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Stereoselective synthesis of an *ansa*-zirconocene in a spirane scaffold

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Abstract

Methodology is described for the preparation of a rigid C_2-bridged zirconocene catalyst system where the C_2-bridge is embedded in a spirane scaffold. The ligand was prepared from 3,4-dihydro-2*H*-fluoren-1(9*H*)-one. Initially, the oxo group was converted into a spirocyclobutanone function. Further conversion to a fulvene was followed by regio- and stereoselective saturation to provide the ligand *cis*-2-(cyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9*H*-spiro[cyclobutane-1,1′-fluorene]. The ligand was dilithiated and reacted with zirconium tetrachloride to provide the corresponding (η^5-cyclopentadienyl)-spiro[cyclobutane-1,1′-(η^5-fluorenyl)]zirconium dichloride complex. The structure of the zirconocene dichloride has been established by crystal X-ray analysis.

Keywords: Zirconocene C_2-spirane-bridges; Spirane scaffold; Rigid *ansa*-zirconozene; Stereoselective ligand synthesis; Dilithiation and zirconation

1. Introduction

The bridging unit between the two η^5-coordinated aromatic ligands in *ansa*-zirconocene dichloride complexes largely controls the bite angle between the cyclopentadienyl units and have a profound influence on the catalytic properties of these complexes [1–3]. The substitution patterns of the commonly studied C_1-, Si_1- and C_2-bridges also affect the bite angle and hence the reactivity as catalyst for polymerisation, and consequently the polymer microstructures. We aim to prepare highly rigidified metallocenes. The rotational flexibility of C_1-bridged metallocenes has been greatly reduced by incorporation of the C_1-bridge carbon as the C-4 carbon in 4-cyclopentadienyl-4,5,6,7-tetrahydroindenyl derived zirconium derivatives [4,5]. Our interest for C_2-bridged *ansa*-zirconocenes [1,2,6] has been directed towards methods for the preparation of rigid C_2-bridges in a zirconocene catalyst system where the C_2-unit constitutes a part of a spirane scaffold. Methods for the stereoselective preparation of sandwiched bisaryls bridged by spiranes have been reported [7,8]. In the targeted zirconocene **A** in Fig. 1, one of the spirane substituents is a cyclopentadienyl unit whereas the second cyclopentadienyl unit is part of a tetrahydrofluorene system where the C-1 carbon is also the spiro carbon in the scaffold. From models it appears that the bite angle in the spirane and the free C_2-bridges would not be greatly different.

2. Results and discussion

The synthesis of the targeted ligand **5** is outlined in Scheme 1. The substrate was the 1-fluorenone (**1**) [9]. An initial attempt to form an adduct between the ketone **1** and lithiated cyclopropyl phenyl sulfide failed [10]. The former acted as a base with abstraction of an acidic indene proton in preference to nucleophilic addition to the oxo group as indicated by the dark red coloration of the reaction medium. We therefore turned to less basic organometallic species. An organometallic derivative of cerium trichloride was appropriate [11]. The metallated species was available by quenching lithiated cyclopropyl phenyl sulfide with cerium trichloride. Adduct formation proceeded in the cold to provide the alcohol adduct **2**. ^{1}H NMR spectra of the crude product showed full conversion. Part of the material was lost on chromatographic purification, probably because of ready elimination of water, the isolated yield being 66%. By analogy to the rearrangements

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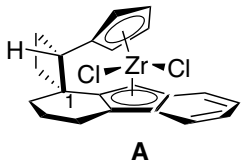


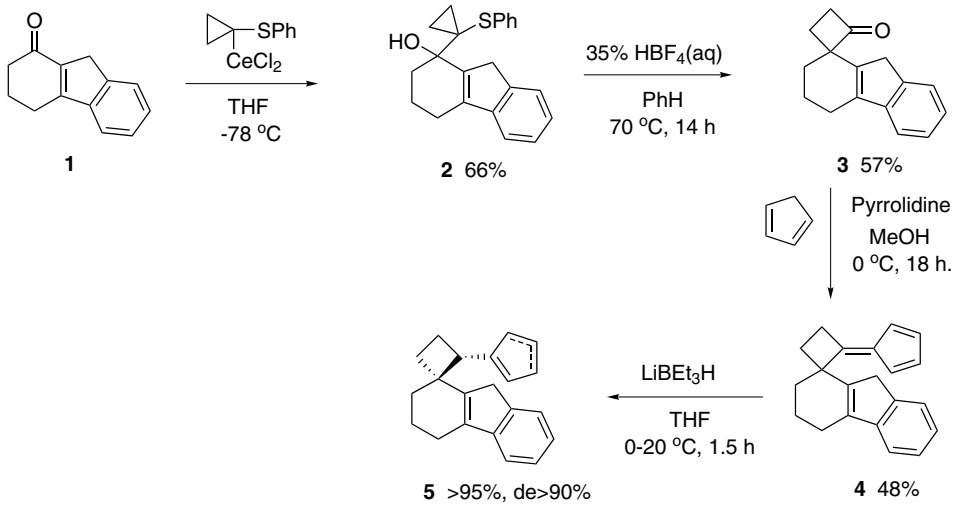
A

Fig. 1. C_2-bridged zirconocene with the C_2-bridge embedded in a rigid spirane scaffold.

reported by Trost [12], the cyclopropyl phenyl sulfide **2** could be rearranged by acid catalysis under the influence of aqueous fluoroboric acid in benzene to furnish the cyclobutanone **3** in 57% yield. In the subsequent step, the ketone was to be converted into a fulvene derivative **4**. In general, several methods are available for fulvene formation [13]. In this work the ketone **3** was reacted with cyclopentadiene in the presence of pyrrolidine as a base to provide the fulvene **4**.

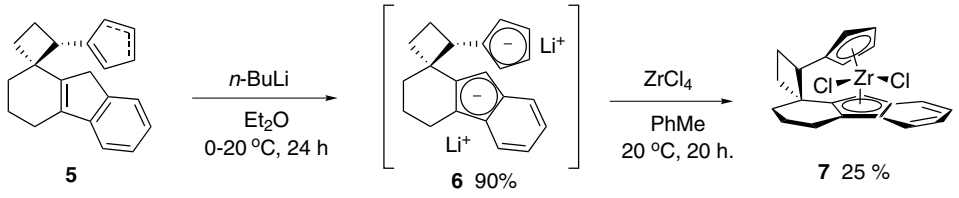
In the final step, a stereoselective reduction of the fulvene double bond was required. Only in the *cis*-configuration, as in structure **5**, can the zirconium metal become coordinated or attached to the fluorenyl and cyclopentadienyl moieties in a sandwiched zirconocene structure. The *cis*-configuration, however, leads to a significant repulsive interaction with the larger part of the fluorene component, and is thermodynamically the less favourable structure of the two geometrical isomers. The sterical shielding of the two faces of the fulvene unit in the spirane **4** differs significantly. Stereoselective saturation of the fulvene exocyclic double bond was required for the generation of the *cis*-isomer **5**. Regioselectivity in the saturation was provided by metal hydride reactions. Initially, simple metal hydride reagents had provided mixtures of stereoisomers. For steric reasons, a bulky metal hydride reagent was required. The requirement was met by the use of lithium triethylborohydride which cleanly provided the *cis*-isomers **5** in high yield. The stereoselectivity is due to addition of the metal hydride reactant to the less shielded side of the cyclobutyl fulvene double bond. The cyclobutadienyl substituent is thereby forced into the *cis*-configuration. ^{1}H NMR showed the crude product to consist mainly of two endocyclic double bond isomers in the cyclopentadiene unit. The product was chemolabile in that only about 30% was recovered after a flash chromatographic operation on silica gel. The crude ligand product was therefore used in the subsequent metallation work.

For the zirconocene formation, the ligand **5** was lithiated and subsequently treated with $ZrCl_4$ (Scheme 2). Addition of one molar equivalent of *n*-BuLi to a solution of the ligand in diethyl ether gave a clear solution. Addition of a second molar equivalent of *n*-Buli led to precipitation of a tan dilithiated powder which was isolated by filtration and was washed with pentane. The dilithiated product was added to toluene without any further characterisation and treated with solid $ZrCl_4$ which had been purified by sublimation. The zirconocene **7** was isolated in 25% yield. The modest yield was not significantly improved by the use of the $ZrCl_4(THF)_2$ complex for the zirconation. In



1 **2** 66% **3** 57% **4** 48% **5** >95%, de>90%

Scheme 1.



5 **6** 90% **7** 25 %

Scheme 2.

part, the modest yield may be explained by the face selectivity during the zirconation. A sandwich complex requires an intramolecular reaction where the zirconium reactant becomes attached to the inner face of the fluorene ring. When $ZrCl_4$ becomes attached to the other outer face of the ring, intermolecular products are likely to be formed. The zirconocene was extremely sensitive to oxygen. Solutions turned dark green, and only small amounts of impure **7** could be isolated from such solutions.

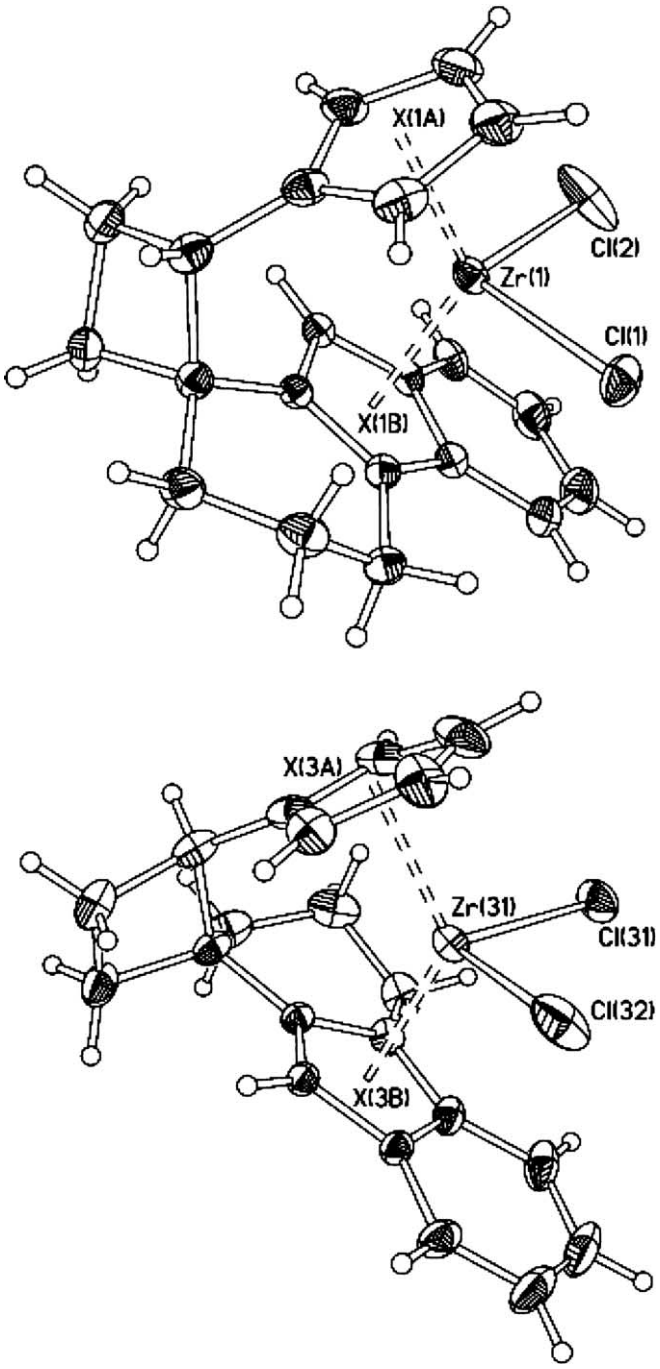


Fig. 2. ORTEP plot of the two crystallographically independent molecules of compound **7**. Ellipsoids are shown at 50% probability. Selected angles (°) and bond lengths (Å) in the molecules: X(1A)–Zr(1)–X(1B) = 125.7, Cl(1)–Zr(1)–Cl(2) = 98.5, Zr(1)–Cl(1) = 2.423, Zr(1)–Cl(2) = 2.420, Zr(1)–X(1A) = 2.200, Zr(1)–X(1B) = 2.243; X(3A)–Zr(31)–X(3B) = 125.8, Cl(31)–Zr(31)–Cl(32) = 98.8, Zr(31)–Cl(31) = 2.432, Zr(31)–Cl(32) = 2.424, Zr(31)–X(3A) = 2.199, Zr(31)–X(3B) = 2.241. Estimated standard deviations are 0.1° in angles and 0.001 Å in bond lengths.

The zirconocene structure **7** has been established by a single-crystal X-ray analysis and is shown by the ORTEP plots of the crystal in Fig. 2. Crystals suitable for X-ray analysis were obtained by slow evaporation of a toluene solution of the zirconocene **7** at room temperature. The crystal unit consisted of two crystallographically independent molecules of compound **7**. Using other solvents like CH_2Cl_2 and Et_2O led to decomposition with dark green coloration. The toluene solution also turned slightly green after a few days, even though it was standing in a glovebox.

The target molecule in this project was to be a conformationally highly constrained C_2-*ansa*-zirconocene. A comparison of the X-ray data will show that the selected torsion angles and the bond distances are similar to the corresponding torsion angles and bond distances in the simple ethylene-bridged C_2-symmetric *rac*-ethylenebis-(1-indenyl)]$ZrCl_2$ [14], and the homologue *rac*-[ethylenbis(4,7-dimethyl-1-indenyl)]$ZrCl_2$ [15].

The properties of the zirconocene complex as a propene polymerisation precatalyst was briefly studied with MAO in toluene under a propene pressure of 1.1 bar at 30 °C. The product was atactic PP. Activity of the zirconocene was calculated to be 0.47×10^6 g PP/mol[Zr]*[C_3]*h. The molecular weight was estimated by ^{1}H NMR end-group analysis [16], $M_w = 600$ g/mol.

3. Conclusion

Methodology for the synthesis of a C_2-bridged zirconocene, (η^5-cyclopentadienyl)spiro[cyclobutane-1,1′-(η^5-fluorenyl)]zirconium dichloride, is described. The C_2-bridge in the ligand is embedded in a rigid spirane scaffold conferring rigidity onto the organometallic complex. As a polymerisation precatalyst, the complex provided atactic PP.

4. Experimental section

The ^{1}H NMR spectra were recorded at 500 MHz with a Bruker DPX 500 instrument, at 300 MHz with a Bruker DPX 300 instrument, or at 200 MHz with a Bruker DPX 200 instrument. The ^{13}C NMR spectra were recorded at 125, 75 or 50 MHz using the same instruments. ^{1}H and ^{13}C spectra were referenced to residual protons in the solvent. Mass spectra were recorded at 70 eV ionizing voltage and are presented as *m*/*z* (% rel. int.). Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany. All organometallic reactions were run under an argon atmosphere using Schlenk and glovebox techniques. THF, Et_2O and toluene were distilled from sodium/benzophenone and CH_2Cl_2 from CaH_2. $CeCl_3$ was bought as the heptahydrate and dried according to the literature [17].

4.1. X-ray crystallographic analysis for zirconocene (7)

X-ray data were collected on a Siemens SMART CCD diffractometer [18] using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection method: ω-scan, range 0.6°, crystal to detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP programs [18]. Absorption corrections were applied by the use of the SADABS program [19]. The structures were determined and refined using the SHELXTL program package [20]. The non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located from difference Fourier maps and refined with isotropic thermal parameters. X-ray structural data for zirconocene **7** have been deposited at the Cambridge Crystallographic Data Centre, deposition number CCDC 266324.

Crystal data for $C_{21}H_{20}Cl_2Zr$ (**7**) $M = 434.49$, triclinic, $P\bar{1}$, $a = 11.123(1)$ Å, $b = 12.807(1)$ Å, $c = 12.930(1)$ Å, $\alpha = 101.62(1)°$, $\beta = 99.13(1)°$, $\gamma = 90.09(1)°$, $V = 1780.1(2)$ Å^3, $Z = 4$, $D_x = 1.621$ Mg m^{-3}, $\mu = 0.917$ mm^{-1}, $T = 150(2)$ K, measured 36,306 reflections in 2θ range 3.2–80.6°, $R_{int} = 0.0148$. 593 parameters refined against 19,480 F^2, $R = 0.030$ for $I_0 > 2\sigma(I_0)$ and 0.046 for all data.

4.2. 1,2,3,4-Tetrahydro-9H-1-[1-(phenylthio)cyclopropyl] fluoren-1-ol (2)

n-BuLi (1.6 M in hexane, 4.40 mL, 7.0 mmol) was added to a solution of cyclopropyl phenyl sulfide [10] (1.05 g, 7.05 mmol) in THF (10 mL) at 0 °C, the mixture stirred at this temperature for 30 min, the temperature lowered to −78 °C and the solution cannulated into a solution of anhydrous $CeCl_3$ (2.08 g, 8.23 mmol) in THF (20 mL) at −78 °C. The resultant mixture was stirred at −78 °C for 3 h. A solution of 3,4-dihydro-2*H*-fluoren-1(9*H*)-one (**1**) (865 mg, 4.7 mmol) in THF (5 mL) was added dropwise, and the reaction mixture allowed to reach room temperature overnight. Water (50 mL) was added, the mixture extracted with diethyl ether (3 × 100 mL), the ether extracts dried ($MgSO_4$), the solution evaporated to dryness and the residual material subjected to flash chromatography on silica gel using EtOAc:hexane 1:10; yield 1.04 g (66%) of a light yellow oil. (Anal. Calc. for $C_{22}H_{22}OS$: C, 79.00; H, 6.63. Found: C, 78.54; H, 6.59%). HRMS(EI): M 334.1359. Anal. Calc. for $C_{22}H_{22}OS$: 334.1391. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.1–1.2 (m, 2H), 1.4–1.6 (m, 2H), 1.9–2.1 (m, 4H), 2.4–2.5 (m, 2H), 3.2–3.5 (m, 2H), 7.2–7.4 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.5, 13.8, 19.2, 22.3, 33.3, 35.1, 36.6, 72.1, 118.7, 123.6, 125.0, 126.0, 126.03, 128.3, 130.2, 136.2, 141.2, 142.5, 143.1, 144.5. MS(EI): 334 (M^+, 3%), 316 (4), 185 (100), 165 (7), 150 (50), 128 (9), 55 (5).

4.3. 1′,2′,3′,4′-Tetrahydro-9H-spiro[cyclobutane-1,1′-fluoren]-2-one (3)

Aqueous 35% HBF_4 (1.3 mL) was added to a solution of 1,2,3,4-tetrahydro-9*H*-1-[1-(phenylthio)cyclopropyl]fluoren-1-ol (**2**) (628 mg, 1.9 mmol) in dry benzene (25 mL) and the mixture heated at 70 °C for 10 h. Dichloromethane (100 mL) was added to the cold reaction mixture and the solution extracted with saturated aqueous $NaHCO_3$ (30 mL), and water (10 mL), the organic solution dried ($MgSO_4$), evaporated and the residual material subjected to flash chromatography on silica gel using EtOAc:hexane 1:20; yield 243 mg (57%) of a light yellow oil which solidified on storage in the refrigerator. (Anal. Calc. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.59; H, 7.20%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.8–2.1 (m, 5H), 2.2–2.4 (m, 1H), 2.5 (m, 2H), 3.0–3.4 (m, 4H), 7.1–7.4 (m, 4H). ^{13}C NMR (75 MHz): δ 19.9, 22.1, 25.3, 32.2, 36.8, 43.1, 66.8, 118.4, 123.5, 124.6, 126.3, 137.7, 138.8, 142.4, 144.9, 213.0. MS(EI): 224 (M^+, 3%), 196 (91), 182 (100), 16 (81), 152 (22), 141 (20), 115 (11), 82 (5).

4.4. 2-(Cyclopenta-2,4-dienylidene)-1′,2′,3′,4′-tetrahydro-9H-spiro[cyclobutane-1,1′-fluorene] (4)

Pyrrolidine (6.7 mL, 80 mmol) was added dropwise to a solution of 1′,2′,3′,4′-tetrahydro-9*H*-spiro[cyclobutane-1,1′-fluoren]-2-one (**3**) (4.5 g, 20 mmol) and cyclopentadiene (8.1 mL, 100 mmol) in methanol (60 mL) and dichloromethane (10 mL) at 0 °C and the mixture stirred at this temperature for 18 h. The reaction mixture was poured into ice-cold 0.5 M HCl (100 mL), the resultant mixture extracted with hexane (3 × 100 mL), the hexane extracts dried ($MgSO_4$), the solution evaporated and the residual material subjected to flash chromatography on silica gel using EtOAc:hexane 1:40; yield 2.6 g (48%) of a dark yellow oil. (Anal. Calc. for $C_{21}H_{20}$: C, 92.60; H: 7.40. Found: C, 92.49; H, 7.58%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.8–2.4 (m, 5H), 2.6 (m, 1H), 2.7 (m, 2H), 3.2–3.4 (m, 2H), 3.5 (s, 2H), 6.23 (dt, $J = 1.7$, 5.2 Hz, 1H), 6.48 (m, 1H), 6.55 (dt, $J = 1.8$, 5.1 Hz, 1H), 6.61 (d, 1H), 7.33 (m, 1H), 7.46 (m, 2H), 7.55 (d, $J = 7.3$ Hz, 1H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 20.5, 23.0, 27.9, 31.6, 37.6, 37.7, 51.9, 118.9, 120.4, 121.0, 124.1, 125.0, 126.8, 130.6, 131.3, 137.6, 139.7, 143.5, 144.5, 145.9, 166.5. MS(EI): 272 (M^+, 100%), 257 (15), 243 (49), 228 (16), 182 (14), 165 (16), 115 (9), 91 (5).

4.5. cis-2-(Cyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9H-spiro[cyclobutane-1,1′-fluorene] (5)

One molar $LiBEt_3H$ in THF (2.8 mL) was added dropwise to 2-(cyclopenta-2,4-dienylidene)-1′,2′,3′,4′-tetrahydro-9*H*-spiro[cyclobutane-1,1′-fluorene] (**4**) (500 mg, 1.8 mmol) in THF (10 mL) at 0 °C. The mixture stirred at room temperature for 1.5 h and poured into ice/water (100 mL) and dichloromethane (100 mL), the two layers separated, the water phase extracted with dichloromethane (2 × 50 mL), the combined organic solutions washed with water (3 × 10 mL), dried ($MgSO_4$) and the residual material subjected to flash chromatography on silica gel using CH_2Cl_2:hexane 1:40; yield 151 mg (30%) of a colourless oil

consisting of a 1:1 mixture of two double bond isomers. HRMS(EI): M 274.1723. Anal. Calc. for $C_{21}H_{22}$: 274.1721. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.9–3.6 (m, 15H), 6.1 (m, 1H), 6.3 (m, 1.5H), 6.4 (m, 0.5H), 7.1–7.4 (m, 4H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 20.3, 20.5, 21.6, 22.0, 23.02, 23.03, 32.1, 32.3, 38.7, 38.9, 40.0, 40.1, 41.3, 43.4, 46.0, 46.7, 47.4, 48.8, 118.17, 118.24, 123.5, 123.6, 124.1, 124.2, 125.8, 126.2, 126.3, 126.4, 131.6, 132.3, 133.8, 134.6, 137.0, 137.2, 143.6, 143.8, 145.88, 145.90, 145.99, 146.0, 149.3, 151.9. MS(EI): 274 (M^+, 8%), 195 (12), 182 (100), 167 (17), 153 (7), 141 (9), 91 (7). MS(CI, CH_4): 275 (M^+, 63%), 211 (17), 195 (15), 183 (100), 93 (75), 79 (8), 49 (9).

4.6. 2-(η^5-Cyclopentadienyl)-1′,2′,3′,4′-tetrahydrospiro[cyclobutane-1, 1′-(η^5-fluorenyl)]zirconium dichloride (7)

1.6 M *n*-BuLi in hexane (4.2 mL, 6.8 mmol) was added to a solution of *cis*-2-(cyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9*H*-spiro[cyclobutane-1,1′-fluorene] (**5**) (890 mg, 3.25 mmol) in diethyl ether (40 mL) under argon at 0°. The reaction mixture was allowed to reach ambient temperature overnight. A tan coloured precipitate was formed. Filtration, washing with pentane and drying under high vacuum gave 836 mg (90%) of the dilithiated ligand. The product was suspended in toluene (30 mL), the temperature lowered to 0 °C and solid zirconium tetrachloride was added in one portion. The reaction mixture was allowed to reach room temperature overnight. The solution was then filtered through a glass sinter, and the resultant clear dark yellow solution was concentrated to approximately 3 mL. Pentane (40 mL) was added and a light yellow precipitate was formed. The precipitate was filtered, washed with pentane (15 mL) and dried under high vacuum; yield: 317 mg (25%) of a light yellow solid. Slow evaporation of a toluene solution yielded crystals suitable for X-ray analysis. (Anal. Calc. for $C_{21}H_{20}Cl_2Zr$: C, 58.05; H, 4.64. Found: C, 58.27; H, 5.03%). HRMS(EI): M 431.9997. Anal. Calc. for $C_{21}H_{20}Cl_2Zr$: 431.9989. ^{1}H NMR (CD_2Cl_2, 300 MHz): 1.50–1.56 (m, 1H), 1.93–1.96 (m, 2H), 2.01–2.09 (m, 2H), 2.36–2.39 (m, 2H), 2.57–2.62 (m, 1H), 2.72–2.77 (m, 1H), 3.17 (dt, $J = 2.0$, 9.5 Hz, 1H), 3.75 (t, $J = 5.2$ Hz, 1H), 6.01 (q, $J = 1.5$, 3.1 Hz, 1H), 6.18 (q, $J = 1.9$, 3.3 Hz, 1H), 6.59 (q, $J = 2.0$, 3.3 Hz, 1H), 6.73 (q,$J = 1.6$, 3.2 Hz, 1H), 7.08–7.11 (m, 1H), 7.17–7.21 (m, 1H), 7.37 (dd, $J = 0.5$, 5.1 Hz, 1H, 7.47 (dd, $J = 0.5$, 5.1 Hz, 1H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 19.5, 20.1, 23.9, 30.6, 38.5, 49.1, 50.8, 95.7, 108.2, 113.5, 118.6, 120.0, 123.2, 123.5, 125.1, 126.1, 126.4, 126.5, 132.7, 138.2, 142.1. MS(EI): 432 (M^+, 95%), 396 (20), 341 (47), 303 (22), 251 (68), 182 (56), 165 (70), 152 (31), 91 (25).

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