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(CYCLOPENTADIENYL)(1-METHYLALLYL)(BUTADIENE)TITANIUM

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Summary

(Cyclopentadienyl)(1-methylallyl)(butadiene)titanium, $C_{13}H_{18}Ti$, has been obtained from the reaction between $(C_5H_5)TiCl_3$ or $(C_5H_5)TiCl_2$ and 1-methylallylmagnesium bromide in ether. The brown compound is diamagnetic and thermally stable, but very sensitive to oxygen. The nature of the new compound has been elucidated from its reaction with bromine and by IR, ^1H and ^{13}C NMR, and mass spectral analysis.

Introduction

In recent years a number of allylic complexes of the early transition metals containing two C_5H_5 or one C_8H_8 group have been reported [1-6]. So far, we have not been able to isolate allylic complexes of the type $(C_5H_5)Ti(\text{allyl})_n$. Attempts to synthesize such complexes by reaction of $(C_5H_5)TiCl_3$ or $(C_5H_5)TiCl_2$ with (methyl)allylmagnesium bromides were unsuccessful, except for the reaction involving 1-methylallylmagnesium bromide. However, this reaction did not lead to a diallylic complex, but gave the compound $(h^5\text{-}C_5H_5)Ti(h^4\text{-}C_4H_6)(h^3\text{-}C_4H_7)$. We describe below the synthesis and characterization of this new compound.

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. Crotyl bromide was distilled before use; $(C_5H_5)TiCl_3$ [7] and $(C_5H_5)TiCl_2$ [8] were prepared by published procedures. Elemental analyses were carried out in the Microanalytical Department of this University.

Mass spectra were recorded with an AEI MS9 mass spectrometer. Operating conditions: energy 70 eV; resolution 1000; accelerating voltage 8 kV; inlet temperature ca. 85°C. The sample was introduced directly into the ion source using a metal probe. The most important peaks of the mass spectrum are listed in Table 2.

IR spectra were measured with a Hitachi EPI-G spectrophotometer. The samples were examined as mulls in hexachlorobutadiene (4000-1200 cm^{-1}) and Nujol (4000-400 cm^{-1}) between KBr discs. Absorptions are found at: 3090 m, 3050 m, 3015 w, 2960 m, 2925 m, 2900 w, 2870 w, 2845 m, 2720 w, 1530 m, 1480 s, 1460 m, 1440 m, 1430 m, 1370 s, 1231 s, 1204 s, 1174 s, 1057 s, 1012 vs, 968 m, 931 m, 910 m, 878 m, 864 s, 845 s, 816 vs, 798 vs, 621 s, 594 m, 525 m, 476 m, 409 s.

^1H NMR spectra were recorded with a Varian A60 high-resolution instrument (C_6D_6 solution, 40°C). The ^{13}C NMR spectra were obtained with a Varian XL-100/15 Fourier Transform spectrometer with proton decoupling at 25.2 MHz (C_6D_6 solution, 10°C). Undecoupled spectra were obtained by the gated decoupler technique.

Synthesis of $(C_5H_5)(C_4H_7)(C_4H_6)Ti$

$(C_5H_5)TiCl_3$ (4.4 g, 20 mmol) was suspended in ether (100 ml) and 80 ml of a 0.75 *M* solution of crotylmagnesium bromide was added dropwise at room temperature. After addition of the Grignard reagent, the brown mixture was refluxed for 15 min. The solvent was removed under reduced pressure and the brown residue was extracted with n-pentane. On cooling of the extract to −78°C, brown crystals separated. Recrystallization from n-pentane gave the pure product. The yield of $C_{13}H_{18}Ti$ was 1.0 g (2.5 mmol, 13%). (Found: C, 70.25, 70.17; H, 8.21, 8.39; Ti, 21.62, 21.47. $C_{13}H_{18}Ti$ calcd.: C, 70.27; H, 8.17; Ti, 21.56%.)

The same compound was obtained from the reaction of $(C_5H_5)TiCl_2$ and two equivalents of the Grignard reagent.

Results and discussion

The reaction of $(C_5H_5)TiCl_3$ or $(C_5H_5)TiCl_2$ with three and two equivalents of 1-methylallylmagnesium bromide, respectively, in ether, gives a brown diamagnetic compound. This compound is very sensitive to water and oxygen both in solution and in the solid state. Differential thermal analysis (heating rate: 2°C/min) indicates that the compound decomposes at 85°C.

The first indications that the new compound contains an 1-methylallyl and a butadiene group (instead of two 1-methylallyl groups), were obtained from decomposition reactions with Br_2. After reaction with Br_2, the following bromine-containing organic compounds were identified by GLC, NMR or IR spectroscopy: 1-bromo-2-butene, C_4H_7Br; 1,2,3-tribromobutane, $C_4H_7Br_3$; 1,4-dibromo-2-butene, $C_4H_6Br_2$, and 1,2,3,4-tetrabromobutane, $C_4H_6Br_4$. The presence of the compounds C_4H_7Br and $C_4H_7Br_3$ indicates that the complex contains a 1-methylallyl ligand, since the same products are formed by reaction of $(C_5H_5)_2Ti$(1-methylallyl) with Br_2. The formation of the 1,4- and 1,2,3,4-bromo derivatives indicates that the second C_4-group is present in the molecule as a butadiene moiety. Reaction of the new compound with HCl in ether gave $(C_5H_5)TiCl_3$, indicating the presence of a h^5-C_5H_5 group; thus the structure $(C_5H_5)Ti(C_4H_7)(C_4H_6)$ was indicated.

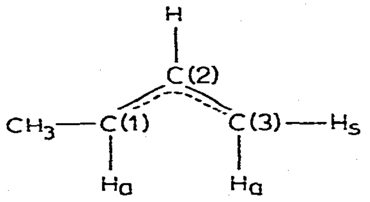
Further evidence for this structure was obtained from the IR spectrum. The C_5H_5 ring absorptions are found in the usual range. Absorptions around 1500 cm^{-1} are characteristic for π-bonded allyl groups [1,2]. In $(C_5H_5)_2Ti$-(1-methylallyl), for instance, the asymmetric C=C stretching frequency of the π-bonded allyl group is found at 1533 cm^{-1} [1]. This value closely agrees with the frequency of 1530 cm^{-1} found in the IR spectrum of the new complex. From a comparison of the IR spectrum of this complex with that of π-butadiene complexes [9,10], it can be concluded that the absorption bands at 1480, 1460, 1440 and 1370 cm^{-1} arise from a π-bonded butadiene moiety.

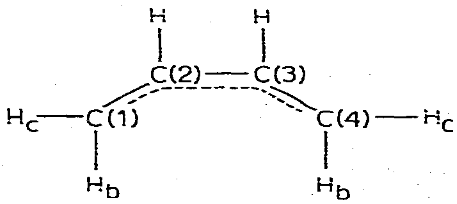
The ^{13}C NMR spectrum (Table 1) of the complex is also in agreement with the presence of a 1-methylallyl and a butadiene group. The ^1H-decoupled ^{13}C NMR spectrum was assigned with the aid of the ^{13}C—^1H coupled spectrum and by comparison with published data [11,12]. The non-equivalence of carbons 1 and 4 of the butadiene group [and the broadened signal from C(2) and C(3)] arises from the asymmetry introduced by the methyl substituent on the allyl group. This is assigned to the *syn*-position on the basis of its IR peak at 1530 cm^{-1}, analogous to that of $(C_5H_5)_2Ti$(*syn*-1-methylallyl) (1533 cm^{-1}) [1,13], whereas *anti*-methyls give rise to absorption at lower frequency [2].

The ^1H NMR spectrum of the compound is more complicated. Absorptions are found around δ 6.0, 1.8, 1.2, 1.0 ppm. Around δ 6.0 ppm a singlet of the protons of the C_5H_5 ring appears, together with various multiplets which can be assigned to the protons on the carbon atoms 2 and 3 of the butadiene group and to the proton on the central carbon atom of the allyl group. Resonance signals at rather low field are reported for the corresponding protons in similar complexes [14]. The resonance signals around δ 1.8 ppm probably belong to the protons in the *syn*-position of the 1-methylallyl group and the protons H_c of the butadiene group (for the numbering of the protons see Table 1). The two protons of the allyl group in the *anti*-position and the protons H_b of the butadiene group have their resonances around δ 1.0 ppm. This signal is somewhat distorted by partial overlap with the doublet of the *syn*-methyl group at δ 1.2 ppm (*J* 5.5 Hz).

TABLE 1

^{13}C NMR DATA OF $(h^5\text{-}C_5H_5)(h^4\text{-}C_4H_6)(h^3\text{-}C_4H_7)Ti$[a,b]





	C_5H_5	CH_3	C(1)	C(2)	C(3)	C(1,4)	C(2,3)
δ	110.0	19.8	80.9	124.4	57.7	61.4, 58.5	114.2
J^c	170(d)	125(q)	155(d)	*d*	155(t)	155(t)	160(d)

[a] Values are given in δ (ppm) relative to TMS. [b] C_6D_6 solution, 10°C. [c] Coupling constants are given in Hz, d = doublet, t = triplet, q = quartet. [d] Coupling constant could not be observed due to overlap with C_6D_6.

TABLE 2

MASS SPECTRUM OF $(C_5H_5)(C_4H_7)(C_4H_6)Ti$: ONLY PEAKS CORRESPONDING TO THE ISOTOPE ^{48}Ti ARE LISTED

	m/e	Rel. int. (%)	Ion		*m/e*	Rel. int. (%)	Ion
1	222	13.1	$C_{13}H_{18}Ti^+$	13	126	5.5	$C_6H_6Ti^+$
2	218	9.3	$C_{13}H_{14}Ti^+$	14	113	93.1	$C_5H_5Ti^+$
3	206	1.0	$C_{12}H_{14}Ti^+$	15	88	6.0	$C_3H_4Ti^+$
4	192	1.6	$C_{11}H_{12}Ti^+$	16	87	34.5	$C_3H_3Ti^+$
5	190	1.3	$C_{11}H_{10}Ti^+$	17	86	19.7	$C_3H_2Ti^+$
6	178	7.2	$C_{10}H_{10}Ti^+$	18	85	13.4	C_3HTi^+
7	168	46.6	$C_9H_{12}Ti^+$	19	74	7.8	$C_2H_2Ti^+$
8	166	16.6	$C_9H_{10}Ti^+$	20	73	16.2	C_2HTi^+
9	154	5.5	$C_8H_{10}Ti^+$	21	55	7.6	$C_4H_7^+$
10	152	4.8	$C_8H_8Ti^+$	22	54	4.8	$C_4H_6^+$
11	140	100.0	$C_7H_8Ti^+$	23	48	17.9	Ti^+
12	138	44.8	$C_7H_6Ti^+$	24	39	25.5	$C_3H_3^+$

Metastable peaks m^*: 191.2 (1→3): 136.0 (11→12): 127.1 (1→7): 116.7 (7→11): 112.2 (3→10): 91.2 (11→14): 89.9 (2→11): 67.0 (14→16): 39.1 (11→19): 28.2 (22→24).

In the mass spectrum of the compound (see Table 2) a number of metastable peaks give information on the fragmentation process. In one route, (1→3→10), the parent ion, $(C_5H_5)(C_4H_7)(C_4H_6)Ti^+$, loses a CH_4 group and the ion thus formed breaks down by elimination of a C_4H_6 fragment; so it is likely that the CH_4 group is eliminated from the C_4H_7 ligand. In a second route, (1→7→11), the parent ion loses a C_4H_6 group, thus giving the ion $(C_5H_5)(C_4H_7)Ti^+$, which, in turn, loses a C_2H_4 group to give the ion $(C_5H_5)(C_2H_3)Ti^+$. The latter ion breaks down by elimination of either H_2 or C_2H_3 or C_5H_6, resulting in the ions $(C_5H_5)(C_2H)Ti^+$, $(C_5H_5)Ti^+$ and $(C_2H_2)Ti^+$, respectively. The fragmentation of the 1-methylallyl ligand given above agrees with the degradation of this group in other 1-methylallyltitanium complexes, for instance $(C_5H_5)_2Ti(C_4H_7)$ [15] and $(C_8H_8)Ti(C_4H_7)$ [5].

It may be concluded that in the compound $C_{13}H_{18}Ti$ three organic ligands are present, viz. a h^5-C_5H_5, a h^3-1-methylallyl and a h^4-butadiene group. The titanium atom thus achieves a 16 electron configuration, which is compatible with the observed diamagnetism.

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