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DIRECTIVE EFFECT OF A METHYL SUBSTITUENT IN THE EXCHANGE REACTION OF RING HYDROGEN WITH MOLECULAR DEUTERIUM IN DICYCLOPENTADIENYLTITANIUM COMPLEXES

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SUMMARY

Hydrogenated (1-methylallyl)dicyclopentadienyltitanium(III) exchanges its ring hydrogen atoms with deuterium gas. The deuterated complex can be oxidized with hydrogen chloride and air to $(C_5D_5)_2TiCl_2$. In the related methyl-substituted complex, obtained by hydrogenation of allylbis(methylcyclopentadienyl)titanium(III), only the ring hydrogen atoms in β-position to the methyl substituent exchanged with deuterium, the hydrogen in α-position to the substituent proved to be relatively unreactive. In the exchange reaction, an intermediate is proposed having a structure with a bridged π- as well as σ-bonded C_5H_4 or $C_5H_3CH_3$ group.

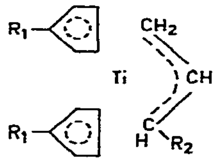
INTRODUCTION

Deuteration of cyclopentadienyl ligands in metallocenes by deuterium oxide has been effected by acid and base catalysis[1]. Further specific isotopic exchange with molecular deuterium in triphenylphosphine and triphenyl phosphite complexes of Group VIII metals has been reported for *ortho*-phenyl hydrogen atoms[2]. We have observed that hydrogenated dicyclopentadienyltitanium allyl complexes, besides their catalytic properties in the hydrogenation and isomerization of alkenes[3], also exchange cyclopentadienyl hydrogen with deuterium gas[4].

This exchange reaction, its use for the synthesis of deutero dicyclopentadienyltitanium complexes and the effect of methyl substitution on ring hydrogen exchange is described.

RESULTS

Allylbis(methylcyclopentadienyl)titanium(III) (allyl-BMCT) was synthesized in 40% yield along the same lines as the unsubstituted complex (allyl-DCT) from BMCT dichloride and allylmagnesium chloride[5]. The black-violet, crystalline and air-sensitive complex was crystallized from pentane and characterized by titanium analysis, chemical evidence and its mass spectrum (experimental part).



$R_1 = CH_3$; $R_2 = H$ (allyl-BMCT)
$R_1 = H$; $R_2 = H$ (allyl-DCT)
$R_1 = H$; $R_2 = CH_3$ (crotyl-DCT)

The IR spectrum of allyl-BMCT shows a strong band at 1508 cm^{-1} with a shoulder at 1498 cm^{-1}, assigned to the antisymmetric (C$\cdots$C stretch of the π-allyl and the π-methylcyclopentadienyl ligand respectively, analogous to the absorptions at 1509 cm^{-1} found for allyl-DCT and at 1495 cm^{-1} for BMCT dichloride. The oxidation state of titanium is known to exert virtually no influence on the absorption of the cyclopentadienyl ligand[6].

In the visible light spectrum of allyl-BMCT (in cyclohexane solution), an absorption at 506 nm is found. Comparison with the absorption at 512 nm of allyl-DCT and at 539 nm for crotyl-DCT[7] suggests that methyl substitution in the cyclopentadienyl ligand has less influence on the electronic system of the complex than substitution in the π-allyl ligand.

Allyl-BMCT, which decomposes at 68°, is less stable than allyl-DCT and crotyl-DCT and more soluble in common organic solvents. Analogous to allyl-DCT and crotyl-DCT, allyl-BMCT can be hydrogenated leading to a product that shows catalytic activity in the hydrogenation and isomerization of alkenes. The spectrum of the hydrogenated complex in the 400–1000 nm range is quite similar to that of the unsubstituted analog (absorption at 495 and 635 nm in cyclohexane); again, reaction with hydrogen chloride and air quantitatively produces BMCT dichloride[5]. The catalytic activity, however, is distinctly smaller than for the unsubstituted analog[3]: the isomerization of 1,5-cyclooctadiene is much slower, while hydrogenation of cyclohexene is incomplete, due to rapid decomposition of the catalyst.

Exchange reaction with deuterium

When cyclohexane solutions of hydrogenated allyl complexes, carefully freed

TABLE 1

THE RELATIVE PARENT PEAK INTENSITIES IN THE MASS SPECTRA OF DICYCLOPENTADIENYLTITANIUM DICHLORIDE COMPLEXES

DCT dichloride				BMCT dichloride			
Untreated		Deuterated		Untreated		Deuterated	
m/e	*I*	*m/e*	*I*	*m/e*	*I*	*m/e*	*I*
		255	3.1				
246	10.3	256	12.2	274	12.5	278	14.1
247	9.7	257	25.6	275	11.3	279	34.3
248	100.0	258	100.0	276	100.0	280	100.0
249	24.2	259	26.2	277	28.8	281	59.6
250	69.0	260	66.7	278	70.0	282	75.8
251	12.3	261	13.1	279	15.1	283	31.3
252	15.0	262	12.9	280	17.5	284	19.2
253	1.8	263	2.1			285	6.7
254	0.7	264	0.9				

of hydrogen, are exposed to pure deuterium gas, hydrogen can be detected in the gas phase after some time by mass spectrometry. After repeating this procedure until no more hydrogen appeared in the gas phase, the products were converted into the more conveniently handled DCT dichloride and BMCT dichloride respectively by treatment with hydrogen chloride and air.

The relative parent peak intensities in the mass spectrum of deuterated DCT dichloride and the untreated compound exhibit analogous trends (Table 1) demonstrating the almost completed cyclopentadienyl hydrogen exchange. The mass spectrum of BMCT dichloride, however, indicated that only about 4 hydrogen atoms (of the 14 available) are substituted by deuterium with minor amounts of the D_3 and D_5 compounds. Apart from this feature, identical fragmentation patterns were obtained for the deuterated and undeuterated complexes for DCT dichloride as well as for BMCT dichloride.

The IR spectra of deuterated DCT dichloride and BMCT dichloride are shown in Fig. 1. The aliphatic C–H stretch absorption of BMCT dichloride (between 2800 and 3000 cm^{-1}) appears to be unchanged upon deuteration. As no absorption is observed in the corresponding C–D region, it may be concluded that no exchange has occurred in the methyl group. Both an aromatic C–H and a C–D stretch absorption

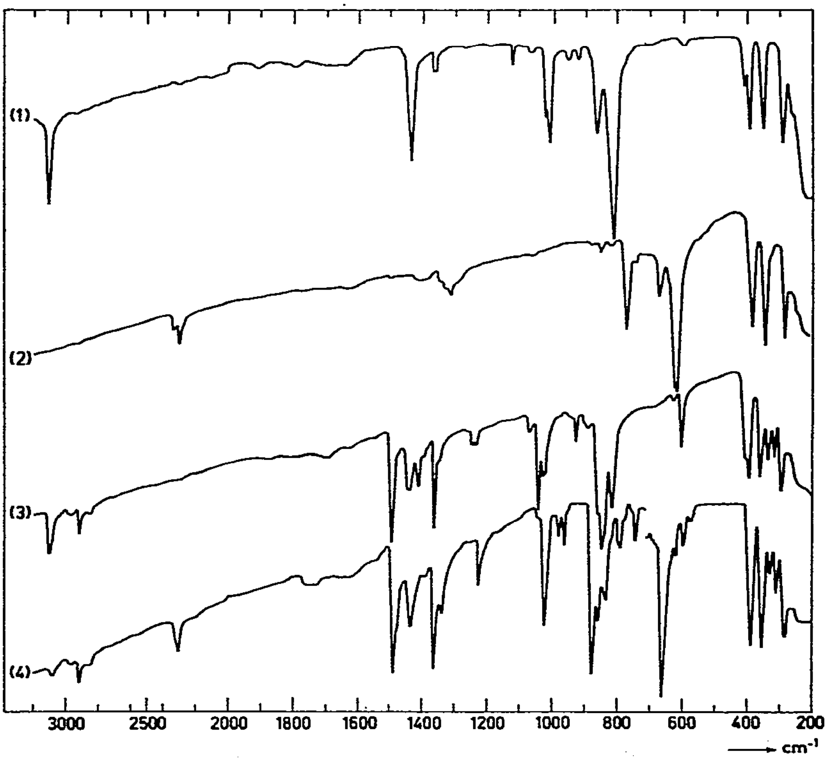


Fig. 1. IR spectra of (1) dicyclopentadienyltitanium dichloride, (2) perdeuterodicyclopentadienyltitanium dichloride, (3) bis(methylcyclopentadienyl)titanium dichloride and (4) deuterobis(methylcyclopentadienyl)-titanium dichloride (PMR data show 10% deuteration in H_α and full deuteration in H_β in the latter compound).

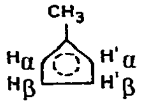
(at 3080 cm^{-1} and 2305 cm^{-1} respectively), are present indicating that, in this compound, exchange of ring protons has taken place only partially. In the spectrum of undeuterated DCT dichloride, the cyclopentadienyl C–H stretch absorption is observed at 3105 cm^{-1} with a weak shoulder at 3085 cm^{-1} (the latter being more pronounced upon cooling). For the perdeutero compound, the corresponding C–D stretching vibration is split (bands at 2307 cm^{-1} and 2338 cm^{-1}). Splitting in C–H and C–D stretch may be attributed to the lower molecular symmetry[8,9]. In the 60 MHz PMR spectrum of DCT dichloride in perdeuteroacetone, only one singlet (δ 6.62) was detectable (in agreement with ref. 9). A second singlet, ascribed to hindered ring rotation[10] was not observable, even with a 220 mHz instrument. The IR frequency shifts observed upon deuteration, confirm the band assignments reported for DCT dichloride[9]. Further, a remarkably low intensity of the antisymmetric C=C stretch absorption (at 1438 cm^{-1} in DCT dichloride) is observed in D_{10}-DCT dichloride; this is also observed, but to a less pronounced extent, in the spectrum of perdeuteroferrocene[11].

Similar systems showing the exchange reaction are formed by careful hydrogenation of dimethyl-DCT in solution[4] * and by reduction of DCT dichloride with sodium naphthalene (2 moles) in dimethoxyethane in the presence of deuterium (or hydrogen). In the latter system, however, also unreactive and undeuterated "titanocene" is formed in considerable amounts (*cf.* ref. 12). Remarkably, in the system DCT dichloride with excess of bromoisopropylmagnesium, no exchange was observed.

The related complexes allyldicyclopentadienylniobium(III)[13] and diallyldicyclopentadienylzirconium(IV)[14] were found to be unreactive towards hydrogen and deuterium.

Directive effect of the methyl substituent

Since the mass spectral data indicate incomplete deuteration in the methyl substituted ligand of BMCT dichloride, the possible specificity of the exchange reaction was investigated by PMR spectroscopy. The PMR spectrum of BMCT dichloride shows a methyl singlet (δ 2.28) and two triplets (δ 6.29 and δ 6.55 with $J(H_\alpha–H_\beta) \approx J(H_\alpha–H'_\beta) \approx 2.6$ Hz). The higher field triplet is slightly broadened, due to spin-coupling with the methyl protons [$J(H_\alpha–H_{methyl}) \approx 0.5$ Hz]. This would indicate that the protons responsible for this triplet are α to the methyl group, *i.e.* H_α protons.



A spin simulation, using the above-mentioned parameters, resulted in a perfect match of the experimental spectrum as expected, including the broadening of the higher field triplet. It also showed the irrelevance of the magnitude of coupling constants between protons with equal chemical shift and that $J(H_\alpha–H_\beta)$ and $J(H_\alpha–H'_\beta)$ have equal signs.

On deuteration, the lower field triplet gradually disappears with concomitant

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* After completion of this manuscipt, we became aware of a communication by Marvich and Brintzinger[20], in which the isolation of a hydride from such a system is reported.

TABLE 2

EXTENT OF DEUTERATION OF RING PROTONS (in %), OBTAINED FROM PMR DATA AFTER CONVERSION TO BMCT DICHLORIDE

Reaction time (h)	H_α	H_β
1	0	28
7	0	79
240[a]	36	100

[a] After four days reacting, reexposed to pure deuterium

further broadening of the H_α triplet.

The unchanged methyl band intensity in the IR spectrum and the fact that the PMR methyl singlet remains unsplit during the deuteration prove that the methyl hydrogens are not replaced. This makes the PMR methyl signal a convenient intensity standard.

Table 2 shows the extent of deuterium exchange of the methylcyclopentadienyl hydrogen atoms after various times of exposure to deuterium, determined after conversion to BMCT dichloride.

These results demonstrate the preference of the β-hydrogen atoms for the deuterium exchange reaction, as compared with those in α-position to the methyl group.

DISCUSSION

During the hydrogenation of (1-methylallyl)-DCT, the allyl moiety is converted to butane; the resulting hydrogenation product is an active catalyst for the hydrogeneration and isomerization of alkenes. As a π-allyl mechanism for the isomerization is improbable, it is reasonable to assume the catalyst to be a hydride[3,4] (dimeric, according to freezing point determinations). Further, the isomerization of alkenes has been found to be markedly enhanced by small amounts of hydrogen, indicating a system in equilibrium with hydrogen[3]. This is supported by the exchange reaction with deuterium, which further suggests that a ring hydrogen is involved in the equilibrium system. In two-component systems, *i.e.* DCT dichloride/main group organometallics, investigated for their nitrogen reduction properties, participation of a cyclopentadienyl hydrogen in the reduction reaction has also been observed[15]. In these two-component systems, however, no exchange of ring hydrogen with molecular deuterium as described in this paper, occurs. Also "titanocene" $(C_{20}H_{20}Ti_2)$[16], which is also formed irreversibly by heating of the DCT/hydrogen system, fails to show this reaction[4].

The most probable mechanism for the exchange with molecular deuterium seems to be oxidative addition of the ring C–H bond to titanium, leading to a structure with a bridged π- and σ-bonded C_5H_4 or $C_5H_3CH_3$ ring. Such an intramolecular hydrogen abstraction may be reversible upon coordination with deuterium, which is thus incorporated. A similar structure with a π- as well as σ-bonded bridged C_5H_4 ring has been reported for $(C_5H_5)(CO)Mo$-μ-$C_5H_4Mn(CO)_4$[17]. This view may account for the low rate of exchange of H_α compared to H_β (Table 2) in the methyl-substituted cyclopentadienyl ring, as σ-bonding of titanium to carbon α to the methyl substituted one may be hampered by steric hindrance.

EXPERIMENTAL

All operations were carried out under pure argon.

IR spectra were measured on a Perkin–Elmer 521 spectrometer in KBr pellets and for air-sensitive compounds in nujol; visible light absorption spectra were obtained on cyclohexane solutions in a 2 mm cell with a Cary 14 spectrophotometer. Mass spectra were recorded on a G.E.C.-A.E.I. MS 902 spectrometer. PMR spectra were measured at 60 MHz and 220 MHz on deuteroacetone solutions, with Varian A-60 and HR-220 spectrometers at 40° and 20° respectively. Chemical shifts are quoted in ppm downfield from internal tetramethylsilane (δ values). Spin simulations were performed with the Varian Spectro system 100 interfaced with the recorder of the HA-100 spectrometer.

Deuterium was passed through a 15% solution of triethylaluminium in paraffin oil. Solvents were distilled from lithium aluminium hydride or sodium benzophenone.

Crotyl-DCT was prepared according to ref. 3 and BMCT dichloride according to ref. 18. BMCT dichloride was synthesized in THF as the only solvent and the reaction mixture was acidified with gaseous hydrogen chloride before evaporation to dryness. The solid residue was treated with 2 *N* hydrochloric acid and chloroform; after drying over sodium sulphate and evaporation of chloroform, crude solid BMCT dichloride was obtained, which was crystallized once from boiling toluene. (Found: Cl, 25.3; Ti, 16.9. $C_{12}H_{14}Cl_2Ti$ calcd.: Cl, 25.6; Ti, 17.29%.)

*Synthesis of allyl-BMCT**

A solution of allylmagnesium chloride (40 mmoles, 1.202 *M*, determined by double titration[19]) in THF was added dropwise to a stirred solution of 20 mmoles of BMCT dichloride in 40 ml THF. After half of the Grignard solution had been added, the reaction mixture was refluxed for 2 h, cooled to 20° and the remainder of the Grignard solution added. The colour of the reaction mixture changed from brown-violet to deep violet on stirring for 4 h at 20°. The solvent was then removed in vacuum and the residue extracted with 180 ml pentane at room temperature. After filtration and evaporation to 130 ml, the pentane solution was cooled to −80° and black-violet crystals of allyl-BMCT separated and were freed from pentane by filtration and evaporation in vacuum at room temperature; yield 8.1 mmoles (40%). (Found: Ti as TiO_2, 19.1. $C_{15}H_{19}Ti$ calcd.: Ti, 19.38%.) Volumetric determination of propene (evolved upon addition of oxygen-free 4 *N* hydrochloric acid[5]): calcd.: 90 ml/g; found: 91 ml/g, containing 95% propene and 7 minor impurities (GLC).

Upon addition of air-free hydrogen chloride in ether to allyl-BMCT or hydrogenated allyl-BMCT (see below) first brown-green monochloride is observed, which is oxidized to brown-red BMCT dichloride when agitated in air.

In the mass spectrum, expected isotope patterns for Ti containing fragments were found. Characteristic ^{48}Ti-containing ions were found at *m/e* ratios of: 247

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* Synthesized by Mr. J. A. Bakker, student of the Delft University of Technology.

(9.5%), parent ion; 206 (100%), $(CH_3C_5H_4)_2Ti$; 168 (1.0%), $(CH_3C_5H_4)TiC_3H_5$; 127 (6.5%), $(CH_3C_5H_4)Ti$; 79 (5%), $CH_3C_5H_4$; 41 (4%), C_3H_5. A minute amount of $(C_5H_5)(CH_3C_5H_4)Ti$ ion originated from an impurity in the starting material.

Synthesis of deuterated compounds

Solutions of 0.5 to 1 mmole of crotyl-DCT or allyl-BMCT in 30 to 50 ml cyclohexane were hydrogenated. Then all hydrogen was removed by evacuating and the reaction mixture exposed to about 5 mmoles of deuterium gas while stirring at 20° and 760 mm Hg for 24 h. The hydrogen content of the gas phase was 30–50% (calculated from the H_2, HD and D_2 ratios in the mass spectrum). Exposure to pure deuterium was repeated until less than 2% hydrogen was detectable in the gas phase.

After addition of 2.4 equivalents of air-free 0.1 *N* hydrogen chloride in ether and subsequent stirring in air, red perdeutero-DCT dichloride and red-brown deutero-BMCT dichloride were filtered off, washed with pentane and dried. Yields were about 80%. Both compounds were recrystallized from toluene saturated with hydrogen chloride.

To measure the time dependence of the exchange reaction, samples of 0.16 mmole hydrogenated allyl-BMCT in 10 ml cyclohexane (saturated with argon) were rigorously stirred with 9.2 mmole deuterium for defined periods. Treatment with hydrogen chloride in ether, washing of the precipitate with pentane, drying and immediate extraction with perdeuteroacetone produced the solutions for PMR measurements.

For long exposure times, the methyl-substituted compound underwent substantial selfhydrogenation, which, on treatment with hydrogen chloride and air, resulted in the formation of more insoluble material and less BMCT dichloride.

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