6588 *Inorg. Chem.* **2001,** *40,* 6588−6597

Group 4 Dimethylmetallocenes: Improved Synthesis and Reactivity Studies

Davide Balboni, Isabella Camurati, Giansiro Prini, and Luigi Resconi*

Basell Polyolefins, Centro Ricerche G. Natta, 44100-Ferrara, Italy

Simona Galli, Pierluigi Mercandelli, and Angelo Sironi

Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Via Venezian 21, 20133 Milano, Italy

Received January 4, 2001

Group 4 dimethylmetallocenes are catalyst precursors for the methylmetallocenium/borate catalyst systems for olefin polymerization, and they are usually prepared by methylation (with MeMgCl or MeLi) of the parent metallocene dichlorides. We describe here a simpler preparation of a series of bisindenyldimethylmetallocenes carried out by reacting the π-ligand with a 2-fold excess of MeLi, and then $MtCl_4$ (Mt = Ti, Zr, Hf). This simple, one-pot method produces the dimethylated complexes in higher overall yield, and saves on reaction time and solvents. Ind_2MtMe_2 (**1**, Mt = Ti; **2a**, Mt = Zr; **3**, Mt = Hf), $(4,7\text{-}Me_2Ind)_2ZrMe_2$ (**4**), *rac/meso*-$[C_2H_4(Ind)_2]ZrMe_2$ (**5**), *meso*-$[C_2H_4(4,7\text{-}Me_2Ind)_2]ZrMe_2$ (*m*-**6a**), and *meso*-$[C_2H_4(4,7\text{-}Me_2Ind)_2]HfMe_2$ (*m*-**7a**) have been prepared in 40−80% isolated yields. **2a** reacts with 1−4 equiv of *t*-BuOH to give the mono-*tert*-butoxy derivative **2b**, $Ind_2ZrMe(O\text{-}t\text{-}Bu)$, while reaction with 2 equiv of C_6F_5OH cleanly affords $Ind_2Zr(OC_6F_5)_2$ (**2c**). Analogously, in the presence of 2 equiv of *t*-BuOH, *m*-**6a** gives *meso*-$[C_2H_4(4,7\text{-}Me_2Ind)_2]ZrMe(O\text{-}t\text{-}Bu)$ (*m*-**6b**) with replacement of the outward methyl group only, as established by NMR analysis; *meso*-$[C_2H_4(4,7\text{-}Me_2Ind)_2]Zr(OC_6F_5)_2$ (*m*-**6c**) is obtained by reaction with 2 equiv of C_6F_5OH. The molecular structures of *m*-**6a** and *m*-**6c** are also described.

Introduction

The success of metallocene-based catalyst systems for olefin polymerization[1] has increased the efforts directed at improving their preparation methods.[2] The two σ-ligands on the transition metal of group 4 metallocene precatalysts are usually chloride, because the most used synthetic procedures involve the reaction between $MtCl_4$ (Mt = Ti, Zr, Hf) and the π-ligand anion, usually as its lithium or potassium salt.[3] Metallocene dichlorides are perfectly suitable as catalyst precursors when the cocatalyst is methylalumoxane. However, dialkylmetallocenes, particularly dimethyls, are required as catalyst components of the alkylmetallocenium/borate catalyst systems for olefin polymerizations, where the cocatalyst of choice is a borane Lewis acid, e.g., $B(C_6F_5)_3$, or a borate salt, e.g., $[Ph_3C][B(C_6F_5)_4]$ or $[PhNHMe_2][B(C_6F_5)_4]$.[4] The dialkylmetallocenes can be prepared in several ways:

(a) by reaction of the metallocene dichloride with a suitable alkylating agent, such as MeLi, MeMgCl, or Me_2Mg, in an ethereal solvent;[5,6]

(b) by alkylation of a metallocene bisamide with excess $AlMe_3$;[6]

(c) by reaction of the neutral ligand with a zirconium alkyl compound, e.g., $Zr(CH_2Ph)_4$;[7]

(d) by reaction of the π-ligand anion with $ZrCl_2Me_2$, preformed from $ZrCl_4$ and MeLi in THF at low temperature;[8]

(e) by alkylation in situ of the metallocene dichloride with an excess of an AlR_3 compound (which also acts as a scavenger during the polymerization of olefins).[9]

While the latter method is in some instances convenient compared to the first one, it does not proceed to full alkylation of the metallocene, the major product being the metallocene alkyl chloride.[10] On the other side, method (a) does not always give satisfactory yields: the combined yields of the two-step process from the ligand to the final dialkylmetallocene are very often in the range 20−50%. For instance, the preparation of

---

(1) See for example: (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Gupta, V. K.; Satish, S.; Bhardwaj, I. S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34* (3), 439. (d) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1.

(2) For recent reviews on the synthesis of group 4 metallocenes, see: Halterman, R. In *Metallocenes. Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1, p 455.

(3) See for example: Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986. Wild, F.; Zsolnai, L.; Huttner, G.; Brintzinger, H.-H. *J. Organomet. Chem.* **1982**, *232*, 233. Wild, F.; Wasiucionek, M.; Huttner, G.; Brintzinger, H.-H. *J. Organomet. Chem.* **1985**, *288*, 63. Grossman, R.; Doyle, R. A.; Buchwald, S. *Organometallics* **1991**, *10*, 1501.

(4) Chen, E.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285.

(5) (a) Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263. (b) Samuel, E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1976**, *113*, 331. (c) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301. (d) Siedle, A. R.; Newmark, R. A. *J. Organomet. Chem.* **1995**, *497*, 119.

(6) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024. Kim, I.; Jordan, R. F. *Macromolecules* **1996**, *29*, 489.

(7) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649.

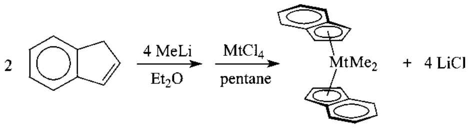
(8) Park, T. J.; Woo, B. W.; Yoon, S. C.; Shim, S. C. *J. Organomet. Chem.* **1997**, *535*, 29.

(9) Matsumoto, J.; Okamoto, T.; Watanabe, M.; Ishihara, N. (Idemitsu). Eur. Pat. Appl. 513 380, 1992. Chien, J. C. W.; Tsai, W.-M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 141.

(10) See for example: Negishi, E.; van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, *107*, 6639. Beck, S.; Brintzinger, H. H. *Inorg. Chim. Acta* **1998**, *270*, 376.

10.1021/ic010018q CCC: $20.00

Scheme 1



Ind_2ZrCl_2 by reaction of the lithium salt of indene with $ZrCl_4$ gives at best a yield of 58%.[5c] The conversion of Ind_2MtCl_2 (Mt = Ti, Zr, Hf) to the corresponding dimethyl derivative using MeLi proceeds in yields of 36−57%.[5a]

Analogously, the laborious preparation of *rac*-[C_2H_4(1-indenyl)$_2$]$ZrCl_2$ by reaction of the dilithium salt of bis(1-indenyl)ethane with $ZrCl_4$ gives at best a yield of 66%.[11] The following conversion of *rac*-[C_2H_4(1-indenyl)$_2$]$ZrCl_2$ to the corresponding dimethyl derivative using MeLi proceeds in yields of 20−25%.[12] Better results were obtained by Jordan, who prepared *rac*-[C_2H_4(1-indenyl)$_2$]$ZrMe_2$ by reaction of the corresponding dichloride with Me_2Mg in Et_2O followed by workup with dioxane, with a yield of 90%.[13] While the yield is higher, this approach requires the additional preparation of Me_2Mg. All other methods, too, require the additional synthesis of the appropriate Zr compound ($Zr(NMe_2)_4$, $Zr(CH_2Ph)_4$, or $ZrCl_2Me_2$) from $ZrCl_4$, and, especially in method d, the use of low (−78 °C) reaction temperatures.

At the end of 1996 we discovered that, by synthesizing the dianions of bridged bisindenyl ligands in diethyl ether in the presence of excess MeLi, the *ansa*-metallocene chloromethyl or dimethyl derivatives were obtained. We have since improved the direct synthesis of group 4 dimethylmetallocenes and cyclopentadienylsilylamido dimethyl complexes of Ti and Zr, which consists of the reaction of the π-ligand with a 2-fold excess of MeLi, and $MtCl_4$ (Mt = Ti, Zr, Hf).[14] This one-pot method produces the dimethylated complexes in higher overall yield, reduces the overall reaction time, and simplifies the reaction procedures. Here we report the synthesis of a series of group 4 metal bisindenyl complexes and a preliminary investigation of their reactivity toward alcohols, including the synthesis of *meso*-[C_2H_4(4,7-Me_2Ind)$_2$]ZrMe(O-*t*-Bu) and *meso*-[C_2H_4(4,7-Me_2Ind)$_2$]$Zr(OC_6F_5)_2$. The molecular structures of the latter and *meso*-[C_2H_4(4,7-Me_2Ind)$_2$]$ZrMe_2$ are also described.

Results and Discussion

Synthesis. Reaction of the π-ligand precursor with a 2-fold excess of MeLi in Et_2O generates the ligand anion without detectable side reactions (potentially arising from the excess MeLi). Subsequent addition of $ZrCl_4$ as a slurry in pentane gives the dimethylzirconocenes directly (Scheme 1). Evaporation of the solvents followed by extraction with toluene or refluxing pentane (depending on the solubility of the complex) gives fully soluble, spectroscopically pure (^{1}H NMR) complexes in good to high yields (Table 1). Although in earlier experiments the two mixtures were in some cases cooled before being mixed, and then allowed to react overnight, we found that reactions at room temperature for shorter times (1−4 h) give higher yields. All the products were characterized by ^{1}H and ^{13}C NMR spectroscopy, in some cases by alcoholysis, and by comparison with literature data or with samples prepared by methylation of the parent metallocene dichlorides.

Table 1. Synthesis of Dimethylmetallocenes

entry	complex	yield (%)^a	*rac*:*meso*	$T_{mix}/T_{rxn}{}^b$ (°C)
1	Ind_2TiMe_2	70		rt/rt
2	Ind_2ZrMe_2	77		rt/rt
3^c	Ind_2ZrMe_2	85		rt/rt
4^d	Ind_2ZrMe_2	87		rt/rt
5	Ind_2HfMe_2	74		rt/rt
6^c	Ind_2HfMe_2	83		rt/rt
7	(4,7-Me_2Ind)$_2$$ZrMe_2$	74		rt/rt
8	C_2H_4(Ind)$_2$$ZrMe_2$	75	38:62	rt/rt
9^e	CH_2(3-*t*-BuInd)$_2$$ZrMe_2$	55	90:10	−30/−30 to rt
10	C_2H_4(4,7-Me_2Ind)$_2$$ZrMe_2$	75	38:62	−80/−80 to rt
11	C_2H_4(4,7-Me_2Ind)$_2$$ZrMe_2$	ca. 100^f	20:80	rt/rt
12	C_2H_4(4,7-Me_2Ind)$_2$$HfMe_2$	75	8:92	rt/rt

^{a} Isolated yields based on the metal. ^{b} T_{mix} = temperature at which the two suspensions are mixed; T_{rxn} = temperature of reaction. ^{c} Using titrated MeLi. ^{d} Using indene of 98% GC purity. ^{e} Data from ref 14c. ^{f} Crude yield by ^{1}H NMR.

We first evaluated this new method in the synthesis of the three simplest bisindenyl dimethyl complexes of Ti (**1**), Zr (**2a**), and Hf (**3**). Technical indene, percolated over activated alumina and deaerated (indene purity 91−94% by GC), was used without further purification: yields turned out to be quite good, and similar for the three metals (70−77%), despite the relatively low purity of the starting indene. At this point, Ind_2MtMe_2 complexes are the simplest group 4 metallocenes to make. Using higher purity indene (98%) further improves the yield (see entry 4 in Table 1), but the use of technical indene still provides the best cost/yield balance. We noted that an excess of alkylating agent (over the 2 equiv of MeLi/equiv of indene) leads to reduced yields of Ind_2MtMe_2. At first, we used the producer's nominal MeLi concentration (1.6 M) to determine the amount of MeLi solution to be used. A black residue (traces of which are extracted by toluene or ether, affecting the color of the final metallocene) was obtained in several cases. Finally, MeLi solutions were titrated, and found to exceed the nominal concentration by as much as 10%. The use of the exact stoichiometry then led to even higher yields (see entries 3 and 6 in Table 1), as high as 85% in the case of Ind_2ZrMe_2.

Ind_2TiMe_2 was found to have limited stability in the solid state at room temperature, a behavior that prevented an accurate elemental analysis, whereas both Ind_2ZrMe_2 and Ind_2HfMe_2 are stable under nitrogen for a prolonged time both as solids and in solution: for example, Ind_2ZrMe_2 is stable in CD_2Cl_2 for up to 48 h, and in benzene for several days and up to 70 °C for at least several hours. In addition, their higher solubility with respect to their dichloride counterparts makes their isolation much simpler. In our hands, Ind_2ZrMe_2 shows improved stability with respect to the commercial Ind_2ZrCl_2.

The reverse addition, that is adding 4 equiv of MeLi in Et_2O to $ZrCl_4$ (at −30 °C in pentane) and then adding 2 equiv of indene, was tested as well (see the Experimental Section for details), but the conversion to **2a** was less than 5%, thus ruling out the possible intermediacy of Me_2ZrCl_2.[8]

---

(11) (a) Lee, I.-M.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115. (b) Piemontesi, F.; Camurati, I.; Resconi, L.; Balboni, D.; Sironi, A.; Moret, M.; Zeigler, R.; Piccolrovazzi, N. *Organometallics* **1995**, *14*, 1256. (c) Yang, Q.; Jensen, M. D. *Synlett* **1996**, 147. (d) van Beek, J. A. M. (DSM). Eur. Pat. Appl. 530 908, 1993.

(12) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570. Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633.

(13) Rodewald, S.; Jordan, R. F. *J. Am. Chem. Soc.* **1994**, *116*, 4491.

(14) (a) Resconi, L.; Balboni, D.; Prini, G. (Montell). Int. Appl. WO 99/36427, 1999. (b) Resconi, L. (Montell). Int. Appl. WO 00/75151, 2000. Balboni, D.; Prini, G.; Rinaldi, M.; Resconi, L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41* (1), 456. (c) Resconi, L.; Balboni, D.; Baruzzi, G.; Fiori, C.; Guidotti, S. *Organometallics* **2000**, *19*, 420.

High yields can also be obtained with alkyl-substituted indenes: for example, $(4,7\text{-Me}_2\text{Ind})_2\text{ZrMe}_2$ (**4**) was obtained in 74% isolated yield from 4,7-dimethylindene.[15]

We then turned our attention to the *ansa*-zirconocenes. $[\text{C}_2\text{H}_4(\text{Ind})_2]\text{ZrMe}_2$ (**5**), the dimethyl derivative of Brintzinger's catalyst,[1a,b,11] was obtained in 75% yield and ca. 40:60 *rac*:*meso* ratio (entry 8 in Table 1). The synthesis of *rac*-$[\text{CH}_2(3\text{-}t\text{-Bu-Ind})_2]\text{ZrMe}_2$ has already been reported by us (entry 9 in Table 1).[14c] The complex $[\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2]\text{ZrMe}_2$ (**6a**), was targeted because both the corresponding dichlorides, *rac*- and *meso*-$[\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2\text{ZrCl}_2$, are precatalysts with excellent performances in ethylene (co)polymerization.[16a−c] In the synthesis of **6a**, variation of the reaction temperature seems to have little influence on the yield of the reaction but a significant one on the *rac*:*meso* ratio. Thus, we obtained **6a** in a 20:80 *rac*:*meso* ratio, in a nearly quantitative yield, carrying out the reaction at room temperature, whereas a 40:60 *rac*:*meso* ratio was obtained at −80 °C (compare entries 10 and 11 in Table 1). Washing the 20:80 *rac*:*meso* sample with pentane to remove the more soluble racemic isomer, followed by toluene extraction, gave the *meso* isomer *m*-**6a** in 54% isolated yield and 99% diastereoisomeric purity. $[\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2]\text{ZrCl}_2$ had been previously obtained in 44% yield in a *rac*:*meso* ratio of 2.33:1, whereas the pure *rac* and *meso* diastereoisomers could be obtained by transmetalation from *rac*- and *meso*-$\text{C}_2\text{H}_4(3\text{-SiMe}_3\text{-}4,7\text{-Me}_2\text{Ind})_2$ in 40% and 30% yields, respectively (based on the starting ligand, 1,2-bis(4,7-dimethylindenyl)ethane).[16d] Analogously, the new *meso*-$[\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2]\text{HfMe}_2$ (*m*-**7a**) was obtained in 75% yield and 8:92 *rac*:*meso* ratio. In this case, substituting Hf for Zr brings about a slight increase in *meso* selectivity.

As apparent from the data shown in Table 1, our synthetic method affords dimethylmetallocenes in a simple, rapid, and inexpensive way, leading to the desired products with a one-pot procedure starting from the ligands. Furthermore, our process leads to final yields which are in most cases higher than those obtainable with the usual procedures. Even if the combined yields of the two-step process (synthesis of the metallocene dichloride followed by its methylation) were comparable to the yield of our direct method, the latter is more convenient because of the simpler procedure and the savings in reagents and solvents.

It is worth pointing out that this synthetic method is not limited to metallocene-type complexes, but is quite general. We have already extended the scope of our process to the cyclopentadienyl amido "constrained geometry" complexes of both Zr and Ti,[14b] showing that also catalytically important Ti complexes can be produced conveniently with our procedure, while Schrock and co-workers have applied a similar method to the synthesis of bisamidotitanium and -zirconium complexes.[17]

Scheme 2

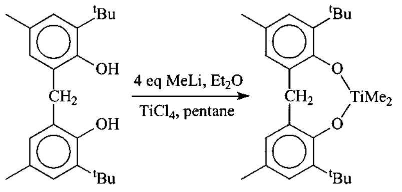
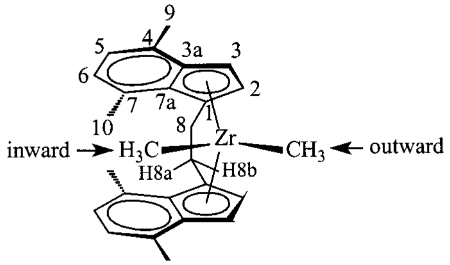


Chart 1



To further show the generality of the method, we reacted a diol, the commercially available 2,2′-methylene-bis(6-*tert*-butyl-4-methylphenol), with 4 equiv of MeLi and then 1 equiv of TiCl_4, and isolated the known[18] $\text{CH}_2(6\text{-}t\text{-Bu-4-Me-phenoxy})_2\text{TiMe}_2$ in 70% yield as a light yellow powder (Scheme 2). The ^{1}H NMR spectrum, which shows two singlets for the two different CH_3 groups and two doublets (AB system) for the two diastereotopic hydrogens in the methylene bridge, matches that already reported for this compound.[18]

Reactivity. The ready availability of the bisindenylmetal dimethyl complexes prompted us to start an investigation on their reactivity. The reactivity of the Mt−Me bond toward alcohols was briefly investigated on two complexes, $\text{Ind}_2\text{ZrMe}_2$ and *meso*-$[\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2]\text{ZrMe}_2$, the latter chosen because of the two diastereotopic (*inward* and *outward* with respect to the two indenyl ligands) methyl groups on zirconium, which are anticipated to have a different reactivity due to the fact that the inward methyl group is sterically shielded by the *ansa*-ligand framework (Chart 1). $\text{Ind}_2\text{ZrMe}_2$ (**2a**) cleanly reacts with *t*-BuOH to give $\text{Ind}_2\text{Zr(O-}t\text{-Bu)Me}$ (**2b**), irrespectively of the *t*-BuOH:Zr ratio (from 1 to 4). Excess *t*-BuOH eventually leads to partial liberation of indene. Reaction with 2 equiv of $\text{C}_6\text{F}_5\text{OH}$ yields $\text{Ind}_2\text{Zr(OC}_6\text{F}_5)_2$ (**2c**) without detectable byproducts.[19] The inertness of **2b** toward alcoholysis with *t*-BuOH is not due to steric hindrance: whereas CH_3OH does not react with **2b**, the reaction of 1 equiv of $\text{C}_6\text{F}_5\text{OH}$ with **2b** proceeds with complete conversion to $\text{Ind}_2\text{Zr(O-}t\text{-Bu)(OC}_6\text{F}_5)$.

Analogously, *meso*-$[\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2]\text{ZrMe}_2$ (*m*-**6a**) undergoes clean replacement of only one methyl group when exposed to 2 equiv of *t*-BuOH, to give the outward mono-*tert*-butoxy derivative only, *meso*-$[\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2]\text{Zr(O-}t\text{-Bu)-Me}$, where the position of the *tert*-butoxy substituent was determined by 2D NMR experiments (see the next section). The corresponding reaction of *m*-**6a** with 2 equiv of $\text{C}_6\text{F}_5\text{OH}$ yields *meso*-$[\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2]\text{Zr(OC}_6\text{F}_5)_2$ (*m*-**6c**).

Reaction of **2a** or **3** with 1 equiv of $\text{B(C}_6\text{F}_5)_3$ in toluene proceeds with quantitative conversion to the ion pairs $[\text{Ind}_2\text{MtMe}][\text{MeB(C}_6\text{F}_5)_3]$ (Mt = Zr, Hf) as already reported by Siedle.[5d] Finally, also *m*-**6a** reacts cleanly and quantitatively with $\text{B(C}_6\text{F}_5)_3$ to give the corresponding ion pair {*meso*-$[\text{C}_2\text{H}_4(4,7\text{-}$

---

[15] For the synthesis of $(4,7\text{-Me}_2\text{Ind})_2\text{ZrCl}_2$, see ref 11a and Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098.

[16] (a) Dall'Occo, T.; Resconi, L.; Balbontin, G.; Albizzati, E. (Montell). Int. Appl. WO 95/35333, 1995. (b) Resconi, L.; Dall'Occo, T.; Giannini, U. In *Metallocene Catalysts*, Kaminsky, W., Scheirs, J., Eds.; Wiley: New York, 1999; pp 69−101. (c) Galimberti, M.; Piemontesi, F.; Fusco, O. In *Metallocene Catalysts*; Kaminsky, W., Scheirs, J., Eds.; Wiley: New York, 1999; pp 309−343. (d) Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Zeigler R. *Organometallics*, **1996**, *15*, 5046.

[17] Liang, L.-C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797.

[18] Okuda, J.; Fokken, S.; Kang, H.-C.; Massa, W. *Chem. Ber.* **1995**, *128*, 221. Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66.

[19] For related bis(pentafluorophenoxy) derivatives of group 4 metallocenes, see: (a) Howard, W. A.; Trnka, T. M.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900. (b) Amor, J. I.; Burton, N. C.; Cuenca, T.; Gómez-Sal, P.; Royo, P. *J. Organomet. Chem.* **1995**, *485*, 153.

$Me_2Ind)_2]ZrMe_{inw}\}$ $[MeB(C_6F_5)_3]$.[20] As in the case of the reaction with *t*-BuOH, only the outward methyl group reacts, as shown by the fact that only the peak assigned to the outer methyl group is broadened (0.15 ppm in C_6D_6), whereas the inner one remains a sharp singlet (−1.76 ppm).

In our hands, $[Ind_2MtMe][MeB(C_6F_5)_3]$ proved stable at room temperature and in the solid state for a few days, while {*meso*-$[C_2H_4(4,7\text{-}Me_2Ind)_2]ZrMe_{inw}\}[MeB(C_6F_5)_3]$ decomposed more quickly (hours) to insoluble products. A more thorough investigation of the reactions of bisindenylzirconium dimethyl complexes with strong Lewis acids is in progress in our laboratories.

NMR Analysis. The NMR analysis of *m*-**6a**, prepared by methylation of the parent dichloride, was reported by us in a preliminary communication.[21] The diastereotopic methyl groups in *m*-**6a** were assigned from the NOESY spectrum[22] (see the Supporting Information): the inward methyl protons (see Chart 1) are at −2.12 ppm, while the outward ones are at −0.023 ppm. These assignments correct those erroneously reported in ref 21. A weak coupling between the two methyls on Zr was observed in the COSY-gs spectrum.[23]

The presence of through-metal homo- and heteronuclear long-range couplings was already observed by us in the case of *m*-**6a**,[21] as well as in [Me$_2$Si(Cp′)(*t*-BuN)]MtMe$_2$ complexes.

The ^1H spectrum of *meso*-$[C_2H_4(4,7\text{-}Me_2Ind)_2]ZrMe(O\text{-}t\text{-}Bu)$ is assigned from the NOESY spectrum from cross-peaks between protons H3 and H9 and H2 and H8b. Owing to the cross-peaks between the zirconium methyl protons and the aromatic H5 and H6, the Zr methyl group is assigned to be inward. Protons H5 and H6 are assigned from their cross-peaks with methyl protons H9 and H10, respectively.

The ^{13}C spectrum is assigned from $^1H-^{13}C$ HSQC[24] and $^1H-^{13}C$ HMBC[25] 2D experiments. In the $^1H-^{13}C$ HMBC spectrum carbon C1 is identified from its cross-peaks with H2 and H3 and as expected does not show any cross-peaks with methyl H9 and H10. The quaternary carbon of the O-*t*-Bu group is identified from the cross-peak with its methyl protons. The cross-peaks of methyl H9 and carbons C3a, C4, and C5 and methyl H10 and carbons C7a, C7, and C6 allow carbons C5 and C6 to be assigned and C3a and C4 to be distinguished from C7a and C7. Carbons C3a and C7a are then distinguished from C4 and C7, respectively, for their strong cross-peaks with H2 and H3.

The ^1H spectrum of *m*-**6c** is assigned from the NOESY spectrum from cross-peaks between protons H3 and H9, H5 and H9, H2 and H8b, and H6 and H10. These assignments are confirmed from the COSY spectrum from cross-peaks H9−H5, H10−H6, H2−H3, and H5−H6. The ^{13}C spectrum is assigned from $^1H-^{13}C$ HSQC and $^1H-^{13}C$ HMBC 2D experiments; C10 is a doublet owing to the coupling with one ^{19}F of the OC_6F_5 group.[26] This is also confirmed by the molecular structure of this complex (see the next section). In the $^1H-^{13}C$ HMBC, C1 is identified from its cross-peaks with H2, H3, H8a, and H8b and as expected does not show any cross-peak with methyls H9 and H10. The cross-peaks between methyl H9 and carbons C3a, C4, and C5 and methyl H10 and carbons C7a, C7, and C6 allow carbons C3a and C4 to be distinguished from carbons C7a and C7. Carbons C3a and C7a are then distinguished from C4 and C7, respectively, for their strong cross-peaks with H2 and H3. In aromatic systems $J^3 \approx 7-10$ Hz and $J^2 \approx 1$ Hz, and therefore only couplings C4−H6 and C7−H5 are present.

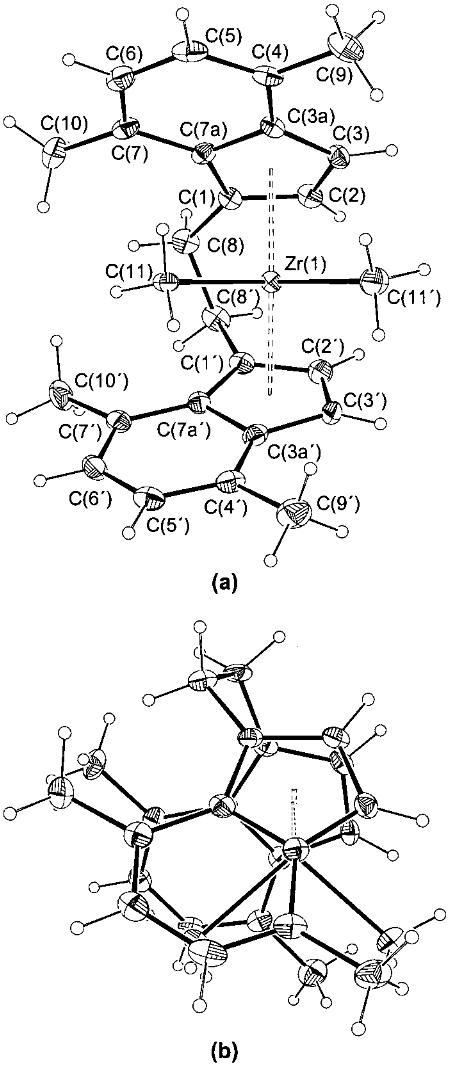


Figure 1. ORTEP drawings of *meso*-[ethylenebis(4,7-dimethyl-η^5-1-indenyl)]dimethylzirconium (*m*-**6a**): (a) viewed down the C(11)−Zr(1)−C(11′) bisector; (b) top view. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are given arbitrary radii. Atoms and primed atoms are not related by symmetry.

Crystal and Molecular Structures of *meso*-[Ethylenebis(4,7-dimethyl-η^5-1-indenyl)]dimethylzirconium (*m*-6a) and *meso*-[Ethylenebis(4,7-dimethyl-η^5-1-indenyl)]bis(pentafluorophenoxy)zirconium (*m*-6c). The molecular structure of compounds *m*-**6a** and *m*-**6c** has been determined by X-ray analysis. Two different ORTEP views of *m*-**6a** and *m*-**6c** are shown in Figures 1 and 2, respectively. Table 2 contains the most relevant bonding parameters for the two compounds. Table 3 collects the angles between some relevant least-squares planes, a few slip-fold indicators, and the geometrical parameters described in Figure 3 for the two compounds and for the strictly related dichloro derivative (*m*-**6d**),[27] whose pertinent bonding parameters have been properly permuted to compare species with similar conformations and labeling.

---

(20) Prini, G. Ph.D. Thesis, Centro Ricerche G. Natta, Ferrara, 1999.

(21) Prini, G.; Balboni, D.; Camurati, I.; Resconi, L.; Traverso, O. *Inorg. Chem. Commun.* **1999**, *2*, 41.

(22) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

(23) Hurd, R. E. *J. Magn. Reson.* **1990**, *87*, 422.

(24) (a) Palmer, A. G., III; Cavanagh, J.; Wright, P. E.; Rance, M. *J. Magn. Reson.* **1991**, *93*, 151. (b) Kay, L. E.; Keifer, P. Saarinen, T. *J. Am. Chem. Soc.* **1992**, *114*, 10663.

(25) Wilker, W.; Leibfritz, D.; Kerssebaum, R.; Bermel, W. *Magn. Reson. Chem.* **1993**, *31*, 287.

(26) Jones, C. R.; Parlow, J. J.; Schnur, D. M. *J. Heterocycl. Chem.* **1996**, *33*, 1835.

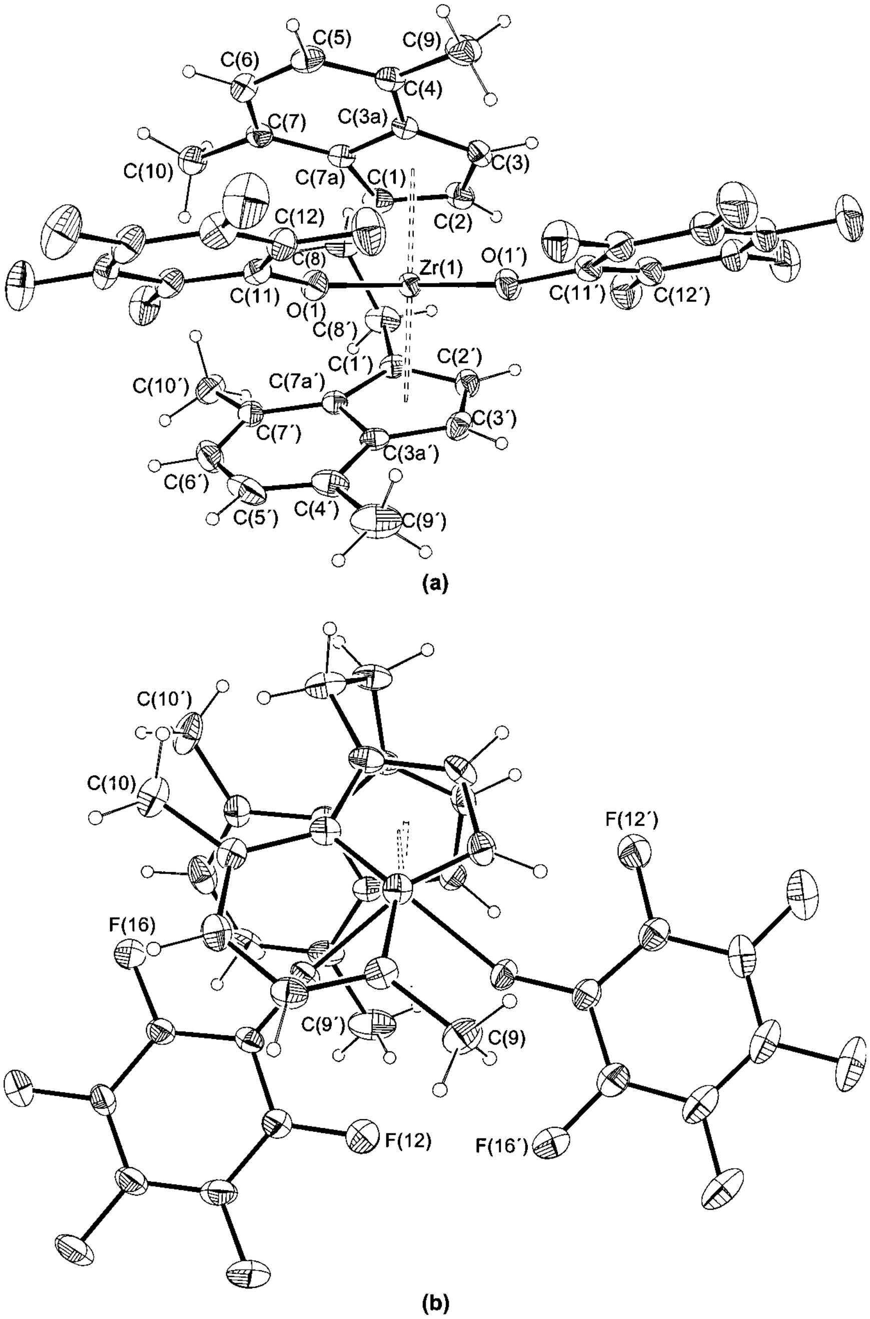


Figure 2. ORTEP drawings of *meso*-[ethylenebis(4,7-dimethyl-η^5-1-indenyl)]bis(pentafluorophenoxy)zirconium (*m*-**6c**): (a) viewed down the O(1)−Zr(1)−O(1′) bisector; (b) top view. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are given arbitrary radii. Atoms and primed atoms are not related by symmetry.

In these compounds the metal atom is *pseudo*tetrahedrally coordinated by the two cyclopentadienyl groups of the ethylene-bridged bisindenyl moiety and by two equatorial ligands (methyl, pentafluorophenoxy, and chloro for *m*-**6a**, *m*-**6c**, and *m*-**6d**, respectively). As usual for bent sandwich complexes, the overall coordination environment is best described by the set of parameters reported in Figure 3, which can be related to zirconium accessibility. In particular, the smaller the bite angle β and the bigger the cp−Zr−cp′ α one, the more the metal is tucked into the ligand envelope. These parameters are very sensitive to differences in the number and type of the *ansa* atoms, while the presence of substituents on the ligand leads only to minor changes in the local stereochemistry of the metal atom.[28] Data reported in Table 3 show that also the nature of the equatorial ligands only slightly affects the coordination of the bisindenyl moiety to the metal center (at least for the limited set of compounds examined here).

In these *meso* derivatives the steric environments of the two equatorial ligands (X and X′ refer to the inward and outward σ-ligands, respectively) are markedly dissimilar, leading to a significant asymmetry of the Zr−X bond lengths (see Table 2; for *m*-**6d** the values are Zr(1)−Cl(1) = 2.4505(4) Å and Zr(1)−Cl(1′) = 2.4105(4) Å) and, for *m*-**6c**, to different degrees of distortion of the Zr−O−C bond angles (vide infra). Note, for *m*-**6c** and *m*-**6d** the outward ligands have longer Zr−X bond lengths, whereas for *m*-**6a** the opposite is true. The two indenyl

---

(27) Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Zeigler, R. *Organometallics* **1996**, *15*, 5046.

(28) Dang, V. A.; Yu, L.-C.; Balboni, D.; Dall'Occo, T.; Resconi, L.; Mercandelli, P.; Moret, M.; Sironi, A. *Organometallics* **1999**, *18*, 3781.

Table 2. Selected Bond Lengths (Å) and Angles (deg)[a]

	m-**6a**		*m*-**6c**	
	I	II	I	II
Zr(1)−cp(1)	2.235(3)	2.239(3)	2.224(2)	2.250(2)
Zr(1)−X	2.269(6)	2.242(6)	1.979(3)	2.022(3)
Zr(1)−C(1)	2.481(5)	2.518(5)	2.487(4)	2.541(4)
Zr(1)−C(2)	2.486(6)	2.492(6)	2.489(4)	2.469(4)
Zr(1)−C(3)	2.531(6)	2.508(6)	2.529(4)	2.490(4)
Zr(1)−C(3a)	2.609(5)	2.598(6)	2.570(4)	2.601(4)
Zr(1)−C(7a)	2.588(5)	2.607(5)	2.577(4)	2.655(4)
C(1)−C(2)	1.402(8)	1.413(8)	1.409(6)	1.406(5)
C(1)−C(7a)	1.440(7)	1.419(7)	1.438(5)	1.431(5)
C(2)−C(3)	1.521(8)	1.520(8)	1.515(5)	1.516(5)
C(2)−C(8)	1.389(8)	1.408(9)	1.389(6)	1.392(6)
C(3)−C(3a)	1.417(8)	1.420(8)	1.425(6)	1.415(5)
C(3a)−C(4)	1.423(8)	1.425(8)	1.419(5)	1.418(6)
C(3a)−C(7a)	1.435(8)	1.448(8)	1.434(5)	1.432(5)
C(4)−C(5)	1.361(9)	1.352(9)	1.358(6)	1.356(7)
C(4)−C(9)	1.498(9)	1.506(9)	1.503(6)	1.505(7)
C(5)−C(6)	1.408(9)	1.405(8)	1.416(6)	1.406(7)
C(6)−C(7)	1.355(9)	1.364(8)	1.361(6)	1.358(7)
C(7)−C(7a)	1.445(8)	1.419(8)	1.428(5)	1.437(6)
C(7)−C(10)	1.496(9)	1.508(8)	1.500(5)	1.499(6)
C(8)−C(8′)	1.535(8)		1.530(6)	
cp(1)−Zr(1)−cp(1′)	125.4(1)		124.41(8)	
cp(1)−Zr(1)−X	107.5(2)	108.6(2)	108.7(1)	108.7(1)
cp(1)−Zr(1)−X′	107.8(2)	107.3(2)	106.1(1)	106.3(1)
X−Zr(1)−X′	96.4(2)		99.96(12)	
C(2)−C(1)−C(7a)	106.2(5)	107.4(5)	106.7(4)	106.2(4)
C(2)−C(1)−C(8)	124.0(5)	121.6(5)	122.4(4)	124.6(4)
C(7a)−C(1)−C(8)	129.8(5)	131.0(6)	130.9(4)	129.2(4)
C(1)−C(2)−C(3)	110.9(6)	110.1(5)	110.2(4)	110.6(4)
C(2)−C(3)−C(3a)	107.5(5)	107.0(5)	108.0(4)	107.5(4)
C(3)−C(3a)−C(4)	130.8(5)	130.1(6)	129.8(4)	130.4(5)
C(3)−C(3a)−C(7a)	107.8(5)	108.1(5)	107.5(3)	107.7(4)
C(4)−C(3a)−C(7a)	121.4(6)	121.7(5)	122.7(4)	121.8(4)
C(3a)−C(4)−C(5)	116.6(6)	116.9(6)	116.0(4)	115.8(5)
C(3a)−C(4)−C(9)	120.1(6)	120.5(6)	120.4(4)	119.9(5)
C(5)−C(4)−C(9)	123.3(6)	122.6(6)	123.6(4)	124.3(5)
C(4)−C(5)−C(6)	122.2(6)	122.0(6)	122.0(4)	122.8(5)
C(5)−C(6)−C(7)	124.1(7)	123.2(6)	123.8(4)	123.8(5)
C(6)−C(7)−C(7a)	116.0(7)	118.0(6)	116.6(4)	115.7(4)
C(6)−C(7)−C(10)	121.3(6)	120.3(6)	120.6(4)	120.5(5)
C(7a)−C(7)−C(10)	122.7(6)	121.7(6)	122.8(4)	123.6(4)
C(1)−C(7a)−C(3a)	107.4(5)	107.3(5)	118.9(4)	107.8(4)
C(1)−C(7a)−C(7)	132.9(6)	134.5(6)	133.6(4)	132.2(4)
C(3a)−C(7a)−C(7)	119.7(6)	118.0(5)	107.5(4)	119.8(4)
C(1)−C(8)−C(8′)	113.2(5)	114.4(5)	110.5(4)	112.2(3)
Zr(1)−O(1)−C(11)			167.1(3)	152.2(3)
cp(1′)−Zr(1)−cp(1)−C(1)	35.3(3)	−23.3(3)	27.9(3)	−10.6(3)
C(1)−cp(1)−cp(1′)−C(1′)	13.4(4)		19.7(4)	
C(1)−C(8)−C(8′)−C(1′)	40.7(7)		46.1(6)	
O(1′)−Zr(1)−O(1)−C(11)			47.3(12)	−156.0(6)
Zr(1)−O(1)−C(11)−C(12)			−32.4(14)	−31.4(8)

[a] cp refers to the centroid of the five-membered ring of the indenyl ligand. X refers to the C(11) and O(1) atoms for *m*-**6a** and *m*-**6c**, respectively. I and II indicate atoms (I) and primed atoms (II) of *m*-**6a** and *m*-**6c** as shown in Figures 1 and 2.

Table 3. Relevant Geometrical Parameters[a]

	m-**6a**		*m*-**6c**		*m*-**6d**	
	I	II	I	II	I	II
α	125.4		124.4		123.8	
β	60.3		59.1		62.4	
γ	4.4	3.5	1.9	3.2	3.5	2.0
δ	86.3	86.6	87.4	85.0	86.2	86.4
al−*bz*	6.6	6.4	4.2	7.0	8.6	6.7
ZrX$_2$−*cp*	30.7	29.6	30.2	28.9	31.8	30.6
bz−cp−cp'−bz'	12.5		18.9		14.5	
Ω	4.3	3.9	2.6	3.1	6.2	3.9
Δ	0.14	0.13	0.10	0.20	0.15	0.14

[a] All quantities in degrees, apart from Δ (Å). The angles α, *β*, *γ*, and *δ* are defined in Figure 3. *al*, *bz*, *cp*, and *ZrX$_2$* refer to the least-squares planes defined by the allylic moiety [C(1), C(2), C(3)], the aromatic six-membered ring, the five-membered ring, and the ZrX_2 atoms, respectively. bz refers to the centroid of the six-membered ring of the indenyl ligand. Ω is the angle between the plane defined by the allylic moiety [C(1), C(2), C(3)] and the least-squares plane defined by the atoms C(1), C(7a), C(3a), and C(3); Δ is the distance between the perpendicular projection of the heavy atom on the ring least-squares plane and the ring centroid.

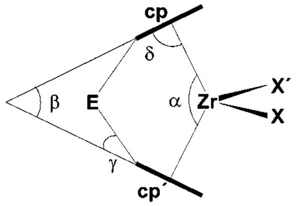


Figure 3. Schematic representation of an *ansa*-zirconocene molecule detailing the angles listed in Table 3. α is the angle cp−Zr−cp′, *β* is the angle between the least-squares planes of the two cyclpentadienyl ligands, *γ* is the angle between the C(1)−C(8) vector and the *cp* least-squares plane, and *δ* is the angle between the Zr−cp vector and the *cp* least-squares plane.

groups, which are effectively identical in the time-averaged C_s symmetric structure observed in solution, show some differences in the solid state. In particular, for the *δ*,*R*,*S* conformers (vide infra), the Zr(1)−C(1) and Zr(1)−C(7a) bond lengths are somewhat shorter than the Zr(1)−C(1′) and Zr(1)−C(7a′) ones, respectively (see Table 2; for the dichloro derivative *m*-**6d** the pertinent values are Zr(1)−C(1) = 2.462(2) Å, Zr(1)−C(1′) = 2.498(2) Å, Zr(1)−C(7a) = 2.599(2) Å, and Zr(1)−C(7a′) = 2.602(2) Å).

The bisindenyl ligand adopts a skewed, asymmetric conformation with respect to the two equatorial ligands, the *ansa* ethylene bridge being almost *trans* to the X′ atom. The degree of rotation of the two indenyl moieties about the Zr−cp vector is different in the three compounds, as can be seen by comparing the values of the cp′−Zr−cp−C(1) and cp−Zr−cp′−C(1′) angles (see Table 2; for *m*-**6d** the values are cp(1′)−Zr(1)−cp(1)−C(1) = 38.9(3)° and cp(1)−Zr(1)−cp(1′)−C(1′) = −25.0(3)°). These minor conformational differences could be related to the different steric demands of the equatorial ligands in the three compounds. However, they may be a consequence of different crystalline environments, the crystals being neither isomorphous nor isostructural.

The Zr−O bond lengths in *m*-**6c** (inward, 1.979(3) Å; outward, 2.022(3) Å) are quite short when compared to the sum of the covalent radii for zirconium and oxygen (2.16 Å),[29] and the Zr−O−C bond angles (inward, 167.1(3)°; outward, 152.2(3)°) show a significant deviation toward a linear geometry. Large Zr−O−C bond angles and short Zr−O bond lengths are consistent either with an enhanced *π* donation from the alkoxy ligand oxygen lone pairs to the electron-deficient metal center[30] or with a partial ionic character of the zirconium−oxygen bond (i.e., $Zr^{\delta+}-O^{\delta-}$) perhaps combined with unfavorable steric interactions with other ligands bound to the metal.[19a] Nevertheless, the Zr−O−C angles found in *m*-**6c** are smaller and the Zr−O distances are longer than those found in compounds for which a strong p*π*−d*π* interaction has been claimed, $[Cp_2Zr(O\text{-}t\text{-}Bu)(thf)]^+$ (Zr−O−C = 172.3°, Zr−O = 1.890 Å)[30] and $Cp_2Zr(O\text{-}t\text{-}Bu)RuCp(CO)_2$ (Zr−O−C = 169.6°, Zr−O = 1.910 Å),[31] and are very similar to those found for the related biscyclopentadienyl derivative $Cp_2Zr(OC_6F_5)_2$ (Zr−O−C = 163.7°, Zr−O = 1.991 Å).[19b]

---

(29) (a) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960. (b) Howard, W. A.; Waters, M.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.

(30) Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092.

Table 4. Selected C···F Distances (Å) for *m*-**6c**

C(9)···F(12)	3.574(6)	C(9′)···F(16′)	5.397(7)
C(9′)···F(12)	4.745(7)	C(10)···F(16)	3.407(5)
C(9)···F(16′)	3.756(6)	C(10′)···F(16)	3.933(7)

According to an adaptation by Schlögl[32] of the Cahn–Ingold–Prelog rules, the stereoisomers of *m*-**6a** and *m*-**6c** represented in Figures 1 and 2 have an *R*,*S* configuration of the bridgehead carbon atoms C(1) and C(1′) and a δ conformation of the Zr(1)–C(1)–C(8)–C(8′)–C(1′) metallacycle. However, in solution, due to the very low energy barrier associated with the rotation about the C(8)–C(8′) bond, their λ,*S*,*R* enantiomers are also present and the molecules show dynamic C_s symmetry.

Table 4 gives a list of selected distances between the carbon atoms of the methyl substituents of the bisindenyl moiety and the *o*-fluoro substituents of the pentafluorophenoxy ligands F(12), F(16), and F(16′) (see Figure 2b). Pertinent F(12′)···C distances are somewhat longer and are not reported in Table 4. Assuming a rapid process of enantiomeric exchange in solution, the mean distance of the backward methyl groups C(10) and C(10′) from F(16) (3.67 Å) is sensibly shorter than the mean distance of the forward methyl groups C(9) and C(9′) from both F(12) and F(16′) (4.16 and 4.57 Å, respectively).

Conclusions

We have described here a facile, highly efficient synthesis of dimethylmetallocenes by the reaction of the ligand with a 2-fold excess of MeLi, and $MtCl_4$ (Mt = Ti, Zr, Hf). This simple, one-pot procedure saves on reaction time, solvents, and number of reactors, and produces the dimethylmetallocenes in higher overall yield compared to the known methods. This convenient procedure paves the way to the synthesis of a large number of metal methyl complexes which were previously more difficult to obtain, and hopefully will ease the study of the chemistry of group 4 alkylmetal cations. The reactivity of **2a** and *m*-**6a** toward alcohols has been investigated. Only the mono-*tert*-butoxy derivative is obtained in both cases, while reaction of both **2a** and *m*-**6a** with C_6F_5OH gives the bisaryloxide derivatives. The reactivity of the *m*-**6a** complex, which has two diastereotopic metal-bonded methyl groups, with *tert*-BuOH shows that, as expected, the outward methyl is more reactive toward alcoholysis with aliphatic alcohols than the inward methyl.

Experimental Section

General Procedures and Materials. All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were purified by being degassed with N_2 and passed over activated (8 h, N_2 purge, 300 °C) Al_2O_3, and stored under nitrogen. MeLi (Acros), $TiCl_4$ (Aldrich), $ZrCl_4$ (Aldrich), $HfCl_4$ (Roc-Ric, 99.99% Hf), $B(C_6F_5)_3$ (Boulder Scientific), and 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) (LOWINOX 22M46, Great Lakes) were used as received. Technical indene (Aldrich) was purified by being passed over activated Al_2O_3; 4,7-dimethylindene (99.7% by GC) and 1,2-bis(4,7-dimethylindenyl)-ethane (97.2% by GC), both from Boulder Scientific Co., were used as received. 1,2-Bis(indenyl)ethane (Boulder Scientific) was purified to 98.4% (GC) by crystallization from EtOH followed by extraction with pentane, as described in ref 11b. All compounds were analyzed on an DPX 200 Bruker spectrometer, by ^1H NMR (200.13 MHz, $CDCl_3$, referenced against the peak of residual $CHCl_3$ at 7.25 ppm, or C_6D_6, referenced against the peak of residual C_6D_5H at 7.15 ppm) and ^{13}C NMR (50.323 MHz, broad-band decoupling, C_6D_6, referenced to the central line of C_6D_6 at 128.00 ppm). All NMR solvents were dried over P_4O_{10} or CaH_2 and distilled before use. GC–MS analyses were carried out on an HP 5890 series 2 gas chromatograph and an HP 5970 mass spectrometer. All dimethylmetal complexes were isolated by extraction with toluene at room temperature, or by continuous extraction with refluxing pentane in a modified Soxhlet apparatus equipped with a glass filter, as described in ref 11b. *CAUTION: The solid residues after extraction of the reaction mixture might be reactive toward water and alcohols and must be carefully decomposed (e.g., with EtOH) under nitrogen.* The metal contents were determined by inductively coupled plasma (ICP) on an ARL3580 instrument.

Ind_2TiMe_2. A 31.0 mL sample of 1.6 M MeLi in Et_2O (49.6 mmol) was added with stirring at room temperature to a solution of 3 g of indene (94% by GC, 24.3 mmol) in 30 mL of diethyl ether over a period of about 10 min (exothermic reaction). The Schlenk tube was kept in a water bath to remove the heat of reaction. The reaction mixture was stirred for 30 min. After this time the solution turned from light yellow to orange. A 1.34 mL sample of $TiCl_4$ (99%, 12.2 mmol) was dissolved in 30 mL of pentane, and this solution was quickly added to the Li salt solution (exothermic reaction). The reaction mixture was stirred for 2 h at room temperature with final formation of a dark brown suspension. The solvents were then removed under reduced pressure. The brown solid obtained was extracted in a Soxhlet apparatus with 80 mL of pentane. The filtrate was evaporated to dryness under reduced pressure, to give 2.62 g of a yellow-brown powder (70% metal-based yield).

Anal. Calcd for $C_{20}H_{20}Ti$: C, 77.93; H, 6.54; Ti, 15.53. Found: C, 77.0; H, 6.5; Ti, 14.6; Cl, <0.05.

^1H NMR (C_6D_6, δ, ppm): −0.50 (s, $TiCH_3$, 6H), 5.37 (t, Cp H(2), 2H, $J = 3.24$ Hz), 5.78 (d, Cp H(1,3), 4H, $J = 3.24$ Hz), 6.90–6.95 (m, Ar, 4H), 7.16–7.22 (m, Ar, 4H).

Ind_2ZrMe_2 (a). Operating as in the case of Ind_2TiMe_2, 29.6 mL of a solution of 1.6 M MeLi in Et_2O (47.4 mmol) was added at room temperature to a solution of 3 g (23.7 mmol) of indene (91.8% by GC) in 30 mL of Et_2O in about 5 min (exothermic reaction). The mixture was stirred for 30 min, to give an orange solution. A 2.76 g sample of $ZrCl_4$ (11.84 mmol) were slurried in 30 mL of pentane. The $ZrCl_4$ slurry in pentane was quickly added to the Li salt solution in Et_2O (exothermic reaction). The reaction mixture was stirred for 2 h and then brought to dryness under reduced pressure. The light brown solid was extracted with 100 mL of pentane (Soxhlet, 4.5 h), and then the filtrate was evaporated to dryness under reduced pressure, to give 3.2 g (77% yield) of a light yellow solid, which was characterized by ^1H NMR as spectroscopically pure Ind_2ZrMe_2.

Anal. Calcd for $C_{20}H_{20}Zr$: C, 68.32; H, 5.73; Zr, 25.94. Found: C, 67.1; H, 5.8; Zr, 23.5; Cl, <0.05.

^1H NMR (C_6D_6, δ, ppm): −0.78 (s, $ZrCH_3$, 6H), 5.62 (t, Cp H(2), 2H, $J = 3.32$ Hz), 5.80 (d, Cp H(1,3), 4H, 3.32 Hz), 6.87–6.92 (m, Ar, 4H), 7.19–7.23 (m, Ar, 4H).

$^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 35.65 ($ZrCH_3$), 99.84 (CH, Cp C1,3), 114.83 (CH, Cp C2), 124.10 (C, C3a,7a), 124.47 (CH, Ar C5,6), 124.96 (CH, Ar C4,7).

Ind_2ZrMe_2 (b). The same experiment was carried out using a purer indene. A 15.8 mL sample of a solution of 1.6 M MeLi in Et_2O (25.3 mmol) was added at room temperature to a solution of 1.5 g (12.6 mmol) of indene (Aldrich, 97.9% by GC) in 30 mL of Et_2O in about 5 min (exothermic reaction). The mixture was stirred for 30 min, to give an orange solution. A 1.47 g sample of $ZrCl_4$ (6.33 mmol) was slurried in 30 mL of pentane. The $ZrCl_4$ slurry in pentane was quickly added to the Li salt solution in Et_2O (exothermic reaction). The reaction mixture was stirred for 30 min, and the yellow-brown suspension was treated as described above, to give 1.92 g (86.5% yield) of a light yellow solid, which was characterized by ^1H NMR as spectroscopically pure Ind_2ZrMe_2.

Anal. Calcd for $C_{20}H_{20}Zr$: C, 68.32; H, 5.73; Zr, 25.94. Found: C, 67.3; H, 5.75; Cl, <0.05.

Ind_2ZrMe_2 (c). The inverse addition was tested in a separate experiment. A 2.24 g sample of $ZrCl_4$ (9.61 mmol) was slurried in 50 mL of pentane, the slurry was cooled to −30 °C, and 24.0 mL of a solution of 1.6 M MeLi in Et_2O (38.44 mmol) was added. No color change was observed. This mixture was stirred for 4 h at −30 °C. A

---

(31) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665.

(32) Schlögl, K. *Top. Stereochem.* **1966**, *1*, 39.

solution of 2.38 g of indene (94%, 19.22 mmol) in 50 mL of Et_2O was cooled to −30 °C and added to the $ZrCl_4$/MeLi slurry. The mixture was stirred for 2 h at −30 °C, to give a light yellow suspension. The reaction mixture was slowly allowed to reach room temperature and stirred overnight, to give a black suspension, which was then brought to dryness under reduced pressure. The black paste was analyzed by ^1H NMR, which shows only limited conversion (<5%) to the desired product.

Ind$_2$HfMe$_2$. Operating as in the previous case, 21.5 mL of 1.6 M MeLi in Et_2O (34.4 mmol) was slowly added at room temperature (exothermic reaction) to a stirred solution of 2 g of indene (91.8%, 15.81 mmol) in 30 mL of diethyl ether over a period of about 10 min. The reaction mixture was stirred for 4 h. After this time the solution became orange from light-yellow. A 2.76 g sample of $HfCl_4$ (8.62 mmol) was slurried in 30 mL of pentane, and the $HfCl_4$ slurry in pentane was quickly added to the stirred Li salt solution (exothermic reaction). The reaction mixture was stirred overnight with final formation of a gray-black suspension. The solvents were then removed under reduced pressure. The black solid obtained was extracted in a Soxhlet apparatus with 100 mL of pentane. The filtrate was evaporated to dryness under reduced pressure, to give 2.8 g of a light yellow powder (74% yield), which was characterized by ^1H NMR as spectroscopically pure Ind$_2$HfMe$_2$.

Anal. Calcd for $C_{20}H_{20}Hf$: C, 54.74; H, 4.59; Hf, 40.67. Found: C, 54.1; H, 4.6; Hf, 40.3 (Zr, 1200 ppm); Cl, 0.09.

^1H NMR (C_6D_6, δ, ppm): −0.93 (s, $HfCH_3$, 6H), 5.57 (t, Cp H(2), 2H, $J = 3.3$ Hz), 5.69 (d, Cp H(1,3), 4H, $J = 3.3$ Hz), 6.87−6.92 (m, Ar, 4H), 0.7.19−7.23 (m, Ar, 4H).

$^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 40.59 ($HfCH_3$), 98.79 (CH, Cp C1,3), 115.18 (CH, Cp C2), 123.86 (C, C3a,7a), 124.63 (CH, Ar C5,6), 124.94 (CH, Ar C4,7).

Methyllithium Titration. A 2 mL sample of a 1.4 or 1.6 M MeLi solution in diethyl ether (Aldrich and Fluka, respectively) was charged at room temperature under nitrogen atmosphere into a 50 mL Schlenk flask. Then 20 mL of deionized water was added dropwise at room temperature. *CAUTION: During the addition a strong exothermicity and a gas evolution (CH_4) are generated.* The final colorless solution was potentiometrically titrated with a 1 M HCl solution; then the exact molarity value of the starting MeLi solution was determined.

The two following experiments were carried out by using the exact molarity value of the MeLi solution.

Ind$_2$ZrMe$_2$ in Et$_2$O/Heptane, ∼1:1 Vol/Vol. A 1.717 M MeLi solution in Et_2O (Aldrich, 25.3 mL, 43.44 mmol) was added over a period of about 5 min at room temperature to a solution of indene (93.4% by GC, 2.70 g, 21.71 mmol) in 25 mL of Et_2O in a 100 mL Schlenk flask. During the addition exothermicity and gas evolution were observed. The yellow-orange solution so-obtained was stirred for 40 min at room temperature and then added at the same temperature to a slurry of $ZrCl_4$ (Aldrich, 2.53 g, 10.86 mmol) in 50 mL of heptane in a 250 mL Schlenk flask (exothermic reaction). The light brown reaction mixture was stirred for 90 min at room temperature and then filtered on a G4 frit. An additional 10 mL of heptane was used to completely transfer the final suspension onto the frit. The brown filtrate was evaporated to dryness under reduced pressure, to give 3.24 g of a yellow powder (85% metal-based yield), which was characterized by ^1H NMR as spectroscopically pure Ind$_2$ZrMe$_2$.

Ind$_2$HfMe$_2$ in Et$_2$O/Heptane, ∼1:1 Vol/Vol. A 30.1 mL sample of MeLi in Et_2O (Fluka, 1.66 M, 50.0 mmol) was added over a period of about 5 min at room temperature to a solution of 3.09 g of indene (93.4% by GC, 24.8 mmol) in 30 mL of Et_2O in a 100 mL Schlenk flask (exothermic reaction). The so-obtained yellow-orange solution was stirred for 30 min at room temperature and then added to a suspension of 4.00 g of $HfCl_4$ (12.5 mmol) in 60 mL of heptane in a 250 mL Schlenk flask (exothermic reaction). The light yellow reaction mixture was stirred for 4 h at room temperature and then filtered on a G4 frit. An additional 10 mL of heptane was added to wash the residue on the frit. The yellow filtrate was evaporated to dryness under reduced pressure, to give 4.90 g of a yellow powder, which was characterized by ^1H NMR as spectroscopically pure Ind$_2$HfMe$_2$ (89.3% metal-based yield). Anal. Calcd for $C_{20}H_{20}Hf$: C, 54.74; H, 4.59; Hf, 40.67. Found: C, 53.0; H, 4.6.

^1H NMR (C_6D_6, δ, ppm): identical to that reported above.

^1H NMR (CD_2Cl_2, δ, ppm): −1.30 (s, 6H, $HfCH_3$); 5.93 (t, 2H, Cp H(2), $J = 3.33$ Hz); 6.03 (d, 4H, Cp H(1,3), $J = 3.33$ Hz); 7.11−7.20 (m, 4H, Ar); 7.41−7.50 (m, 4H, Ar).

Ind$_2$Zr(O-*t*-Bu)Me. *tert*-Butyl alcohol (0.26 g, 3.55 mmol) in 1 mL of C_6D_6 was added dropwise at room temperature to a suspension of Ind$_2$ZrMe$_2$ (1.25 g, 3.55 mmol) in 2.5 mL of C_6D_6. Gas evolution was observed (CH_4 by ^1H NMR in C_6D_6, $\delta = 0.15$ ppm); a homogeneous yellow solution was obtained. The solution was stirred for 1 h at room temperature. The yellow solution was brought to dryness and the residue taken up in 6 mL of pentane, cooled to −40 °C, and stirred at this temperature for 1 h to precipitate a white solid, which was isolated by siphoning off the pentane layer and then by drying the residue under vacuum, to give a white, deliquescent solid. Yield: 1.40 g, 96%.

^1H NMR (C_6D_6, δ, ppm): −0.13 (s, 3H, $ZrCH_3$), 0.93 (s, 9H, ZrO-*t*-Bu), 5.64−5.67 (m, 2H, Cp H1,3); 5.76 (t, Cp H2, 2H, $J = 3.3$ Hz), 5.88−5.91 (m, Cp H3,1, 2H), 6.84−6.98 (m, Ar H5,6, 4H), 7.28−7.37 (m, Ar H4,7, 4H).

$^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 23.78 ($ZrCH_3$), 31.87 ($ZrOC(\mathit{C}H_3)_3$), 78.91 ($ZrO\mathit{C}(CH_3)_3$), 97.81−99.30 (CH, Cp C1,3), 117.20 (CH, Cp C2), 123.50−123.74 (CH, Ar C5,6), 124.11−124.20 (CH, Ar C4,7), 125.32−126.12 (C, C3a,7a).

Ind$_2$Zr(O-*t*-Bu)(OC$_6$F$_5$). Ind$_2$Zr(O-*t*-Bu)Me (0.83 g, 0.20 mmol) was dissolved in 2 mL of C_6D_6, C_6F_5OH (140 mg, 0.20 mmol) was added at room temperature, and the solution was stirred for 1 h.

^1H NMR (C_6D_6, δ, ppm): 1.00 (br s, ZrO-*t*-Bu, 9H), 5.73 (d, 4H, Cp H1,3, $J = 3.37$ Hz); 6.16 (t, Cp H2, 2H, $J = 3.37$ Hz), 6.67−6.74 (m, 4H, Ar), 7.01−7.07 (m, 4H, Ar).

Ind$_2$Zr(OC$_6$F$_5$)$_2$. Pentafluorophenol (0.995 g, 5.4 mmol) in 3 mL of toluene was added dropwise to a solution of Ind$_2$ZrMe$_2$ (0.95 g, 2.7 mmol) in 30 mL of toluene at 0 °C. The yellow solution was stirred for 1 h at room temperature. The solution was brought to dryness, and the residue was slurried in 5 mL of pentane, stirred, then filtered, and dried under vacuum, to give a straw-yellow powder. Yield: 1.7 g, 92% yield.

Anal. Calcd for $C_{30}H_{14}F_{10}O_2Zr$: C, 52.40; H, 2.05; F, 27.63; O, 4.65; Zr, 13.27. Found: C, 49.4; H, 1.6.

^1H NMR (C_6D_6, δ, ppm): 5.73 (d, 4H, Cp H2, $J = 3.38$ Hz), 6.16 (t, 2H, Cp H1,3, $J = 3.38$ Hz), 6.64−6.74 (m, 4H, Ar), 7.00−7.07 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 101.52 (CH, Cp C1,3), 121.50 (CH, Cp C2), 123.43 (CH, Ar C4,7), 126.05 (CH, Ar C5,6), 128.48 (C, C3a,7a).

Reaction of Ind$_2$ZrMe$_2$ with B(C$_6$F$_5$)$_3$. A 1.07 g sample of Ind$_2$ZrMe$_2$ (3.04 mmol) was dissolved in 30 mL of toluene in a 100 mL Schlenk flask, and then 1.56 g of $B(C_6F_5)_3$ in 20 mL of toluene (3.04 mmol) was added at once at room temperature. A slight exothermicity was observed. The dark brown solution was stirred for 15 min and then evaporated under reduced pressure, to give a yellow solid, which was analyzed by ^1H NMR.

^1H NMR (C_6D_6, δ, ppm): −0.58 (s, 3H, $ZrCH_3$), −0.2 (br, 3H, BCH_3), 6.5−7.0 (m, 8H, Ar).

After 3 days, the ^1H NMR spectrum was unchanged, but the product became partially insoluble.

(4,7-Me$_2$Ind)$_2$ZrMe$_2$. Operating as in the case of Ind$_2$ZrMe$_2$, 26.0 mL of a 1.6 M solution of MeLi in Et_2O (41.6 mmol) was added at room temperature to a solution of 3 g (20.8 mmol) of 4,7-dimethylindene in 30 mL of Et_2O in about 5 min (exothermic reaction). The mixture was stirred for 1 h at room temperature; after 15 min a white solid started to precipitate. A 2.42 g sample of $ZrCl_4$ (10.4 mmol) was slurried in 40 mL of pentane. The $ZrCl_4$ slurry in pentane was quickly added to the Li salt solution in Et_2O (exothermic reaction). The reaction mixture was stirred for 2 h and then brought to dryness under reduced pressure. The light brown powder was taken up in 50 × 3 mL of toluene and filtered, and then the filtrate was evaporated to dryness under reduced pressure, to give 3.14 g (74% yield) of a white solid, which was characterized by ^1H NMR as spectroscopically pure (4,7-Me$_2$-Ind)$_2$ZrMe$_2$.

Anal. Calcd for $C_{24}H_{28}Zr$: C, 70.70; H, 6.92; Zr, 22.37. Found: C, 62.2; H, 5.5; Cl, <0.05.

^1H NMR (C_6D_6, δ, ppm): −0.84 (s, $ZrCH_3$, 6H), 2.18 (s, $ArCH_3$, 12H), 5.77 (t, Cp H(2), 2H, $J = 3.32$ Hz), 5.89 (d, Cp H(1,3), 4H, $J =$

3.32 Hz), 6.70 (s, Ar, 4H). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 18.97 ($ArCH_3$), 34.20 ($ZrCH_3$), 98.95 (CH, Cp C1,3), 112.79 (CH, Cp C2), 124.04 (CH, Ar C5,6), 125.27 (C, C3a,7a), 131.41 (C, C4,7).

C_2H_4(1-Ind)$_2$ZrMe$_2$. A 22.2 mL sample of 1.6 M MeLi in Et_2O (35.6 mmol) was added, in about 10 min, to a solution of 2.33 g of 1,2-bis(indenyl)ethane (98.4% by GC, 8.88 mmol) in 40 mL of Et_2O at room temperature. The mixture was stirred for 3 h. A thick light yellow suspension was obtained. To this suspension was quickly added a slurry of 2.07 g of $ZrCl_4$ (8.88 mmol) in 20 mL of pentane (mildly exothermic reaction). The mixture was stirred at room temperature for 1 h, to give a light gray suspension. The reaction mixture was then brought to dryness under reduced pressure, to give a light gray solid. This solid was extracted with 2 × 100 mL of toluene at 40 °C. After filtration the toluene solution was evaporated to dryness under reduced pressure, to give 2.51 g (75% yield) of a light yellow solid. The ^1H NMR analysis showed the presence of spectroscopically pure C_2H_4(1-Ind)$_2$ZrMe$_2$ (*rac*:*meso* = 38:62). ^1H NMR (δ, ppm, C_6D_6), *rac*: −0.97 (s, $ZrCH_3$, 6H), 2.6−3.1 (m, CH_2 bridge, 4H), 5.65 (d, Cp H, 2H, *J* = 3.33 Hz), 6.42 (d, Cp H, 2H, *J* = 3.33 Hz), 6.9−7.4 (m, Ar, 8H). ^1H NMR (δ, ppm, C_6D_6), *meso*: −2.20 (s, $ZrCH_3$, 3H), 0.12 (s, $ZrCH_3$, 3H), 2.6−3.1 (m, CH_2 bridge, 4H), 5.70 (d, Cp H, 2H, *J* = 3.33 Hz), 6.46 (d, Cp H, 2H, *J* = 3.33 Hz), 6.8−7. 4 (m, Ar, 8H).

Anal. Calcd for $C_{22}H_{22}Zr$: C, 69.97; H, 5.87; Zr, 24.16. Found: C, 69.2; H, 5.7; Cl, 0.065.

The structure of the product was confirmed by comparison with literature data and a sample prepared by methylation of C_2H_4(1-Ind)$_2$-ZrCl$_2$.

C_2H_4(4,7-Me$_2$Ind)$_2$ZrMe$_2$. A 25.4 mL sample of 1.6 M MeLi in Et_2O (40.6 mmol) was added, in about 10 min, to a solution of 3.25 g of 1,2-bis(4,7-dimethylindenyl)ethane (10.1 mmol) in 30 mL of Et_2O at room temperature. The mixture was stirred for 3 h. A thick white suspension was obtained, which was diluted with an additional 100 mL of Et_2O to improve stirring. To this suspension, cooled to −80 °C, was quickly added a slurry of 2.36 g of $ZrCl_4$ (10.1 mmol) in 50 mL fo pentane, previously cooled to −80 °C. The mixture was allowed to warm slowly to room temperature overnight (about 16 h), and a dark brown solution was finally obtained. The reaction mixture was then brought to dryness under reduced pressure, to give a brown solid, which was extracted with 300 mL of toluene, and then the filtrate was evaporated to dryness under reduced pressure, to give 3.3 g (75% yield) of a pale yellow solid. The ^1H NMR analysis showed the presence of spectroscopically pure C_2H_4(4,7-Me$_2$Ind)$_2$ZrMe$_2$ (*rac*:*meso* = 38/62).

***meso*-C_2H_4(4,7-Me$_2$Ind)$_2$ZrMe$_2$.** A 40.0 mL sample of 1.6 M MeLi in Et_2O (64.0 mmol) was added, in about 10 min, to a solution of 5 g of 1,2-bis(4,7-dimethylindenyl)ethane (16.0 mmol) in 50 mL of Et_2O at room temperature. The mixture was stirred for 3 h. A thick white suspension was obtained, which was diluted with an additional 100 mL of Et_2O to improve stirring. To this suspension was quickly added a slurry of 3.7 g of $ZrCl_4$ (15.9 mmol) in 50 mL of pentane (mildly exothermic reaction). The mixture was stirred at room temperature overnight (about 16 h) and a light brown suspension was finally obtained. The reaction mixture was then brought to dryness under reduced pressure, to give a light brown solid, which analyzes (^1H NMR) as a 20:80 *rac*:*meso* mixture of C_2H_4(4,7-Me$_2$-1-Ind)$_2$ZrMe$_2$, apparently free from organic byproducts. This solid was washed with 200 mL of pentane to remove the racemic isomer and then extracted with 5 × 100 mL of toluene. The toluene solution was evaporated to dryness under reduced pressure, to give 3.75 g (54% yield) of a light yellow solid. The ^1H NMR analysis showed the presence of spectroscopically pure *meso*-C_2H_4(4,7-Me$_2$-1-Ind)$_2$ZrMe$_2$ (*rac*:*meso* = 1:99). This compound is stable for months under nitrogen in the solid state.

Anal. Calcd for $C_{26}H_{30}Zr$: C, 72.00; H, 6.97. Found: C, 71.4; H, 7.1; Cl, <0.05.

^1H NMR (C_6D_6, δ, ppm), *meso*: −2.12 (s, inward $ZrCH_3$, 3H), 0.023 (s, outward $ZrCH_3$, 3H), 2.30 (s, $ArCH_3$, H10, 6H), 2.32 (s, $ArCH_3$, H9, 6H), 2.67−2.78 (m, CH_2 bridge, 8b, 2H), 3.23−3.34 (m, CH_2 bridge, 8a, 2H), 5.82 (d, *J* = 3.49 Hz, Cp H2, 2H), 6.50 (d, *J* = 3.49 Hz, Cp H3, 2H), 6.66 (s, Ar, 4H). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 19.06 (CH_3, C9), 20.91 (CH_3, C10), 26.29 ($ZrCH_3$, outward), 31.13 (CH_2, bridge, C8), 41.22 ($ZrCH_3$, inward), 100.98 (CH, Cp C3), 112.91 (C, Cp C1), 114.79 (CH, Cp C2), 123.29 (C, C7a), 123.79 (CH, Ar C5,6), 126.24 (CH + C, Ar C5,6 + C3a), 131.92 (C, Ar C4 or C7), 132.08 (C, Ar C7 or C4). Crystals of *m*-**6a** suitable for X-ray diffraction analysis were grown at −20 °C from a concentrated pentane solution.

***meso*-C_2H_4(4,7-Me$_2$Ind)$_2$ZrMe(O-t-Bu).** *tert*-Butyl alcohol (0.17 g, 2.30 mmol) in 6 mL of toluene was added dropwise at room temperature to a solution of *meso*-C_2H_4(4,7-Me$_2$Ind)$_2$ZrMe$_2$ (0.5 g, 1.15 mmol) in 30 mL of toluene. Gas evolution was observed (CH_4 by ^1H NMR in C_6D_6, δ = 0.15 ppm). The solution was stirred overnight at room temperature. The yellow solution was brought to dryness and the residue taken up in 20 mL of pentane and then dried again under vacuum, to give a yellow powder. Yield: 0.56 g, 99%.

^1H NMR (C_6D_6, δ, ppm): −1.94 (s, $ZrCH_3$, 3H), 1.17 (s, ZrO-*t*-Bu, 9H), 2.25 (s, CH_3 H9, 6H), 2.34 (s, CH_3 H10, 6H), 2.81−2.92 (m, CH_2 8b, 2H), 3.26−3.37 (m, CH_2 8a, 2H), 6.23 (d, Cp H3, 2H, *J* = 3.32 Hz), 6.37 (d, Cp H2, 2H, *J* = 3.32 Hz), 6.63 (d AB, Ar H5, 2H, *J* = 6.84 Hz), 6.70 (d AB, Ar H6, 2H, *J* = 6.84 Hz).

$^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 19.24 (CH_3, C9), 21.16 (CH_3, C10), 29.77 ($ZrCH_3$), 30.22 (CH_2 C8), 77.29 (CO-*t*-Bu), 100.37 (CH, Cp C3), 110.57 (CH, Cp C2), 115.62 (C, Cp C1), 123.11 (CH, Ar C5), 124.04 (C, C7a) 126.10 (CH, Ar C6), 126.65 (C, C3a), 131.00 (C, Ar C7), 131.25 (C, Ar C4).

***meso*-C_2H_4(4,7-Me$_2$Ind)$_2$Zr(OC$_6$F$_5$)$_2$.** Pentafluorophenol (0.10 g, 0.54 mmol) in 10 mL of toluene was added dropwise to a solution of *meso*-C_2H_4(4,7-Me$_2$Ind)$_2$ZrMe$_2$ (0.12 g, 0.28 mmol) in 30 mL of toluene at −20 °C. The solution was stirred for 1 h at −20 °C and then for 3 h at room temperature. The pale yellow solution was brought to dryness and the residue taken up in 30 mL of pentane and then dried again under vacuum, to give a yellow powder. Yield: 0.21 g, 99%. Anal. Calcd for $C_{36}H_{24}F_{10}O_2Zr$: C, 56.17; H, 3.14. Found: C, 56.5; H, 3.2; Cl, <0.05.

^1H NMR (C_6D_6, δ, ppm): 1.99 (s, CH_3 H9, 6H), 2.45 (s, CH_3 H10, 6H), 2.98−3.18 (m, CH_2 8b, 2H), 3.54−3.74 (m, CH_2 8a, 2H), 6.06 (d, Ar H5, 2H, *J* = 7.05 Hz), 6.18 (d, Cp H3, 2H, *J* = 3.52 Hz), 6.31 (d, Ar H6, 2H., *J* = 7.05 Hz), 6.40 (d, Cp H2, 2H, *J* = 3.52 Hz).

$^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 17.96 (CH_3, C9), 20.82 (d, CH_3 ,C10, *J* = 4.44, CF), 31.68 (CH_2, C8), 108.53 (CH, Cp C3), 118.05 (CH, Cp C2), 118.54 (C, Cp C1), 124.03 (CH, Ar C5), 127.25 (C, C3a), 127.81 (C, C7a), 128.23 (CH, Ar C6), 129.85 (C, Ar C7), 131.00 (C, Ar C4).

Crystals of *m*-**6c** suitable for X-ray diffraction analysis were grown at −20 °C from a concentrated toluene solution.

Reaction of *meso*-C_2H_4(4,7-Me$_2$Ind)$_2$ZrMe$_2$ with B(C$_6$F$_5$)$_3$. A 0.4 g sample of *meso*-C_2H_4(4,7-Me$_2$Ind)$_2$ZrMe$_2$ (0.92 mmol) was dissolved in 30 mL of toluene in a 100 mL Schlenk flask, and then 0.47 g of $B(C_6F_5)_3$ (0.92 mmol) in 20 mL of toluene was added dropwise at room temperature in 15 min. The solution was stirred for 3 h at room temperature. A yellow solution was obtained and evaporated under reduced pressure, and the residue was slurried in 30 mL of pentane and brought to dryness. The obtained powder was dried under high vacuum and characterized by ^1H NMR.

^1H NMR (C_6D_6, δ, ppm): −1.76 (s, inward $ZrCH_3$, 3H), 0.15 (br s, outward $ZrCH_3$, 3H), 1.86 (s, $ArCH_3$, H10, 6H), 1.81 (s, $ArCH_3$, H9, 6H), 2.44−2.56 (m, CH_2 bridge, 8b, 2H), 2.79−2.91 (m, CH_2 bridge, 8a, 2H), 6.11 (d, Cp H3, 2H), 6.07 (d, Cp H2, 2H), 6.43 (d AB, Ar H5, 2H), 6.45 (d AB, Ar H6, 2H).

***meso*-C_2H_4(4,7-Me$_2$Ind)$_2$HfMe$_2$.** A 18.4 mL sample of 1.6 M MeLi in Et_2O (29.44 mmol) was added, in about 10 min, to a solution of 2.37 g of 1,2-bis(4,7-dimethylindenyl)ethane (7.34 mmol) in 50 mL of Et_2O at room temperature. The mixture was stirred for 3 h. A white suspension was obtained, to which was quickly added a slurry of 2.35 g of $HfCl_4$ (7.34 mmol) in 50 mL of pentane (mildly exothermic reaction). The mixture was stirred at room temperature 3 h, and a light brown suspension was finally obtained. The reaction mixture was then brought to dryness under reduced pressure, to give a light brown solid, which was taken up in 200 mL of toluene and filtered, the residue was washed with an additional 100 mL of toluene, and the filtrates were combined and evaporated under reduced pressure, to give 2.85 g (74.6% yield) of an 8:92 *rac*:*meso* mixture of C_2H_4(4,7-Me$_2$-1-Ind)$_2$HfMe$_2$, containing traces of organic byproducts (^1H NMR). The powder was taken up in 100 mL of pentane, the slurry stirred for 15 min and filtered, and the filtrate evaporated to dryness under reduced pressure, to give

2.15 g of spectroscopically pure *meso*-$C_2H_4(4,7\text{-}Me_2\text{-}1\text{-}Ind)_2HfMe_2$, as a white powder.

Anal. Calcd for $C_{26}H_{30}Hf$: C, 59.94; H, 5.80. Found: C, 59.15; H, 5.85; Cl, <0.05.

^{1}H NMR (C_6D_6, δ, ppm) *meso*: −2.38 (s, inward $ZrCH_3$, 3H), −0.19 (s, outward $ZrCH_3$, 3H), 2.28 (s, $ArCH_3$, H10, 6H), 2.33 (s, $ArCH_3$, H9, 6H), 2.74−2.93 (m, CH_2 bridge, 8b, 2H), 3.24−3.43 (m, CH_2 bridge, 8a, 2H), 5.78 (d, J = 3.33 Hz, Cp H2, 2H), 6.41 (d, J = 3.33 Hz, Cp H3, 2H), 6.65 (s, Ar H5,6, 4H).

$^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 19.15 (CH_3, C9), 20.90 (CH_3, C10), 30.70 (CH_2, bridge, C8), 32.88 ($HfCH_3$, outward), 43.81 ($HfCH_3$, inward), 100.28 (CH, Cp C3), 111.16 (C, Cp C1), 114.48 (CH, Cp C2), 123.28 (C, C7a), 123.81 (CH, C5), 125.62 (C, C3a), 126.47 (CH, C6), 131.75 (C, C7), 132.06 (C, C4).

CH_2(6-*t*-Bu-4-Me-phenoxy)$_2$TiMe$_2$. A 2.0 g sample of 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) (5.9 mmol) was dissolved in 50 mL of Et_2O in a 100 mL Schlenk tube and the solution cooled to −80 °C. A 14.7 mL sample of 1.6 M MeLi in Et_2O (23.5 mmol) was added dropwise over 15 min with stirring. The solution was allowed to warm to room temperature and stirred for 2 h. A light yellow solution was obtained. A 0.65 mL sample of $TiCl_4$ (Aldrich 99%, 5.9 mmol) was dissolved in 50 mL of pentane. The two solutions were both cooled to −80 °C, and the $TiCl_4$ solution in pentane was quickly added to the Li salt in Et_2O. The reaction mixture was allowed to warm slowly to room temperature overnight (about 16 h), and a dark green suspension was finally obtained. The reaction mixture was then brought to dryness under reduce pressure. The thus obtained dark green solid was extracted with 100 mL of pentane in a Soxhlet apparatus, and then the filtrate was evaporated to dryness under reduced presure, to leave 1.7 g of light yellow CH_2(6-*t*-Bu-4-Me-phenoxy)$_2$TiMe$_2$. Isolated yield: 70%. ^{1}H NMR (C_6D_6, δ, ppm): 1.358 (s, 3H, $TiCH_3$), 1.374 (s, 3H, $TiCH_3$), 1.604 (s, 18H, *t*-Bu), 2.108 (s, 6H, $ArCH_3$), 3.21 (AB system, J = 14.20 Hz, 1H, CH_2), 3.38 (AB system, J = 14.20 Hz, 1H, CH_2), 6.98−7.02 (m, 4 H, Ar H).

X-ray Diffraction Structural Analysis. (a) Collection and Reduction of X-ray Diffraction Data. Suitable crystals of *m*-**6a** and *m*-**6c** were mounted in air on a glass fiber tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. Unit cell parameters were determined by a least-squares fit of the setting angles of 25 randomly distributed intense reflections with 10° < θ < 14°. Data collection was performed by the ω scan method with variable scan speed (maximum time per reflection 70 and 50 s for *m*-**6a** and *m*-**6c**, respectively) and variable scan range (1.00 + 0.35 tan θ (deg) and 0.80 + 0.35 tan θ (deg), respectively). Crystal stability under diffraction was checked by monitoring three standard reflections every 180 min. The measured intensities were corrected for Lorentz, polarization, decay, and background effects and reduced to F_o^2. An empirical absorption correction was applied using ψ scans of three suitable reflections having χ values close to 90°.[33] Crystal data and data collection parameters are summarized in Table 5.

(b) Structure Solution and Refinement. The structures were solved by direct methods[34] and subsequent Fourier synthesis; they were refined by full-matrix least-squares on F^2 [35] using reflections with $I > 2\sigma(I)$. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the internal library of SHELX97.[35] Weights were assigned to individual observations according to the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; a and b were chosen to give a flat analysis of variance in terms of F_o^2. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions (d_{C-H} = 0.93, 0.96, and 0.97 Å for aromatic, methylene, and methyl hydrogen atoms, respectively) and refined riding on their parent atom with an isotropic displacement parameter 1.2 times that of the pertinent carbon atom. The correctness of the absolute structure for *m*-**6a** was checked, and the Flack parameter[36] for the correct enantiomer was 0.03(8). The final difference electron density map showed no features of chemical significance, with the largest peaks lying close to those of the metal atoms. Final conventional agreement indexes and other structure refinement parameters are listed in Table 5.

Table 5. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters

	m-**6a**	*m*-**6c**
	Crystal Data	
empirical formula	$C_{26}H_{30}Zr$	$C_{36}H_{24}F_{10}O_2Zr$
fw	433.72	769.77
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$ (no.19)	$P2_1/c$ (no.14)
a (Å)	11.290(2)	15.301(4)
b (Å)	11.942(2)	15.289(6)
c (Å)	15.458(2)	14.334(5)
β (deg)		114.52(2)
V (Å^3)	2084.1(6)	3050.8(18)
Z	4	4
F(000)	904	1544
density (g cm^{-3})	1.382	1.676
abs coeff (mm^{-1})	0.535	0.456
cryst descriptn	yellow prism	yellow prism
cryst size (mm)	0.20 × 0.18 × 0.12	0.26 × 0.14 × 0.14
	Data Collection	
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
scan mode	ω	ω
θ range (deg)	$3.1 \leq \theta \leq 24.9$	$3.0 \leq \theta \leq 25.0$
index ranges	$0 \leq h \leq 13$	$0 \leq h \leq 18$
	$0 \leq k \leq 14$	$-18 \leq k \leq 0$
	$0 \leq l \leq 18$	$-16 \leq l \leq 14$
intens decay (%)	9	3
abs correctn	ψ scan	ψ scan
min rel transm factor	0.882	0.946
no. of measd reflns	2091	5544
no. of independent reflns	2091	5341
R_{int}, R_σ[a]	−, 0.0493	0.0357, 0.0756
no. of reflns with $I > 2\sigma(I)$	1524	3211
	Refinement	
no. of data/params	1524/250	3211/442
weights (a, b)[b]	0.040, 0.69	0.034, 1.09
goodness-of-fit $S(F^2)$[c]	1.080	1.082
$R(F)$[d]	0.0293	0.0351
$R_w(F^2)$[e]	0.0664	0.0709
largest difference, peak and hole (e Å^{-3})	0.450, −0.224	0.198, −0.256

[a] $R_{int} = \sum|F_o^2 - F_{mean}^2|/\sum|F_o^2|$; $R_\sigma = \sum|\sigma(F_o^2)|/\sum|F_o^2|$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters. [d] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Acknowledgment. We thank Antonio Cascio and Simona Guidotti for helping with the experiments using titrated MeLi, Marcello Colonnesi for the ^{1}H NMR spectra, Fabrizio Piemontesi for helpful discussions on the NMR assignments, and R. Selleri and D. Bedendo for the elemental analyses.

Supporting Information Available: 2D NMR spectra of *m*-**6a**, *m*-**6b**, and *m*-**6c** and tables of additional crystallographic data, final atomic coordinates, anisotropic displacement parameters, and full bond lengths and angles for *m*-**6a** and *m*-**6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010018Q

---

(33) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(34) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, C.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(35) Sheldrick, G. M. *SHELX97: program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

(36) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.