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TETRACYCLOPENTADIENYLTITANIUM(IV) AND TRICYCLOPENTADIENYLTITANIUM(III)

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SUMMARY

The syntheses and properties of the complexes $(C_5H_5)_4Ti$ and $(C_5H_5)_3Ti$ are described. IR and NMR spectra show that these complexes have the structures $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$ and $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$ respectively. The spectra and properties of the two compounds are compared with those of $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2$ and $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_5H_5)$. The compound $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_5H_5)_2$ could not be prepared.

INTRODUCTION

Studies on the preparation and stability of complexes of general formula $(\pi\text{-}C_5H_5)_2MR_n$ (where M is a transition metal and R an alkyl or aryl group, which is σ-bonded to the metal) led to the isolation of stable complexes of the types: $(\pi\text{-}C_5H_5)_2TiR_2$ (ref. 1), $(\pi\text{-}C_5H_5)_2VR$ (ref. 2) and $(\pi\text{-}C_5H_5)_2NbR_2$ (refs. 3 and 4). The compounds tricyclopentadienylvanadium[2] and tetracyclopentadienylniobium[3] were found to be representatives of the types mentioned, with $R = \sigma\text{-}C_5H_5$.

In contrast, the constitution $(\pi\text{-}C_5H_5)_3Ti$ had been assigned to tricyclopentadienyltitanium[5]. No details are known on tetracyclopentadienyltitanium. The synthesis of this compound (probably impure and partly polymerized) was reported by Breederveld and Waterman[11], but no details of its structure and properties were given.

The present paper describes the synthesis and isolation of tetracyclopentadienyltitanium by reaction of one mole of $(\pi\text{-}C_5H_5)_2TiCl_2$ with two moles of C_5H_5Na. Thermal decomposition of the compound yields tricyclopentadienyltitanium, identical with the product described by Fischer and Löchner[5]. Evidence is given that the constitution of the two complexes is $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$ and $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$ respectively, contrary to Fischer and Löchner's suggestion[5] on the constitution of $(C_5H_5)_3Ti$. Attempts to prepare $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_5H_5)_2$ led to reduction of the metal.

RESULTS AND DISCUSSION

Tetracyclopentadienyltitanium was prepared in a way analogous to the preparation of diphenyldicyclopentadienyltitanium[1]:

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2\,C_6H_5Li \rightarrow (\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2 + 2\,LiCl$$

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2\,C_5H_5Na \xrightarrow{0^\circ} (C_5H_5)_4Ti + 2\,NaCl$$

When very dry tetrahydrofuran was used as solvent and the temperature was kept below room temperature tetracyclopentadienyltitanium was easily obtained as a thermally stable, violet-black complex. In contrast with other dicyclopentadienyltitanium(IV) complexes, tetracyclopentadienyltitanium is sensitive to oxygen. It can be converted into tricyclopentadienyltitanium(III) by heating in vacuum. Both complexes react with hydrogen chloride under formation of cyclopentadiene:

$$(C_5H_5)_4Ti^{IV} + 2\,HCl \rightarrow (\pi\text{-}C_5H_5)_2Ti^{IV}Cl_2 + 2\,C_5H_6$$

$$(C_5H_5)_3Ti^{III} + HCl \rightarrow \tfrac{1}{2}\,[(\pi\text{-}C_5H_5)_2Ti^{III}Cl]_2 + C_5H_6$$

These reactions with hydrogen chloride suggest the presence of σ-bonded cyclopentadienyl groups in both complexes, as is the case with tetracyclopentadienylniobium[3] and tricyclopentadienylvanadium[2].

The NMR spectrum of tetracyclopentadienyltitanium shows a very broad peak around τ 4.3, which is overlapped by a sharp peak at τ 4.2 (with TMS as internal standard); this indicates that not all the cyclopentadienyl protons are equivalent. Furthermore, the IR spectrum of tetracyclopentadienyltitanium shows a striking

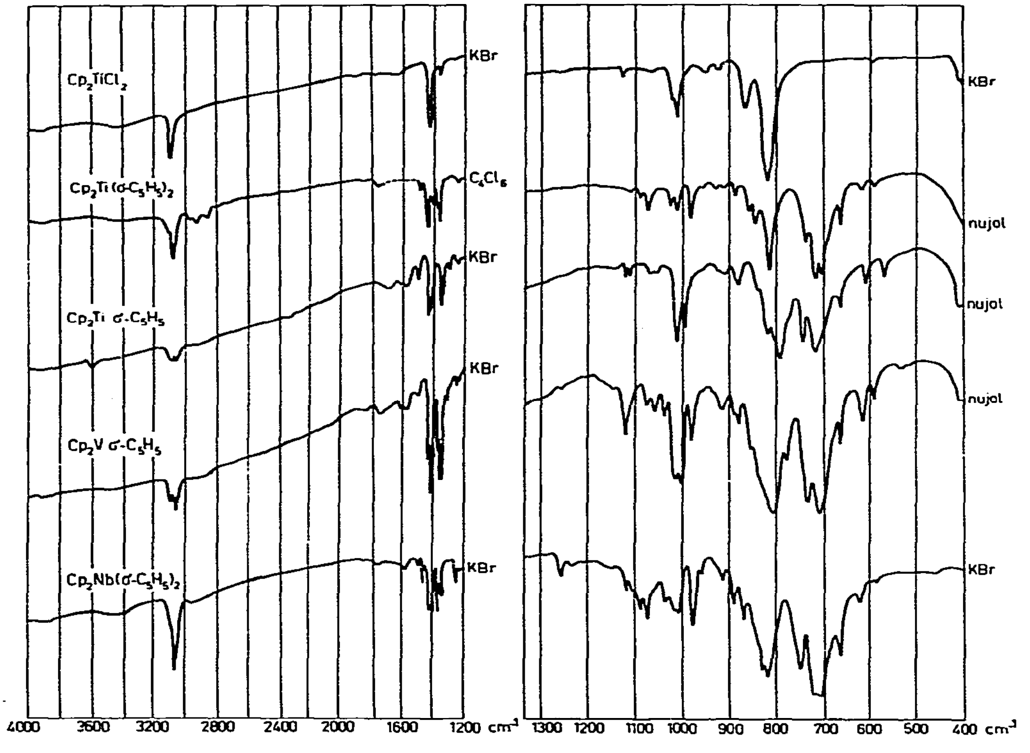

Fig. 1. Infrared spectra of $(\pi\text{-}C_5H_5)_2TiCl_2$, $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$, $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$, $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_5H_5)$ and $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2$. Cp = $\pi\text{-}C_5H_5$. The infrared spectrum of $(\pi\text{-}C_5H_5)_2TiCl_2$ is given in order to indicate the vibrations of π-bonded cyclopentadienyl groups.

analogy with that of tetracyclopentadienylniobium (Fig. 1); the absorption bands expected for π- and σ-bonded cyclopentadienyl groups are present[10]. Therefore, tetracyclopentadienyltitanium must be given by the formula $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$.

The IR spectra of tricyclopentadienyltitanium and tricyclopentadienylvanadium are closely similar and they are analogous to those of tetracyclopentadienyltitanium and -niobium (Fig. 1). It is seen that the absorption bands attributed to σ-bonded C_5H_5 groups are clearly present in the spectra of $(C_5H_5)_3Ti$ and $(C_5H_5)_3V$, although they are less intense than in the spectra of $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$ and $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2$. This leads us to assign the formulae $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$ and $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_5H_5)$ to the tricyclopentadienyl complexes; the structure of the vanadium compound was confirmed by its NMR spectrum[2]. Our observations are not compatible with the structure $(\pi\text{-}C_5H_5)_3Ti$ proposed by Fischer and Löchner[1].

The reaction of one mole of $(\pi\text{-}C_5H_5)_2VCl_2$ with two moles of C_5H_5Na yielded $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_5H_5)$; the metal was reduced to the trivalent state as is generally the case for substitution reactions starting from $(\pi\text{-}C_5H_5)_2VCl_2$ (refs. 6 and 7). Thermal decomposition of $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_5H_5)$ at 125° yielded vanadocene, $(\pi\text{-}C_5H_5)_2V$.

The analogy between the cyclopentadienyl complexes of titanium and vanadium can be illustrated by the following reactions:

$$(\pi\text{-}C_5H_5)_2Ti^{IV}Cl_2 + 2\ C_5H_5Na \xrightarrow{0^\circ} (\pi\text{-}C_5H_5)_2Ti^{IV}(\sigma\text{-}C_5H_5)_2 + 2\ NaCl$$

$$(\pi\text{-}C_5H_5)_2Ti^{IV}(\sigma\text{-}C_5H_5)_2 \xrightarrow{125^\circ} (\pi\text{-}C_5H_5)_2Ti^{III}(\sigma\text{-}C_5H_5) + C_5H_5^{\cdot}$$

$$(\pi\text{-}C_5H_5)_2V^{IV}Cl_2 + 2\ C_5H_5Na \xrightarrow{0^\circ} (\pi\text{-}C_5H_5)_2V^{III}(\sigma\text{-}C_5H_5) + C_5H_5^{\cdot} + 2\ NaCl$$

$$(\pi\text{-}C_5H_5)_2V^{III}(\sigma\text{-}C_5H_5) \xrightarrow{125^\circ} (\pi\text{-}C_5H_5)_2V^{II} + C_5H_5^{\cdot}$$

The reactions with C_5H_5Na show the usual difference between titanocene and vanadocene complexes, *viz.* reduction of the metal in the case of reactions starting from $(\pi\text{-}C_5H_5)_2VCl_2$.

Our results indicate that tetracyclopentadienyltitanium may occur as an intermediate species in the synthesis of $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ from $(\pi\text{-}C_5H_5)_2TiCl_2$ and two equivalents of C_5H_5Na, followed by treatment with carbon monoxide[9], and in the synthesis of tricyclopentadienyltitanium from $(\pi\text{-}C_5H_5)_2TiCl_2$ and an excess of C_5H_5Na (ref. 5).

EXPERIMENTAL

All experiments were carried out in an atmosphere of purified nitrogen. Solvents were purified by conventional methods; before use they were freed from oxygen by repeated degassing and saturating with nitrogen. Tetrahydrofuran was distilled from $LiAlH_4$ under nitrogen. The starting materials were prepared according to published procedures [2,8]. Elementary analyses of C, H, Ti and V were carried out at the Micro Analytical Department of this University under supervision of Mr. W. M. Hazenberg. The (uncorrected) melting points were observed in sealed glass capillaries. IR spectra were measured by means of a Hitachi EPI-G spectrophotometer. NMR spectra were measured with a Varian A 60 high-resolution instrument.

Tetracyclopentadienyltitanium

Dicyclopentadienyltitanium dichloride (2.49 g, 10.0 mmoles) was dissolved in 200 ml of tetrahydrofuran at 0°, in the first bulb of a double-Schlenk-type vessel. White solid sodium cyclopentadienide (13.7 g, 155 mmoles) was added. The color of the reaction mixture immediately changed from orange to violet. The reaction mixture was stirred during 45 min at 0°. The solvent was removed at 0° in vacuum and the residue evaporated to complete dryness. 200 ml of ether (0°) were added. The mixture was stirred for 30 min, the solution filtered into the second bulb and cooled to −78°. Violet-black cystals separated. The mother liquor was removed and 1.20 g of tetracyclopentadienyltitanium were isolated; yield 39%; m.p. 128°. (Found: C, 77.57; H, 7.01; Ti, 14.60. $C_{20}H_{20}Ti$ calcd.: C, 77.91; H, 6.54; Ti, 15.54%.)

Tricyclopentadienyltitanium

Tetracyclopentadienyltitanium (277 mg, 0.9 mmole) was heated at 125° in a vacuum of 10^{-3} mm. A green product sublimed. Isolation gave 91 mg of tricyclopentadienyltitanium; yield 41%; m.p. 138–140° with decomposition. (Found: C, 73.91; H, 6.11; Ti, 19.71. $C_{15}H_{15}Ti$ calcd.: C, 74.07; H, 6.18; Ti, 19.75%.)

Dicyclopentadienyltitanium dichloride (2.00 g, 8.0 mmoles) was mixed with 75 ml of ether at room temperature. White solid sodium cyclopentadienide (1.50 g, 17.0 mmoles) was added. After stirring for 45 min the blue-black reaction mixture was evaporated to dryness. Sublimation of the residue at 125° (10^{-3} mm) gave a green product. The IR spectrum of this product was identical with that of the product obtained from the first synthesis. 150 mg of tricyclopentadienyltitanium were isolated; yield 7.5%. (Found: C, 74.41; H, 6.02; Ti, 18.67. $C_{15}H_{15}Ti$ calc.: C, 74.07; H, 6.18; Ti, 19.75%.)

Attempted synthesis of tetracyclopentadienylvanadium

Dicyclopentadienylvanadium dichloride (2.25 g, 9.0 mmoles) was mixed with 75 ml of ether at 0°, in the first bulb of a double-Schlenk-type vessel. White solid sodium cyclopentadienide (1.70 g, 19.3 mmoles) was added. After stirring for 30 min the reaction mixture had turned brown-black. The solvent was removed at 0° in vacuum and the residue evaporated to complete dryness. 100 ml of ether (0°) were added. The mixture was stirred for 10 min, the solution filtered into the second bulb and concentrated to 30 ml. On cooling at −78° tricyclopentadienylvanadium separated as black crystals. The mother liquor was removed and 0.17 g of product were isolated; yield 7.5%; m.p. 98°. The IR spectrum of this product was identical with that of tricyclopentadienylvanadium obtained from dicyclopentadienylvanadium monochloride and sodium cyclopentadienide as described earlier[2]. (Found: C, 74.41; H, 6.09. $C_{15}H_{15}V$ calcd.: C, 73.17; H, 6.14; V, 20.69%.)

Decomposition of tricyclopentadienylvanadium to vanadocene

Tricyclopentadienylvanadium (184 mg, 0.7 mmole) was heated at 125° in a vacuum of 0.25 mm. A violet product sublimed. This was identified as vanadocene by its analysis, melting point and infrared spectrum; yield 37%. (Found: C, 66.89; H, 5.61; V, 27.36. $C_{10}H_{10}V$ calcd.: C, 66.30; H, 5.57; V, 28.13%.)

Analysis of the σ-bonded cyclopentadienyl group(s) of $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$ *and* $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$

Tetracyclopentadienyltitanium reacted with hydrogen chloride in toluene under formation of dicyclopentadienyltitanium dichloride and cyclopentadiene:

$$(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2 + 2\,HCl \rightarrow (\pi\text{-}C_5H_5)_2TiCl_2 + 2\,C_5H_6$$

Tricyclopentadienyltitanium reacted with hydrogen chloride in toluene under formation of cyclopentadiene and dicyclopentadienyltitanium monochloride. The latter compound was oxidized by hydrogen chloride and oxygen:

$$2\,(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5) + 2\,HCl \rightarrow [(\pi\text{-}C_5H_5)_2TiCl]_2 + 2\,C_5H_6$$
$$[(\pi\text{-}C_5H_5)_2TiCl]_2 + 2\,HCl + \tfrac{1}{2}\,O_2 \rightarrow 2\,(\pi\text{-}C_5H_5)_2TiCl_2 + H_2O$$

Cyclopentadiene was quantitatively determined by gas chromatography; $(\pi\text{-}C_5H_5)_2TiCl_2$ was identified by its IR spectrum. The following results were obtained:

Starting material	Moles of C_5H_6 per mole of starting material
$(C_5H_5)_4Ti$	1.80
$(C_5H_5)_3Ti$	0.85
$(C_5H_5)_3V$ (ref. 2)	0.92

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