

Influence of solvents on the insertion of methacrolein into zirconacycloprenes¹

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Abstract

The reaction of $\text{Cp}_2\text{Zr}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{L} = \text{THF}, \text{py}$) with equimolar amounts of $\text{H}_2\text{C}=\text{CMe}-\text{CHO}$ at room temperature depends strongly on the ligands L and the solvents that are used. With $\text{L} = \text{THF}$, in THF solution the insertion product $\text{Cp}_2\text{Zr}-\text{O}-\text{CH}(\text{CMe}=\text{CH}_2)-\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$ **1** was isolated, whereas by conducting the reaction in n -hexane solution an alkyne substitution with 1,4-coordination of the methacrolein takes place and the binuclear complex $[\text{Cp}_2\text{Zr}-\text{O}-\text{CH}=\text{CMe}-\text{CH}_2]_2$ **2** was obtained. In contrast, with $\text{L} = \text{py}$ (a stronger ligand) only a 1:1 ratio of **1** and **2** was observed in both THF and in n -hexane. At 50°C complex **1** was converted into **2** and the alkyne was eliminated quantitatively.

Complexes **1** and **2** were characterized by IR and NMR spectroscopical measurements and **1** by an additional X-ray structure determination.

Keywords: Zirconium; Carbonyl; Early transition metals; Group 4; X-ray diffraction; Trimethylsilyl

1. Introduction

Alkyne complexes of Group 4 bent metallocenes are interesting organometallic building blocks which can be used synthetically for many purposes (for reviews, see Ref. [1]). They can be considered as metallacycloprenes which insert carbonyl compounds to yield metalladihydrofurans [1,2]. This reaction was frequently applied after hydrolysis to provide configurationally pure allylic alcohols [3,4] starting from unsymmetrically substituted alkynes, ketones and aldehydes. Recently, the steric [5–8] and electronic [9] influence on regiochemical control was investigated.

In this and other reactions of stable complexes with bis(trimethylsilyl)acetylene, e.g. $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ [2–9] and $\text{Cp}_2\text{Zr}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{L} = \text{THF}$ [10], py [11]), the insertion competes with the generation of 'Cp₂M'. Both types of reaction are drasti-

cally influenced by the different metals, ligands L and substrates [12]. The steric hindrance of alkyne and carbonyl compound substituents was assumed to be the reason for a dissociation of the insertion products initially formed, giving no coupling of $\text{C}\equiv\text{C}$ and $\text{C}=\text{O}$ bonds at all. This indicates the steric limitations of the coupling reaction of alkynes with ketones and aldehydes by metallocene complexes.

Here we report on the influence of the solvents tetrahydrofuran (THF) and n -hexane on the products in the interaction of $\text{Cp}_2\text{Zr}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{L} = \text{THF}, \text{py}$) and methacrolein as a functionalized olefinic aldehyde.

2. Results and discussion

The reaction of $\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with equimolar amounts of $\text{H}_2\text{C}=\text{CMe}-\text{CHO}$ in THF at room temperature (Eq. (1)) gives, in isolated yield, 68% air- and moisture-sensitive orange crystals identified as

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¹ In memory of Professor Hidemasa Takaya († 4 October 1995).

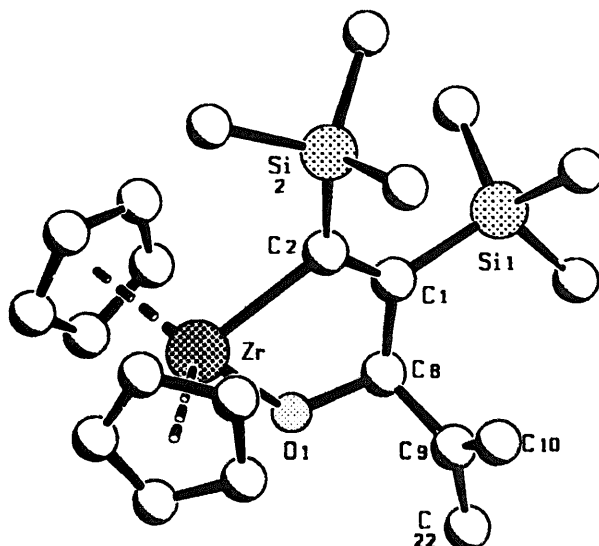
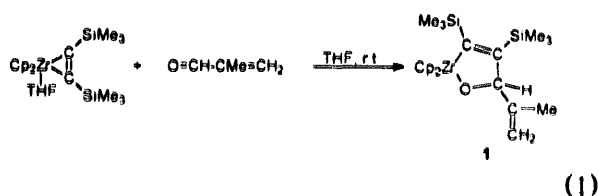
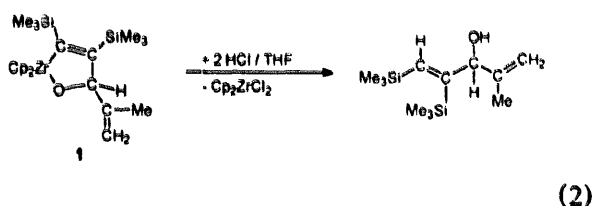


Fig. 1. Molecular structure of **1**; selected bond lengths (Å) and angles (deg): C(1)–C(2), 1.365(7); C(1)–C(8), 1.525(7); C(1)–Si(1), 1.897(5); C(2)–Si(2), 1.859(5); C(2)–Zr, 2.312(5); C(8)–O(1), 1.427(6); C(8)–C(9), 1.535(8); C(9)–C(10), 1.337(9); C(9)–C(22), 1.461(8). C(2)–C(1)–C(8), 119.3(4); C(2)–C(1)–Si(1), 128.3(4); C(1)–C(2)–Si(2) 128.2(4); C(1)–C(2)–Zr 107.7(3); C(8)–O(1)–Zr, 122.2(3); O(1)–Zr–C(2), 78.8(2); O(1)–C(8)–C(1), 111.0(4); C(1)–C(8)–C(9), 112.6(4).

the insertion product $\text{Cp}_2\text{Zr}-\text{O}-\text{CH}(\text{CMe}=\text{CH}_2)-\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$ **1**:



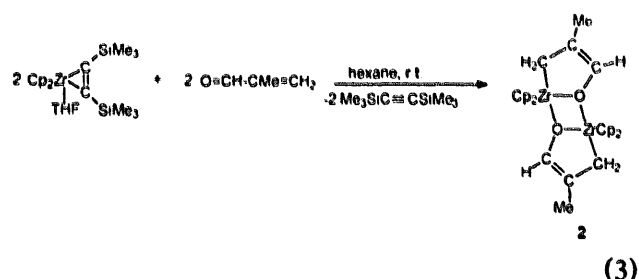
By treating **1** with two equivalents of anhydrous HCl an adequate amount of allylic alcohol could be detected by GC-MS and NMR (Eq. (2)).



The signals of the acetylenic C atoms at 185.4 and 222.2 ppm in the ^{13}C NMR spectrum of complex **1**, typical of analogous complexes [13], indicate a zirconadihydrofuran structure. The crystal structure of **1** [6] is shown in Fig. 1, along with selected bond lengths and angles. (Crystal data for **1** (obtained from a solution of *n*-hexane–THF): crystal dimensions $0.4 \times 0.4 \times 0.3$ mm³; prism; orange; $a = 15.884(3)$ Å, $b = 8.955(2)$ Å, $c = 16.697(3)$ Å; $\alpha = 90.00^\circ$, $\beta = 93.20(1)^\circ$, $\gamma = 90.00^\circ$; space group $P21/n$; $Z = 4$; mol. wt. 460.86 for $\text{C}_{22}\text{H}_{33}\text{Si}_2\text{OZr}$, (calcd) = 1.291 g cm⁻³; $R = 0.0661$, $R_w = 0.1517$.) The structure is very similar to those of

corresponding insertion products with acetone or benzaldehyde. Table 1 gives some relevant data.

Conducting the reaction of $\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with equimolar amounts of $\text{H}_2\text{C}=\text{CMe}-\text{CHO}$ in *n*-hexane solution (Eq. (3)) an alkyne substitution is more favoured as the insertion reaction and a 1,4-coordination of the methacrolein takes place. The resulting air- and moisture-sensitive pale yellow crystals of the binuclear complex $[\text{Cp}_2\text{Zr}-\text{O}-\text{CH}=\text{CMe}-\text{CH}_2]_2$ **2** were isolated in a yield of 65%.



In the ^1H and ^{13}C NMR spectra of **2** the signals of the methylene group (1.58, 48.3 ppm) are not in the typical region of olefins, and less downfield shifted than complex **1** (5.06, 4.88; 112.1 ppm).

Complex **2** was also characterized by an X-ray structure analysis. The results confirmed the presence of a homodinuclear two-fold oxygen-bridged complex in which, however, a disordering of the zirconium atoms and the Cp-ring systems did not allow the determination of bond lengths and angles. Nevertheless, the dinuclear structure has been established.

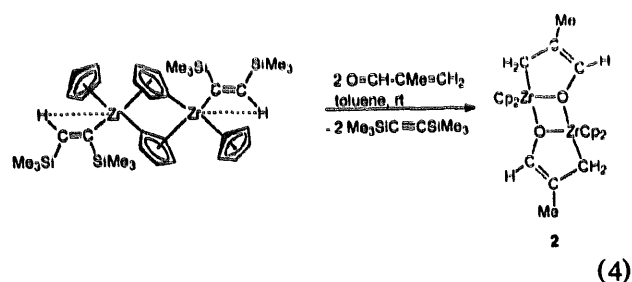
Detailed NMR experiments gave further evidence for

Table 1
Comparison of structural data of zirconacyclic complexes $\text{Cp}_2\text{Zr-OCR}^1\text{R}^4\text{-C(R}^2\text{)=C(R}^1\text{)}$

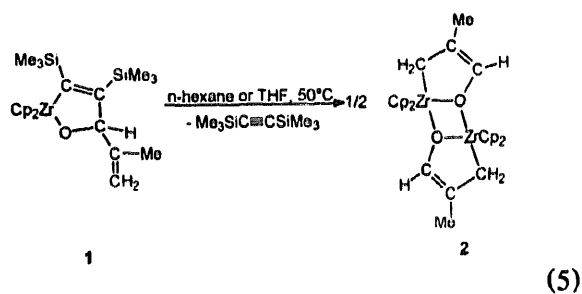
Compound	$\text{R}^1 = \text{R}^2 = \text{SiMe}_3, \text{R}^3 = \text{R}^4 = \text{Me}^{13}$	$\text{R}^1 = \text{R}^2 = \text{SiMe}_3, \text{R}^3 = \text{H}, \text{R}^4 = \text{Ph}^{12}$	$\text{R}^1 = \text{R}^2 = \text{SiMe}_3, \text{R}^3 = \text{H}, \text{R}^4 = \text{CMe} = \text{CH}_2$ 1
Distances (Å)			
Zr–C α	2.324(4)	2.324(3)	2.312(5)
C α –C β	1.371(7)	1.365(4)	1.365(7)
C β –C R^3R^4	1.544(7)	1.527(5)	1.525(7)
Angles (deg)			
R 1 –C α –C β	128.4(4)	126.8(3)	128.2(4)
R 2 –C β –C α	125.6(4)	129.3(3)	128.3(4)

the insertion reaction in THF to **1** on the one hand, and of the alkyne elimination to **2** in *n*-hexane on the other hand. Reacting the components in THF-*d*₈ gave 87% **1** and 13% **2**. In *n*-hexane, only 12% **1**, 73% **2**, as well as 15% oxygen-bridged oligomers, were detected after evaporation of the solvent and measurement in toluene-*d*₈.

Carrying out the reaction with methacrolein by using the stronger ligand-containing complex $\text{CpZr}(\text{py})(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$, no significant difference and a nearly 1:1 ratio of **1** and **2** could be observed in both solvents, *n*-hexane and THF. One explanation for this is the stronger interaction of the py ligand, compared with the THF ligand, with the zirconium atom, which is better at preventing substitution by the aldehyde; thus, substitution of the alkyne as the first step should be favoured, giving more complex **2**. The other explanation is the reduced stability of the THF complex in *n*-hexane, which rearranges to the $\eta^1:\eta^5$ Cp-bridged alkylidene complex $\{[\mu-\eta^1:\eta^5\text{-C}_5\text{H}_4]\text{CpZr-C}(\text{SiMe}_3)=\text{CHSiMe}_3\}_2$ [10]; this reacts in another way to yield complex **2**, as shown by Eq. (4).



Interestingly, heating *n*-hexane as well as THF solutions of **1** gave a quantitative yield of **2** and the bis(trimethylsilyl)acetylene (Eq. (5)).

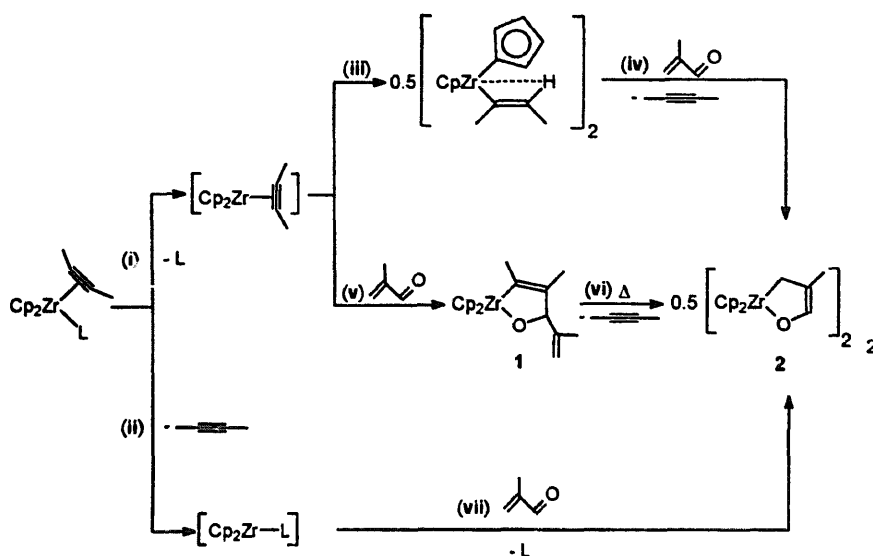


The corresponding insertion product to **1** with benzaldehyde, $\text{Cp}_2\text{Zr-O-CHPh-C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$ **3**, is stabilized by loss of half of the alkyne and the formation of a dinuclear complex $\{[\text{Cp}_2\text{Zr-O-CHPh-C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)]\text{Cp}_2\text{Zr}(\eta^2\text{-OCHPh})\}$ **4** [12]. The additional involvement of the methylene group to a 1,4-coordinated methacrolein seems to favour the total elimination of the alkyne on going from **1** to **2**, compared with the formation of **4** from **3**. An analogous, not isolated insertion product of benzophenone ' $\text{Cp}_2\text{Zr-O-CPh}_2\text{-C}(\text{SiMe}_3)=\text{CSiMe}_3$ ' also reacts by quantitative elimination of the acetylene to ' $\text{Cp}_2\text{Zr}(\eta^2\text{-OCPH}_2)$ '; this is stabilized either by a bridging 1,2 coordination of C=O in *n*-hexane $[\text{Cp}_2\text{Zr}(\eta^2\text{-OCPH}_2)]_2$, or by an alternative coordination of a THF ligand in THF as solvent complex $\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-OCPH}_2)$. The Zr–O–Zr–O four-membered ring systems in the coordination dimers are the thermodynamically more stable products.

The different reaction pathways to complexes **1** and **2** can be explained in general by Scheme 1.

In principle, the way to different products is determined by the different dissociation tendencies of the ligands (i) or the bis(trimethylsilyl)acetylene (ii). For THF as ligand in THF as solvent, the reactions (i) and (v) with a substitution of THF by the methacrolein occur. In *n*-hexane, after the dissociation of THF (i) and the intramolecular stabilization (iii) in the reaction with methacrolein, or after dissociation of the alkyne (ii), directly (vii), the coordination dimer **2** is formed. The formation of complex **2** after ligand dissociation (i), coupling with methacrolein (v) to complex **1** and elimination of the alkyne (vi) is excluded at room temperature (Eq. (5)). With pyridine as ligand, the alkyne dissociation (ii) can compete with the ligand dissociation (i) giving complex **2** after reaction (vii) with methacrolein. For THF as ligand in *n*-hexane as solvent, it is not yet known whether the product **2** is formed by the proved steps (i), (iii) and (iv) (Eq. (4)), or directly by the alternative combination (ii) and (vii).

The conclusion is that coupling reactions of carbonyl compounds with alkynes by zirconocene complexes occur more easily in donating solvents, e.g. THF. The preparation of zirconocene complexes of carbonyl compounds starting from alkyne complexes should be carried out in non-coordinating solvents, e.g. *n*-hexane.



Scheme 1.

3. Supplementary material available

The following material is available: tables of crystal structure and details of data collection, bond angles and distances, and atomic positional and thermal parameters **1**; listings of observed and calculated structure factors of **1**. Ordering information is given on any current masthead page.

4. Experimental section

All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. The following spectrometers were used: NMR, Bruker ARX 400; IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. Melting points were measured in sealed capillaries on a Büchi 535 apparatus; X-ray diffraction data were collected on a STOE-IPDS diffractometer using Mo K α radiation. The structures were solved by direct methods [14] and refined by full-matrix least squares techniques against F^2 [15]; structural representation: (XP, Siemens).

4.1. Preparation of $Cp_2Zr(O-CH(CMe=CH_2)-C(SiMe_3)_2) \cdot C(SiMe_3)_2$ **1**

0.45 g (0.97 mmol) of $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$ was dissolved in 20 ml of THF and treated with 0.08 ml (9.7 mmol) of methacrolein. The colour immediately changed to light orange. The volume was reduced by half and *n*-hexane was added. On standing a few days

at -30°C , 0.304 g (68%) orange crystals appeared, which were dried in vacuo. M.p.: at 85°C (elimination of alkyne). Anal. Found: C, 56.9; H, 7.24. $C_{22}H_{33}OSi_2Zr$ (460.88). Calc.: C, 57.33; H, 7.22%. IR(Nujol mull): 1244 cm^{-1} δ_s ($CH_3 - (Si)$), 1644 cm^{-1} $\nu(C=C)$, 1055 cm^{-1} $\nu(C-O-(Zr))$. 1H NMR (THF- d_6) δ /ppm: 0.08, 0.16 $SiMe_3$ (9H each), 1.66 CH_3 (3H), 4.72 CH (1H), 4.88, 5.06 CH_2 (1H each), 6.31, 6.34 Cp (5H each); ^{13}C NMR (THF- d_6) δ /ppm: 2.3, 4.6 $SiMe_3$, 21.3 CH_3 , 88.5 CO, 112.1 CH_2 , 113.8, 114.3 Cp, 149.7 CMe, 222.2 C α , 185.4 CB. MS (70eV) 220 Cp_2Zr^+ , 73 $SiMe_3^+$.

4.2. Preparation of $[Cp_2Zr(O-CH=CH-CMe-CH_2)]_2$

To 0.540 g (1.16 mmol) of $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$, a solution of 0.096 ml (1.16 mmol) methacrolein in 20 ml *n*-hexane was added. The solution immediately showed a yellow colour. After filtration and standing at 0°C light brown crystals appeared, which after recrystallization from *n*-hexane showed a pale yellow colour (0.439 g, 65%). M.p.: $253-254^\circ\text{C}$. Anal. Found: C, 57.2; H, 5.52. $C_{28}H_{32}O_2Zr_2$ (583). Calc.: C, 57.69; H, 5.53%. IR(Nujol mull): 1648 cm^{-1} $\nu(C=C)$, 1119 cm^{-1} $\nu(C-O-(Zr))$. 1H NMR (C_6D_6) δ /ppm: 1.58 CH_2 (2H), 1.90 CH_3 (3H), 5.62 Cp (10H), 5.88 CH (1H); ^{13}C NMR (C_6D_6) δ /ppm: 19.5 CH_3 , 48.3 CH_2 , 110.1 Cp, 124.0 CMe, 143.3 CH. MS (70eV) 290 $M^+/2$, 220 Cp_2Zr^+ .

4.3. NMR investigations

0.1 g (2.2 mmol) of $Cp_2Zr(THF)(Me_3SiC_2SiMe_3)$ was dissolved in 5 ml of THF (or *n*-hexane) and 0.018 ml (2.2 mmol) of methacrolein was added. After removal of

the solvent, the residue of the THF-attempt was treated with THF- d_8 , whereas that from *n*-hexane was treated with toluene- d_8 . The ratio of **1** and **2** was detected by integration of the signals.

4.4. Preparation of $\text{Me}_3\text{SiCH}=\text{C}(\text{SiMe}_3)\text{-CHOHMe}=\text{CH}_2$

To 300 mg of **1** (0.65 mmol) dissolved in THF, 1.30 ml (1.3 mmol) of 1.0 M HCl was added. The solution turned immediately colourless. After evaporation of solvent the residue was dissolved in C_6D_6 and filtered. MS (70 eV) m/z : 241 $\text{M}^+ - \text{H}$, 225 $\text{M}^+ - \text{OH}$, 171 $\text{Me}_3\text{SiCH}=\text{CSiMe}_3^+$. ^1H NMR δ/ppm : 0.18, 0.24 SiMe_3 (9H each), 1.68 Me (3H), 4.68 (1H), 4.90, 5.09 CH_2 (1H each), 6.78 (1H), 6.81 $=\text{CH}$ (1H); 6.06 Cp_2ZrCl_2 .

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