$ anion can be π-bonded with a planar conformation and a C_{8v} symmetry or the ring is bent [15] and asymmetrically bonded with a local C_s symmetry.

In the infrared spectrum (Fig. 1), two bands of medium intensity at 3010 and 3035 cm^{-1} are observed; these bands may be assigned to aromatic C—H

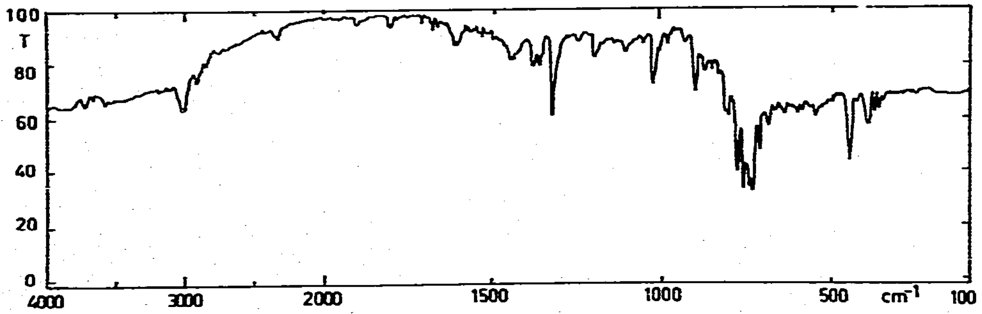


Fig. 1. Infrared spectrum of $C_9H_7TiC_8H_8$.

TABLE 1

IR SPECTRA OF SOME ORGANOTITANIUM COMPOUNDS (Frequencies in cm^{-1})

$(C_5H_5)_3Ti$[a]	$C_5H_5TiC_8H_8$[b]	$C_5D_5TiC_8H_8$[b]	$C_9H_7TiC_8H_8$	$C_8H_8TiC_8H_8$[c]
	227 vw	222 vw	225 vw	
	245 vw	245 vw	237 vw	
	253 vw	253 vw	253 vw	
		265 vw		260 vw
	280 vw	277 vw	277 vw	
		288 vw	287 vw	
	303 vw	302 vw	304 vw	
			355 w	357 w
372 m	377 s	369 s	368 m	
413 vs	435 m	407 w	393 m(br)	
			422 vw	
				440 m
			459 s	
	535 m(br)	514 w	548 w	
		556 m		
570 m		595 s		
609 m		606 s		
	619 vw			625 w
662 vw	665 w	665 m	642 w	
	670 w			
		682 w	689 w	686 vs
		710 w	715 w	
			738 vs	734 vs
745	748 vs	748 vs	745 vs	
	761 vs	762 vs	763 vs	765 vs
	793 w(sh)		781 s	784 m
798	797 vs	798 w	809 m	811 vs
	815 w	818 m	815 w	
		829 vw		
	855 vw	842	858 w	
	875 vw	873 vw(sh)	882 w	877 w
	911 s	910 s	909 m	905 w
			940 w	
	1003 s			
	1012 s	1010 w	1016 vw	
		1051 w	1039 m	1040 w
	1066 w	1062 w	1065 w	
1119	1108 m	1105 w	1117 w	
		1220 vw	1208 w	
	1265 w	1255 vw		
		1287 vw		
	1323 m	1322 m	1330 s	1325 w
	1369 m	1368 m	1368 w	
			1385 w	
	1427 s			1433 m
	1441 m	1432 vw	1445 m	1435 w
		1439 vw		
1447		1453 m	1455 w	
	1490 w			
		1537 w		
	1581 w(br)			
		1620 w(br)	1615 w(br)	
	1680 w(br)	1695 w		
	1780 vw			
	1811 w	1814 w		1810 w
	1891 vw	1892 vw		

(continued)

TABLE 1 (continued)

$(C_5H_5)_3Ti$	$C_5H_5TiC_8H_8$	$C_5D_5TiC_8H_8$	$C_9H_7TiC_8H_8$	$C_8H_8TiC_8H_8$
	1906 vw	1908 vw		1955 w
		2330 vw		
		2355 vw		
		2850 vw		
2907	2930 vw	2925 w	2920 w	2920 m
	3010 w	3020 w	3010 m	3000 m
3030	3040 w		3035 m	

[a] Refs. 11 and 12. [b] Ref. 13. [c] Ref. 14.

stretching vibrations of C_5, C_6 and C_8 rings. It is in this region (3100-3000 cm^{-1}) that all ν(C—H) stretching frequencies must lie in a π structure. In a structure with a σ-bond, the corresponding bands are found between 3000 and 2800 cm^{-1} [16]. The absence of a strong absorption band in the 1600-1650 cm^{-1} region indicates no localized C=C bonds are present in the compound; it seems probable, therefore, that the cyclooctatetraenyl and the indenyl rings are both π-bonded. The band at 1445 cm^{-1} is due to C—C vibrations, probably ω (C—C); it lies in the range where these vibrations for aromatic C_5 and C_6 rings could be expected. This band is also found in $C_5D_5TiC_8H_8$ [13] and in triindenylactinide(IV) chlorides [17].

In the absence of data for deuterated ring systems, a complete assignment is somewhat difficult in the 1200-100 cm^{-1} region, however it is possible to put forward a number of hypotheses: *(a)* the spectra of $C_9H_7TiC_8H_8$ and $C_5H_5TiC_8H_8$ exhibit between 1050 and 1000 cm^{-1} bands of high intensity, strongly affected by the deuteration of the cyclopentadienyl ring [13], *(b)* they correspond probably to δ(C—C) vibrations. The most important bands of the spectrum are observed between 800 and 700 cm^{-1}, originating probably from (C—H) vibrations

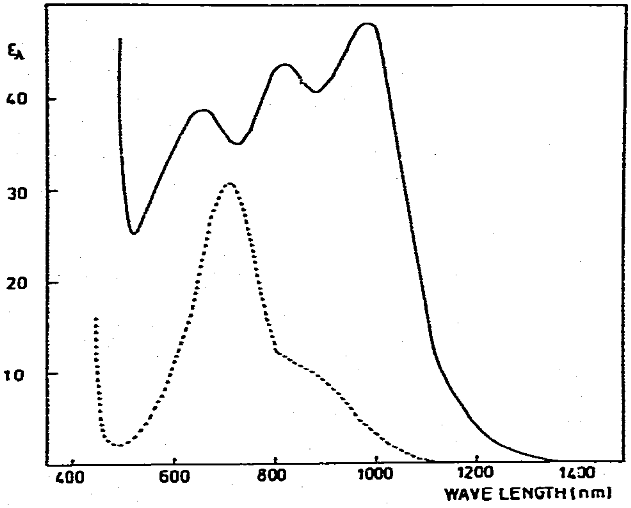


Fig. 2. Electronic absorption spectrum (—) $C_9H_7TiC_8H_8$ (1.4 × 10^{-2} *M*, THF), (- - -) $C_5H_5TiC_8H_8$ (2.0 × 10^{-4} *M*, THF).

of the C_5 and C_6 rings. The absorption band found at 459 cm^{-1} belongs to (C—C) vibrations of the C_6 ring of the indenyl ligand [9].

The electronic absorption spectrum of $C_9H_7TiC_8H_8$ in the visible and near infrared regions is compared with that of $C_5H_5TiC_8H_8$ in Fig. 2. A detailed interpretation of the former spectrum is being attempted.

Conclusions

The color, poor solubility in organic solvents, good thermal stability, sublimation behavior and sensitivity to oxygen of both $C_5H_5TiC_8H_8$ and $C_9H_7TiC_8H_8$ suggest that they are structurally similar. EPR has shown [10] that in both cases Ti^{IV} is reduced to Ti^{III} during synthesis. The IR spectra provide evidence for the aromatic character of the indenyl and the cyclooctatetraenyl rings and for the sandwich structure of the new compound [10].

Acknowledgements

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