Notes

Preparation and First X-ray Structure of a Zirconocene *β*-Keto Ester Enolate

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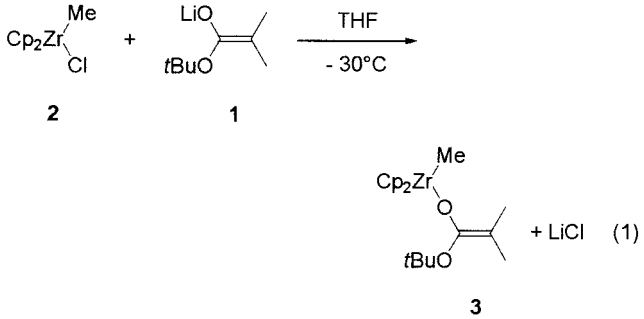
Summary: The reaction of methyl 2-ethylbutyrate with an equimolar amount of lithium diisopropylamide (LDA) leads to the formation of the lithium enolate of methyl 2,2,4-triethyl-3-oxohexanoate. Further reaction with bis-(cyclopentadienyl)zirconium(methyl)chloride yields a crystalline zirconocene enolate complex, the structure of which was determined by X-ray diffraction.

Introduction

Collins et al. found that methyl methacrylate is polymerized in a living manner with the neutral zirconocene enolate complex $Cp_2Zr(Me)(OC(O\mathit{t}Bu){=}CMe_2)$ (**3**) as the initiator and the cationic zirconocene complex $Cp_2Zr(Me)(thf)(BPh_4)$ as the catalyst.[1,2] Following Collins[1] we prepared the enolate complex **3** starting from *tert*-butyl isobutyrate, LDA, and $Cp_2Zr(Me)Cl$ (**2**). In the first step the lithium enolate **1** was obtained according to Collum et al.,[3] a white insoluble powder precipitated upon treatement of *tert*-butyl isobutyrate with LDA in hexane at 0 °C. Reaction of the lithium enolate **1** in THF with $Cp_2Zr(Me)Cl$ (**2**) resulted in the zirconocene enolate **3** as a yellow oil (eq 1).



We prepared the ester enolate **3** according to Collins[1] and characterized it by means of NMR spectroscopy. We were not able to crystallize this species in order to determine its structural parameters, though. Titanocene enolate complexes seem to have a higher tendency to crystallize than the corresponding zirconocene enolate complexes,[4] e.g., the titanocene ester enolate complex $Cp_2Ti(Cl)(OC(OMe){=}CMe_2)$ has been structurally characterized by X-ray diffraction.[5] To the best of our knowledge up to now no zirconocene ester enolate of the general formula $Cp_2Zr(X)(OC(OR){=}CR'R'')$ (X = Me, Cl; R = alkyl; R′, R″ = H, alkyl) has been characterized by means of X-ray diffraction.

Our attempt to synthesize a crystalline zirconocene ester enolate led to an unexpected result. Crystals of the zirconocene *β*-keto ester enolate **6** were obtained by using methyl 2-ethylbutyrate (**4**) instead of *tert*-butyl isobutyrate in the described reaction sequence (eq 1); the crystal structure was determined by means of X-ray diffraction.

Results and Discussion

Equimolar amounts of freshly prepared LDA and methyl 2-ethylbutyrate (**4**) were reacted at 0 °C in hexane to obtain the corresponding lithium ester enolate **7** (cf. Scheme 1). In analogy with the lithium enolate **1** which was obtained from *tert*-butyl isobutyrate we expected a white powder as the product. Instead we isolated a viscous pale yellow oil **5**, which upon treatment with $Cp_2Zr(Me)Cl$ (**2**) (cf. eq 2) yielded a red-orange viscous oil **6**, from which yellow crystals were formed after prolonged storage time at 0 °C. The structure of these crystals was determined by means of X-ray diffraction (Figure 1).

6 forms molecular crystals without exceptionally short-range intermolecular interactions. The overall molecular structure corresponds to that of a bent metallocene. However, to our surprise the structure

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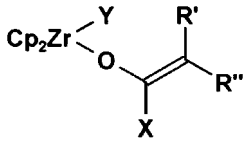
Table 1. Bond Lengths and Angles in Zirconocene Enolate Complexes $Cp_2Zr(Y)[OC(X)=C(R')(R'')]$



entry	X	Y	R′	R″	Zr−O (Å)	Zr−Y (Å)	Zr−O−C (deg)	lit
1	$CEt_2(COOMe)$	Me	Et	Et	1.952(4)	2.277(7)	163.6(4)	this
2	Me	Me	Ph	Ph	1.975(3)	2.289(8)	150.8(3)	9
3	Fer[a]	Cl	H	H	1.935(4)	2.462(2)	164.0(4)	10
4	$(CO)_3CrMes$[b]	Cl	H	H	1.977(2)	2.463(1)	154.6(2)	11
5	$SiMe_3$	Cl	Ar[c]	H	1.950(4)	2.469(2)	157.7(3)	12
6	PPh_2	Cl	H	H	1.960(3)	2.457(1)	163.6(3)	13
7	PPh_2	Cl	H	Me	1.955(5)	2.464(3)	160.5(5)	14
8	NPh_2	Cl	H	H	1.976(3)	2.461(1)	147.3(3)	15
9	NPh_2	Cl	Me	H	1.981(2)	2.475(1)	151.0(2)	16

[a] Ferrocenyl, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$. [b] $[\eta^6\text{-}2,4,6\text{-}Me_3C_6H_2Cr(CO)_3]$-fragment substituted in position 1 of the aromatic cycle. [c] 9-Anthryl.

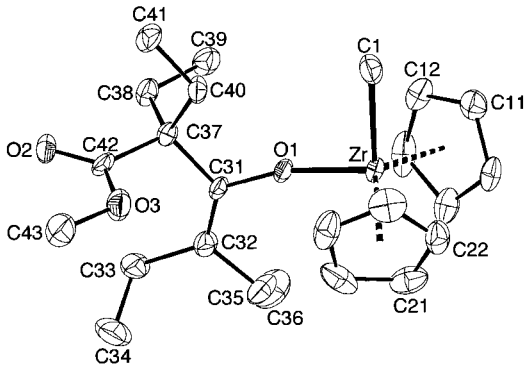
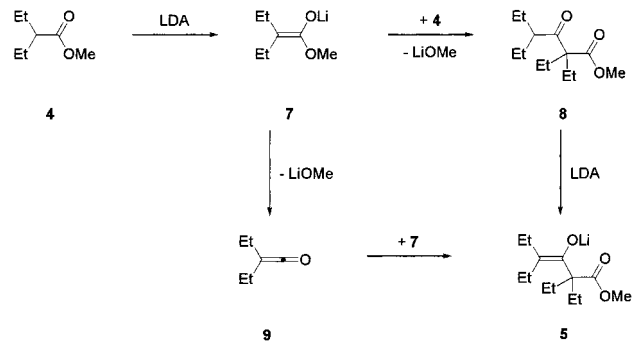
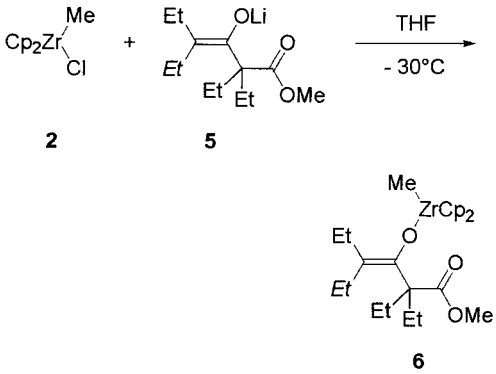


Figure 1. PLATON[6] drawing for complex **6** (30% ellipsoides). Selected intramolecular distances [Å] and angles [deg]: Zr−O(1) 1.952(4), Zr−C(1) 2.277(7), Zr−Centroid(C11−C15) 2.233, Zr−Centroid(C21−C25) 2.197, O(1)−C(31) 1.357(6), O(2)−C(42) 1.204(7), O(3)−C(43) 1.462(8), C(31)−C(32) 1.332(8); O(1)−Zr−C(1) 98.8(2), Centroid(C11−C15)−Zr−Centroid(C21−C25) 130.3, C(31)−O(1)−Zr 163.6(4).

Scheme 1. Formation of Lithium Enolate 5 by Reaction of Equimolar Amounts of Methyl 2-Ethylbutyrate with LDA (cf. Experimental Section)



determination revealed a β-keto ester enolate as a ligand which is linked with the β-enole oxygen to the metal center, the Zr−O1 bond distance amounting to 1.952(4) Å. The angle Zr−O1−C31 [163.6(4)°] deviates significantly from the tetrahedral angle expected for an sp^3-hybridized oxygen; this is an indication of a partly sp-hybridized oxygen due to a $p_\pi-d_\pi$ interaction between the zirconium and the oxygen. This conclusion has also been drawn by other authors for nearly linear metal−oxygen−carbon bonds in titanocene (e.g., Beckhaus[7]) and zirconocene (e.g., Collins[8]) complexes. In Table 1 our values are compared with values of other zirconocene ketone enolate complexes. The results indicate an inverse correlation between the magnitude of the bond angle Zr−O−C and the Zr−O bond distance (cf. entries 1, 2 and 3−9), which is in agreement with the above-mentioned $p_\pi-d_\pi$ interaction between zirconium and oxygen. The bond distance Zr−Cl (cf. entries 3−9) does not show such a trend but is sensitive to a change of R′ with respect to R″ from H to Me (cf. entries 6−9).



On the basis of the molecular structure of **6** the reaction of **2** with **5** is represented by eq 2.

The formation of the lithium enolate **5** is explained in Scheme 1. The reaction of LDA with methyl 2-ethylbutyrate (**4**) results in the corresponding ester enolate **7**. However, the ester **4** reacts with the lithium enolate **7** according to a Claisen type condensation rather than with LDA, and the β-keto ester **8** is formed. After complete reaction of the methyl 2-ethylbutyrate half of the initial quantity of LDA is still present and reacts with the β-keto ester **8** with deprotonation to produce the lithium enolate **5**. Since the α-position to the ester-carbonyl is fully substituted, the abstracted proton has to stem from the α-position to the ketone-carbonyl (γ-position to the ester-carbonyl). An alternative reaction pathway proposed by Seebach et al.[17] comprises the

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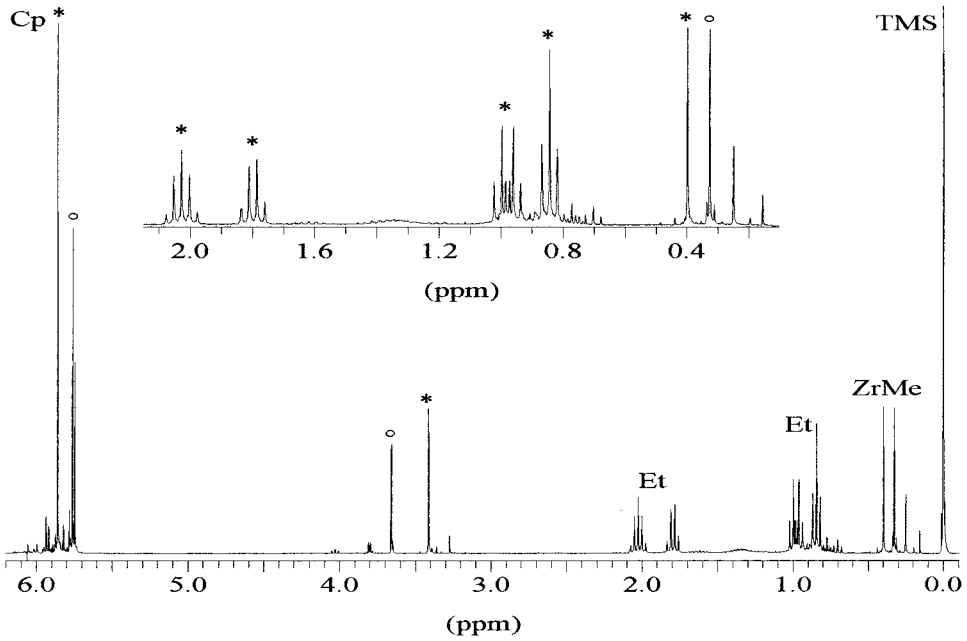

Figure 2. ^{1}H NMR spectrum (C_6D_6, TMS = tetramethylsilane) of **6**. [Assignment of resonances: ∗ = **6**, ○ = $Cp_2Zr(Me)(OMe)$].

elimination of Li-methoxide from the enolate **7** and the intermediate formation of the ketene **9**. Nucleophilic addition of the enolate **7** to the ketene **9** eventually results in the Li-enolate **5**. Both reaction path ways are based on the higher solubility in hexane of the lithium enolate **7** as compared with that of the lithium enolate **1**.

The ^{1}H NMR spectrum of the zirconocene β-ketone enolate complex was assigned after the crystal structure was obtained (Figure 2). The diastereotopic ethyl groups that are situated at the olefinic double bond show two separated triplets (methyl resonances) at 1.0 ppm and two only slightly separated quartets (methylene resonances) that merge to form a quintet at 2.0 ppm. A detailed assignment of the resonances is given in the Experimental Section. The resonances marked with a circle (○) in Figure 2 are assigned to $Cp_2Zr(Me)(OMe)$, which stems from the reaction of LiOMe with **2**.

Conclusion

The reaction of methyl 2-ethylbutyrate (**4**) with LDA causes an ester condensation to form a β-keto ester, which was isolated in its metalated form **5**. The reaction of **5** with $Cp_2Zr(Me)Cl$ (**2**) leads to the zirconocene β-ketone enolate complex **6**; the molecular structure of **6** was determined by single-crystal X-ray diffraction.

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Experimental Section

All reactions were carried out in a dry argon atmosphere. Solvents were dried and distilled before use following standard methods. ^{1}H NMR spectra were measured on a 300-DPX Bruker instrument.

Synthesis of 1. Butyllithium (31.5 mmol, 15.0 mL of a 2.1 M solution in cyclohexane) was added to a solution of diisopropylamine (3.33 g, 33 mmol) in 50 mL of hexane at 0 °C and stirred for 30 min. *tert*-Butyl isobutyrate (5.11 g, 35.4 mmol) was added at 0 °C. After 3 h the suspension was filtered and the lithium enolate **1** was isolated as a white powder in 96% yield (4.55 g, 30.3 mmol).

Synthesis of 2. Cp_2ZrCl_2 (7.49 g, 25.6 mmol) was suspended in 60 mL of diethyl ether, and MeLi (25.2 mmol, 14.0 mL of a 1.8 M solution in diethyl ether) was added at 0 °C. After 3 h at 0 °C the reaction mixture was stirred at room temperature overnight, then the solvent was removed in vacuo. The residue was treated with 30 mL of toluene and stirred at 80 °C for 24 h, then cooled to room temperature, and the LiCl was filtered off. From the filtrate, **2** crystallized in 68% yield (4.68 g, 17.2 mmol) as yellow crystals. ^{1}H NMR ($CDCl_3$): [ppm] δ 0.32 (s, Me, 3 H), 6.24 (s, Cp, 10 H).

Synthesis of 3. A solution of **2** (4.68 g, 16.8 mmol) in 20 mL of THF was added at −78 °C to a solution of **1** (3.06 g, 20.4 mmol) in 30 mL of THF. Within 4 h the reaction mixture was warmed to room temperature. Then the solvent was evaporated, and 7 mL of pentane was added to the residual oil. LiCl was removed by filtration. Pentane was evaporated, leaving a yellow oil as residue. ^{1}H NMR (C_6D_6): [ppm] δ 0.40 (s, $Zr-CH_3$, 3 H), 1.27 (s, $-C(CH_3)_3$, 9 H), 1.62 and 1.82 (s, $=C(CH_3)_2$, 3 H), 5.82 (s, Cp, 10 H).

Synthesis of 5. Butyllithium (30.0 mmol, 15.0 mL of a 2.0 M solution in cyclohexane) was added to a solution of diisopropylamine (3.03 g, 30.0 mmol) in 50 mL of hexane at 0 °C and stirred for 30 min. Methyl 2-ethylbutyrate (4.20 g, 32.0 mmol) was added at 0 °C, and after 90 min the volatiles were evaporated, leaving 4.10 g of a yellow, viscuos oil.

Synthesis of 6. A solution of **2** (8.20 g, 30.0 mmol) in 35 mL of THF was added at −78 °C to a solution of **5** (4.10 g, 30.0 mmol) in 40 mL of THF. The reaction mixture was stirred and warmed to room temperature within 4 h. The solvent was evaporated, and 7 mL pentane was added to the residual oil. LiCl was removed by filtration. Pentane was evaporated from

Table 2. Crystal Data, Data Collection Parameters, and Convergence Results for 6

formula	$C_{24}H_{36}O_3Zr$
fw	463.77
system	orthorhombic
space group (no.)	*Fdd*2 (43)
a, Å	28.382(7)
b, Å	41.846(9)
c, Å	8.03(1)
U, Å^3	9535(10)
Z	16
d_{calc}, g cm^{-3}	1.29
μ, cm^{-1}	4.71
θ_{max}, deg	26.1
temperature, K	203
λ, Å	0.71073
cryst dimens, mm^3	0.35 × 0.20 × 0.20
no reflns.	10962
no variables	259
R (obsd reflns)	0.0513
*wR*2 (all reflns)	0.1030
GOF	0.825
peak/hole res el dens, e Å^{-3}	0.539 /−0.759
enantiomorph polarity param	−0.06(6)

the filtrate, leaving a viscous red-orange oil. From this oil crystals formed slowly so that after 6 months at 0 °C more than 50% of the oil had transformed into a crystalline substance.

Analysis by X-ray diffraction of a crystal revealed the structure $Cp_2Zr(Me)(OC(CEt_2(COOMe))=CEt_2)$. ^{1}H NMR ($C_6D_6$): [ppm] δ 0.40 (s, Zr−CH_3, 3 H), 0.84 (t, >C(CH_2CH_3)$_2$, 6 H), 0.96 and 1.00 (t, =C(CH_2CH_3)$_2$, 3 H), 1.80 (q, >C(CH_2-CH_3)$_2$, 4 H), 2.02 (2 x q, =C(CH_2CH_3)$_2$, 4 H), 3.41 (s, OCH_3, 3 H), 5.86 (s, Cp, 10 H).

X-ray Structure Determination of 6. Geometry and intensity data were collected with Mo Kα radiation on an ENRAF-Nonius CAD4 diffractometer equipped with an incident beam graphite monochromator. A summary of crystal data, data collection parameters, and convergence results are compiled in Table 2. Due to the low linear absorption coefficient, no absorption correction had to be applied to the experimental data. The structure was solved by direct methods[18] and refined on intensities.[19] In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were included as riding on the corresponding carbon atoms (C−H = 0.98 Å, U_{iso}(H) = 1.3 U_{eq}(C)).

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137534. Copies of available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0) 1223-336033 or e-mail: deposit@chemcrys.cam.ac.uk).

Supporting Information Available: Crystallographic data for compound **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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