

Fulvene having substituents only on 1-, 4-, and 6-positions: a key intermediate for novel *ansa*-metallocene complexes

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Abstract

A synthetic route for 1,4-dimethyl-6-phenylfulvene (**4**) and 1,4-dimethyl-6,6-diphenylfulvene (**5**), which are characteristic in that they have substituents only on 1-, 4-, and 6-positions, is developed. The synthetic route is straightforward from 2-bromo-3-methyl-2-cyclopenten-1-one ethylene ketal (**1**), which can be easily synthesized in 100-g scale. Overall yield from **1** is 50 and 47% for **4** and **5**, respectively. Synthesis of an *ansa*-metallocene complex, [Ph(H)C(fluorenyl)(1,3-Me₂Cp)]ZrCl₂ (**7**), is demonstrated using **4**. Much higher comonomer incorporation in ethylene/1-hexene copolymerization and dramatic increase of molecular weight in 1-hexene polymerization are observed with **7** when the reactivity compared with that of the one not having methyl substituents, [Ph(H)C(fluorenyl)(Cp)]ZrCl₂.

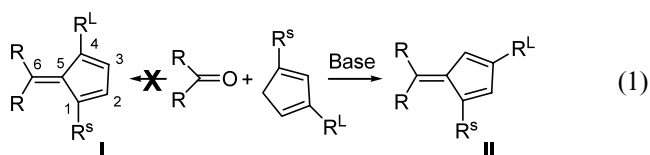
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Keywords: Fulvene; Metallocenes; Zirconium; Polymerization; Cyclopentadienyl

1. Introduction

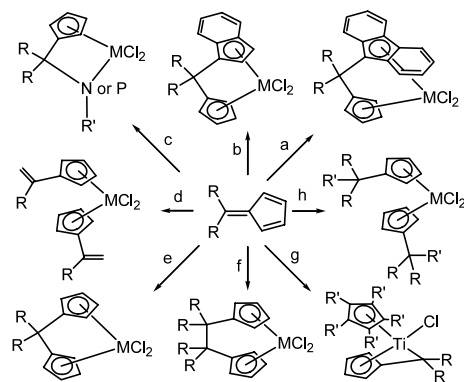
Various metallocene complexes, which can serve as catalysts for the polymerization of olefins, can be synthesized from fulvenes. Scheme 1 shows its versatility [1]. Fulvenes are also substrates for cycloaddition reaction by which useful organic compounds can be provided [2,3]. Fulvenes are obtained by coupling reaction of cyclopentadiene or substituted cyclopentadienes with aldehydes or ketones [3,4]. When 1,3-disubstituted cyclopentadiene is used, the substituents are situated in 1,3-positions in the resulting fulvene by steric reason (**II** in Eq. (1)) [5]. Other routes for fulvene derivatives have been developed but, in those cases, the products still have substituents on 1- and 3-positions [6]. Syntheses of 1,2,3,4-tetramethylfulvene and 1,2,3,4,6-

pentamethylfulvene were developed and they were used successfully for the syntheses of novel metallocene complexes [7]. However, until now, synthetic route for fulvenes having substituents only on 1-, 4-, and 6-positions (**I** in Eq. (1)) has not been developed. Herein, we disclose a synthetic route for these fulvenes. Synthesis of an *ansa*-metallocene complex is demonstrated using the fulvene and its reactivities to the olefin (co)polymerizations are studied. The *ansa*-metallocene complexes derived from the fulvene are characteristic in that substituents on the cyclopentadienyl ligand are located adjacent to the bridge point [8]. With the complexes, the steric congestion at the reaction site is kept minimum, while electronic effect is controlled by the substituents.



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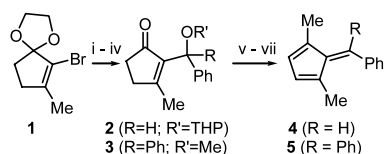
Scheme 1. Metallocene complexes from a fulvene.

2. Results and discussion

2.1. Syntheses of 1,4-dimethyl-6-phenylfulvene (**4**) and 1,4-dimethyl-6,6-diphenylfulvene (**5**)

A fulvene having substituents only on 1-, 4-, and 6-positions are synthesized by the route shown in Scheme 2. Starting material **1** can be easily synthesized in 100-g scale from commercially available 3-methyl-2-cyclopenten-1-one by two steps. The novel route consists of two steps. The first step is composed of four individual reactions: (a) lithiation of **1** with *n*-BuLi; (b) addition of a ketone or an aldehyde; (c) deprotection of ketal group; and (d) protection of the generated hydroxyl group. It can be conducted in one pot with overall high yields (70 and 68% for **2** and **3**, respectively). Deprotection of ketal group is carried out successfully by treatment of aqueous 1 N HCl briefly. In the case of addition of benzaldehyde, the generated secondary alcohol can be protected with tetrahydropyranyl (THP) without problems but, in the case of addition of benzophenone, a tertiary alcohol is generated which is difficult to be protected with THP group [9]. Protection even to methyl ether by NaH/methyl iodide condition is not successful. The protection problem can be overcome by transforming the generated lithium alkoxide in the second reaction directly to methyl ether by the addition of methyl iodide. The deprotection of ketal is carried out after the formation of methyl ether.

The second step is composed of three individual reactions: (a) 1,2-addition of methyllithium to the carbonyl; (b) dehydration to give cyclopentadiene deri-

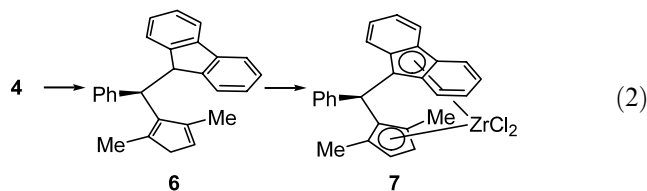


Scheme 2. (i) *n*-BuLi, -78°C ; (ii) RCOPh (R = H or Ph); (iii) 1 N HCl for **2** (or MeI for **3**); (iv) dihydropyran, *p*-TsOH for **2** (or 1 N HCl for **3**); (v) MeLi; (vi) 2 N HCl; and (vii) NaOMe/THF.

vatives; and (c) treatment with base to furnish fulvenes. Overall yields for the second step are fairly good (72 and 69% for **4** and **5**, respectively). Dehydration is carried out simply by shaking ethyl acetate solution of the generated tertiary alcohol with aqueous 2 N HCl for several minutes [10]. The final reaction was conducted by reacting the generated cyclopentadiene with NaOMe/MeOH in THF. The appearance of red color indicates the formation of fulvene and the structures are confirmed by ^1H - and ^{13}C -NMR spectra and elemental analyses. Two vinyl proton signals at 6.03 and 6.10 ppm (C_6D_6) and two methyl proton signals at 1.79 and 2.00 ppm are observed for **4** in ^1H -NMR spectrum. A vinyl proton signal at 6.05 ppm (CDCl_3) and a methyl proton signal at 1.40 ppm are observed for **5**.

2.2. Synthesis of $[\text{Ph}(\text{H})\text{C}(\text{fluorenyl})(1,3\text{-Me}_2\text{Cp})]\text{ZrCl}_2$ (**7**)

Synthesis of an *ansa*-metallocene complex is demonstrated (Eq. (2)) using **4**. Nucleophilic attack of fluorenyl anion to **4** gives the desired ligand **6** (86%). The deprotonation of **6** with two equivalents of *n*-BuLi and subsequent reaction of the resulting dianion with $\text{ZrCl}_4(\text{THF})_2$ in pentane afford clearly the desired *ansa*-zirconocene complex **7** as red solid (77%). Two Cp–H signals are observed separately at 6.02 and 6.06 ppm as doublet ($J = 3.6$ Hz) in ^1H -NMR spectrum due to destroyed symmetry by the phenyl group. Signal of proton attached on bridge carbon is observed at 6.25 ppm as singlet. Methyl proton signals are observed at 1.72 and 1.84 ppm as singlet. Fulvene **5** is inert to the nucleophilic attack of fluorenyl anion.



Single crystals suitable for X-ray crystallography are obtained by vapor phase addition of pentane to a benzene solution. Fig. 1 shows the ORTEP drawing of **7** with selected bond lengths and angles. Cp(centroid)–Zr–fluorenyl(centroid) angle, the value of which indicates how far the zirconium atom displaces from the cyclopentadienyl and fluorenyl ligand, is 118.8° . The value is slightly bigger than that observed for $[\text{Ph}_2\text{C}(\text{Cp})(\text{fluorenyl})]\text{ZrCl}_2$ (117.6°) [11] indicating that the Zr atom in $[\text{Ph}_2\text{C}(\text{Cp})(\text{fluorenyl})]\text{ZrCl}_2$ is located slightly further out of the mouth of the ligand. The angle of Cl–Zr–Cl ($98.77(10)^{\circ}$) is slightly bigger than that of $[\text{Ph}_2\text{C}(\text{Cp})(\text{fluorenyl})]\text{ZrCl}_2$ (95.9°). Methyl substituents are slightly above the cyclopentadienyl plane. Dihedral angles of C21–C19–C18–C17 and C20–C16–C17–C18 are -172.5° and 173.8° , respectively.

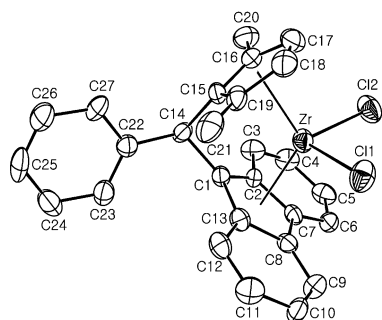


Fig. 1. ORTEP view of **7**, showing the atom numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Zr–Cl(1), 2.412(3); Zr–Cl(2), 2.421(3); Zr–C(1), 2.401(9); Zr–C(2), 2.554(9); Zr–C(7), 2.659(8); Zr–C(15), 2.447(9); Zr–C(16), 2.488(11); Zr–C(17), 2.533(11); C(14)–C(15), 1.527(12); C(1)–C(14), 1.523(12); C(16)–C(20), 1.532(13); C(19)–C(21), 1.518(12); Cl(1)–Zr(1)–Cl(2), 98.77(10); C(1)–C(14)–C(15), 101.6(7); Cp(centroid)–Zr(1)–Cp(centroid), 117.15.

2.3. Polymerization studies

The complex was tested in ethylene, propylene, 1-hexene, ethylene/1-hexene, and ethylene/norbornene (co)polymerizations. The reactivity is compared with that of an *ansa*-zirconocene complex not having methyl substituents, [PhCH(fluorenyl)(Cp)]ZrCl₂ (**8**) [12], to investigate the effects of the methyl substituents. In the ethylene and propylene polymerizations, rather lower activity and lower molecular weight are observed with **7** (entries 1–4 in Table 1). Capability to control tacticity is not reduced by the methyl substituents in propylene polymerization. Both catalysts give syndiotacticity-rich poly(propylene) having almost same T_m (139 and 137 °C for **7** and **8**, respectively) and [r] content (65 and 66% for **7** and **8**, respectively). In 1-hexene polymerization (entries 5 and 6), molecular weight is increased drama-

tically by the methyl substituents. The polymer obtained with **7** is rubbery solid (M_w , 1050 000) while that obtained by the comparison catalyst **8** is oily (M_w , 100 000). Capability to control tacticity is not reduced severely in this case as well ([rrrr], 83 and 87% for **7** and **8**, respectively). Almost same ¹³C-NMR spectra are observed for both copolymers. In ethylene/1-hexene copolymerization, rather lower molecular weight and lower activity are observed with complex **7** (entries 7 and 8) but 1-hexene incorporation is increased dramatically. Complex **7** produces a copolymer having 15 mol% 1-hexene content while complex **8** gives a copolymer having only 4.0 mol% 1-hexene content under the same polymerization condition. In the ethylene/norbornene copolymerization, both complexes show the similar reactivity in terms of activity, norbornene content, and molecular weight.

3. Conclusion

A synthetic route for 1,4-dimethyl-6-phenylfulvene (**4**) and 1,4-dimethyl-6,6-diphenylfulvene (**5**), which are characteristic in that they have substituents only on 1-, 4-, and 6-positions, is developed and synthesis of an *ansa*-metallocene complex, [Ph(H)C(fluorenyl)(1,3-Me₂Cp)]ZrCl₂ (**7**), is demonstrated using **4**. When the polymerization reactivity of **7** is compared with that of the one not having methyl substituent, [Ph(H)C(fluorenyl)(Cp)]ZrCl₂ (**8**), molecular weight (M_w) is increased by 10 times in 1-hexene polymerization and incorporation of 1-hexene is increased dramatically in ethylene/1-hexene copolymerization. Various fulvenes and hence various novel metallocene complexes are expected to be synthesized by using the synthetic route described in this paper. We are currently studying the syntheses and

Table 1
Polymerization results

Entry	Catalyst	Monomer	Activity (kg mol ⁻¹ h ⁻¹)	T_m (°C)	M_w^a	M_w/M_n^a
1	7	Ethylene	6.0	131	262000	2.5
2	8 ^b	Ethylene	13.4	133	302000	3.2
3	7	Propylene	1.8	139	153000	1.8
4	8	Propylene	2.9	137	210000	1.9
5	7	1-Hexene	5.3	ND	1050000	2.4
6	8	1-Hexene	7.7	ND	100000	2.0
7 ^c	7	Ethylene + 1-hexene	13.9	ND	90400	1.9
8 ^d	8	Ethylene + 1-hexene	25.3	113	129000	1.9
9	7	Ethylene + norbornene	139	121 ^e	404000	4.6
10	8	Ethylene + norbornene	130	122 ^e	483000	3.7

ND, not detected.

^a Determined by GPC in 1,2,4-trichlorobenzene at 140 °C against polystyrene standards.

^b [PhCH(fluorenyl)(Cp)]ZrCl₂.

^c 15 mol% 1-hexene content by ¹³C-NMR study.

^d 4.0 mol% 1-hexene content.

^e T_g value instead of T_m .

polymerization reactivities of the metallocene complexes.

4. Experimental

4.1. General considerations

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, THF, diethyl ether, and C₆D₆ were distilled from benzophenone ketyl. Anhydrous grade DMSO was purchased from Aldrich and used without further purification. Toluene used for polymerization reaction was purchased from Aldrich (anhydrous grade) and purified further by distillation over Na–K alloy. 1-Hexene was purified by distillation over Na–K alloy. Norbornene was dissolved in toluene (3.54 M) and the solution was purified by distillation over Na–K alloy. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo (7.6 wt.% of Al, MMAO type 4). Ethylene and propylene were purchased from Conley Gas (99.9%) and MG industry, respectively, and purified by contacting with molecular sieves and copper overnight under the pressure of 150 psig. NMR spectra were recorded on a Varian Mercury plus 400 spectrometer. Elemental analyses were carried out on a Fisons EA1108 micro-analyzer. IR spectra were recorded on Nicolet Magma-IR 550. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using Waters Model 150-C+ GPC and the data were analyzed using a polystyrene analyzing curve. Differential scanning calorimetry (DSC) was performed on a Thermal Analysis 3100. Compound **1** was reported but experimental details and spectroscopic data are missing in the literature [13]. We have developed 100-g scale synthesis of the compound.

4.2. 2-Bromo-3-methyl-2-cyclopenten-1-one

3-Methyl-2-cyclopenten-1-one (142 g, 1.24 mol) was dissolved in CCl₄ (760 ml) in 3.0-l three neck flask. The solution was cooled to 0 °C with an ice bath. Bromine (260 g, 1.63 mol) dissolved in CCl₄ (760 ml) was added dropwise for 5 h while keeping the temperature below 5 °C. The solution should be stirred with mechanical stirrer because thick slurry was formed. The liquid phase was removed by cannula, a tip of which is capped with filter paper, while keeping the temperature at 0 °C. CCl₄ (250 ml) was added and the slurry was stirred. The liquid phase was removed by the cannula again. This washing process was repeated twice. The washing process should be conducted in a hood because HBr gas was evolved from the decanted solution. Diethyl ether (760 ml) was added to dissolve the obtained yellow solid and the

solution was cooled to 0 °C. Concentrated aqueous NaHCO₃ solution (1.2 l) was added dropwise while keeping the temperature below 5 °C. Vigorous evolution of CO₂ gas was detected. After solid NaHCO₃ (ca. 100 g) was added additionally at 0 °C, the aqueous solution became slightly basic and evolution of CO₂ gas ceased. Ether phase was collected and dried with MgSO₄. Removal of solvent with rotary evaporator gave a solid which was dissolved in ethyl acetate (250 ml) and hexane (500 ml). When the solution was stored at –20 °C overnight, white crystals were deposited, which were collected by filtration (106 g). The solvent in the mother liquor was removed by rotary evaporator. The residue was dissolved in ethyl acetate (100 ml) and hexane (300 ml) again. Storing the solution at –20 °C overnight gave the second crops (20 g). The total isolated yield was 50% (126 g). m.p. 54 °C. ¹H-NMR (400 MHz, CDCl₃, 25 °C): δ = 2.20 (s, 3 H, CH₃), 2.54–2.56 (m, 2 H, CH₂), 2.68–2.70 (m, 2 H, CH₂) ppm. ¹³C{¹H}-NMR (100 MHz, CDCl₃, 25 °C): δ = 19.02 (CH₃), 32.19 (CH₂), 33.25 (CH₂), 122.73 (C=C), 173.35 (C=C), 201.10 (C=O) ppm. IR (neat, KBr): $\tilde{\nu}$ = 1610 and 1710 (C=C–C=O) cm^{–1}. C₆H₇BrO (175.03)—Anal. Calc.: C, 41.2; H, 4.04. Found: C, 41.0; H, 4.37%.

4.3. Bromoketal compound **1**

2-Bromo-3-methyl-2-cyclopenten-1-one (93.0 g, 0.531 mol), ethylene glycol (230 g, 3.70 mol), and triethyl orthoformate (235 g, 1.59 mol) were mixed in 1.0-l one neck flask. *p*-Toluenesulfonic acid monohydrate (2.0 g) was added and the solution was stirred for 4 h at room temperature (r.t.). KOH (2.4 g) dissolved in 500 ml water was added to the solution. The compound was extracted with hexane (500 ml × 3). The volatiles were removed by rotary evaporator. TLC study shows only two spots, product and reactant. The reactant was removed by solubility difference. The reactant is soluble in water but sparingly soluble in hexane. The product is soluble in hexane but insoluble in water. Thus, the residue was dissolved in hexane (1.25 l) again and the solution was poured into a 3.0-l separatory funnel. The solution was washed with distilled water (1.0 l × 10). The hexane phase was dried briefly with minimum amount of anhydrous MgSO₄. The solvent was removed by rotary evaporator. The residue was distilled under full vacuum (500 mTorr, 65–70 °C) to give white solid (93.5 g, 81%). Special care should be exerted during distillation. The distillation temperature should be lowered as far as possible. Decomposition of the compound was observed when the bath temperature was above 120 °C. The boiling temperature can be lowered by connecting the glass joints with vacuum grease and by cooling the collecting flask with dry ice/acetone bath. The condenser should be cooled with ambient air. The compound is solidified inside the

condenser if it was cooled with cooling water. m.p. 35 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C): δ = 1.80 (s, 3 H, CH_3), 2.15–2.18 (m, 2 H, CH_2), 2.34–2.37 (m, 2 H, CH_2), 3.93–4.00 (m, 2 H, OCH_2), 4.13–4.21 (m, 2 H, OCH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3 , 25 °C): δ = 16.53 (CH_3), 32.85, 34.44, 65.66, 118.05, 118.74, 144.15 ppm. $\text{C}_8\text{H}_{11}\text{BrO}_2$ (219.09)—Anal. Calc.: C, 43.9; H, 5.07. Found: C, 44.2; H, 5.35%.

4.4. Compound 2

To a Schlenk flask containing **1** (5.00 g, 23.0 mmol) in THF (25 ml) was added *n*-BuLi at -78°C (6.39 g, 2.5 M in hexane, 23.0 mmol) dropwise and the solution was stirred for 1 h at -78°C . Benzaldehyde (2.45 g, 23.0 mmol) was added and the solution was stirred for 2 h at -78°C . The solution was poured into a separatory funnel containing water (30 ml) and the product was extracted with ethyl acetate (40 ml $\times$ 2). The combined organic layer was shaken with 1 N aqueous HCl solution (40 ml) for about 30 s, in which step the ketal group was deprotected to furnish a carbonyl. The organic layer was washed with concentrated aqueous NaHCO_3 solution (40 ml). The solution was dried over anhydrous MgSO_4 and the solvent was removed to give a residue which was used for the next step without further purification (yield: 96%). The residue was dissolved in CH_2Cl_2 (50 ml) and dihydropyran (4.85 g, 57.6 mmol) and *p*-toluenesulfonic acid monohydrate (44 mg, 0.23 mmol) were added at r.t. The solution was stirred for 2 h and then diluted with ethyl acetate (25 ml). The solution was washed with saturated aqueous NaHCO_3 solution. The organic phase was collected and dried over anhydrous MgSO_4 . Removal of solvent by rotary evaporator gave a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 3:1). Yield was 4.60 g (overall 70%). Two diastereomers are observed in $^1\text{H-NMR}$ spectrum. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C): δ = 1.51–1.74 (m, 6 H), 2.15 (s, 1.5 H, CH_3), 2.27 (s, 1.5 H, CH_3), 2.32–2.41 (m, 2 H, CH_2), 3.42–3.54 (m, 1 H, OCH_2), 3.76–3.88 (m, 1 H, OCH_2), 4.57 (dd, $^3J_{\text{H,H}}$ = 2.9, 4.6 Hz, 0.5 H, OCHO), 4.64 (t, $^3J_{\text{H,H}}$ = 3.3 Hz, 0.5 H, OCHO), 5.78 (s, 0.5 H, PhC-H), 5.82 (s, 0.5 H, PhC-H), 7.21–7.46 (m, 5 H, Ph-H) ppm. Spectral data of the intermediate hydroxyl compound are as follows. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C): δ = 2.10 (s, 3 H, CH_3), 2.35–2.45 (m, 2 H), 2.50–2.60 (m, 2 H), 4.58 (d, $^3J_{\text{H,H}}$ = 9.1 Hz, 1 H, OC-H), 5.59 (d, $^3J_{\text{H,H}}$ = 9.1 Hz, 1 H, O-H), 7.20–7.36 (m, 5 H, phenyl-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3 , 25 °C): δ = 17.49 (CH_3), 32.07, 34.58, 70.14 (C-OH), 125.73, 127.44, 128.48, 140.04, 142.85, 172.18, 210.60 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 1639 and 1690 (C=C-C=O), 3420 (br, OH) cm^{-1} .

4.5. Compound 3

To a Schlenk flask containing **1** (1.13 g, 5.20 mmol) in THF (6.0 ml) was added *n*-BuLi at -78°C (1.44 g, 2.5 M in hexane, 5.20 mmol) dropwise and the solution was stirred for 1 h at -78°C . A solution of benzophenone (0.948 g, 5.20 mmol) in THF (1.0 ml) was added and the solution was stirred for 2 h at -78°C . The solution was warmed to r.t. and the solvent was removed under vacuum. DMSO (7.5 ml) and MeI (0.85 ml, 13.8 mmol) were added successively. The solution was stirred overnight. Aqueous saturated NH_4Cl solution (1.0 ml) and aqueous 1 N HCl solution (0.3 ml) was added successively. The mixture was stirred for 10 min. Aqueous saturated NaHCO_3 solution (4.0 ml) was added and the product was extracted with diethyl ether (8.0 ml $\times$ 5). The product was dissolved in hot hexane and ethyl acetate (v/v, 10:1). White crystals were obtained by storing the solution in a freezer (-20°C). Yield was 68% (1.04 g). m.p. 130 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C): δ = 2.29–2.36 (m, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 2.48–2.51 (m, 2 H, CH_2), 2.89 (s, 3 H, OCH_3), 7.20–7.30 (m, 6 H, ph-H), 7.39–7.42 (m, 4 H, ph-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3 , 25 °C): δ = 19.70, 33.33, 35.02, 51.21, 84.93, 126.93, 127.37, 128.04, 141.09, 141.46, 173.69, 206.48 (C=O) ppm. $\text{C}_{20}\text{H}_{20}\text{O}_2$ (292.40)—Anal. Calc.: C, 82.1; H, 6.91. Found: C, 82.0; H, 6.88%.

4.6. 1,4-Dimethyl-6-phenylfulvene (4)

To a Schlenk flask containing **2** (2.17 g, 7.57 mmol) in diethyl ether (24 ml) was added MeLi (6.05 ml, 1.5 M in diethyl ether, 9.08 mmol) at -78°C dropwise. The solution was allowed to warm to r.t. and stirred for 5 h. Water (20 ml) was added. Diethyl ether was removed by rotary evaporator. Ethyl acetate (60 ml) was added to the residue and the mixture was poured into a separatory funnel. The aqueous layer was removed and aqueous 2 N HCl solution (40 ml) was added. The mixture was shaken vigorously for 3 min. The aqueous layer was removed and the organic layer was washed with saturated aqueous NaHCO_3 solution (40 ml). The organic layer was collected and dried over anhydrous MgSO_4 . Solvent was removed by rotary evaporator to give a residue. To the residue were added NaH (0.19 g, 8.0 mmol) and THF (20 ml) under nitrogen atmosphere. Methanol (2.0 ml) was added via syringe, upon which hydrogen gas was evolved and the solution turned to red. The solution was stirred for 3 h at r.t. under nitrogen. The solution was poured into a separatory funnel containing water (20 ml) and hexane (60 ml). The organic layer was collected and dried over anhydrous MgSO_4 . Removal of solvent gave a red residue which was purified by column chromatography on silica gel eluting with hexane and toluene (v/v, 10:1). Yield was

0.920 g (72%). $^1\text{H-NMR}$ (400 MHz, C_6D_6 , 25 °C): δ = 1.79 (s, 3 H, CH_3), 2.00 (s, 3 H, CH_3), 6.03 (dq, $^3J_{\text{H,H}} = 3.6$, $^4J_{\text{H,H}} = 2.0$ Hz, 1 H, $\text{CH}_3\text{-C=CH}$), 6.10 (dq, $^3J_{\text{H,H}} = 3.6$, $^4J_{\text{H,H}} = 2.0$ Hz, 1 H, $\text{CH}_3\text{-C=CH}$), 7.03–7.16 (m, 6 H) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, C_6D_6 , 25 °C): δ = 13.08 (CH_3), 17.15 (CH_3), 127.58, 127.94, 128.08, 129.59, 130.11, 132.70, 133.51, 134.03, 137.15, 147.24 ppm. $\text{C}_{14}\text{H}_{14}$ (182.28)—Anal. Calc.: C, 92.2; H, 7.76. Found: C, 92.0; H, 7.52%.

4.7. 1,4-Dimethyl-6,6-diphenylfulvene (5)

The compound was prepared according to the same procedure and condition for **4**. The product was purified by column chromatography on silica gel eluting with hexane and toluene (v/v, 10:1). Yield was 69%. m.p. 98 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C): δ = 1.40 (s, 6 H, CH_3), 6.05 (s, 2 H, vinyl-H), 7.16–7.20 (m, 4 H, Ph-H), 7.27–7.31 (m, 6 H, Ph-H) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, CDCl_3 , 25 °C): δ = 16.92 (CH_3), 127.75, 128.13, 130.54, 130.62, 132.39, 142.44, 144.32, 151.37 ppm. $\text{C}_{20}\text{H}_{18}$ (258.38)—Anal. Calc.: C, 93.0; H, 7.04. Found: C, 93.1; H, 7.02%.

4.8. Ligand 6

To a stirred solution of fluorene (0.162 g, 1.0 mmol) in cold THF (5 ml, –30 °C) was added *n*-BuLi (0.277 g, 2.5 M in hexane, 1.0 mmol) dropwise inside a glove box. The resulting solution was stirred for 1 h. Compound **4** (0.182 g, 1.0 mmol) in THF (1.0 ml) was added at –30 °C and the solution was stirred for 2 h at r.t. Saturated aqueous NH_4Cl solution (5 ml) was added and the product was extracted with diethyl ether. The collected organic layer was dried over anhydrous MgSO_4 . Removal of solvent by rotary evaporator gave a residue which was purified by column chromatography on silica gel eluting with hexane and toluene (v/v, 20:1). Yield was 0.298 g (86%). m.p. 133 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C): δ = 1.87 (s, 3 H, CH_3), 1.92 (d, $^4J_{\text{H,H}} = 1.6$ Hz, 3 H, CH_3), 2.81 (d, $^3J_{\text{H,H}} = 2.0$ Hz, 2 H, CH_2), 3.80 (d, $^3J_{\text{H,H}} = 11.6$ Hz, 1 H, PhC-H or Flu-H), 4.87 (d, $^3J_{\text{H,H}} = 11.6$ Hz, 1 H, PhC-H or Flu-H), 5.87 (s, 1 H, vinyl-H), 6.48 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 1 H), 6.94 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 1 H), 7.0–7.4 (m, 9 H), 7.70 (d, $^3J_{\text{H,H}} = 7.2$ Hz, 2 H) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, CDCl_3 , 25 °C): δ = 15.22, 16.65, 44.43, 48.43, 48.51, 119.23, 119.36, 125.28, 125.80, 125.99, 126.11, 126.20, 126.36, 126.82, 126.90, 127.98, 129.38, 138.78, 140.82, 140.91, 141.57, 142.72, 144.02, 145.88, 146.30 ppm. $\text{C}_{27}\text{H}_{24}$ (348.51)—Anal. Calc.: C, 93.0; H, 6.96. Found: C, 93.2; H, 7.07%.

4.9. $[\text{Ph}(\text{H})\text{C}(\text{fluorenyl})(1,3\text{-Me}_2\text{Cp})]\text{ZrCl}_2$ (7)

To a stirred solution of **6** (0.100 g, 0.287 mmol) in cold THF (3 ml, –30 °C) was added *n*-BuLi (0.159 g, 2.5 M in hexane, 0.574 mmol) dropwise. The solution was stirred overnight. The solvent was removed by vacuum and the residue was washed with pentane (4.0 ml) and benzene (4.0 ml). $\text{ZrCl}_4(\text{THF})_2$ (0.108 g, 0.287 mmol) and pentane (5.0 ml) was added to the red dilithium salt and the slurry was stirred for 24 h. The solvent was decanted and the product was extracted with benzene (ca. 12 ml). Removal of solvent gave a red solid which is quite pure by the analysis of ^1H - and ^{13}C -NMR spectra. Yield was 0.11 g (77%). The single crystals suitable for X-ray crystallography and elemental analysis were obtained by vapor phase addition of pentane to a benzene solution overnight at r.t. $^1\text{H-NMR}$ (400 MHz, C_6D_6 , 25 °C): δ = 1.72 (s, 3 H, CH_3), 1.84 (s, 3 H, CH_3), 6.02 (d, $^3J_{\text{H,H}} = 3.6$ Hz, 1 H, Cp-H), 6.06 (d, $^3J_{\text{H,H}} = 3.6$ Hz, 1 H, Cp-H), 6.25 (s, 1 H), 6.66 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 1 H), 6.91 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 1 H), 7.02–7.20 (m, 5 H), 7.26 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 2 H), 7.45 (dd, $^3J_{\text{H,H}} = 6.4$, $^4J_{\text{H,H}} = 1.2$ Hz, 2 H), 7.73 (dd, $^3J_{\text{H,H}} = 8.4$, 6.0 Hz, 2 H) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, C_6D_6 , 25 °C): δ = 16.51, 19.30, 41.67, 73.96, 99.41, 121.28, 122.34, 122.66, 123.14, 123.70, 123.81, 123.99, 124.40, 124.82, 124.84, 124.92, 125.02, 126.27, 126.63, 126.70, 127.36, 128.35, 128.72, 138.45 ppm. $\text{C}_{27}\text{H}_{22}\text{Cl}_2\text{Zr}$ (508.56)—Anal. Calc.: C, 63.8; H, 4.37. Found: C, 63.5; H, 4.15%.

4.10. Polymerization

In a dry box, to a dried 70-ml glass reactor was added 30 ml of toluene, 1-hexene, norbornene solution in toluene (3.54 M), or 1-hexene solution in toluene (0.50 M). The reactor was assembled and brought out from the dry box. The reactor was immersed in an oil bath whose temperature had been set to a given value and stirred for 15 min. An activated catalyst prepared by mixing a given amount of catalyst and MAO was added via a syringe. Ethylene or propylene was fed immediately under the predetermined pressure. After polymerization had been conducted for a given time, it was quenched by venting ethylene or propylene gas and pouring the mixture to a solution of methanol and concentrated aqueous HCl (v/v, 1:1). The resulting white slurry was stirred for several hours. White precipitates were collected by filtration, washed with methanol, and dried under vacuum. Detailed conditions for each polymerization reactions are as follows: 0.5 μmol catalyst, Al/Zr = 4000, 60 °C, 75 psig, 6 min for ethylene polymerization; 2.0 μmol catalyst, Al/Zr = 2000, r.t., 75 psig, 20 min for propylene polymerization; 1.0 μmol catalyst, Al/Zr = 4000, r.t., 30 min for 1-hexene polymerization; 0.5 μmol catalyst, Al/Zr = 4200, 75 psig,

60 °C, 10 min for ethylene/1-hexene copolymerization; 0.25 μmol catalyst, Al/Zr = 6000, 100 psig, 60 °C, 5 min for ethylene/norbornene copolymerization. ^{13}C -NMR spectra of ethylene/1-hexene copolymers were recorded at 100 °C with 70° flip angle, acquisition time of 1.5 s, and a delay time of 4.0 s. The copolymers (ca. 80 mg) were dissolved in a mixed solvent (0.5 ml) of $\text{C}_2\text{D}_2\text{Cl}_4$ and $\text{C}_6\text{H}_3\text{Cl}_3$ (v/v, 1:2). The 1-hexene contents were calculated according to the literature method [14]. ^{13}C -NMR spectra of the poly(propylene) were recorded at 125 °C with 45° flip angle, acquisition time of 2.3 s, and a delay time of 2.0 s. The copolymers (ca. 60 mg) were dissolved in $\text{C}_2\text{D}_2\text{Cl}_4$ (0.5 ml). The $[\text{r}]$ contents were calculated according to the literature method [15]. Table 1 summarizes the polymerization results.

4.11. Crystallographic studies

Crystals coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf-Nonius CCD single crystal X-ray diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXS-97) [16] and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions.

Crystal data for 7: $\text{C}_{13.50}\text{H}_{11}\text{ClZr}_{0.50}$, $M = 254.28$, $a = 8.2574(7) \text{ \AA}$, $b = 9.1131(7) \text{ \AA}$, $c = 15.6296(16) \text{ \AA}$, $\alpha = 106.437(4)^\circ$, $\beta = 102.150(4)^\circ$, $\gamma = 92.759(4)^\circ$, $Z = 4$, $d = 1.542 \text{ g cm}^{-3}$, triclinic, space group $P\bar{1}$, crystal size $0.2 \times 0.2 \times 0.1 \text{ mm}^3$, $T = 293(2) \text{ K}$, scan type $\omega/2\theta$, $1.40 \leq \theta \leq 27.21$, $-9 \leq h \leq 9$, $-10 \leq k \leq 11$, $-17 \leq l \leq 19$, 5515 measured reflections, 3501 independent reflections ($R_{\text{int}} = 0.0954$), $\mu = 0.758 \text{ mm}^{-1}$, $R_1 [F^2 > 2\sigma(F^2)] = 0.0542$, $wR_2 = 0.1213$.

5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 205363 for compound 7. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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