

TRI-1-METHALLYL- AND 1-METHALLYL-BUTADIENE GROUP IV TRANSITION METAL COMPLEXES

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Summary

Reaction of $\text{Cp}'\text{MCl}_3$ ($\text{Cp}' = \eta^5\text{-C}_5(\text{CH}_3)_5$; $\text{M} = \text{Ti, Zr, Hf}$) with 2-butenylmagnesium bromide at low temperatures gives $\text{Cp}'\text{M}(\text{1-methallyl})_3$, which is readily converted into $\text{Cp}'\text{M}(\eta^3\text{-1-methallyl})(\eta^4\text{-butadiene})$ on heating. Only $\text{Cp}'\text{Hf}(\text{1-methallyl})_3$ could be isolated; it is fluxional and its NMR and IR spectra indicate that it consists of a complex mixture of isomers containing interconverting η^1 - and η^3 -1-methallyl groups. The compounds $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ are much more thermally stable; they show fluxional behaviour, but this is limited to the η^3 -1-methallyl group. These complexes are very reactive towards a large variety of organic substrates.

Introduction

The interest in the butadiene and allyl chemistry of early transition metals has increased strongly in recent years. Allylic compounds of zirconium and hafnium, e.g. $\text{M}(\text{allyl})_4$ [1], $\text{C}_8\text{H}_8\text{M}(\text{allyl})_2$ [2] and $\text{Cp}_2\text{Zr}(\text{allyl})_2$ [3] have been extensively studied by several groups. However, few studies have been made of Group IV metal butadiene complexes. The preparation and reactions of $\text{M}(\eta^4\text{-butadiene})_2(\text{dmpe})$ ($\text{M} = \text{Ti, Zr}$) [4] and $\text{Cp}_2\text{M}(\eta^4\text{-diene})$ ($\text{M} = \text{Zr}$ [5,6], Hf [6]) were recently reported. Some years ago our group described a complex containing both η^4 -butadiene and η^3 -1-methallyl ligands, $\text{CpTi}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ [7]. We tried to extend this work to zirconium and hafnium, initially with little success. However, use of permethylcyclopentadienyl in place of the cyclopentadienyl group led to facile formation of the compounds $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ ($\text{Cp}' = \eta^5\text{-C}_5(\text{CH}_3)_5$; $\text{M} = \text{Ti, Zr, Hf}$) and $\text{Cp}'\text{Hf}(\text{1-methallyl})_3$ [8]. These syntheses and the properties of the complexes are described in this paper.

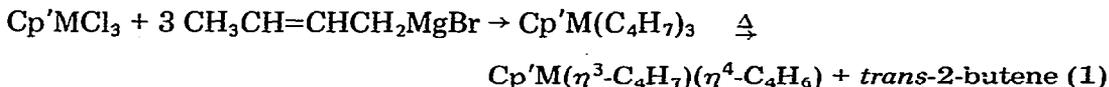
Results and discussion

Formation of $Cp'M(\eta^3-C_4H_7)(\eta^4-C_4H_6)$ ($M = Ti, Zr, Hf$)

Reaction of $Cp'MCl_3$ ($Cp' = \eta^5-C_5(CH_3)_5$; $M = Ti, Zr$) with 3 mol of 2-butenylmagnesium bromide in ether at room temperature gives intensely coloured solutions from which the crystalline compounds $Cp'M(\eta^3-C_4H_7)(\eta^4-C_4H_6)$ can be isolated (Table 1). The corresponding hafnium compound is not formed in this way, and instead the reaction gives a yellow-orange oil, identified as the tri-1-methallyl compound $Cp'Hf(C_4H_7)_3$ (Table 2). On heating, e.g. on refluxing in THF, this compound is converted into $Cp'Hf(\eta^3-C_4H_7)(\eta^4-C_4H_6)$ (Table 1) and *trans*-2-butene.

The formation of the titanium and zirconium methallyl-butadiene complexes probably also proceeds via the trimethallyl complexes $Cp'M(C_4H_7)_3$. The reaction of $Cp'ZrCl_3$ with 2-butenylmagnesium bromide at $-78^\circ C$ gives a yellow product, presumably $Cp'Zr(C_4H_7)_3$, which is stable in ether up to about $-40^\circ C$, but decomposes at higher temperatures to give $Cp'Zr(\eta^3-C_4H_7)(\eta^4-C_4H_6)$ and *trans*-2-butene. The titanium compound $Cp'Ti(C_4H_7)_3$ is even less stable and decomposes at $-78^\circ C$.

The observations indicate the reaction sequence as shown in eq. 1 and a thermal stability sequence of the intermediate compounds $Cp'M(C_4H_7)_3$ of $Hf > Zr > Ti$.



The intermediacy of the triallyl complexes prompted us to study the stable compound $Cp'Hf(C_4H_7)_3$.

Properties of $Cp'Hf(C_4H_7)_3$

At room temperature $Cp'Hf(C_4H_7)_3$ is an air sensitive, yellow-orange oil. It was characterized by IR and 1H and ^{13}C NMR spectroscopy (Table 2).

The interpretation of the spectra of compounds with two or more allyl groups is difficult. As basis we use the analysis by Hoffmann et al. [2] for the related compounds $(\eta^3-C_8H_8)M(1\text{-methallyl})_2$ ($M = Zr, Hf$).

TABLE 1

 $Cp'M(\eta^3-C_4H_7)(\eta^4-C_4H_6)$, ANALYTICAL AND PHYSICAL DATA

Compound M =	Colour	Yield (%)	Mol. weight ^a (calcd.)	Dec. temp. ($^\circ C$)	IR ^b $\nu(C=C)$ (cm^{-1})	Analysis (found (calcd.)) (%)		
						C	H	M
Ti	brown	30	—	116	1533	73.86 (73.96)	9.62 (9.65)	16.08 (16.39)
Zr	red	83	328 (336)	135	1534	63.93 (64.41)	8.38 (8.41)	27.27 (27.18)
Hf	orange	72	—	>200	1533	51.37 (51.12)	6.92 (6.67)	42.21 (42.20)

^a Cryoscopically in benzene. ^b KBr/Nujol.

TABLE 2
SPECTROSCOPIC DATA FOR $\text{Cp}'\text{Hf}(\text{C}^\alpha\text{H}_2\text{C}^\beta\text{H}=\text{C}^\gamma\text{HC}^\delta\text{H}_3)_3$

IR ^a $\nu(\text{CC})$ (cm^{-1})	¹ H NMR ^{b, c} δ (ppm), ³ J(H, H) (Hz)	¹³ C NMR ^{b, c} δ (ppm), ¹ J(¹³ C, H) (Hz)
1647 } (η^1 -C ₄ H ₇)	1.22(d, 6 H, CH ₂ , J($\alpha\beta$) 9.5)	11.4(q, C ₅ (CH ₃) ₅ , J 127)
1629 } (η^1 -C ₄ H ₇)	1.80(d, 9 H, CH ₃ , J($\gamma\delta$) 6.0)	17.2(q, C ^{δ} , J 130)
	1.82(s, 15 H, Cp')	67.1(t, C ^{α} , J 128)
1576 (η^3 -C ₄ H ₇)	4.66(dq, 3 H, C ^{γ} H, J($\beta\gamma$) 14.5)	112.4(d, C ^{γ} , J 154)
	5.45(dt, 3 H, C ^{β} H)	117.2(s, C ₅ (CH ₃) ₅)
		133.8(d, C ^{β} , J 145)

^a KBr/Nujol. ^b Chemical shifts relative to internal TMS in benzene-*d*₆. ^c Multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Systems with three 1-methallyl groups per metal atom are, in principle, rather complicated because of the possibility of: a) dynamic behaviour of the ligands ($\eta^1 \rightleftharpoons \eta^3$), b) the presence and interconversion of isomers (*syn-anti* η^3 -1-methallyl ligands and *cis-trans* η^1 -1-methallyl ligands, and c) isomers with varying numbers of η^1 - and η^3 -1-methallyl groups. IR spectroscopy is a useful technique to study the presence of such isomers, since it gives spectra that are superpositions of all the components of the mixture. For $\text{Cp}'\text{Hf}(\text{C}_4\text{H}_7)_3$ the spectrum (Fig. 2) shows three bands in the 1700–1500 cm^{-1} range. The bands at 1647 and 1629 cm^{-1} are assigned to two different η^1 -C₄H₇ ligands, possibly due to *cis* and *trans* configurations of the 1-methallyl group. The band at 1576 cm^{-1} indicates the presence of η^3 -1-methallyl ligands. This position is rather high compared with that for $(\eta^8\text{-C}_8\text{H}_8)\text{M}(\eta^1\text{-C}_4\text{H}_7)(\eta^3\text{-C}_4\text{H}_7)$ (M = Zr, Hf), for which the absorptions are found at 1560 (M = Zr) and 1540 cm^{-1} (M = Hf) [2], but corresponds almost exactly with that of the η^3 -1-methallyl band in $\text{Cp}_2\text{Zr}(\eta^1\text{-C}_4\text{H}_7)(\eta^3\text{-C}_4\text{H}_7)$ at 1582 cm^{-1} (the bands for the η^1 -C₄H₇ groups are found in this case at 1638 and 1620 cm^{-1}) [9]. The band at 1576 cm^{-1} is broad and shows unresolved splitting. This suggests various η^3 -1-methallyl groups, e.g. *syn* or *anti*, or even two η^3 -1-methallyl groups per metal centre. The presence of *cis* and *trans* η^1 -C₄H₇ groups may originate from the starting Grignard reagent, but isomerization on the transition metal atom is much more likely, since the NMR spectra exclude the presence of non-interconverting *cis* and *trans* isomers.

The room temperature NMR spectra (Table 2) at first sight are simple, and in agreement with the presence of only η^1 -1-methallyl groups. The ¹H NMR spectrum (Fig. 1) shows resonances at positions and with intensities compatible with the presence of three η^1 -1-methallyl groups. A ³J(H, H) coupling constant between the olefinic protons of 14.5 Hz is close to that expected for a *trans* configuration. However, all the ¹H NMR resonances, are slightly broadened at 25°C and broaden further on cooling, thus confirming the indications from the IR spectra, that $\text{Cp}'\text{Hf}(\text{C}_4\text{H}_7)_3$ is a mixture of interconverting isomers. The broadening continues below -85°C, indicating that the activation energies are very small [2].

The ¹³C NMR spectrum shows broad resonances for C ^{α} , C ^{γ} and C ^{δ} . The chemical shifts and coupling constants, ¹J(C, H), are typical of η^1 -1-methallyl ligands [10].

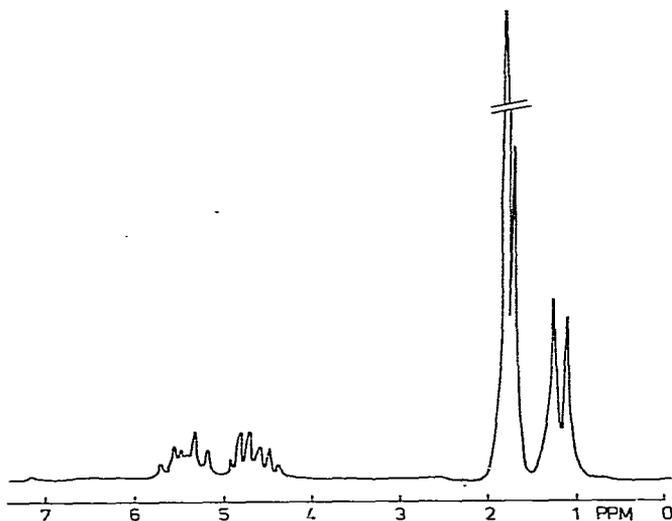
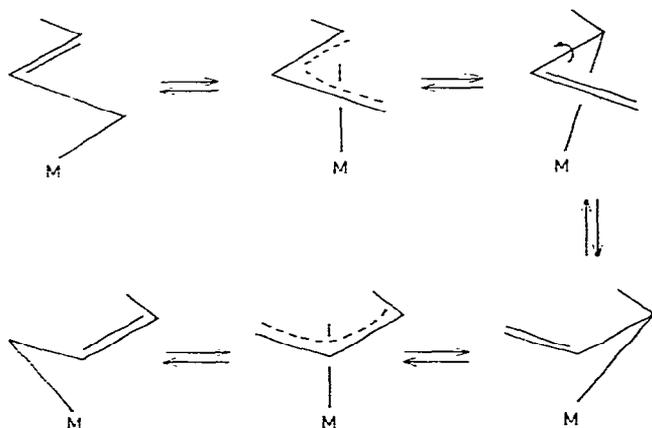


Fig. 1. ^1H NMR spectrum of $\text{Cp}'\text{Hf}(\text{C}_4\text{H}_7)_3$ in benzene- d_6 at room temperature.

The exact nature of these dynamic processes cannot be established without further and detailed investigations of the NMR spectra at various temperatures, but we feel justified in regarding the IR and NMR data as evidence for the presence of a complicated mixture of readily interconverting isomers (Scheme 1).

SCHEME 1



Conversion into $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$

The conversion of $\text{Cp}'\text{Hf}(\text{C}_4\text{H}_7)_3$ into $\text{Cp}'\text{Hf}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ and *trans*-2-butene, according to eq. 1, was monitored by ^1H NMR and IR spectroscopy. In C_6D_6 (60°C) the original $\text{Cp}'\text{Hf}(\text{C}_4\text{H}_7)_3$ ^1H NMR spectrum (Fig. 1) is changed into a new complicated one, which is compatible with the presence of $\eta^5\text{-Cp}'$, $\eta^4\text{-C}_4\text{H}_6$ and $\eta^3\text{-C}_4\text{H}_7$ ligands. However, there are two Cp' singlets (δ 1.80 and 1.90 ppm) and a complex resonance from the CH-CH_3 part of the $\eta^3\text{-C}_4\text{H}_7$ ligand, indicating that two isomers (*syn* and *anti*) are present. On prolonged

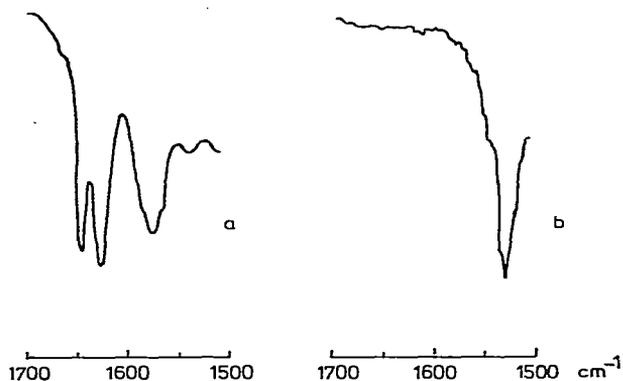
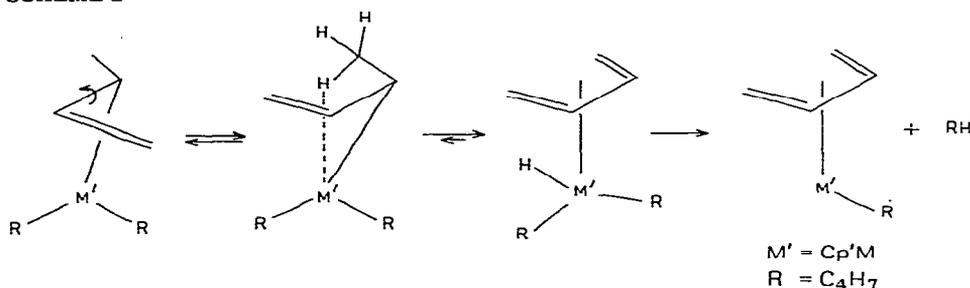


Fig. 2. The IR allyl region of (a) $\text{Cp}'\text{Hf}(\text{C}_4\text{H}_7)_3$ and (b) $\text{Cp}'\text{Hf}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$.

heating the Cp' singlet at δ 1.90 ppm increases at the expense of the singlet at δ 1.80 ppm. Simultaneously the CH-CH_3 resonances also become simpler and the spectrum of $\text{Cp}'\text{Hf}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ is finally reached. At 60°C in THF the region between $1650\text{--}1500\text{ cm}^{-1}$ in the IR spectrum of $\text{Cp}'\text{Hf}(\text{C}_4\text{H}_7)_3$ changes significantly. The absorptions at $1647/1629\text{ cm}^{-1}$ ($\eta^1\text{-C}_4\text{H}_7$) and 1576 cm^{-1} ($\eta^3\text{-C}_4\text{H}_7$) disappear and a new absorption at 1533 cm^{-1} of the now η^3 -bonded methallyl ligand [11] in $\text{Cp}'\text{Hf}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ appears (Fig. 2).

A plausible mechanism of formation of $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ from $\text{Cp}'\text{M}(\text{C}_4\text{H}_7)_3$ is shown in Scheme 2. The formation of η^1 -1-methyl-2-propen-1-yl leads to a β -H abstraction, which is followed by reductive elimination of *trans*-2-butene.

SCHEME 2

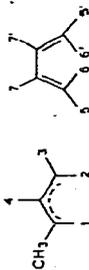


A rearrangement of the three η^1 -1-methallyl ligands into $\eta^3\text{-C}_4\text{H}_7$ and $\eta^4\text{-C}_4\text{H}_6$ with formation of 2-butene is not surprising, since the compounds $\text{Cp}'\text{M}(\eta^1\text{-C}_4\text{H}_7)_3$ and its isomers with η^1 - and $\eta^3\text{-C}_4\text{H}_7$ groups are coordinatively highly unsaturated.

Properties of $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$

The IR spectra of the compounds $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ all are very similar, showing characteristic $\eta^5\text{-Cp}'$ bands at 2915m , 2870m , 1485s , 1425s , 1380s , 1070m , 1025s and 800m cm^{-1} . The assignment of the $\eta^4\text{-C}_4\text{H}_6$ absorptions, usually found between $1500\text{--}1350\text{ cm}^{-1}$ [12], is problematic as they

TABLE 3
 ^1H NMR SPECTROSCOPIC DATA FOR $\text{Cp}^*\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ a,b



Compound M =	$\eta^5\text{-Cp}^*$	CH_3	H(1)	H(2)	H(3)	H(4)	H(5,5')	H(6,6')	H(7,7')	$^3J(1,4)$	$^3J(2,4)$	$^3J(3,4)$
Ti	1.79 (s, 15 H)	1.30 (d, 3 H)	1.3 ^d (m, 1 H)		1.0 (br, 2 H)	6.45 (m, 1 H)	1.3 ^d (m, 2 H)	-0.68 (m, 2 H)	6.00 (m, 2 H)			
Zr	1.92 (s, 15 H)	1.43 (s, 3 H)	1.43 (m, 1 H)	0.59 (dd, 1 H)	1.6 ^d (m, 1 H)	5.98 (dt, 1 H)	1.6 ^d (m, 2 H)	-0.58 (m, 2 H)	5.53 (m, 2 H)	12.5	12.5	9.5
Hf	1.94 (s, 15 H)	1.55 (d, 3 H)	1.5 ^d (m, 1 H)		1.0 (br, 2 H)	6.00 (m, 1 H)	1.5 ^d (m, 2 H)	-0.83 (t, 2 H)	5.56 (m, 2 H)	13.0	10.5	10.5

^a In benzene-d₆ at room temperature, values given in δ (ppm) relative to internal TMS. ^b Coupling constants $^3J(\text{H}, \text{H})$ are given in Hz. ^c Coupling not observed. ^d Partially overlapped by other resonances.

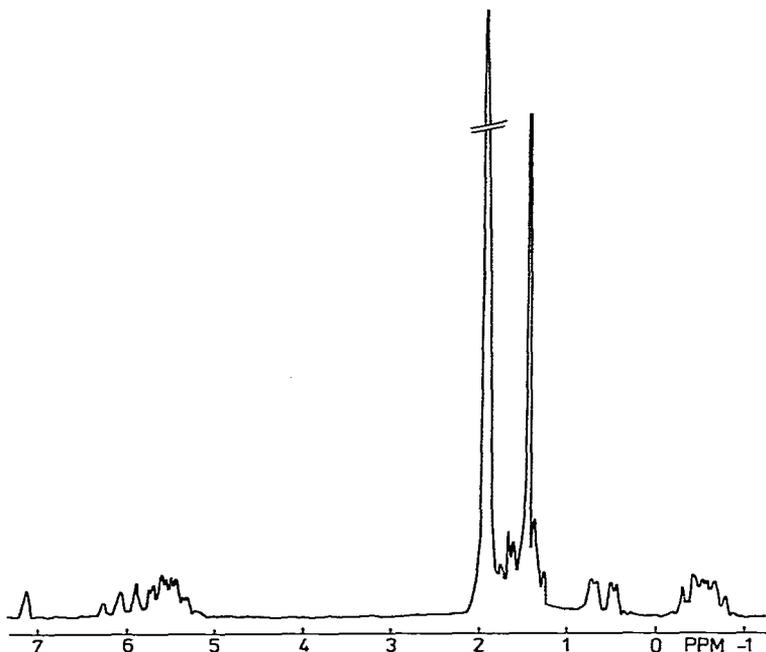


Fig. 3. ^1H NMR spectrum of $\text{Cp}'\text{Zr}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ in benzene- d_6 at room temperature.

coincide with the Cp' absorptions. A medium to strong absorption near 1530 cm^{-1} is characteristic of an η^3 -1-methyl group with the methyl group in a *syn* position [11].

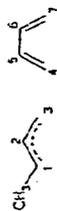
The ^1H NMR spectra of the compounds $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ (Table 3) all show resonances characteristic of $\eta^5\text{-Cp}'$, $\eta^4\text{-C}_4\text{H}_6$ and $\eta^3\text{-C}_4\text{H}_7$ ligands, and are temperature dependent. In Fig. 3 is shown the room temperature ^1H NMR spectrum of $\text{Cp}'\text{Zr}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$.

Below the coalescence temperature (for $\text{M} = \text{Ti} -8^\circ\text{C}$; $\text{Zr } 30^\circ\text{C}$; $\text{Hf } 10^\circ\text{C}$) the $\eta^3\text{-C}_4\text{H}_7$ fragment in the complex is static, i.e. the rate of exchange of the *syn* and *anti* protons 2 and 3 is slow on the NMR time scale and the protons 2 and 3 appear at different positions*. The value found for $^3J(\text{H}(1), \text{H}(4))$ ($\sim 13\text{ Hz}$) also indicates that the methyl group is in a *syn* position [2]. At higher temperatures an equilibration of the *syn* and *anti* protons, due to rotation about the C—C single bond in the $\eta^1\text{-C}_4\text{H}_7$ form (see Scheme 3b), occurs and a $\text{AMX}_2(\text{Z}_3)$ spin system results. At the same time, the two partially overlapping triplets (Fig. 4) due to two different inner methylene protons 6 and 6' of the $\eta^4\text{-C}_4\text{H}_6$ ligand coalesce, and at higher temperatures a broad triplet due to equivalent inner methylene protons results (Fig. 4).

The temperature-dependent ^{13}C NMR spectra (Table 4) below the coalescence temperature also show two different methylene carbon atoms, which

* The free energy of activation (ΔG^\ddagger) for this process could not be calculated.

TABLE 4

 ^{13}C NMR SPECTROSCOPIC DATA FOR $\text{Cp}^*\text{M}(\eta^3\text{-C}_5\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ a,b

Compound	T (°C)	C ₅ (CH ₃) ₅	C ₅ (CH ₃) ₅	CH ₃	C(1)	C(2)	C(3)	C(4)	C(5,6)	C(7)
Ti ^c	25	118.0	12.3	19.3	80.4	127.1	58.7	^e	115.1	^e
Zr ^c	25	117.6	(q, 127) 12.1	(q, 128) 18.3	(d, 151) 77.3	(d, 152) 128.0	(t, 153) 53.2	^e 48.4	(d, 156) 113.0	52.0
Hf ^d	-23	116.8	(q, 127) 12.3	(q, 126) 18.6	(d, 145) 74.7	(d, 150) 129.1	(t, 151) 50.0	(t, 146) 50.2	(d, 161) 112.4/ 112.7	(t, 146) 45.6
	25	116.6	12.0	18.1	74.7	128.9	50.0	^e	112.5	^e
	60	117.0	(q, 127) 12.1	(q, 128) 18.1	(d, 145) 75.2	(d, 151) 129.4	(t, 148) 50.4	^e 48.0	(d, 158) 112.9	48.0

^a Values given in δ (ppm) relative to TMS. ^b $^1\text{J}(^{13}\text{C}, \text{H})$ given in Hz in parentheses. ^c Benzene- d_6 . ^d Toluene- d_8 . ^e Not observed.

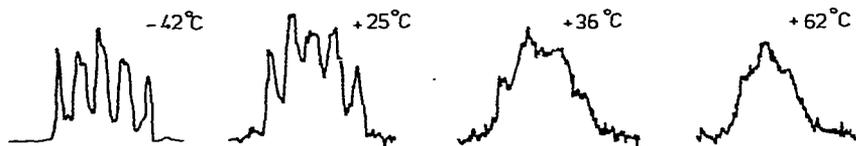


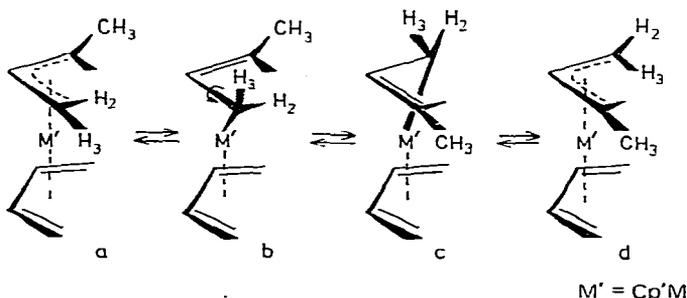
Fig. 4. Temperature-dependent ^1H NMR spectra (H(6), H(6') region) of $\text{Cp}'\text{Zr}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$.

upon heating coalesce to one signal. The ^{13}C -H coupling constants in the butadiene fragment (Table 4), determined from gated decoupled ^{13}C NMR spectra, are typical of η^4 -bonded butadiene [5,13] and so a metallacyclopentene structure is unlikely [4b].

There is no doubt that the $\eta^4\text{-C}_4\text{H}_6$ ligand in the complex has a *cis* arrangement. The NMR resonances and coupling constants of the $\eta^4\text{-C}_4\text{H}_6$ fragment are in agreement with those found in bis(η^5 -cyclopentadienyl)(η^4 -*cis*-butadiene)zirconium [5].

From the combined spectroscopic evidence it is possible to propose a structure for the compound $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$, and a possible arrangement for the $\eta^3\text{-C}_4\text{H}_7$ and $\eta^4\text{-C}_4\text{H}_6$ fragments is shown in Scheme 3. It is easy to see that a

SCHEME 3



static $\eta^3\text{-C}_4\text{H}_7$ group is responsible for two different methylene groups of the $\eta^4\text{-C}_4\text{H}_6$ fragment (Scheme 3a). When the $\eta^3\text{-C}_4\text{H}_7$ ligand becomes fluxional, the methylene groups of the butadiene ligand will become equivalent (Scheme 3b, c, d).

Chemical properties of $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$

The compounds $\text{Cp}'\text{M}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-C}_4\text{H}_6)$ are very reactive. They are air sensitive and react with dry oxygen to give 1,3-butadiene and inorganic products containing oxygen, Cp' and probably methyl groups. With HCl (gas, excess) $\text{Cp}'\text{MCl}_3$ is formed, together with a mixture of butenes and chlorobutanes. The composition of this mixture depends strongly on the metal. For $\text{M} = \text{Zr}$ we found 1-butene, *trans*-2-butene, 1-chlorobutane and 2-chlorobutane (ratio 1 : 5 : 3 : 41).

Attempts to replace the butadiene ligand by other dienes, e.g. 2,3-dimethyl-1,3-butadiene, isoprene, 1,3-pentadiene (hydrocarbon solvents, temperatures up to 70°C) were unsuccessful, and no dimerization of the dienes was observed under these conditions. With acetylene a smooth reaction took place under mild conditions (1 atm, room temperature, hydrocarbon solvent) with formation of polyacetylene and traces of benzene and cyclooctatetraene.

The complexes are also very reactive towards small substrate molecules like CO, CO₂ and H₂, and these reactions are under investigation.

Experimental

General

All experiments were done under purified nitrogen. Solvents were distilled from sodium benzophenone ketyl or LiAlH₄.

Elemental analyses were performed in the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga.

¹H NMR spectra were measured at 60 MHz with Perkin-Elmer R-24B and JEOL 60 HL spectrometers. ¹³C NMR spectra were measured at 25.2 MHz with a Varian XL-100 spectrometer. IR spectra were measured on a JASCO-IRA-2 spectrophotometer using Nujol mulls or THF solutions.

GC analyses were carried out with a Packard 428 Laboratory Gas Chromatograph using a 6-ft Poropak Q column. Decomposition temperatures were measured by differential thermal analysis (DTA); heating rate 2–3°C/min.

Preparation of Cp'TiCl₃ *

Cp'TiCl₃ was prepared by a modification of a published procedure [14]. A suspension of 9.96 g (26.9 mmol) of TiCl₃ · 3 THF and 3.82 g (26.9 mmol) of Cp'Li [15] in THF was stirred for 12 h. Subsequently, THF was removed in vacuo and the dark green solid was oxidized with a HCl-ether-pentane solution. After evaporation of the solvent, the red Cp'TiCl₃ was obtained by sublimation (120°C/0.001 mmHg). Yield 5.52 g (70%). Anal.: Found: Ti, 16.46; Cl, 36.60. TiC₁₀H₁₅Cl₃ calcd.: Ti, 16.54; Cl, 36.74%. ¹H NMR (δ, CDCl₃): 2.37 ppm (s).

Preparation of Cp'MCl₃, M = Zr, Hf

A suspension of 32.0 mmol of MCl₄ and 32.0 mmol of Cp'Li in *o*-xylene was stirred for 12 h, then the suspension was filtered and the solid washed with *n*-pentane. Sublimation (M = Zr: 160°C/0.001 mmHg; M = Hf: 140°C/0.001 mmHg) gave yellow (M = Zr) or green-yellow (M = Hf) Cp'MCl₃. Yield 21.0 mmol (65%). Anal. Cp'ZrCl₃: Found: Zr, 27.47; Cl, 31.98. ZrC₁₀H₁₅Cl₃ calcd.: Zr, 27.41; Cl, 31.96%. ¹H NMR Cp'ZrCl₃ (δ, CDCl₃): 2.17 ppm (s). Anal. Cp'HfCl₃: Found: Hf, 42.52; Cl, 25.48. HfC₁₀H₁₅Cl₃ calcd.: Hf, 42.49; Cl, 25.32%. ¹H NMR Cp'HfCl₃ (λ, CDCl₃): 2.28 ppm (s).

Preparation of Cp'Hf(C₄H₇)₃

A solution of 14.1 mmol of 2-butenylmagnesium bromide in ether was added dropwise during 15 minutes to a stirred suspension of 1.97 g (4.7 mmol) of Cp'HfCl₃ in 25 ml of ether at 0°C. After stirring for 3 h at 0°C, the solvent was removed in vacuo. Extraction of the resulting solid with *n*-pentane and evaporation of the extract gave a yellow-orange oil, Cp'Hf(C₄H₇)₃. Yield 2.01 g (90%).

* Unless mentioned otherwise reactions were performed at room temperature.

Preparation of $Cp'M(\eta^3-C_4H_7)(\eta^4-C_4H_6)$, $M = Ti, Zr$

A solution of 25.5 mmol of 2-butenylmagnesium bromide in ether was added dropwise during 15 minutes to a stirred suspension of 8.5 mmol of $Cp'MCl_3$ in 40 ml of ether. After 2 h, when the evolution of *trans*-2-butene had stopped, the solvent was removed in vacuo and the resulting solid was extracted with n-pentane, and recovered by removal of the solvent. Recrystallization from n-pentane gave analytically pure $Cp'M(\eta^3-C_4H_7)(\eta^4-C_4H_6)$ (Table 1).

Preparation of $Cp'Hf(\eta^3-C_4H_7)(\eta^4-C_4H_6)$

Either sublimation (90°C/0.001 mmHg) of $Cp'Hf(C_4H_7)_3$ or reflux in THF and subsequent recrystallization from n-pentane gave pure $Cp'Hf(\eta^3-C_4H_7)(\eta^4-C_4H_6)$ (Table 1).

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