Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

DIALLYLDICYCLOPENTADIENYLZIRCONIUM AND SOME RELATED COMPLEXES

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(Received April 24th, 1968)

SUMMARY

The complexes $Cp_2Zr(C_3H_5)_2$, $Cp_2ZrCl(C_3H_5)$ (impure) and $Cp_4Zr_2Cl(C_3H_5)_3$ were prepared in crystalline form by reaction of Cp_2ZrCl_2 with allylmagnesium chloride in THF. In a similar way, the 2-methylallyl complexes $Cp_2Zr(C_4H_7)_2$ and $Cp_2ZrCl(C_4H_7)$ were obtained as oils. The complexes are air sensitive. Infrared spectroscopy shows that the allylic ligands in $Cp_2ZrCl(C_3H_5)$ and $Cp_2ZrCl(C_4H_7)$ are σ-bonded to the metal, while in $Cp_2Zr(C_3H_5)_2$ and $Cp_2Zr(C_4H_7)_2$ one of the allylic ligands is π-bonded, the other σ-bonded. In $Cp_4Zr_2Cl(C_3H_5)_3$, which is probably a molecular complex, one allyl group is π-bonded, the other two σ-bonded. The NMR spectra of the allylic ligands are of the dynamic type. The bonding of the allylic ligands and their CC stretching frequencies are discussed and compared with corresponding titanium and vanadium complexes; it is found that substitution of the hydrogen atom at 2-C of the allyl group by a methyl group leads to an increase of the CC stretching frequency of σ-allylic ligands, but to a decrease in the case of π-allylic ligands.

INTRODUCTION

Reaction of dicyclopentadienyltitanium(IV) dichloride with allylmagnesium chloride leads to reduction of the metal to the trivalent state with formation of the π-allyl complex $Cp_2Ti(\pi\text{-}C_3H_5)$[1,2]. Dicyclopentadienylzirconium(IV) dichloride is much more resistant to reduction than the analogous titanium compound; we found that Cp_2ZrCl_2 is not reduced by zinc powder or isopropylmagnesium bromide under conditions where Cp_2TiCl_2 is reduced[2,3,4]. It seemed of interest, therefore, to study the reaction of Cp_2ZrCl_2 with allylmagnesium chloride.

SYNTHESIS AND CHEMICAL PROPERTIES

By reaction of 2 moles of allylmagnesium chloride with 1 mole of dicyclopentadienylzirconium dichloride in tetrahydrofuran we obtained cream-coloured crystals of diallyldicyclopentadienylzirconium(IV) according to:

$$Cp_2ZrCl_2 + 2\,C_3H_5MgCl \rightarrow Cp_2Zr(C_3H_5)_2 + 2\,MgCl_2 \qquad (1)$$

The homologue bis(2-methylallyl)dicyclopentadienylzirconium(IV), $Cp_2Zr(C_4H_7)_2$,

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was prepared in a similar way, but this compound was obtained as a yellow oil which could not be purified. The reaction of Cp_2ZrCl_2 with 1,3-dimethylallylmagnesium chloride in molar ratio 1:2 in THF evolved some heat and a deep red solution was obtained; the complex formed, however, was too unstable to be isolated at room temperature.

Diallyldicyclopentadienylzirconium is air sensitive. Ampules of the compound kept under nitrogen at room temperature and in daylight darken after several hours; if stored in darkness at −18° the compound remains unchanged for several months. When heated, $Cp_2Zr(C_3H_5)_2$ decomposes from about 87° without melting. Solutions of the compound in cyclohexane show no absorption band in the visible range from 350 to 850 mμ (the same is observed for Cp_2ZrCl_2).

Reaction of $Cp_2Zr(C_3H_5)_2$ with 4 *N* hydrochloric acid or pure water gives propene, as expected (*cf.* ref. 2). However, a slow further hydrolysis takes place with formation of cyclopentadiene; after some days a white residue is obtained which does not contain cyclopentadienyl ligands. By reaction of $Cp_2Zr(C_3H_5)_2$ with hydrogen chloride in ether solution white Cp_2ZrCl_2 is regenerated. During the reaction a transient yellow colour is observed, probably due to the intermediate product $Cp_2ZrCl(C_3H_5)$; the transient yellow colour was also observed during the preparation according to reaction (1). The yellow complex $Cp_2ZrCl(C_3H_5)$ could be isolated in an impure state as the product of the reaction of $Cp_2Zr(C_3H_5)_2$ with dichloromethane in hexane solution.

It was also attempted to prepare allyldicyclopentadienylzirconium chloride by reaction of Cp_2ZrCl_2 and C_3H_5MgCl in a molar ratio of 1:1 in THF. A yellow crystalline compound was isolated; chemical analysis showed, however, that the product was not the expected compound $Cp_2ZrCl(C_3H_5)$, but had the composition $Cp_4Zr_2Cl(C_3H_5)_3 = [Cp_2ZrCl(C_3H_5)\cdot Cp_2Zr(C_3H_5)_2]$. Although the infrared spectrum (in KBr discs) and the NMR spectrum (in benzene or cyclopentane solution) of the product are superpositions of the spectra of $Cp_2Zr(C_3H_5)_2$ and $Cp_2ZrCl(C_3H_5)$, the product is believed to be a molecular compound $Cp_4Zr_2Cl(C_3H_5)_3$ rather than a mixture, since its composition was constant in several experiments, while its X-ray powder pattern differed from those of $Cp_2Zr(C_3H_5)_2$ and $Cp_2ZrCl(C_3H_5)$. The complex $Cp_4Zr_2Cl(C_3H_5)_3$ is air sensitive, but seems to be somewhat more stable than either $Cp_2ZrCl(C_3H_5)$ or $Cp_2Zr(C_3H_5)_2$; no change was observed if the crystals were stored (under nitrogen) for some hours at room temperature or for some months at −18°. Solutions of $Cp_4Zr_2Cl(C_3H_5)_3$ in cyclohexane do not show an absorption band in the visible range.

Reaction of Cp_2ZrCl_2 and 2-methylallylmagnesium chloride in molar ratio 1:1 gave a red oil which could not be purified; the Cl content and the infrared spectrum (see below) indicate that the reaction product is mainly $Cp_2ZrCl(C_4H_7)$.

Infrared and NMR spectra

The method of preparation and the chemical properties of diallyldicyclopentadienylzirconium suggest that the cyclopentadienyl ligands are π-bonded to the metal. This conclusion is supported by the infrared spectrum of the complex (Fig. 1a) in which the normal vibrations of the π-cyclopentadienyl groups are observed at their usual wave numbers[5], as is also the case in the spectra of $Cp_2Ti(C_3H_5)$[2] (Fig. 1b) and $Cp_2V(C_3H_5)$[6] (Fig. 1c).

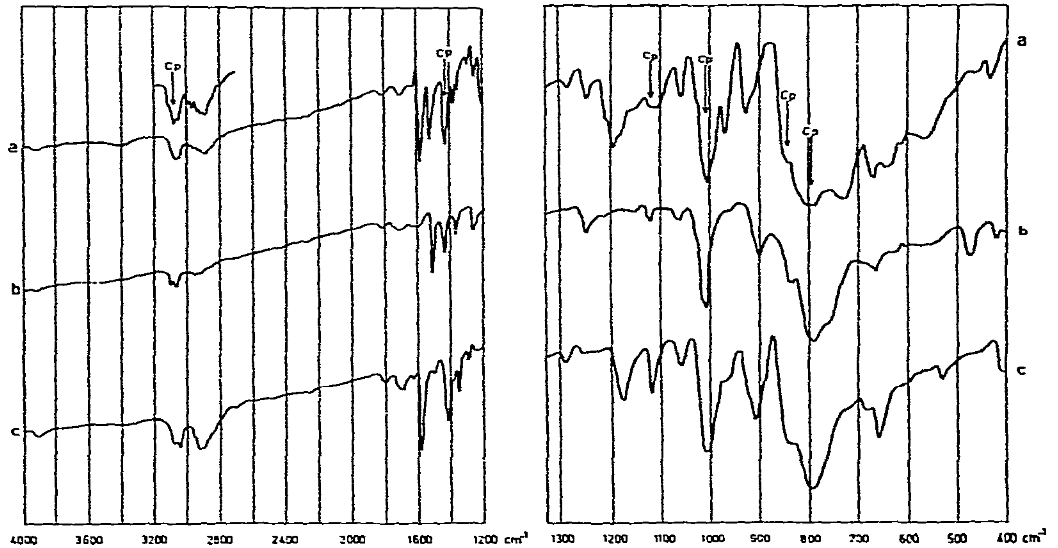

Fig. 1. Infrared spectra of (a) $Cp_2Zr(C_3H_5)_2$; (b) $Cp_2Ti(\pi\text{-}C_3H_5)$[2]; (c) $Cp_2V(\sigma\text{-}C_3H_5)$[6] in KBr discs. The normal vibrations of the $\pi\text{-}C_5H_5$ ligands are indicated.

In $Cp_2Ti(C_3H_5)$ the allyl group is π-bonded to the metal[2,7], in $Cp_2V(C_3H_5)$ the group is σ-bonded[6]. Comparison of Fig. 1b and 1c shows several differences in the absorption of the π-allyl and σ-allyl ligands, *e.g.* in the intensities of the CH stretching bands in the range 3000 to 2900 cm^{-1} and in the wave numbers of the CH deformation bands in the range 1400 to 1150 cm^{-1}. The most characteristic differences, however, are found in the range from 1650 to 1450 cm^{-1}. Complexes with an allylic group σ-bonded to a transition metal [such as $Cp_2V(C_3H_5)$] show a strong absorption band (C=C stretch) in the range 1650 to 1580 cm^{-1}; in complexes with π-bonded allylic ligands the corresponding band (asymmetric CC stretch) is found[7,8,9] in the range 1550 to 1450 cm^{-1}.

The spectrum of diallyldicyclopentadienylzirconium shows two strong absorption bands in the range under discussion, one at 1589 cm^{-1} and one at 1533 cm^{-1}. The spectrum of allyldicyclopentadienylzirconium chloride shows only one band in this range, namely at 1598 cm^{-1}, while the complex $[Cp_2ZrCl(C_3H_5)\cdot Cp_2Zr(C_3H_5)_2]$ gives strong bands at 1598 and 1589 cm^{-1} and a band of medium intensity at 1533 cm^{-1} (Table 1).

Table 1 compares these bands with the corresponding bands of σ-allyl and π-allyl complexes of titanium and vanadium. We deduce that the allyl group in $Cp_2ZrCl(C_3H_5)$ is σ-bonded to the metal, while $Cp_2Zr(C_3H_5)_2$ contains one σ-bonded and one π-bonded allylic ligand. Of the three allyl groups in the complex $Cp_4Zr_2Cl(C_3H_5)_3$ probably one is π-bonded, the other two σ-bonded to zirconium. The other ranges of the infrared spectra are also in agreement with these conclusions; *cf.* the spectrum of $Cp_2Zr(C_3H_5)_2$ in Fig. 1a. Quite similarly, the infrared spectra of the 2-methylallyl complexes (Table 1) show that the allylic ligand is σ-bonded to the metal in $Cp_2ZrCl(C_4H_7)$, while the bis(2-methylallyl) complex $Cp_2Zr(C_4H_7)_2$ has one π-allylic and one σ-allylic ligand.

TABLE 1

ABSORPTION BANDS IN THE RANGE 1450–1650 cm^{-1} IN THE INFRARED SPECTRA OF ALLYL AND 2-METHYLALLYL COMPLEXES OF ZIRCONIUM, TITANIUM AND VANADIUM

The deduced type of bonding of the allylic ligands is also given, as is independent evidence for this type of bonding.

	Wave numbers (cm^{-1})		Bonding	Confirmed by	Ref.
Allyl complexes					
$Cp_2Zr(C_3H_5)_2$	1533 (st)	1589 (st)	π, σ		
$Cp_2ZrCl(C_3H_5)$		1598 (st)	σ		
$Cp_4ZrCl(C_3H_5)_3$	1533 (m)	1589 (st) 1598 (st)	π, σ, σ		
$Cp_2Ti(CH_3)(C_3H_5)$		1597	σ		11
$Cp_2Ti(C_3H_5)$	1509		π	X-ray analysis[a]	7
$Cp_2V(C_3H_5)$		1588	σ	Paramagnetism	6
$Zr(C_3H_5)_4$	1515		π	NMR	10
$Ti(C_3H_5)_3$?		1607	σ		10
$V(C_3H_5)_3$	1505–1520		π		10
2-Methylallyl complexes					
$Cp_2Zr(C_4H_7)_2$	1520 (m)	1603 (st)	π, σ		
$Cp_2ZrCl(C_4H_7)$?		1606 (st)	σ		
$Cp_2Ti(CH_3)(C_4H_7)$		1602	σ		11
$Cp_2Ti(C_4H_7)$	1480		π	X-ray analysis[a]	7
$Cp_2V(C_4H_7)$		1598	σ	Paramagnetism	6

[a] X-ray analysis of (1,2-dimethylallyl)dicyclopentadienyltitanium(III).

Unfortunately, it has not yet been possible to confirm (or reject) the above conclusions by NMR spectroscopy. The proton resonance spectra of $Cp_2Zr(C_3H_5)_2$, $Cp_2ZrCl(C_3H_5)$, $Cp_2Zr(C_4H_7)_2$ and $Cp_2ZrCl(C_4H_7)$ recorded at room temperature (Table 2) indicate that the behaviour of the allylic ligands is of the "dynamic" type[9,12,13].

TABLE 2

NMR SPECTRA OF ALLYL AND 2-METHYLALLYL COMPLEXES OF ZIRCONIUM AT ROOM TEMPERATURE

Chemical shifts are given relative to TMS (τ = 10 ppm) as internal standard.

Compound (solvent)	τ-values (and intensities) of signals assigned to hydrogens attached to				J(H–H) (cps)
	π-C_5H_5	1-C and 3-C	2-C	2-Me	
$Zr(C_3H_5)_4$		Doublet	Quintet		
(in cyclopentane)[10]		7.30(16)	4.76(4)		12
(in $CFCl_3$, −10°)[14]		7.37(16)	4.81(4)		12.5
$Cp_2Zr(C_3H_5)_2$	Singlet	Doublet	Quintet		
(in C_6D_6)	4.87(10)	7.11(8)	4.37(2)		11.5
$Cp_2ZrCl(C_3H_5)$	Singlet	Doublet	Quintet?		
(in C_6D_6)	4.26(10)	6.69(4)	3.89(1?)		11
$Cp_2Zr(C_4H_7)_2$	Singlet	Singlet		Singlet	
(in C_6D_6)	4.41(10)	7.14(8)		8.39(7)	
$Cp_2ZrCl(C_4H_7)$	Singlet	Singlet		Singlet	
(in $CDCl_3$)	3.67(10)	6.91(3)		8.34(3)	

For comparison, the NMR spectrum of $Zr(C_3H_5)_4$ at room temperature[10,14] which also indicates dynamic behaviour of the allyl ligands, is included in Table 2. Below −70° the spectrum of $Zr(C_3H_5)_4$ becomes of the π-allyl type[10,14]. In contrast, we found low-temperature (down to −90°) NMR spectra of $Cp_2Zr(C_3H_5)_2$ and $Cp_2Zr(C_4H_7)_2$ in cyclopentane not to be significantly different from those recorded at room temperature. (The chloro complexes are insufficiently soluble at low temperatures.) It is to be remarked, that the NMR signals of the protons of the allylic ligands in $Cp_2Zr(C_3H_5)_2$ lie at lower fields than those of the π-allyl ligands in $Zr(C_3H_5)_4$, but at higher fields than those of the σ-allyl group in $Cp_2ZrCl(C_3H_5)$ (Table 2).

The apparently conflicting conclusions about the behaviour of the allylic ligands as derived from the NMR and infrared spectra are to be ascribed to the difference of the frequencies employed in the two techniques, and hence to their different time scales. It must also be kept in mind that the infrared spectra refer to the pure compounds (solids or oils), the NMR spectra to solutions. The following discussion will be based on the conclusions from the infrared spectra, summarized in Table 1, namely that σ-bonded and π-bonded allylic ligands can be distinguished.

DISCUSSION

The C=C stretching frequency in the infrared spectra of allyl compounds of the main-group metals (where π-bonding in the usual sense is not possible) increases with increasing electronegativity of the metal[12], *e.g.* from 1535 cm^{-1} in NaC_3H_5 (which is regarded as ionic) to 1575 cm^{-1} in $Mg(C_3H_5)_2$, to 1605 cm^{-1} in $Zn(C_3H_5)_2$ and 1630 cm^{-1} in $B(C_3H_5)_3$; the latter compound may be regarded as nearly homopolar with σ-bonds between borium and the allylic groups.

The infrared bands of $Cp_2Zr(C_3H_5)_2$ and $Cp_2ZrCl(C_3H_5)$ which have been assigned as the C=C stretching frequencies of σ-bonded allyl groups, lie at 1589 and 1598 cm^{-1} respectively (Table 1), in reasonable agreement with the general rule mentioned. [Substitution of the π-allyl ligand of $Cp_2Zr(C_3H_5)_2$ by chloride increases the effective electronegativity of the central metal.] The corresponding bands of the 2-methylallyl complexes $Cp_2Zr(C_4H_7)_2$ and $Cp_2ZrCl(C_4H_7)$ lie at somewhat higher frequencies (Table 1). Similar increase of the C=C stretching frequency by methyl substitution is found in the σ-(2-methylallyl) complexes $Cp_2V(C_4H_7)$[6] and $Cp_2Ti(CH_3)(C_4H_7)$[11] (Table 1) and also in organic compounds where a hydrogen atom attached to one of the carbon atoms linked by a (localised) double bond is substituted by a methyl group.

For allylic anions with delocalized π-electrons, however, the asymmetric CC stretching frequency decreases if the hydrogen at the middle carbon atom of the allylic group is substituted by a methyl group, *e.g.* from 1535 cm^{-1} in allylsodium to 1520 cm^{-1} in 2-methylallylsodium[15]. The asymmetric CC stretching frequency of (2-methylallyl)dicyclopentadienyltitanium also is considerably lower than that of $Cp_2Ti(C_3H_5)$ (Table 1); in these complexes, too, the π-electrons of the allylic ligands are delocalized[7]. A similar, though smaller, shift is found for the asymmetric CC stretches of the π-allylic ligands of $Cp_2Zr(C_3H_5)_2$ and $Cp_2Zr(C_4H_7)_2$ (Table 1). (The few literature data available indicate that the influence of substitution on the CC stretching frequency is less important, if the number of *d*-electrons of the metal is large.)

The bonding in complexes π-Cp_2MR_n ($n=1, 2, 3$) has been discussed by Ballhausen and Dahl[16]; three orbitals of the metal M are available for combining with orbitals of the ligands R. In $Cp_2Ti(\pi\text{-}C_3H_5)$ two of these metal orbitals combine with the (filled) bonding and non-bonding π-orbitals of the $C_3H_5^-$ ligand. The (empty) antibonding π-orbital of this ligand combines with the third metal orbital which contains the unpaired electron ("back-bonding"). The effect will be a weakening of the C–C–C π-bond of the ligand and, therefore, a decrease of its (asymmetric) CC stretching frequency; this frequency is observed at 1509 cm^{-1} compared to 1535 cm^{-1} in $Na^+C_3H_5^-$. In $Cp_2Zr(\sigma\text{-}C_3H_5)(\pi\text{-}C_3H_5)$ one of the metal orbitals is involved in σ-bonding the σ-allyl ligand and is not available for back-bonding to the π-allyl ligand. The C–C–C bond of the latter ligand will be less weakened; indeed, its asymmetric CC stretching frequency is found at 1533 cm^{-1}, almost the same as for allylsodium. Similar reasonings also apply to the corresponding 2-methylallyl complexes (*cf.* Table 1).

By extension of the theory one might expect that $Cp_2V(C_3H_5)$ is diamagnetic ("inert-gas rule") and that the CC stretching frequency of the supposedly π-bonded allyl ligand is still lower than that of $Cp_2Ti(C_3H_5)$. Actually, however, $Cp_2V(C_3H_5)$ is paramagnetic (with two unpaired electrons) and its CC stretching band occurs at 1588 cm^{-1} indicating that the allyl ligand is σ-bonded to the metal[6]. The compound, therefore, conforms to the empirical rule that the Cp_2V group preferably carries one additional (monodentate) ligand, while the Cp_2Ti group preferably has two monodentate ligands or one bidentate ligand, as in $Cp_2Ti(\pi\text{-}C_3H_5)$[6]. The Cp_2Zr group in $Cp_2Zr(C_3H_5)_2$ carries one monodentate σ-allyl ligand and one bidentate π-allyl ligand, the maximum number possible according to Ballhausen and Dahl's theory[16]. The polymerisation of Cp_2ZrH_2[17] also indicates that the Cp_2Zr group preferably carries three additional ligands.

EXPERIMENTAL

Dicyclopentadienylzirconium dichloride was prepared as described by Wilkinson and Birmingham[18], the Grignard reagents as in ref. 2. Spectra in the visible range were recorded with a Unicam spectrophotometer SP 800, infrared spectra of the complexes embedded in KBr discs by means of a Hitachi Grating Infrared Spectrophotometer EPI-G as described in ref. 2. NMR spectra were measured with a Varian A60 high-resolution instrument. X-ray powder patterns were obtained by the Debye–Scherrer method. C and H analyses were carried out at the Microanalytical Department under supervision by Mr. W. M. Hazenberg; the determination of Zr (as ZrO_2) and Cl (by Schöniger's method) were performed at our laboratory under supervision by Drs. B. P. Knol.

Diallyldicyclopentadienylzirconium (IV)

A solution of allylmagnesium chloride (44 mmoles) in THF was added dropwise to a cooled (0°) stirred mixture of 20 mmoles of dicyclopentadienylzirconium dichloride in THF (50 ml) contained in a double Schlenk vessel equipped with a P_3 filter. Initially, the mixture became yellow; at the end of the reaction it had a very pale green colour. When the addition of the reagent was complete, the reaction mixture was stirred for five more minutes at 0°. While the product was kept at 0°, the solvent was removed in vacuum and the product evaporated to complete dryness. The white residue thus obtained was extracted with 150 ml of pentane at room temperature. Cooling the filtrate at −80° gave 0.8 g of cream-coloured crystals, which decompose from about 78°. (Found: C, 63.79; H, 6.60; Zr, 30.69. $C_{16}H_{20}Zr$ calcd.: C, 63.31; H, 6.64; Zr, 30.05%.) A second extraction of the white residue gave another 1.6 g of the compound; total yield 39%.

The allyl content was determined as described in ref. 2. Found: 167 ml and 171 ml of gas (0°, 76 cm Hg) per gram of $Cp_2Zr(C_3H_5)_2$; calcd.: 148 ml of propene per gram of $Cp_2Zr(C_3H_5)_2$. The too high value (by 14%) is explained by slow hydrolysis of the complex with evolution of cyclopentadiene (the infrared spectrum of the evolved gas indicated the presence of cyclopentadiene in addition to propene).

The complex $Cp_4Zr_2Cl(C_3H_5)_3$

The preparation was completely analogous to that described above. 20 mmoles of Grignard reagent were added to 20 mmoles of Cp_2ZrCl_2 in 50 ml of THF. Extraction with 150 ml of pentane gave 1.7 g (28%) of yellow crystals. The analyses indicate a composition of $Cp_4Zr_2Cl(C_3H_5)_3$. (Found: C, 58.13, 58.19; H, 5.76, 5.75; Zr, 30.49, 30.41; Cl, 5.83, 5.67. $C_{29}H_{35}ClZr_2$ calcd.: C, 57.90; H, 5.87; Cl, 5.90; Zr, 30.33%.) (A second extraction with 150 ml of pentane yielded only 0.5 g of impure product.) When the yellow crystals were heated they changed their colour to orange from 45°; at 130° a red oil was formed.

$Cp_2Zr(C_3H_5)_2$ (0.5 mmole) was treated with dichloromethane (30 mmoles) in 20 ml of hexane at 0° for 15 to 60 min. The reaction product was evaporated to dryness in vacuum and the residue recrystallized from hexane. The final product was identical with $Cp_4Zr_2Cl(C_3H_5)_3$. (Found: C, 57.86; H, 5.69%.)

Allyldicyclopentadienylzirconium(IV) chloride

$Cp_2Zr(C_3H_5)_2$ (0.5 mmole) was treated with dichloromethane (30 mmoles) in 20 ml of hexane at 0°, as described above, but the treatment was extended to 6 h. Again, the reaction product was evaporated (in vacuum) to dryness and the residue recrystallized from hexane. Infrared and NMR spectroscopy indicated the final product to be $Cp_2ZrCl(C_3H_5)$, somewhat contaminated by the complex $Cp_4Zr_2Cl(C_3H_5)_3$.

Bis(2-methylallyl)dicyclopentadienylzirconium(IV)

The preparation was carried out at 0°. 66 mmoles of 2-methylallylmagnesium chloride in THF were added dropwise to a stirred mixture of 30 mmoles of Cp_2ZrCl_2 and 30 ml of THF. The solution changed from colourless via orange to brownish-red (after half of the Grignard solution was added) and finally to yellow; the reaction mixture was stirred for another half hour. The solvent was removed *in vacuo*, leaving a mixture of a yellow oil and a white precipitate of $MgCl_2$. 100 ml of cold pentane were added; the mixture was stirred for 15 min at 0° and filtered. On cooling the bright yellow filtrate at −80° a pale yellow precipitate was formed which was isolated at low temperature. It melted at about −15° to a yellow, very air-sensitive oil. Yield 2 g (30%).

(2-Methylallyl)dicyclopentadienylzirconium(IV) chloride

Starting from 25 mmoles of 2-methylallylmagnesium chloride and 25 mmoles of Cp_2ZrCl_2, the synthesis and isolation were carried out as described above. Yield 1.5 g (19%) of a red air-sensitive oil.

ACKNOWLEDGEMENTS

We wish to thank Dr. H. J. DE LIEFDE MEIJER for many helpful discussions, and Miss J. G. HARTSUIKER for her assistence in this investigation, which was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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