Synthesis of functionalised zirconium complexes

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A method for synthesis of cyclic zirconium complexes has been developed. Treating zirconocene complexes having aryl methyl ether substituted ligands with BBr_3 affords cyclic zirconium complexes.

Keywords: zirconium, heterocycle, cleavage reaction

Many kinds of zirconium complexes have been synthesised due to their various usages in many aspects, such as: ring contraction reactions,[1] homologation of propane,[2] asymmetric hydroamination of alkenes,[3] reactions of alkenyl substituted enol ethers,[4] polymerisation,[5] and conversion of amides to nitriles,[6] Syntheses of functionalised zirconium complexes have been the focus of this field.[7] Recently, Gansauer *et al.* reported a modular and effiãent method for synthesis of cyclic titanium complexes by treating titanocence dichloride derivatives having a ligand bearing an ester group with $ZnCl_2$ at room temperature,[8] but did not report synthesis of cyclic zirconium complexes. Reports on synthesis of cyclic zirconium complexes are rare. To prepare them, we synthesised two substituted cyclopentadienyl zirconium dichlorides, then cyclic zirconium complexes were obtained by treating them with BBr_3 (Scheme 1). The conversion involves cleavage of an ether group and substitution of chlorine atoms by bromine and oxygen atoms.

The conversion yield (83%) of **2** to **4** is higher than that of **1** to **3** (33%). The yields show that it is easier to convert when the alkyl substituent is ethyl than when the alkyl substituent is methyl, in the benzyl α-position. With big substituents the complex **2** possesses higher potential energy and is relatively unstable, hence easy to convert. No conversion product was obtained by LiBr instead of BBr_3 in the same conditions.

Conversion was confirmed by comparing the ^{1}H NMR data of **1** and **2** with those of **3** and **4.** For example, the signal of OCH_3 in compound **1** appears at 3.6 ppm as a single peak, and the signal disappears in compound **3,** which indicates there is no methyl of the ether in compound **3**. Two methyl groups on benzyl are equivalent in compound **1**, the signal of the two methyl groups appears at 1.84 ppm as a single peak. But after conversion, Zr is a chiral centre in compound **3,** thus the two methyl groups on benzyl become unequivalent, and the signal of the two methyl groups appears at 1.5 ppm as double peaks.

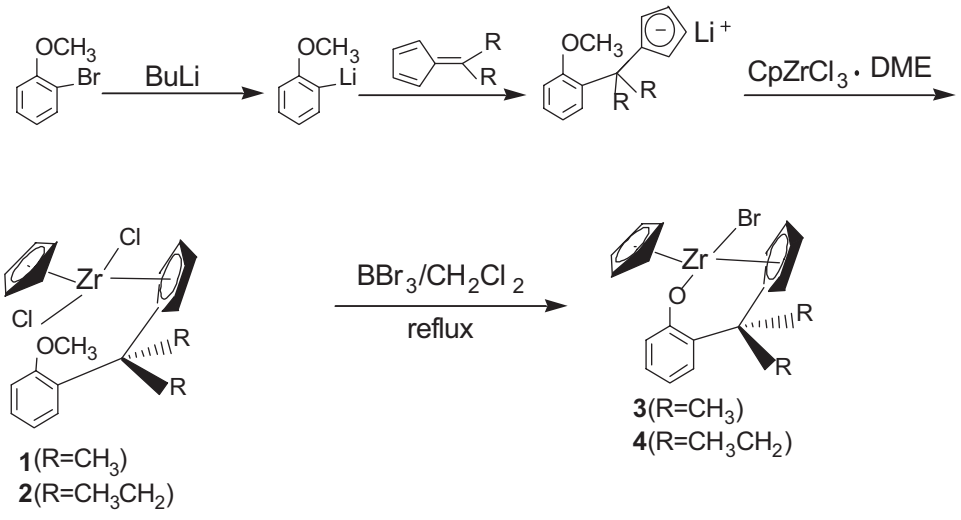
Conversion was also confirmed by MS data. Peaks of the molecular ion all appear in cyclic zirconium complexes **3** (*m/z* = 434, M, 15.5%) and **4** (*m/z* = 462, M, 60%). No peak of the molecular ion appears in zirconium dichloride compounds **1** and **2,** which indicates that cyclic zirconium complexes are more stable than the corresponding zirconium dichlorides. Elemental analysis confirmed conversion further.

Experimental

All reactions were carried out under an inert atmosphere using standard Schlenk techniques. Melting points were uncorrected. ^{1}H NMR spectra were recorded on a GERMINI-300 spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. IR spectra were measured on a NICOLET MAGNA-IR550 spectrometer. MS were obtained on a HP5989A Mass Spectrometer. Elemental analysis were determined using Perkin-Elmer 2400|| elemental analyser.

Synthesis of **1**

A solution of BuLi (1.46N, 4.4 mmol) in hexane (3 ml) was added dropwise to a solution of o-bromoanisole (810 mg, 4.3 mmol) in Et_2O (5 ml) with stirring at 0°C. After addition, the mixture was stirred for 3 h at room temperature. A solution of 6,6-dimethylfulvene (0.45 ml, 4.3 mmol) in hexane (5 ml) was added to above mixture at 0°C. After addition, the mixture was stirred for 2 h at 0°C, to give a solution of the ligand salt. In another Schlenk flask, [$ZrCpCl_3$]•DME (1.53 g, 4.3 mmol) and THF (20 ml) were added, then the above ligand salt solution was added dropwise. After addition, the mixture was stirred for 2 h. After the solvent was removed, the residue was recrystallised from $CHCl_3$-petroleum to afford 1.3 g of a white crystalline solid in 68% yield, m.p. 178–178.5°C. ^{1}H NMR (δppm): 7.28 (m, 2H), 6.9



Scheme 1

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(m, 1H), 6.8 (m, 1H), 6.5 (m, 2H), 6.4 (s, 5H), 6.27 (m, 2H), 3.6 (s, 3H), 1.84 (s, 6H). IR (KBr) 740, 830, 1030, 1090, 1180, 1250, 1380, 1490, 1590, 2950, 3100 cm^{-1}. MS (*m/e*): 419 ($Cp'CpZrClCH_3$, 11), 403 (M–HCl, 7.9), 375 (M–Cp + H, 100), 339 (M–Cp–Cl, 15), 226 (M–Cp', 9.8), 213 (Cp', 4), Cp' = substituted Cp. Anal. Calc. for $C_{20}H_{22}Cl_2OZr$: C, 54.55; H, 5.0. Found: C, 53.9; H, 5.0%.

Synthesis of **2**

Using the identical procedure as for synthesis of **1**, except using 6,6-diethylfulvene instead of 6,6-dimethylfulvene to afford a white crystalline solid in 60% yield, m.p. 153–154°C. ^1H NMR (δppm), 7.3 (m, 2H), 7.0 (m, 2H), 6.58 (m, 2H), 6.29 (m, 2H), 6.02 (s, 5H), 3.85 (s, 3H), 2.34 (m, 4H), 0.75 (t, 6H). IR (KBr) 750, 810, 1020, 1240, 1430, 1460, 1600, 2950, 3080 cm^{-1}. MS (*m/e*): 447 ($Cp'CpZrClCH_3$, 7.6), 431 (M–HCl, 5.5), 402 (M–Cp, 100), 226 (CpZrCl2, 5.8). Anal. Calc. For $C_{22}H_{26}Cl_2OZr$: C, 56.4; H, 5.55. Found C, 56.2; H, 6.0%.

Synthesis of **3**

BBr_3 (0.182 ml, 1.87 mmol) was added to a solution of **1** (390 mg, 0.89 mmol) in CH_2Cl_2 (20 ml). The solution was then stirred for 33 h at reflux. After the solvent was removed, the residue was recrystallised from $CHCl_3$-petroleum to afford 128 mg of pale yellow crystals in 33% yield, m. p. 142–142.5°C. ^1H NMR (δppm): 7.3 (m, 1H), 7.1 (m, 1H), 6.9 (m, 1H), 6.6 (m, 1H), 6.48 (s, 5H), 5.6–6.4 (m, 4H), 1.5 (d, 6H). IR (KBr) 620, 760, 810, 860, 1020, 1140, 1240, 1280, 1440, 1480, 1600, 2980, 3100 cm^{-1}. MS (*m/e*): 434 (M, 60), 419 (M–CH3, 19.5), 369 (M–Cp, 10.5), 354 (M–Br, 15.5), 337 (M–Cp–2CH3–2H, 100), 289 (M–Cp–Br, 37). Anal. Calc. for $C_{19}H_{19}BrOZr$: C, 52.5; H, 4.3. Found C, 52.9, H, 4.55%.

Synthesis of **4**

Using an identical procedure as for synthesis of **3** except using **2** instead of **1,** to afford pale yellow crystals in 83% yield, m. p. 130–131°C. ^1H NMR (δppm): 7.26 (m, 1H), 7.10 (m, 1H), 6.87 (m, 1H), 6.58 (m, 1H), 6.49 (s, 5H), 6.37–5.74 (m, 4H), 1.60–2.12 (m, 4H), 0.625–0.722 (m, 6H). IR (KBr) 630, 750, 810, 860, 1010, 1250, 1430, 1480, 1590, 2980, 3110 cm^{-1}. MS (*m/e*): 462 (M, 15.5), 433 (M–Et, 16.6), 351 (M–Br–CH3–, 100). Anal. Calc. for $C_{21}H_{23}BrOZr$: C, 54.5; H, 5.0. Found C, 54.6; H, 5.1%.

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