

An efficient synthetic method of *ansa*-zirconocene dimethyl complexes via Me_2ZrCl_2

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Abstract

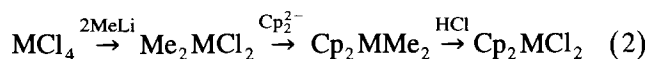
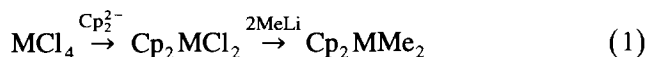
The reaction of ZrCl_4 with 2 equiv. of MeLi to form Me_2ZrCl_2 followed by in situ metalation of Me_2ZrCl_2 with the corresponding *ansa*-ligands produces the respective *ansa*-dimethylzirconocene complexes, *o*-Xyl(Ind)₂ZrMe₂ [**1b**, Ind = η^5 -1-indenyl, *o*-Xyl = C₆H₄(CH₃)₂-1,2], 2-Bn(Ind)₂ZrMe₂ [**2b**, 2-Bu = (-CH₂CH=CHCH₂-)], Et(Ind)₂ZrMe₂ (**3b**), and Me₂Si(Ind)₂ZrMe₂ (**4b**) in high yields. Treatment of **1b–3b** with HCl affords *ansa*-dichlorozirconocene complexes, **1a–3a**, in quantitative yields. Synthesis of *ansa*-dimethylzirconocene via Me_2ZrCl_2 is more efficient than that via Cp_2ZrCl_2 (Cp₂ = *ansa*-ligand) in the conventional methods. © 1997 Elsevier Science S.A.

Keywords: *ansa*-Dimethylzirconocene; Dichlorodimethylzirconium

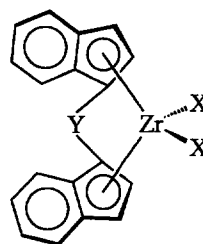
1. Introduction

The cationic, 14-electron metallocene methyl complex $\text{Cp}_2\text{M}(\text{CH}_3)^+$ (M = Group 4 metals) is now well established as the catalytically active species in the polymerization of α -olefins by homogeneous Ziegler–Natta catalysts [1]. One of the major problems in the commercialization of neutral metallocene catalysts has been the need for large amounts of the expensive cocatalyst methylaluminoxane (MAO). Therefore, active polymerization catalysts of the cationic type $[\text{Cp}_2\text{M}(\text{CH}_3)]\text{A}$ (A = ‘noncoordinating’ anion) without MAO cocatalyst have received increasing attention in recent years. High yield synthesis of *ansa*-dimethylmetallocene complex is extremely important in the development of cationic catalysts for the stereospecific α -olefin polymerization since the dimethyl complex is generally employed for the generation of $[\text{Cp}_2\text{M}(\text{CH}_3)]\text{A}$ complexes via methyl abstraction [2,3]. The *ansa*-dimethylmetallocenes have been prepared so far exclusively from the reaction of MCl_4 with *ansa*-ligand dianion (Cp_2^{2-}) to give Cp_2MCl_2 and subsequent treatment of the dichloride with MeLi as shown in Eq.

(1). The second alkylation step in Eq. (1) is capricious and usually results in a low yield of Cp_2MMe_2 [3–8].



We herein report an efficient, synthetic method of *ansa*-dimethylzirconocene complexes according to Eq. (2). *ansa*-Dimethylzirconocene complexes, **1b–4b**, can be prepared in high yields by initial dimethylation of ZrCl_4 with 2 equiv. of MeLi to form Me_2ZrCl_2 and in situ metalation reaction of Me_2ZrCl_2 with the dianion of the corresponding *ansa*-ligand. Furthermore, the *ansa*-dimethylzirconocene complexes **1b–3b** react with HCl to afford the *ansa*-dichlorozirconocene complexes **1a–3a** in quantitative yields.



Y = *o*-Xyl ; X = Cl (**1a**), Me (**1b**)

2-Bu ; Cl (**2a**), Me (**2b**)

Et ; Cl (**3a**), Me (**3b**)

Me₂Si ; Cl (**4a**), Me (**4b**)

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2. Results and discussion

Many research groups have designed and synthesized chiral Group 4 *ansa*-metallocene complexes in order to evaluate the critical structural factors as catalysts for the stereoregularity of α -olefin polymerization. In an effort to address the role of the bridging groups of *ansa*-metallocenes, we have prepared and characterized *o*-Xyl(Ind)₂ZrX₂ [9] [**1a**: X = Cl, **1b**: X = Me, Ind = η^5 -indenyl, *o*-Xyl = C₆H₄(CH₂)_{2-1,2}] and 2-Bn(Ind)₂ZrX₂ [**2a**: X = Cl, **2b**: X = Me, 2-Bn = (-CH₂CH=CHCH₂-)], new *ansa*-zirconocene complexes with rigid, four carbon atoms as the bridging units. When conventional procedures of Eq. (1) were used for the syntheses of **1a–2b**, dilithiation of bis(1-indenyl)-*o*-xylene (**1'**) and 1,4-bis(1-indenyl)-2-butene (**2'**) with 2 equiv. of ⁿBuLi followed by metalation with ZrCl₄, the desired products **1a** (*rac:meso* = 1:1, 51% yield) and **2a** (1:3, 30%) were formed in low yields and syntheses were not reproducible. In addition, attempted dimethylation reactions of both **1a** and **2a** with 2 equiv. of MeLi were not successful and resulted only in demetalation of the *ansa*-ligands.

We considered that the possible problems associated with both the metalation and alkylation reactions might be solved if we were to use pre-dimethylated Me₂ZrCl₂ instead of ZrCl₄ in the metalation step as is shown in Eq. (2). The formation of Me₂ZrCl₂ was monitored by ¹H NMR spectroscopy. Upon addition of ZrCl₄ to a THF-*d*₈ solution of MeLi in an NMR tube at -60°C, the resonances at δ -2.1 to -2.2 due to CH₃Li disappear instantaneously and a new signal at δ 0.18 grows in. This new resonance is considered to be due to (CH₃)₂ZrCl₂, which appears to decompose above -40°C based on the variable-temperature ¹H NMR spectra.

Reactions of dilithiated *ansa*-ligands **1'** and **2'** with Me₂ZrCl₂ generated by treatment of ZrCl₄ with 2 equiv. of MeLi at -78°C proceed successfully to afford diastereomeric mixtures of **1b** (*rac:meso* = 1:3, 78% yield) and **2b** (2:1, 67%) as white solids respectively. Furthermore, treatment of **1b** and **2b** with dry gaseous HCl gives the corresponding dichloro product, **1a** and **2a**, in quantitative yields. Yield data are compared for the synthetic methods according to Eq. (1) and Eq. (2) in Table 1. The mixture of *rac*- and *meso*-isomers in **1a–2b** can be separated by fractional crystallization using appropriate solvents (see Section 3). Dimethylated isomers that exhibit only one ¹H NMR methyl resonance at δ -1.24 (*rac-1b*) and -1.01 (*rac-2b*) are assigned to the chiral C₂-symmetric racemates [11]. The C_s-symmetric *meso*-isomers give rise to two distinct methyl resonances at δ -0.37 and -2.91 (*meso-1b*) and -0.1 and -2.0 (*meso-2b*).

Table 1

Comparison of yield data for the synthesis of **1a–4b** according to Eqs. (1) and (2)

Complexes	Yields ^a (<i>rac:meso</i>) (%)		
	Reported results	Our results	
		Eq. (1)	Eq. (2)
<i>o</i> -Xyl(Ind) ₂ ZrX ₂	X = Cl (1a)	51 (1:1)	78 (1:3)
	X = Me (1b)	0	78 (1:3)
2-Bn(Ind) ₂ ZrX ₂	X = Cl (2a)	30 (1:3)	67 (2:1)
	X = Me (2b)	0	67 (2:1)
Et(Ind) ₂ ZrX ₂	X = Cl (3a)	35 (<i>rac</i>) [10]	60 (1:1)
	X = Me (3b)	21 [3]	40 (1:1) ^b
Me ₂ Si(Ind) ₂ ZrX ₂	X = Cl (4a)	10–25 (<i>rac</i>) [8]	47 (<i>rac</i>)
	X = Me (4b)		0
			88 (1:2)

^a Yields are based on ZrCl₄ used.

^b Yield (40%) is based on **3a** used.

In order to test the generality of the new method (Eq. (2)), the synthetic strategy was applied to the syntheses of the two *ansa*-zirconocene complexes, Et(Ind)₂ZrX₂ [**3a**: X = Cl, **3b**: X = Me, Et = (-CH₂CH₂-)] and Me₂Si(Ind)₂ZrX₂ (**4a**: X = Cl, **4b**: X = Me), whose *rac*-isomers have seen the greatest amount of study for isospecific polymerization of propylene. Brintzinger and coworkers have reported the synthesis of *rac-3a* as an only product in 35% yield [10,12], while our synthetic effort according to the Collins' method [4] gives a mixture of diastereomers **3a** in a ratio of 1:1 (*rac:meso*) in 60% yield. Complex *rac-4a* has been previously prepared in 10 to 25% yield by Herrmann and Rohrmann [8]. Synthesis of dimethylated complex **3b** has been recently reported in 21% yield by Bochmann and Lancaster [3], but that of **4b** has not been reported as yet. Reaction of a diastereomeric mixture (1:1) of **3a** with 2 equiv. of MeLi affords **3b** of the same diastereomeric ratio in 40% yield, nevertheless the attempted synthesis of **4b** similarly results in only demetalation of the *ansa*-ligand. Syntheses of both **3b** and **4b** by the new method (Eq. (2)), however, produce diastereomeric mixtures of **3b** (*rac:meso* = 1:1, 66% yield) and **4b** (1:2, 88%) in high yields respectively. Upon treatment with dry gaseous HCl, **3b** is cleanly converted to **3a**, but **4b** decomposes to our disappointment.

In conclusion, we have developed a very efficient synthetic method for the preparation of *ansa*-dimethylzirconocene complexes in one pot via Eq. (2), which can be a general synthetic route to the *ansa*-dimethylmetallocene complexes. This new synthetic method is very important both in the synthesis of cationic catalysts for the stereospecific polymerization of α -olefins and in the molecular symmetry assignment of Cp₂MCl₂, especially *rac*- and *meso*-isomers, by dimethylation as a symmetry probe.

3. Experimental section

3.1. General comments

All experiments were performed under argon or nitrogen atmosphere by using either glovebox or standard Schlenk techniques. Solvents were freshly distilled under nitrogen from sodium–benzophenone (all hydrocarbons, diethyl ether, THF) or CaH₂ (dichloromethane). Bis(1-indenyl)-*o*-xylene, bis(1-indenyl)ethane [4–7] and bis(1-indenyl)dimethylsilane [13] were prepared according to the literature procedures.

¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were measured on a Hewlett-Packard 5985B mass spectrometer.

3.2. Synthesis of 2'

The *ansa*-ligand, 2', was prepared in 89% yield according to the reported synthetic method [12,10] of bis(1-indenyl)ethane by replacing 1,2-dibromoethane with *cis*-1,4-dichloro-2-butene. ¹H NMR (CDCl₃, 25 °C) δ 7.47–7.18 (m, 8H, C₆ indenyl), 6.25 (t, 2H, CH of C₅ indenyl) 5.83 (t, 2H, CH), 3.42 (d, 4H, CH₂), 3.34 (d, 4H, CH₂ of C₅ indenyl); ¹³C NMR (CDCl₃, 25 °C) δ 145.2, 144.5, 142.7, 128.4, 127.8, 126.0, 124.6, 123.7, 118.9, 37.7, 26.0; MS (70 eV) *m/z* 284 (M⁺).

3.3. Synthesis of 1b

Solid ZrCl₄ (0.42 g, 1.8 mmol) was dissolved in THF (60 ml) in a 250 ml Schlenk flask covered with aluminum foil, and the resulting solution was cooled to –78 °C. To this solution was added 2.6 ml of MeLi (1.55 M ether solution, 2.2 equiv.) and the suspension was stirred for 30 min at –78 °C to generate Me₂ZrCl₂. To a solution of bis(1-indenyl)-*o*-xylene (0.6 g, 1.8 mmol) in THF (40 ml) in a separate 100 ml Schlenk flask was added 2.5 ml of ⁿBuLi (1.6 M hexane solution, 2.2 equiv.) at –78 °C. The pale yellow dianion suspension was allowed to warm to room temperature at which point the dianion was dissolved to give a deep red solution. The red solution was transferred via cannula to a suspension of Me₂ZrCl₂ at –78 °C and then the reaction mixture was allowed to warm to room temperature. The deep red solution was stirred for an additional 14 h at room temperature. The solvent was evaporated under reduced pressure to provide a white solid which was extracted with dichloromethane and then filtered. The filtrate was evaporated in vacuo and the residue was washed with ether (2 × 10 ml) to provide 0.64 g (78%) of a diastereomeric mixture of 1b in a ratio of 1:3 (*rac*:*meso*). Fractional crystallization in dichloromethane–ether at –20 °C gave *rac*-1b as white crystals and subsequent recrystallization in

dichloromethane–hexane produced *meso*-1b as a white solid. *rac*-1b: ¹H NMR (CDCl₃, 25 °C) δ 7.58–7.03 (m, 12H, C₆ indenyl and phenyl), 6.05 (d, 2H, *J* = 3.49 Hz, C₅ indenyl), 5.05 (d, 2H, *J* = 3.49 Hz, C₅ indenyl), 4.34 (dd, 4H, *J* = 15.7 Hz, *J* = 17.2 Hz, CH₂Ph), –1.24 (s, 6H (CH₃)₂Zr). *meso*-1b: ¹H NMR (CDCl₃, 25 °C) δ 7.58–7.06 (m, 12H, C₅ indenyl and phenyl), 5.98 (d, 2H, *J* = 2.97 Hz, C₅ indenyl), 5.03 (d, 2H, *J* = 2.97 Hz, C₅ indenyl), 4.02 (dd, 4H, *J* = 15.6 Hz, *J* = 16.8 Hz, CH₂Ph), –0.37 (s, 3H, CH₃Zr), –2.91 (s, 3H, CH₃Zr).

3.4. Synthesis of *rac*-1a

Dry gaseous HCl was bubbled through a THF solution (40 ml) of *rac*-1b (0.6 g, 1.3 mmol) for 30 s and the solvent was removed in vacuo to give *rac*-1a as a bright yellow solid in a quantitative yield: ¹H NMR (CDCl₃, 25 °C) δ 7.75–7.12 (m, 12H, C₆ indenyl and phenyl), 6.13 (d, 2H, *J* = 3.38 Hz, C₅ indenyl), 5.77 (d, 2H, *J* = 3.38 Hz, 2H, C₅ indenyl), 4.14 (dd, 4H, *J* = 16.3 Hz, *J* = 38.3 Hz, CH₂Ph); MS (70 eV) *m/z* 492 (M⁺).

3.5. Synthesis of *meso*-1a

The same procedure was followed as for the preparation of *rac*-1a. Yellow *meso*-1b was obtained from *meso*-1a in a quantitative yield: ¹H NMR (CDCl₃, 25 °C) δ 7.66–7.10 (m, 12H, C₆ indenyl and phenyl), 6.01 (d, 2H, *J* = 3.4 Hz, C₅ indenyl), 5.90 (d, 2H, *J* = 3.4 Hz, C₅ indenyl), 4.14 (dd, 4H, *J* = 16.3 Hz, *J* = 28.3 Hz, CH₂Ph); MS (70 eV) *m/z* 492 (M⁺).

3.6. Synthesis of 2b

The same procedure was used as for the preparation of 1b. A suspension of Me₂ZrCl₂ in THF (60 ml) was added to a THF solution (40 ml) of *cis*-1,4-bis(1-indenyl)-2-butene (0.645 g, 2.26 mmol) and ⁿBuLi (2.2 equiv.) at –78 °C, affording 2b (0.612 g, 67%) as a white solid after workup. The ¹H NMR spectrum showed that 2b was present in a *rac*/*meso* ratio of 2/1 and repeated washing from hexane afforded pure *rac*-2b: ¹H NMR (CDCl₃, 25 °C) δ 7.58–7.01 (m, 8H, C₆ indenyl), 6.25 (m, 2H, CH), 5.95 (d, 2H, *J* = 3.1 Hz, C₅ indenyl), 5.79 (d, 2H, *J* = 3.1 Hz, C₅ indenyl), 3.44 (m, 4H, CH₂), –1.01 (s, 6H, (CH₃)₂Zr).

3.7. Synthesis of 2a

In a procedure analogous to that used in the preparation of 1a, a mixture of 2b gave the corresponding chloride derivatives 2a quantitatively. Recrystallization from dichloromethane–ether afforded pure *rac*-2a and *meso*-2a. *rac*-2a: ¹H NMR (CDCl₃, 25 °C) δ 7.71–7.15 (m, 8H, C₆ indenyl), 6.43 (t, 2H, CH), 6.39 (d, 2H,

$J = 3.4$ Hz, C₅ indenyl), 5.74 (d, 2H, $J = 3.4$ Hz, C₅ indenyl), 3.78–3.55 (m, 4H, CH₂); MS (70 eV) m/z 444 (M⁺). **meso-2a**: ¹H NMR (CDCl₃, 25 °C) δ 7.65–7.07 (m, 8H, C₆ indenyl), 6.69 (d, 2H, $J = 3.4$ Hz, C₅ indenyl), 6.43 (m, 2H, CH), 6.11 (d, 2H, $J = 3.4$ Hz, C₅ indenyl), 3.69–3.45 (m, 4H, CH₂); MS (70 eV) m/z 444 (M⁺).

3.8. Synthesis of 3b

In a procedure similar to that used in the preparation of **1b**, **3b** was prepared from the reaction of dilithio salt of bis(1-indenyl)ethane (0.6 g, 2.3 mmol) with Me₂ZrCl₂ in a diastereomeric ratio of 3:1 (**rac-3b**:**meso-3b**, 0.56 g, 66%). The two diastereomers were separated by fractional recrystallization from hexane at –20 °C to give each diastereomer as white crystals. These diastereomers were identified by comparing their ¹H NMR spectra with those reported in the literature [3].

3.9. Synthesis of 3a

The two diastereomeric mixtures (**rac-3b**, **meso-3b**) in THF (40 ml) were reacted with HCl to give chloride derivatives quantitatively. The two diastereomers were separated by fractional recrystallization from dichloromethane–ether to afford pure **rac-3a** and **meso-3a**. Both compounds were characterized by comparing their ¹H NMR data with those reported in the literature [3,4,7].

3.10. Synthesis of 4b

According to the similar procedure employed for the preparation of **1b**, **4b** was prepared from the reaction of dilithiated Me₂Si(Ind)₂ (0.524 g, 1.82 mmol) with Me₂ZrCl₂ in a diastereomeric ratio of 1:2 (**rac-4b**:**meso-4b**, 0.65 g, 87.1%). The two diastereomers were separated by fractional recrystallization from hexane at –20 °C to give each diastereomer as bright yellow crystals. **rac-4b**: ¹H NMR (CDCl₃, 25 °C) δ 7.59–6.94 (m, 8H, C₆ indenyl), 6.84 (d, 2H, $J = 3.30$ Hz, C₅ indenyl), 5.90 (d, 2H, $J = 3.30$ Hz, C₅ indenyl), 0.90 (s, 6H, (CH₃)₂Si), –1.42 (s, 6H, (CH₃)₂Zr). **meso-4b**: ¹H NMR (CDCl₃, 25 °C) δ 7.57–7.11 (m, 8H, C₆ indenyl), 6.92 (d, 2H, $J = 3.22$ Hz, C₅ indenyl), 5.92 (d, 2H, $J = 3.22$ Hz, C₅ indenyl), 1.08 (s, 3H, CH₃Si) 0.73 (s, 3H, CH₃Si), –0.19 (s, 3H, CH₃Zr), –2.69 (s, 3H, CH₃Zr).

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