

Novel Synthesis of *ansa*-Metallocenes via the Reductive Dimerization of Fulvenes with Group 4 Metal Divalent Halides¹

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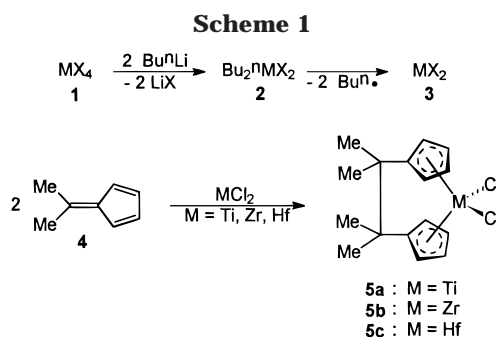
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Summary: Substituted ethylene-bridged *ansa*-metallocenes of group 4 dihalides can be prepared in high yields by the interaction of the titanium, zirconium, or hafnium dihalide with 2 equiv of the appropriate fulvene. The requisite metal dihalides are readily produced by the alkylative reduction of the metal tetrahalide with 2 equiv of an alkyl lithium reagent in THF or in toluene.

Since the introduction of the first soluble metallocene catalyst for olefin polymerization, titanocene dichloride, in 1957,^{2,3} there has been a surging wave of developments that has now, 40 years later, positioned metallocene catalysis at the forefront of the polyolefin industry.⁴ Largely responsible for this prominence have been the remarkable discoveries that chiral *ansa*-metallocenes can promote the stereoselective polymerization of α -olefins in homogeneous media, especially when cocatalyzed by MAO (poly(methylaluminoxane)). Illustrative are the isospecific polymerization of propylene by *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride and MAO⁵ and the syndiospecific polymerization of propylene by a combination of isopropylidene-(cyclopentadienyl)(9-fluorenyl)zirconium dichloride with MAO.⁶ Such outstanding stereoregulation has unleashed a worldwide effort at synthesizing novel metallocenes, whose variegated structures might permit the selective control of such polymer properties as stereochemistry, molecular mass, molecular mass distribution, and bulk density.

The preponderant synthetic route to such unbridged or bridged metallocenes has been the interaction of an alkali or alkaline earth metal salt of the appropriate substituted cyclopentadiene with the desired group 4 metal halide to produce the resulting metallocene halide.⁷ Particularly pertinent to prior syntheses of *ansa*-metallocenes has been the reductive dimerization of fulvenes with alkali or alkaline earth metals and the



subsequent interaction of the resulting dianion with the group 4 or other transition metal halides.^{7b,10} What we wish to report here is a novel and versatile route to *ansa*-metallocene dihalides of group 4 (5), which involves the high-yielding reductive coupling of two units of a substituted fulvene (4) by the appropriate group 4 dihalide (3). The requisite group 4 dihalide 3 is readily prepared by treating the group 4 tetrahalide 1 with 2 equiv of *n*-butyllithium in THF followed by brief warming to complete the reductive elimination of the intermediate di-*n*-butylmetal dihalide.^{8,9} (2) (Scheme 1). With 6,6-dimethylfulvene and MCl₂ (4), the known *ansa*-titanocene dichloride (5a)¹⁰ and *ansa*-zirconocene dichloride (5b),^{10,11} as well as the *ansa*-hafnocene dichloride (5c), can be obtained in over 90% yield (cf. infra) (Scheme 1). The use of 6-substituted fulvenes, such as the 6-phenyl,¹² 6-(1-naphthyl),¹³ and 6-(9-anthryl)¹⁴ derivatives, with TiCl₂ or with ZrCl₂ similarly provides high yields of the corresponding *ansa*-metallocenes but as mixtures of *racemic* (7a–7c) and *meso* (8a–8c) stereoisomers (Scheme 2). The ratio of the *racemic* to *meso* isomer produced (7:8) ranged from 1:1 for the

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(13) 6-(1-Naphthyl)fulvene, prepared according to the procedure, Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, 49, 1849: ¹H NMR (CDCl₃) δ 6.53 (d, 2H), 6.65 (d, 2H), 7.55 (m, 3H), 7.65 (d, H), 7.90 (m, 3H), 8.60 (d, H); ¹³C NMR δ 121.48, 124.44, 125.38, 126.05, 126.15, 126.63, 128.60, 129.36, 130.04, 131.83, 132.03, 133.44, 133.75, 134.85, 135.72, 147.11.

(14) 6-(9-anthryl)fulvene, prepared by the method cited in ref 15: ¹H NMR (CDCl₃) δ 5.88 (s, H), 6.51 (s, H), 6.62 (s, 2H), 7.46 (m, 4H), 7.95 (s, H), 8.02 (m, 2H), 8.15 (m, 2H), 8.48 (s, H); ¹³C NMR δ 122.51, 125.29, 125.35, 125.82, 126.26, 127.68, 128.49, 130.08, 130.62, 131.23, 132.36, 134.25, 134.52, 150.26.

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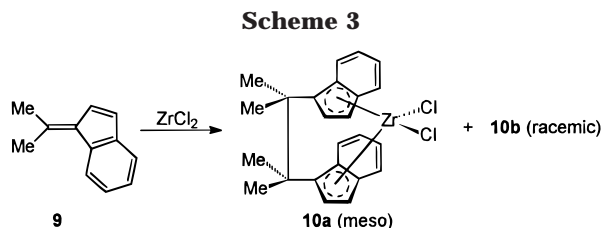
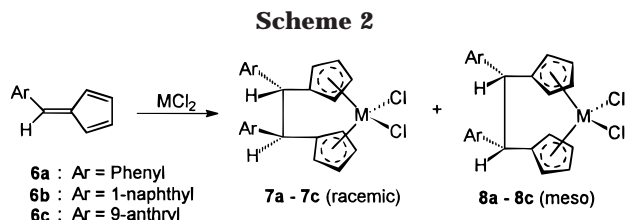
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phenyl isomers (**7a:8a**) through 83:17 for the naphthyl isomers (**7b:8b**) to exclusively the *racemic* isomer (**7c**) for the 9-anthryl derivative.¹⁵ These isomers proved to be separable by flash column chromatography on silica gel by use of a gradient of hexane–chloroform mixtures. The reductive dimerization of 1',1'-dimethylbenzofulvene (**9**) with zirconium dichloride likewise yields about a 1:1 mixture of the *meso*- and *rac*-benzometalocene isomers **10a** and **10b** in an overall yield of over 90%, which are also separable by flash chromatography (Scheme 3).

The following procedures illustrate the preparation of the requisite group 4 metal dihalide and its interaction with the appropriate fulvene to generate the corresponding *ansa*-metallocene dichloride. Thus, under an atmosphere of dry, oxygen-free argon, a solution (TiCl_4) or suspension (ZrCl_4 or HfCl_4) of 10 mmol of the group 4 tetrachloride in 40 mL of purified and anhydrous THF is cooled to -78°C and then treated dropwise with 20.5 mmol of *n*-butyllithium dissolved in hexane. The reaction turned to a dark brown to black color after such addition. The mixture was brought to 20°C and stirred for 20 h. (In the case of ZrCl_2 and HfCl_2 a 2 h warming at 50°C completed the reduction to the divalent state.) Thereupon, the solvents were removed under reduced pressure with warming to leave a residue of the black MCl_2 and byproduct LiCl . Although the LiCl can be removed by selective dissolution of the MCl_2 in a toluene–tetrahydrofuran mixture and removal of LiCl by filtration, it has proved unnecessary for the successful preparation of the *ansa*-metallocenes. For example, the titanium dichloride obtained from such a separation from the lithium chloride byproduct was obtained analytically pure as $\text{TiCl}_2 \cdot 2\text{THF}$.⁸

An illustrative procedure for the preparation of *ansa*-group 4 metallocenes of types **5a–5c** with lithium chloride-containing MCl_2 is the following: The MCl_2 – LiCl solid mixture obtained after evaporation of the THF and hexane can be slurried with 30 mL of dry

toluene at room temperature and then 20 mmol of 6,6-dimethylfulvene added to the suspension. After stirring at 25°C for 1 h and further stirring at reflux for 8 h the suspension is cooled and filtered. The filter cake is washed with CHCl_3 and the filtrate freed of volatiles under reduced pressures to leave a residue of the tetramethylethylenebis(cyclopentadienyl)metal dichloride (**5a–5c**) in $>90\%$ yield: After chromatography pure samples of **5a**, **5b**, and **5c** are obtained whose spectral and TLC properties are wholly in agreement with their structures.¹⁹

Similar reactions of TiCl_2 or ZrCl_2 with 6-phenylfulvene (**6a**) lead to approximately 45:55 mixtures of *meso*- and *rac*-1,2-diphenylethylenebis(cyclopentadienyl)titanium dichlorides (**7a**, **8a**, $\text{M} = \text{Ti}$)²⁰ or -zirconium dichlorides (**7a**, **8a**, $\text{M} = \text{Zr}$),²¹ respectively. With ZrCl_2 6-(1-naphthyl)fulvene (**6b**) gave a 17:83 mixture of *meso*- and *rac*-ansa-zirconocenes dichlorides (**8b:7b**),²² while 6-(9-anthryl)fulvenes with ZrCl_2 yielded essentially only the *racemic* isomer **7c** ($\text{M} = \text{Zr}$).^{15,23} Finally, benzofulvene **9** provided again an equimolar mixture of *meso* and *racemic* isomers, **10a** and **10b**.²⁴

All such *ansa*-metallocenes when combined with MAO in toluene proved capable of polymerizing ethylene with a high activity to linear, high-density polyethylene.²⁵

In conclusion, the ease of preparing, ad libitum, the requisite titanium, zirconium, or hafnium dihalides by the alkylative reduction of the metal tetrahalide with RLi , RMgX , or R_3Al ,^{8,9,26} as well as the accessibility of a wide variety of 6-substituted and 6,6'-disubstituted fulvenes, makes the present preparation of substituted ethylene-bridged *ansa*-metallocenes of group 4 dihalides the synthesis of choice for such commercially important procatalysts required for the production of polyolefin homopolymers and copolymers.

(16) Spectra of **5a**: ^1H NMR (CDCl_3) δ 1.40 (s, 12H); 6.16 (q, 4H); 6.82 (q, 4H); ^{13}C NMR δ 28.16; 45.54; 112.83; 128.83; 145.27.

(17) Spectra of **5b**: ^1H NMR (CDCl_3) δ 1.47 (s, 12H); 6.17 (q, 4H); 6.68 (q, 4H); ^{13}C NMR δ 28.44; 45.13; 108.81; 123.26; 143.47.

(18) Spectra of **5c**: ^1H NMR (CDCl_3) δ 1.46 (s, 12H); 6.02 (q, 4H); 6.57 (q, 4H); ^{13}C NMR δ 29.5; 106.76; 121.77; 142.0.

(19) All such samples displayed appropriate parent ions (M^+) and ions corresponding to $\text{M}^+ - \text{Cl}$ in their mass spectra at 70 eV.

(20) Spectra of separated isomers. **7a** ($\text{M} = \text{Ti}$): ^1H NMR (CDCl_3) δ 4.83 (s, 2H); 6.17 (q, 2H); 6.34 (q, 2H); 6.86 (q, 2H); 7.20 (m, 12H); ^{13}C NMR δ 54.18; 109.85; 117.22; 126.47; 127.58; 127.62; 128.78; 133.91; 137.20; 140.05. **8a** ($\text{M} = \text{Ti}$): ^1H NMR (CDCl_3) δ 5.52 (s, 2H); 6.25 (q, 2H); 6.35 (q, 2H); 7.00 (q, 2H); 7.12 (q, 2H); 7.25 (m, 12H); ^{13}C NMR δ 51.28; 113.75; 126.85; 128.15; 128.43; 130.71; 138.34; 138.45.

(21) Selective ^1H NMR spectral data for **7a** and **8a** ($\text{M} = \text{Zr}$): methine $\text{Ph}-\text{C}-\text{H}$ occurs as a singlet at 4.77 ppm (**7a**) and at 5.50 ppm (**8a**).

(22) Spectral data for the methine 1-naphthyl- $\text{C}-\text{H}$: ^1H NMR δ singlets at 6.28 ppm for **8b** and at 6.52 ppm for **7b** in a ratio of 17:83; ^{13}C NMR δ 44.94; 47.75 ppm.

(23) Spectral data for the methine 9-anthryl- $\text{C}-\text{H}$: ^1H NMR δ singlet at 6.41 ppm for **7c**; ^{13}C NMR δ 48.36 ppm.

(24) Spectral data of the mixture of **10a** and **10b**: ^1H NMR (CDCl_3) δ singlets at 2.30, 2.35, and 2.45 ppm in an intensity ratio of 1:2:1; doublets at 6.75 and 6.85 ppm in a 1:1 ratio; 7.20 (m); 7.75 (d).

(25) Polymerizations were conducted in 250 mL resin-coated glass pressure (Fisher-Porter) bottles provided with magnetic stirring and equipped with a metal head (polymer coated on the inside) bearing a pressure gauge, an outlet for gas and reagents by syringe, and a stopcock for evacuation. The metallocene procatalyst (0.225 mmol) in 100 mL of predried and deoxygenated toluene was treated with 4.5 mmol of MAO ($\text{Al}:\text{Zr} = 20:1$) and the bottle purged with anhydrous ethylene to initiate the polymerization. Under an ethylene overpressure of 40 psi the polymerizations are allowed to proceed for 15–30 min. Usual quench with aqueous HCl and filtration allow the polyethylene to be isolated. Such polyethylene generally melted over 135°C .

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