New syntheses of *ansa*-metallocenes or unbridged substituted metallocenes by the respective reductive dimerization of fulvenes with Group 4 metal divalent halides or with Group 4 metal dichloride dihydrides ☆

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Abstract

Two unprecedented syntheses of Group 4 metallocenes from 6-substituted fulvenes have been discovered and developed into high-yielding processes. In the first route the di-*n*-butylmetal dichlorides of Ti, Zr and Hf are generated in toluene suspensions of LiCl at $-78\,°C$ from the metal tetrachlorides and 2 equiv. of *n*-butyllithium. Bringing the $Bu^n_2MCl_2$ to $25\,°C$ and then heating at reflux for several hours gave complete conversion to slurries of MCl_2 (M = Ti, Zr, Hf). Heating such slurries of MCl_2 with 2 equiv. of 6-substituted or 6,6-disubstituted fulvenes gave high yields of *ansa*-metallocenes or substituted ethylene-bis(cyclopentadienyl)metallocene dichlorides (fulvenes: 6,6-dimethyl-, 6-phenyl-, 6-(1-naphthyl)-, 6-(9-anthryl)-). For 6-substituted fulvenes, both *racemic*- and *meso*-1,2-disubstituted ethylene-*ansa*-metallocene dichlorides are expected to form, but with M = Zr (or Ti), the actual *racemic*- to *meso-ansa*-metallocene dichloride ratios observed were: phenyl, 50:50; 1-naphthyl, 83:17; 9-anthryl, 100:0. Apparently for steric reasons 6,6-diphenylfulvene underwent no *ansa*-metallocene dichloride formation with $ZrCl_2$ but rather produced bis(diphenylmethyl(cyclopentadienyl))zirconium dichloride.

The second route to novel metallocenes involves generating $Bu^n_2MCl_2$ at $-78\,°C$ in toluene slurry, as in the foregoing method, but then adding 2 equiv. of the 6-substituted or 6,6-disubstituted fulvene immediately thereafter at $-78\,°C$. Except with $Bu^n_2TiCl_2$, warming the reaction mixture to $25\,°C$ and then further heating at $65°C$ cause a smooth bis-hydrometallation by transfer to occur, giving good to very good yields of bis(substituted cyclopentadienyl)metal dichlorides (M = Zn, Hf). The instability of $Bu^n_2TiCl_2$, even at $-78\,°C$, rapidly led to a mixture of $TiCl_2$ and $Bu^n_2TiCl_2$ and hence to a mixture of *ansa*-titanocene dichlorides and unbridged, bis(substituted cyclopentadienyl)titanocene dichlorides.

With a detailed study of the attainment and the stereochemistry of the formation of *ansa*-bridged complexes or metallocenes with acetophenone, benzylideneaniline and 6-arylfulvenes, a mechanistic model is developed involving either a three-membered metallo-cycle formed from MCl_2 or an "open-face sandwich" complex of the fulvene and MCl_2. Such intermediates offer a rational steric explanation for the observed stereochemistry of *ansa*-bridge C–C bond formation.

Finally, in comparative polymerizations of ethylene by such metallocenes, cocatalyzed by MAO, the superior catalytic activity of *ansa*-metallocenes in the order, Ti > Zr > Hf and of *ansa*-metallocenes over unbridged substituted metallocenes is attributed to the hyperconjugative stabilization afforded by the *ansa* σ C–C bond to the metallocenium cation at the active olefin-polymerization site.
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Keywords: Group 4 metals; Metallocenes; Fulvenes; Reductive dimerization; Hydrometallation
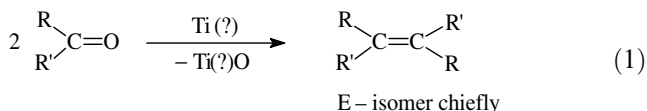
1. Introduction

Over the last decade we have been interested in applying the diverse chemical reactions of subvalent transition metal salts to the methodology of organic synthesis [1–4]. Our attention was especially drawn to the salts of Group 4 metals by the reports of the novel reductive dimerization of carbonyl derivatives to olefins by subvalent titanium reductants of unspecified oxidation state and composition (Eq. (1)).

$$2 \; \underset{R'}{\overset{R}{>}}C{=}O \quad \xrightarrow[-\,Ti(?)O]{Ti\,(?)} \quad \underset{R'}{\overset{R}{>}}C{=}C\underset{R}{\overset{R'}{<}} \qquad (1)$$

E – isomer chiefly

Such reports have issued independently from three different research groups where each utilized an empirical combination of a Ti(III) or Ti(IV) salt with a main-group metal or metal hydride [5–7]. This transformation, which has come to be termed the McMurry coupling after one of its discoverers, has found many valuable applications in organic synthesis [8–10]. But the use of such empirical reductants either in mechanistic studies of the McMurry coupling itself or in the synthesis of transition metal organometallics has up to now proved impractical. Hence, the recent discovery of a convenient, low-temperature route to the Group 4 dichlorides, MCl_2, as bis-THF solvates in THF, or as slurries with LiCl in toluene, has proved crucial for a systematic study of reductive dimerizations [2–4]. In a process termed alkylative reduction the MCl_4 is dialkylated with *n*-butyllithium at -78 °C to form intermediate **1**; warming **1** to 25 °C and above causes the reductive elimination of butyl groups (as butane and butene) and the high-yielding production of **2** (Eq. (2)).

$$\begin{array}{c} MCl_4 \\ M = Ti,\ Zr,\ Hf \end{array} \quad \xrightarrow[\substack{\text{THF solution} \\ \text{or} \\ \text{PhMe slurry}}]{2\ Bu^n Li,\ 78\,^\circ C} \quad \begin{array}{c} 2\ Bu^n_2 MCl_2 \\ \mathbf{1} \end{array}$$

$$\xrightarrow[-\,2\ Bu\cdot]{25\,^\circ C\ to\ 65\,^\circ C} \quad \begin{array}{c} MCl_2 \\ \mathbf{2} \end{array} \qquad (2)$$

in THF : *bis*-THF solvate

in PhMe : slurry with LiCl
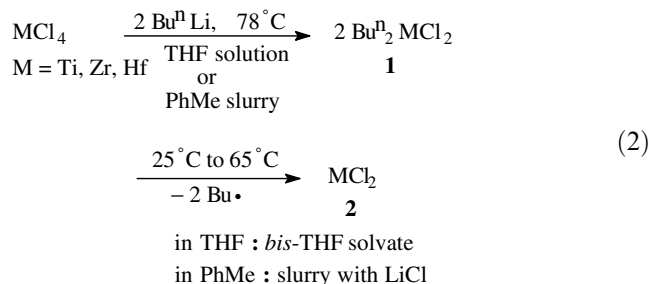
By the use of such reagents as **2** of well-defined valence and stoichiometry, considerable control could be exerted on both the extent and stereochemistry of the reductive coupling of ketones [2]. Acetophenone (**3**), for example, reacts with 2 equiv. of $TiCl_2$ in refluxing THF to give upon hydrolysis 83% of the *racemic*-2,3-diphenyl-2,3-butanediol (**7**) only, while with 4 equiv. of $TiCl_2$ the ketone gives 88% of olefin **8** as a 92:8 mixture of *E* and *Z* isomers. The exclusive formation of *racemic* **7** is consistent with the likely intermediacy of the three-membered ring **4** and the sterically controlled transition state **5** for the insertion of the second ketonic unit to form **6** (Scheme 1) [3,4].

Accordingly, the stereoselective reductive coupling of carbonyl derivatives by $TiCl_2$ depicted in Scheme 1 and the analogous reductive coupling subsequently observed with imines, such as *N*-benzylideneaniline (**9**), as mediated by $TiCl_2$ or $ZrCl_2$ (Scheme 2), have provided excellent model systems with which to assess steric effects in forming C–C bonds in such *ansa*-bridged systems, such as **6** and **10** and **11** (where the bridging O–CH_2–CH_2–O and NPh–CHPh–CHPh–NPh linkages can be envisaged as providing a "handle" (L. *ansa*) on the metal center). In all three systems these intermediate metallocycles can readily be hydrolyzed and the ratio of the resulting *racemic:meso* glycols (**7**) or diamines [(PhCH–NHPh)$_2$ from **10** and **11**] can be determined by ^{1}H NMR spectroscopy. Alternatively, the ratio of the metallocycles **10** and **11** can be estimated directly from their ^{1}H NMR spectra.
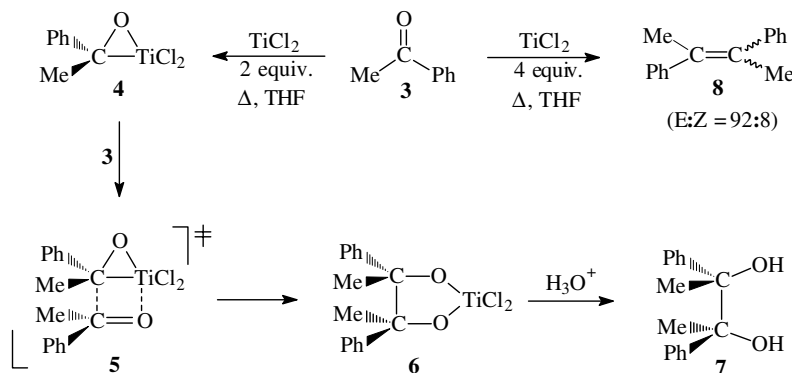
Scheme 1.

Scheme 2.
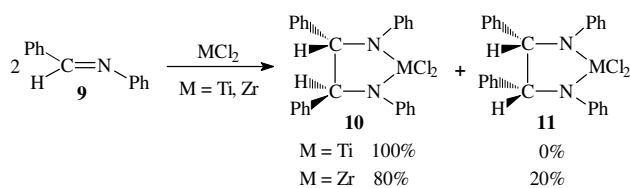
Because of the foregoing success with the efficient and stereoselective reductive dimerizations of both ketones and imines with Group 4 metal dichlorides, we were inspired to attempt a similar dimerization of 6-substituted fulvenes (**12**) with the hope of producing thereby novel *ansa*-metallocenes having some stereochemical preference for the substituents on the *ansa*-bridge (ratio of **13**:**14**) (Eq. (3)) [11,12]. Were such a dimerization to succeed, it would represent a radical departure from established routes to bridged or *ansa*-metallocenes and offer a new approach to stereochemical isomers of such systems as **13** and **14** [12].

$$(3)$$
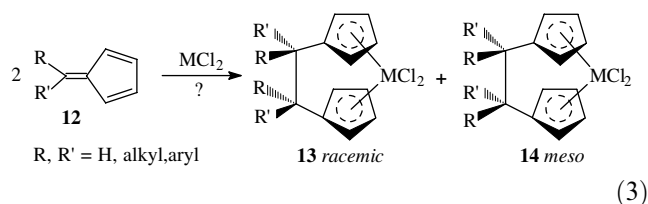
2. Results

2.1. Initial attempts with 6,6-dimethylfulvene (15) and Group 4 metal dihalides

The reactions of 6,6-dimethylfulvene (**15**) with the Group 4 metal dichlorides, $TiCl_2$ (**16**), $ZrCl_2$ (**17**) or $HfCl_2$ (**18**), were initially examined in THF, a solvent in which such salts are readily prepared at room temperature according to Eq. (2) (e.g., $TiCl_2 \cdot 2THF$) [11]. Although *ansa*-metallocene formation (**19–21**) was observed in refluxing THF, such reductive dimerization was slow (Scheme 3). Accordingly, individual slurries

in toluene of **16**, **17** and **18** admixed with LiCl by-product were prepared according to Eq. (2) and allowed to react with 2 equiv. of fulvene **15** at reflux. Although the fulvene was largely consumed and the *ansa*-metallocenes **19–21** formed in good to high yield, moderate to fair yields of unbridged substituted metallocenes (**25–27**) were also obtained. The source of the unbridged metallocenes **25–27** as side-products was traced to the presence of undecomposed Bu_2MCl_2 (**22–24**) in the MCl_2 formed in toluene at 25 °C. Clearly Bu_2MCl_2 performed a bis-hydrometallation by transfer of two moles of fulvene **15** [13].
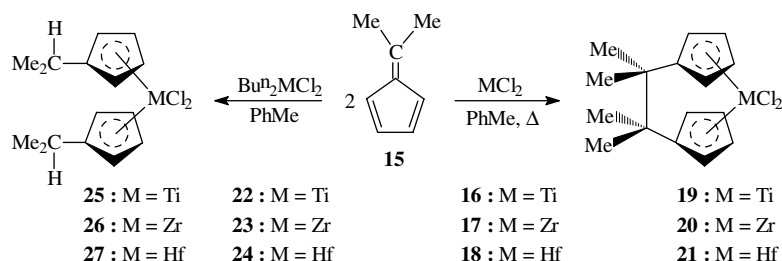
2.2. Preparation of tetramethylethylene-bis(cyclopentadienyl)metal dichlorides 19, 20 and 21

In light of this insight complete conversion of any Bu_2MCl_2 remaining in the toluene suspension to MCl_2 could be assured by heating the reagent at reflux for several hours. Then the reaction of such purified MCl_2 gave yields of over 90% for *ansa*-metallocenes **19–21**, as well as pure product by Soxhlet extraction or flash column chromatography in 80–85% yield.

2.3. Preparation of bis(isopropylcyclopentadienyl)metal dichlorides 25, 26 and 27

The discovery of the interesting bis-hydrozirconation by Bu_2MCl_2 leading to unbridged metallocenes **25–27** prompted us to attempt to maximize this course of reaction by generating the individual $Bu^n_2MCl_2$ at −78 °C in toluene (Eq. (1)) and immediately thereupon adding the 2 equiv. of 6,6-dimethylfulvene. The resulting reaction was warmed to 25 °C and then heated at 65 °C for several hours. This procedure was most effective in producing 75–85% yields of bis(isopropylcyclopentadienyl)-zirconium dichloride (**26**) and bis(isopropylcyclopentadienyl)hafnium dichloride (**27**), which products were shown to be free of the corresponding *ansa*-derivatives (**20** and **21**, respectively) by NMR criteria [13].

However, in the reaction of $TiCl_4$ with *n*-butyllithium in toluene at −78 °C, minutes after admixing the reagents the solution turned black, which signaled formation of $TiCl_2$. Even though the fulvene **15** was then

Scheme 3.

added at −78 °C, subsequent warming of the mixture to 25 °C and then to 65 °C led to an inseparable mixture of bis(isopropylcyclopentadienyl)titanium dichloride (**25**) and tetramethylethylene-bis(cyclopentadienyl)titanium dichloride (**19**), formed in approximately equal amounts.

2.4. ansa-Zirconocenes from 6-substituted fulvenes and zirconium dichloride

In order to investigate steric effects on the stereochemistry of *ansa*-bridge formation a trio of 6-arylfulvenes (**28–30**), where Ar = phenyl, 1-naphthyl or 9-anthryl, was subjected to reductive coupling by pure ZrCl$_2$ (free of Bu$^n_2$ZrCl$_2$, cf. supra). In each reaction *ansa*-bridge formation occurred in satisfactory yield but with different ratios of *racemic*- and *meso*-isomers (Scheme 4). A random ratio of *racemic:meso*-isomers was obtained with Ar equals phenyl (**28a**:**28b** = 50:50), a great preference with Ar equals 1-naphthyl (**29a**:**29b** = 83:17) and an exclusive formation of *racemic*-isomer (**30a**) with Ar = 9-anthryl.

In order to learn whether the covalent radii of Ti (132 pm) and Zr (145 pm) would have any effect on the *racemic–meso*-isomer ratio of *ansa*-bridged product, the reductive dimerization of 6-phenylfulvene (**28**) was also performed with pure TiCl$_2$. In this case, *ansa*-derivative formation also occurred efficiently in 75% yield but again the ratio of *racemic*- and *meso*-isomers obtained was 50:50 (analogous to **28a** and **28b**, with Zr replaced by Ti).

2.5. Structure assignments of the resulting ansa-metallocenes and the unbridged substituted metallocenes

The ultimate structure determination usually is achieved by an XRD analysis of a single crystal of a substance. Although not yet achieved with any of the present metallocenes, partly refined electron-diffraction data however were obtained on the major isomer resulting from the coupling of two units of 6-(1-naphthyl)fulvene by ZrCl$_2$. By plotting such data this 1,2-di(1-naphthyl)ethylene-bis(cyclopentadienyl)zirconium dichloride has been shown unambiguously to be the *racemic*-isomer (**29a**) and that furthermore two chlorine atoms are also bonded to the zirconium center. This structural evidence confirms the assignment made in Section 4.7.4. of the ratio of *racemic*-(**29a**) to *meso*-(**29b**) isomers formed by integration of the methine H singlets at 6.28 and 6.20 ppm in the ^{1}H NMR spectrum of the isomeric mixture.

To substantiate the presence of the MCl$_2$ group in these metallocenes, two representative metallocenes, tetramethylethylene-bis(cyclopentadienyl)titanium dichloride (**19**) and tetramethylethylene-bis(cyclopentadienyl)zirconium dichloride (**20**), were subjected to mass spectrometry by the electrospray technique with NaI. Both **19** and **20** yielded mass spectra having prominent peaks for parent ions containing ^{35}Cl$_2$, ^{35}Cl^{37}Cl and ^{37}Cl$_2$ mass contributions, respectively, in the expected intensity ratios. Therefore, based on the XRD of **29a** and the MS data for **19** and **20**, we can be confident that all these metallocenes resulting from the interaction of 2 equiv. of a fulvene with 1 equiv. of either MCl$_2$ or Bu$^n_2$MCl$_2$ contain the atomic grouping of MCl$_2$ (details in Sections 4.3, 4.6.1 and 4.7.1).

Further structural specification for the individual metallocenes is completely corroborated by NMR spectroscopic data (cf. Section 4.3): (1) the individual ^{1}H NMR spectrum has the proper integral ratio of protons, with each proton having the expected chemical shift and proton–proton coupling; and (2) the individual ^{13}C NMR spectrum of the pure metallocene or isomeric mixture displays exactly the proper number of singlets with the expected chemical shifts; moreover, the ^{13}C NMR spectrum in a DEPT experiment shows the expected number of quaternary C and methine C (C–H) centers.

On the basis of the foregoing array of instrumental analyses we judge that the structures assigned to these novel metallocenes are dependably correct.
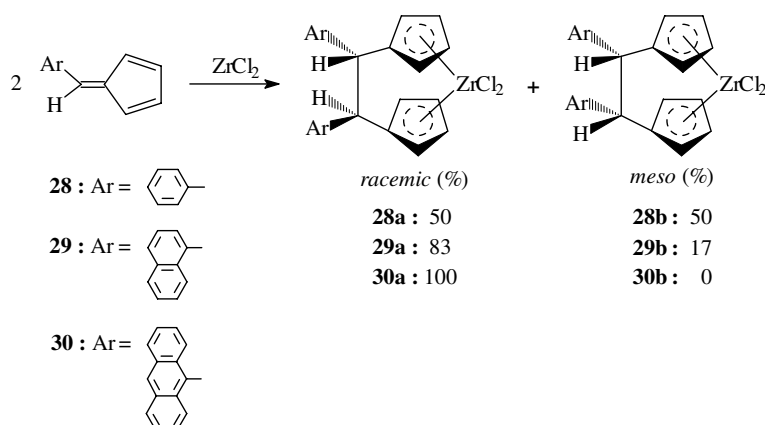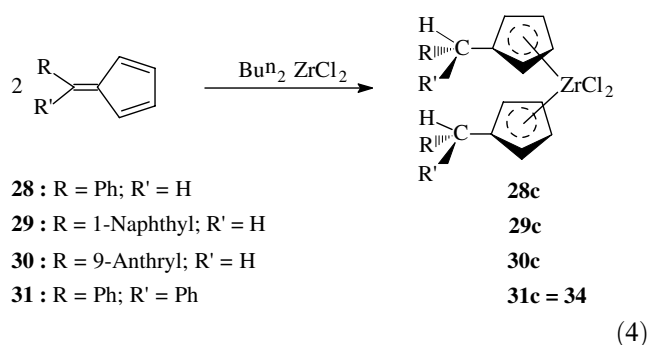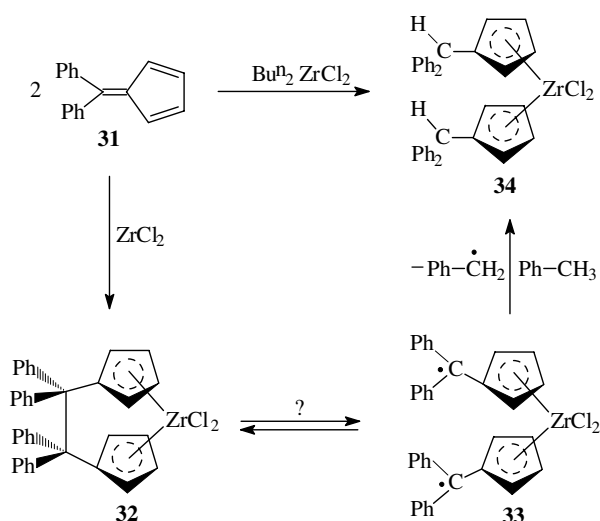

Scheme 4.

2.6. Attempted synthesis of tetraphenylethylene-bis(cyclopentadienyl)zirconium dichloride (32) and the generalized hydrozirconation of fulvenes

Since 6,6-dimethylfulvene (**15**) undergoes efficient reductive dimerization to *ansa*-derivatives **19**, **20** and **21** with the respective metal dichloride, we were curious to determine whether 6,6-diphenylfulvene (**31**) would react similarly (Scheme 5). To an organic chemist, *ansa*-product **32** would have a structure closely similar to the unknown hexaphenylethane, $Ph_3C–CPh_3$, which if fleetingly formed would be expected rapidly to dissociate into stable trityl radicals [14]. When reductive coupling of **31** with $ZrCl_2$ was attempted, no *ansa*-derivative was isolable.

Instead, substituted zirconocene **34** was obtained in 25% yield. Because a number of 6-substituted fulvenes, such as **28**, **29**, **30** and **31**, undergo satisfactory hydrozirconation with Bu^n_2ZrCl (Eq. (4)), an authentic sample of **34**, prepared in an unambiguous manner, was available for spectral comparison and positive identification of product **34** resulting from the attempted synthesis of **32**.

28 : R = Ph; R' = H   **28c**
29 : R = 1-Naphthyl; R' = H   **29c**
30 : R = 9-Anthryl; R' = H   **30c**
31 : R = Ph; R' = Ph   **31c = 34**

(4)

Accordingly, it is reasonable to conclude that the F-strain [15] imposed on the *ansa*-C–C bond of **32** by the near eclipsing of neighboring phenyl groups causes
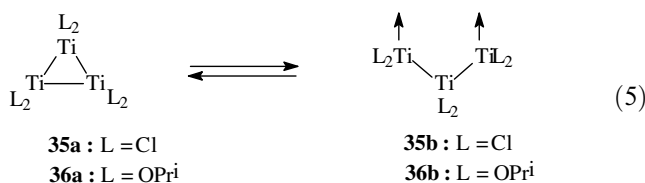
Scheme 5.

dissociation of **32** into stabilized biradical **33**. Eventual H-atom abstraction by **33** from toluene would result in product **34**.

3. Discussion

3.1. Mechanism of the reductive dimerization of the model system, benzylideneaniline (9), with Group 4 metal dichlorides

In considering the reactivity of $TiCl_2$ (**16**), $ZrCl_2$ (**17**) or $HfCl_2$ (**18**) toward a carbonyl (Scheme 1), an imine (Scheme 2) or a fulvene substrate (Eq. (3)), it is important to realize that the monomeric MCl_2 unit delivered must first be detached from a highly associated aggregate $[MCl_2]_x$. For unsolvated MCl_2 generated in toluene such an aggregate could resemble the layer lattice of $TiCl_2$, for example, where infinite layers of Ti atoms are sandwiched between two layers of Cl atoms. But the MCl_2 formed in Eq. (2) clearly can exist in much smaller, oligomeric aggregates. In THF solution the complex $TiCl_2 \cdot 2THF$ (**35**) has been shown to form [2]. Although the degree of association of such a complex is not known, its ready solution in toluene would not be consistent with a polymeric aggregate. Furthermore, such a solution of $TiCl_2$ is diamagnetic and does not show an EPR signal even at low temperatures.
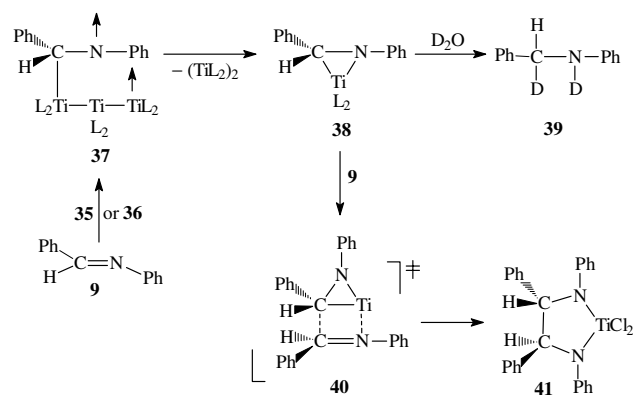
Fortunately, information on the state of aggregation of titanium(II) salts has been obtained from a study of the properties of titanium(II) isopropoxide (**36b**), which can be prepared analogous to $TiCl_2$ (Eq. (2)), by treating $Ti(OPr^i)_4$ with 2 equiv. of *n*-butyllithium. Even when prepared in THF, complex **36b** can be completely freed of THF in vacuo and redissolved in toluene. Such solutions of **36b** exhibit a strong EPR signal indicative of a biradical and hence the presence of two unpaired electrons. The strength of the signal coupling is best in accord with the unpaired electrons being on titanium centers located 1,3 to each other (**36b**), rather than on vicinal or the same Ti center(s) (Eq. (5)) [16,17]. The bulky nature of the isopropoxy ligands may strain the three-membered ring (**36a**) and favor the biradical **36b**. With much smaller chloro ligands the diamagnetic ring in **35a** should be much less strained. There would likely be sufficient room about each Ti atom in **35a** to accommodate two THF units and thereby permit octahedral coordination.

35a : L = Cl   **35b** : L = Cl
36a : L = OPr^i **36b** : L = OPr^i

(5)

The process of forming a three-membered ring or epimetallated product, like **4** for carbonyl substrates or **38** for imines such as **9**, could be viewed as in Scheme 6. Attack of **35** (or **36**) on **9** would lead to biradical **37**, which would close the most rapidly to **38** by intramolecular radical displacement [18]. The presence of **38** in such reductive coupling was corroborated by work-up of the reaction mixture with D_2O and finding the N-phenylbenzylamine dideuterated (**39**).

The observed stereochemistry of reductive coupling can be readily understood by postulating the insertion of a second **9** into the C–Ti bond of **38** via transition state **40** where the phenyl groups would minimize steric repulsion by forming the *racemic* dimer **41** [19]. With little modification the less stereoselective coupling of **9** by $ZrCl_2$ (*racemic:meso* = 80:20) can follow from the longer C–M bond in the Zr intermediate analogous to **38**. The larger covalent radius of Zr over Ti, 145 versus 132 pm, would mean that the two carbon centers would be farther apart in the transition state (similar to **40**) and thus not as sensitive to the steric effects of the phenyl groups.

The only remaining puzzling observation is that made in the attempted transfer-hydrozirconation of **9** by $Bu^n_2ZrCl_2$ (**23**).[1] From our experience with other substrates in hydrozirconation [13], the expected major product should have been N-phenylbenzylamine (**43**), formed via **42**. Although **43** was in fact obtained in 49% yield, yet comparable amounts (51%) of an 80:20 mixture of *racemic*- and *meso*-1,2-dianilinoethanes (**47** and **48**) were also formed, products expected to arise from the reductive coupling of **9** by $ZrCl_2$ (cf. supra). However, at the temperature of reaction, 25 °C, $ZrCl_2$ had not yet formed from the decomposition of

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[1] The generalized reactions discussed in this section, "transfer-hydrometallation" and "transfer-epimetallation", as well as their metal-specific counterparts, "transfer-epititanation, transfer-epizirconation, transfer-hydrotitanation and transfer-hydrozirconation, are reactions that have been studied and established in previous publications of our research group. Transfer-hydrozirconation as described in [13] refers to the transfer of zirconium dichloride dihydride from di-n-butylzirconium dichloride to an unsaturated substrate C = E (carbonyl, imine or fulvene) with release of 1-butene:

$$2 \ \text{>C=E} + Bu^n_2ZrCl_2 \longrightarrow 2\,(H-\overset{|}{\underset{|}{C}}-E-)_2ZrCl_2 + CH_3CH_2-CH=CH_2$$

Analogously, transfer-epizirconation as described in [20] and [21] refers to the transfer of zirconium dichloride from di-n-butylzirconium dichloride to C = E (carbonyl, imine or fulvene) with release of two butyl radicals (or as butane and 1-butene):

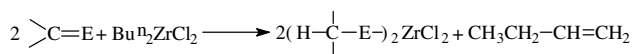$$\text{>C=E} + Bu^n_2ZrCl_2 \longrightarrow -\overset{|}{C}-E + 2CH_3CH_2CH_2\dot{C}H_2$$

Scheme 6.

$Bu^n_2ZrCl_2$ in toluene. We are forced to conclude therefore that epimetallated zirconium intermediate **44** has been formed from **23** by the process of the transfer-epimetallation of **9** (Scheme 7).[1] The generation of the *racemic*- and *meso*-metallocycles (**45** and **46**) would ensue as with the titanium analog (**38** → **41**, Scheme 6). Transfer-epititanation of a wide variety of unsaturated substrates by $Bu^n_2TiCl_2$ (**22**) has been amply demonstrated to be an important process in the functionalization of alkenes and alkynes [20,21], in the Kulinkovich cyclopropanol synthesis [22] and in olefin polymerization [23,24].

3.2. Transfer-hydrometallation of fulvenes and the synthesis of unbridged substituted bis(cyclopentadienyl)metal dichlorides
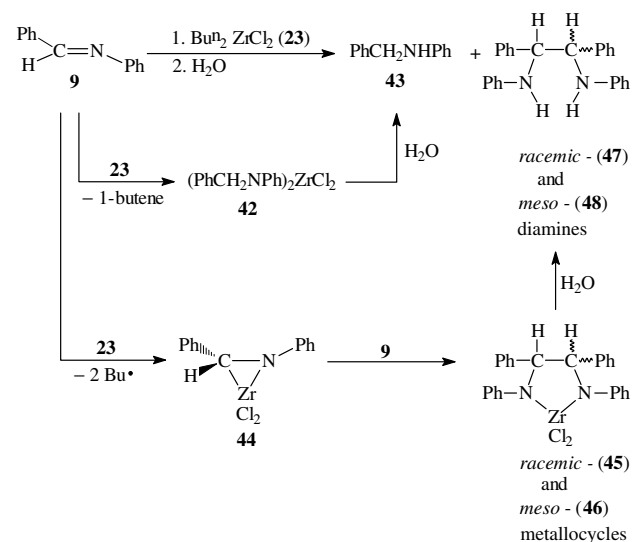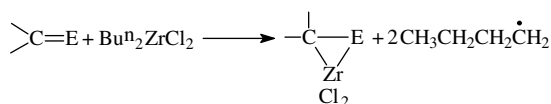
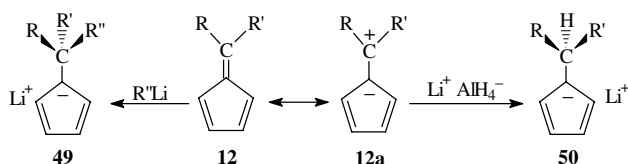### 3.2.1. Chemical and physical properties of fulvenes (12)

Fulvenes (**12**) are colored nonaromatic hydrocarbons possessing a dipole moment and a high degree of chemical reactivity by virtue of their uneven π-electron
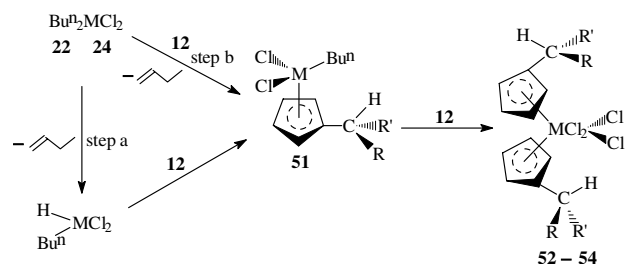
Scheme 7.

Scheme 8.

distribution (**12a** and its resonance structures). Especially for our present purposes, the long-known addition reactions of fulvenes with organolithium reagents (RLi) [25] and with LiAlH$_4$ [26] are especially relevant (Scheme 8). In the formation of adducts **49** and **50** the regioselectivity is driven by the aromatic stabilization attained with the formation of the cyclopentadienyl anion.

3.2.2. Transfer-hydrometallation of fulvenes

Whether the elimination of 1-butene from Bu$^n_2$MCl$_2$ (**22–24**) *precedes* the interaction of Bu$^n_2$MCl$_2$ with the fulvene to produce H$_2$MCl$_2$ (step a) or *accompanies* such an interaction with the fulvene (step b) cannot be decided at present (Scheme 9). Either path produces the "open-face sandwich" (**51**). π-Complexation of **51** with a second **12**, so that the RR′HC-groups on the ring are *anti* to each other, would yield the final metallocenes (**52–54**) with minimal steric hindrance.
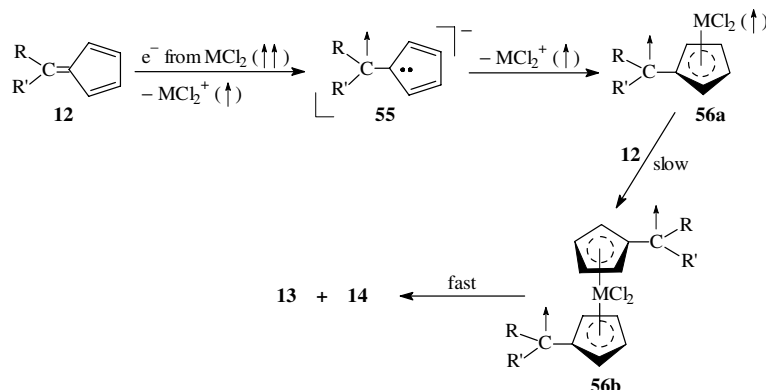

Scheme 9.

3.3. Reductive coupling of fulvenes by union with biradicals

Analogous to the mechanistic insight gained from the reductive dimerization of ketones or of benzylideneaniline by Group 4 metal(II) dichlorides (Schemes 1 and 2), we propose the analogous biradical "open-face sandwich" **56** (Scheme 10), which could be formed via radical-anion **55** by SET from biradical MCl$_2$(↑↑). Interaction of **56a** with a second fulvene **12** would surely be sensitive to steric factors during the formation of the *ansa*-C–C bond. But if the rate of formation of the final *ansa*-complexes **13** and **14** is determined by the complexation of biradical **56a** with a second fulvene **12** to form **56b**, then the subsequent C–C bonding would be fast and steric hindrance would have only an attenuated effect on the *ansa*-racemic- and *meso*-isomeric ratio. Whether R = phenyl and R′ = H or whether M = Ti or Zr in **56b** would then have no large steric effect. Only when R = 1-naphthyl or 9-anthryl and R′ = H would a steric effect become unavoidable. This effect may have nothing to do with steric bias in the relatively rapid *ansa*-C–C bond formation but rather in the rate of complexation of **56a** with the prochiral π-electron cloud surface of the second fulvene.

3.4. Comparative polymerization of ethylene by ansa-metallocene and unbridged metallocene procatalysts with MAO cocatalysis

A complete survey of all the *ansa*- and unbridged catalysts synthesizable from fulvenes has not yet been made. However, the preliminary results obtained thus far and presented in Table 1 permit us to propose three valuable trends in reactivity: first, *ansa*-metallocenes are much more active polymerization catalysts than their unbridged counterparts: for Ti, consider runs 1, 2 and 3; for Zr, compare runs 4, 5 and 6 as well as runs 7 and 9; second, the normal order of polymerization activity for unbridged metallocenes, Zr > Ti > Hf, is changed


Scheme 10.

Table 1
Comparative polymerization of ethylene with metallocene procatalysts and MAO cocatalysts

Run	Metallocene	Polymerization activity[a] (g PE/g M h atm)
1	Tetramethylethylene-bis(cyclopentadienyl)titanium dichloride (**19**)	2640
2	Titanocene dichloride	1100
3	*racemic-* and *meso*-1,2-Diphenylethylene-*bis*(cyclopentadienyl)titanium dichloride, 1:1 mixture (titanium analogue of **28a** and **28b**)	3170
4	*racemic-* and *meso*-1,2-(Diphenylethylene-*bis*(cyclopenta-dienyl)zirconium dichloride (**28a** and **28b**), 1:1 mixture	360
5	Bis(benzylcylcopentadienyl)zirconium dichloride (**28c**)	242
6	Bis[(diphenylmethyl)cyclopentadienyl)]zirconium dichloride (**34**)	62
7	Bis[(1-naphthylmethyl)cyclopentadienyl)]zirconium dichloride (**29c**)	126
8	1,2-Di-[(1-naphthylethylene)-cyclopentadienyl]titanium dichloride (titanium analogue of **29a**)	313
9	1,2-Di-[(1-naphthylethylene)-cyclopentadienyl]zirconium dichloride (83:17 mixture of **29a** and **29b**)	52
10	Bis(isopropylcyclopentadienyl)hafnium dichloride	182

[a] All runs were conducted in toluene at ambient temperature with uncontrolled exotherm employing 0.2–1.0 mmol of metallocene and 50 equiv. of MAO. Comparisons of polymerization activity are reported per grams of metal in the catalyst and are measured for polymerizations proceeding under a constant pressure of ethylene, under the spontaneous exotherm of polymerization and in a reaction mixture turning rapidly from homogeneous to heterogeneous. Therefore, this empirical measure of activity, widely used in industry, cannot be expected to rank polymerization rates of catalysts in an absolute and accurate series. But as employed here, such measurements can readily distinguish among catalysts of high activity, intermediate activity and low activity. Finally, it should be noted that the accurate measurement of initial polymerization rates (the only reliable measure of intrinsic catalyst activity) is a most difficult procedure to carry out in a reproducible and reliable manner (cf. Fischer, D. "Untersuchungen zur Propenpolymerisation an Homogenen Zirconocen/Methylaluminoxan Ziegler-Natta Katalysatoren", *Doctoral Dissertation*, Albert-Ludwig University, Freiburg (Breisgau), Germany, 1992.

for *ansa*-metallocenes, where Ti > Zr > Hf; and third, unbridged substituted zirconocenes have depressed activities, as the steric size of the cyclopentadienyl ring substituent increases: note runs 5, 6 and 7.

The usual reason for the lesser polymerization activity of unbridged titanocenes over analogous zirconocenes is the lower kinetic stability of the titanocenium cation **57**, which has been proposed as the active polymerization site [27]. The greater reactivity for *ansa*-titanocenes over *ansa*-zirconocenes or *ansa*-hafnocenes, therefore, may arise from the greater stabilization of cation **58**. A source of such stabilization of the titanium cation in **58** could be the σ-bond hyperconjugation provided to the backside of the empty sp³-hybridized orbital of the cationic Ti center (**58**).[2] Since such stabilization would be more important in *ansa*-titanocenes than in *ansa*-zirconocenes (better orbital-energy match and shorter distance between the metal center and the σ-electrons of the C–C bond), *ansa*-titanocenes should show a larger increase in polymerization activity than *ansa*-zirconocenes.

57 **58** **59a** **59b**
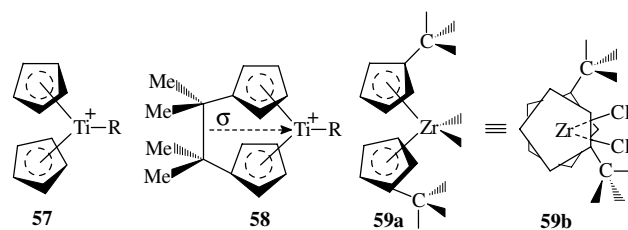
Finally, the reduced polymerization activity of bis(substituted cyclopentadienyl)zirconium dichlorides (with substituents of PhCh₂-, Ph₂CH- and 1-naphthylmethyl (runs 5, 6 and 7)) can be attributed to the favoring of those conformers where the substituents project out of the wider gap between the tilted rings (**59a** and **59b**). Such substituents thereby impede the interaction of such zirconocenes with the MAO cocatalyst and the approach of the ethylene to the zirconocenium cation in the active site.

4. Experimental

4.1. Starting reagents and solvents

Cyclopentadiene was freshly cracked from commercially available dicyclopentadiene and distilled under an atmosphere of dry argon directly before use. 6,6-Dimethylfulvene, 6,6-diphenylfulvene, 1-naphthaldehyde, 9-anthraldehyde, benzylideneaniline, titanium(IV), zirconium(IV) and hafnium(IV) chlorides and *n*-butyllithium in hexane were obtained from

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[2] Such σ-bond hyperconjugation is widely recognized as stabilizing carbenion ions β to silicon as in R₃Si–CH₂–CH₂⁺ (W. Hanstein, H.J. Berwin, T.G. Trayler, J. Am. Chem. Soc. 92 (1970) 829) and in promoting the facile ring-opening of the cyclopropyl carbenium ion to the allyl cation (S.F. Cristol, R.M. Segueira, C.H. DePuy, J. Am. Chem. Soc. 87 (1965) 4007). Since the ansa-C–C bond is closer to the titanium cation, σ-bond hyperconjugation is more likely to be the operative effect than some inductive release of electron density from the *ansa*-carbon centers to the titanium centers but operative through the π-bonding of the rings.

commercial sources in at least 98% purity and were used directly. All solvents employed with organometallic reagents or anhydrous metal salts were dried and distilled from a sodium metal–benzophenone ketyl mixture prior to use [28].

4.2. General procedures

All procedures involving the purification of reaction solvents, the individual preparation of Group 4 metal dialkylmetal dichlorides, Group 4 metal dichlorides and their subsequent reactions leading to metallocenes and their purification were conducted under an atmosphere of anhydrous, oxygen-free argon. The drying and deoxygenation of argon were carried out by means of a purification apparatus previously described [28]. Nonhydrolytic workup of certain reactions to recover the organic ligand was achieved with 3 N aqueous HCl.

4.3. Instrumentation and analysis

After purification the reaction products were routinely subjected to IR and ^{1}H and ^{13}C NMR spectroscopic and, in some cases, mass spectrometric analysis. Since such data served to corroborate the structures assigned to the metallocenes satisfactorily, elemental analyses were considered unnecessary. The IR spectra were recorded with a Perkin–Elmer instrument (model 457) and samples were measured under argon either as mineral oil mulls or as KBr films. The NMR spectra (^{1}H and ^{13}C) were recorded under argon with a Bruker spectrometer (model EM-360) and tetramethylsilane (Me$_4$Si) was used as the internal standard. The chemical shifts reported are expressed on the δ scale in parts per million (ppm) from the Me$_4$Si reference signal. No data on J_{HH} coupling constants exhibited in the ^{1}H NMR spectra have been included because such values are in all cases in the expected range and unexceptional. However, it is worth noting that DEPT measurements in the ^{13}C NMR spectra reported here were able to distinguish quaternary carbon centers (C) from methine–carbon (C–H) centers. The latter but not the former carbon signals underwent resonance with inversion of signal. The number of quaternary C signals and methine–carbon signals observed fit the assigned structure in every case.

The gas chromatographic analyses were carried out with a Hewlett–Packard instrument (model 5880) provided with a 2-m OV-101 packed column or with a Hewlett–Packard instrument (model 4890) having a 30 m SE-30 capillary column. Melting points were determined on a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected.

The mass spectral measurements were performed at the Mass Spectrometry & Proteomics Facility at the Ohio State University and employed a Micromass ESI-Tof™ mass spectrometer (Micromass, Wythensh-

awe, UK) equipped with an orthogonal electrospray source (Z spray) operated in a positive ion mode. The samples were prepared in a solution containing acidified methanol and sodium iodide as an internal mass standard.

4.4. Preparation of Group 4 metal dichlorides

4.4.1. Titanium dichloride (16)

The preparation of titanium dichloride in THF and its isolation as the LiCl-free and analytically supported complex, TiCl$_2 \cdot$ 2THF (35), has been described elsewhere [2]. The complex 35 was analyzed after removal of the THF in vacuo and found to have retained two moles of solvated THF per Ti unit. However, the solvate-free titanium dichloride (16), prepared in hydrocarbon slurry with LiCl, has proved more effective in the following reductive dimerizations of fulvenes. A colorless solution of TiCl$_4$ (5.5 mL, 5.5 mmol) in 20 mL of THF was prepared at −78 °C to avoid cleavage of the THF. Then 6.9 mL of *n*-butyllithium 1.6 M in hexane (11 mmol) was added dropwise at −78 °C causing the formation of a red-brown solution. The dark red solution was brought to RT, stirred for 12 h and then heated at reflux for 3 h. After solvent removal in vacuo the dark residue was diluted with 30 mL of toluene to give a black solution of 16 (5.5 mmol) with suspended LiCl.

4.4.2. Zirconium dichloride (17)

Zirconium dichloride can likewise be prepared in THF and isolated as the LiCl-free and analytically pure complex, ZrCl$_2 \cdot$ 2THF (17). Again, here the complex 17 in toluene slurried with LiCl has proved more effective in *ansa*-metallocene preparations. Thus a clear solution of ZrCl$_4$ (0.20 g, 0.86 mmol), prepared in 20 mL of THF at −78 °C, was treated with 1.1 mL of 1.6 M *n*-butyllithium in hexane (1.72 mmol). The dark red solution was brought to RT, stirred for 12 h and then heated at reflux for 3 h. After solvent removal in vacuo the black residue was treated with 20 mL of toluene to give a black solution of 17 (0.86 mmol) with suspended LiCl.

In a similar manner a suspension of ZrCl$_2$ (5.89 mmol) and LiCl in hexane alone was prepared from 5.89 mmol of ZrCl$_4$ and 11.8 mmol of *n*-butyllithium in a total of 40 mL of hexane.

4.4.3. Hafnium dichloride (18)

Hafnium dichloride (18) prepared in THF appears to form the solvate, HfCl$_2 \cdot$ 2THF, as well but the solvate is not stable upon removal of the THF in vacuo. Thus a clear solution of HfCl$_4$ (3.73 g, 11.6 mmol) in 80 mL of THF at −78 °C was treated with 15 mL of 1.6 M *n*-butyllithium (23.2 mmol). The pale yellow solution was then stirred for 12 h at RT and then heated at reflux for 5 h. The dark brown solution was freed of solvent in

vacuo and the residue of $HfCl_2$ (**18**) and LiCl was suspended in 60 mL of toluene.

4.5. Synthesis of fulvenes

4.5.1. 6-Phenylfulvene (28)

To a solution of freshly distilled benzaldehyde (distilled under argon, 0.40 mL, 4.0 mmol) and freshly cracked cyclopentadiene (0.82 mL, 10 mmol) in 4.0 mL of methanol was added 0.5 mL of pyrrolidine. After 15-min stirring a 0.4 mL-portion of acetic acid was added and the solution stirred for a further 15 min. A mixture of ether and water was added and the organic layer separated and dried over solid $MgSO_4$. Ether removal from the organic layer left pure 6-phenylfulvene (**28**), 584 mg (89%) of dark orange crystals, mp. 33–34 °C. The reaction could be run on a 20-fold scale with little decrease in yield. *Anal*. Calc. for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.65; H, 6.49%.

^1H NMR ($CDCl_3$): 7.59–9.56 (m, 2H), 7.42–7.30 (m, 3H), 7.20 (s, 1H), 6.71–6.64 (m, 2H), 6.52–6.49 (m, 1H), 6.33–6.31 (m, 1H). ^{13}C NMR ($CDCl_3$): 145.3, 138.2, 136.8, 136.4, 130.8, 130.7, 129.0, 128.6, 127.2, 120.3.

4.5.2. 6-(1-Naphthyl)fulvene (29)

To a solution of 1-naphthaldehyde (9.1 g, 58.2 mmol) in 50 mL of methanol was added the fresh cyclopentadiene (12.0 mL, 0.146 mol). After 15-min stirring 7.30 mL of pyrrolidine was introduced, causing the mixture to turn orange during 4 h-stirring at RT. Addition of 5.3 mL of acetic acid, further stirring for 20 min and dilution of the reaction mixture with water and ether yielded a biphasic system. The organic layer was separated, dried over $MgSO_4$ and freed of solvent to provide the crude **29**. Its purification by flash column chromatography on silica gel with a hexane–ethyl acetate eluent gave orange crystals of **29** (9.93 g, 84%), m.p. 52–54 °C.

Anal. Calc. for $C_{16}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.84; H, 6.18%.

^1H NMR ($CDCl_3$): 8.11 (d, 1H), 7.90 (t, 3H), 7.76 (d, 1H), 7.53 (t, 3H), 6.69 (d, 2H), 6.56 (s, 1H), 6.50 (s, 1H). ^{13}C NMR ($CDCl_3$): 147.1, 135.7, 134.9, 133.8, 133.4, 132.0, 131.8, 130.0, 129.4, 128.6, 126.6, 126.2, 126.1, 125.4, 124.4, 121.5.

4.5.3. 6-(9-Anthryl)fulvene (30)

In a procedure analogous to the foregoing, a solution of 9-anthraldehyde (15.0 g, 82.8 mmol) and cyclopentadiene (15.0 mL, 0.182 mol) in 75 mL of methanol was treated with 9.1 mL of pyrrolidine and worked up with water and ether. The crude **30** was purified by flash column chromatography to give orange crystals of **30** (12.6 g, 68%), m.p. 100–101 °C.

Anal. Calc. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.22; H, 5.60%.

^1H NMR ($CDCl_3$): 8.5 (s, 1H), 8.16–8.13 (m, 2H), 8.06–8.01 (m, 2H), 7.94 (s, 1H), 7.51–7.44 (m, 4H), 6.65–6.60 (m, 2H), 6.52–6.49 (m, 1H), 5.89 (d, 1H). ^{13}C NMR ($CDCl_3$): 150.3, 134.5, 134.3, 132.4, 131.2, 130.6, 130.1, 128.5, 127.7, 126.3, 125.8, 125.4, 125.3, 122.5.

4.6. ansa-Metallocene dichlorides of titanium

4.6.1. From 6,6-dimethylfulvene (15)

To a black solution of 10.0 mmol of $TiCl_2 \cdot 2THF$ (**16**) in 30 mL of toluene (cf. Section 4.4.1) were added 20.0 mmol (2.41 mL) of 6,6-dimethylfulvene (**15**) and the resulting mixture heated at reflux for 6 h. Thereupon, the suspension was filtered and the black solid was washed twice with chloroform. The filtrate was freed of volatiles in vacuo to give red-brown **19**, spectrally quite pure, consistently in >90% yield in duplicate runs. Alternatively, the solvent was removed in vacuo, and the solid residue transferred under argon to the thimble of a Soxhlet extraction apparatus. Extraction with hexane over 20 h gave a hexane solution of 1,1,2,2-tetramethylethylene-bis(cyclopentadienyl)titanium dichloride (**19**). By solvent removal, washing with cold pentane and vacuum-drying, product **19** was isolated as a reddish brown solid (2.81 g, 85%). Further purification could be achieved by flash column chromatography with a gradient of hexane–chloroform, starting from pure hexane and ranging to pure chloroform. This metallocene is oxygen- and moisture-sensitive, turning yellowish green in moist air. ^1H NMR ($CDCl_3$): 6.90 (t, 4H), 6.25 (t, 4H), 1.45 (s, 12H). ^{13}C NMR ($CDCl_3$): 145.5, 128.5, 112.5, 45.5, 28.0. MS (electrospray in ESI with N_2 gas; capillary voltage 3000 V, source temperature 110 °C, cone voltage 55 V) prominent parent ion + Na peaks (intensity) at 297 (10), 299 (5), 301 (1), corresponding to the theoretical masses and intensities of $C_{12}H_{12}^{35}Cl_2TiNa$, $C_{12}C_{12}^{35}Cl^{37}ClTiNa$ and $C_{12}C_{12}^{37}Cl_2TiNa$, respectively.

4.6.2. From 6-phenylfulvene (28)

In a similar manner, a solution of 6-phenylfulvene (**28**, 1.54 g, 10.0 mmol) and a solution slurry of $TiCl_2 \cdot 2THF$ (**16**, 5.0 mmol) with the suspended LiCl in 50 mL of toluene were heated at reflux for 6 h. The reaction suspension was filtered and the black filter cake washed twice with chloroform. Removing volatiles from the filtrate gave >90% of a spectrally pure 1:1 mixture of *meso*- and *racemic*-isomers. Alternatively, analogous Soxhlet extraction and subsequent workup provided 85% of a brown-red 1:1 mixture of the *meso-ansa*- and the *racemic-ansa*-isomers of 1,2-diphenylethylene-bis(cyclopentadienyl)titanium dichloride. The conclusion that both isomers are present in such product is drawn from the ^{13}C NMR spectrum, which displays 18 sp^2-carbon and 2 sp^3-carbon

(methine carbon) signals. The ^{1}H NMR signals also come in signal packets of 10:4:4:1:1, consistent with the presence of both *meso-* and *racemic-*isomers. The equal intensity of the methine singlets at 4.85 and 4.35 ppm confirm the presence of a 1:1 mixture. The signal at 4.35 ppm is assigned to the *racemic-*isomer, since its methine H should be shielded by the π-cloud of the adjacent phenyl group. The *meso-* and *racemic-* isomers could be separated by flash column chromatography with a hexane–chloroform gradient. ^{1}H NMR (CDCl₃): 7.16–6.80 (m, 10H), 5.88–5.85 (m, 4H), 5.77–5.76 (m, 4H), 4.85 (s, 1H), 4.35 (s, 1H). ^{13}C NMR (CDCl₃): 140.8, 139.2, 137.4, 136.9, 134.0, 130.6, 129.3, 129.1, 128.8, 128.5, 127.8, 127.5, 126.9, 126.9, 117.7, 116.7, 113.2, 109.4, 53.9, 51.1.

The greater thermal lability and reactivity of the other *ansa*-metallocenes made their isolation more difficult, so a more extensive study of *ansa*-metallocenes was undertaken with zirconium analogues.

4.7. ansa-Metallocene dichlorides of zirconium

4.7.1. From 6,6-dimethylfulvene (15)

A solution of 6,6-dimethylfulvene (**15**, 1.20 mL, 10 mmol) in 60 mL of toluene was combined with a solution slurry of ZrCl2 (**17**, 5.0 mmol, cf. Section 4.4.2.) and LiCl in 50 mL of toluene and the mixture stirred at reflux for 8 h. Filtration of the reaction mixture and washing of the filtered cake twice with chloroform gave an extract, from which volatiles were removed in vacuo. The off-white **20** was spectrally pure and isolated in >90% yield. Alternatively, nonhydrolytic workup and Soxhlet extraction provided 1.31 g of colorless tetramethylene-bis(cyclopentadienyl)zirconium dichloride (**20**) in 70% yield. ^{1}H NMR (CDCl₃): 6.70 (t, 4H), 6.20 (t, 4H), 1.45 (s, 12H). ^{13}C NMR (CDCl₃): 143.5, 123.3, 108.8, 45.2, 28.4. MS (electrospray in ESI with N₂ gas; capillary voltage 3000 V, source temperature 110 °C, cone voltage 55 V) the three most prominent parent ion + Na peaks (intensity) at 339 (1.5), 341 (1.5) and 343 (1.0), corresponding to the theoretical intensities of $C_{12}C_{12}{}^{35}Cl_2ZrNa$, $C_{12}C_{12}{}^{35}Cl^{37}ClZrNa$ and $C_{12}C_{12}{}^{37}Cl_2ZrNa$, respectively.

4.7.2. From 6,6-diphenylfulvene (31), (attempted)

Heating a suspension of ZrCl₂ (**17**, 9.5 mmol) and LiCl with a solution of 6,6-diphenylfulvene (**31**, 2.20 g, 9.5 mmol) in 60 mL of toluene for 18 h gave upon usual nonhydrolytic workup an off-white, air- and moisture-sensitive solid in about 25% yield that proved to be bis(diphenylmethyl(cyclopentadienyl))zirconium dichloride (**34**), rather than the expected *ansa*-metallocene **32**. The presence of a singlet signal for the methine hydrogen at 5.64 ppm provided decisive evidence against the presence of **32**. Moreover, the straightforward hydrozirconative coupling of **31** by dibutylzirconium dichloride (**23**) (Section 4.9.5) provided an

authentic sample of **34** for confirming the structure of this reaction product. ^{1}H NMR (CDCl₃): 7.28–7.09 (m, 20H), 6.05 (t, 4H), 5.78 (t, 4H), 5.64 (s, 2H). ^{13}C NMR (CDCl₃): 143.4, 136.3, 129.0, 128.4, 126.7, 116.0, 115.2, 51.5.

4.7.3. From 6-phenylfulvene (28)

A suspension of ZrCl₂ (**17**, 10.0 mmol) and LiCl in 30 mL of toluene was heated at reflux with 6-phenylfulvene (3.08 g, 20 mmol) for 8 h. Work-up by filtration gave >90% of essentially pure **28a** and **28b**. Alternatively, nonhydrolytic workup and Soxhlet extraction gave 3.53 g (75%) of a colorless 1:1 mixture of the *meso-ansa-*(**28b**) and *racemic-ansa-*(**28a**) isomers of 1,2-diphenylethylene-bis(cyclopentadienyl)zirconium dichloride. Spectral evidence for such a composition of these isomers and the assignment of the methine H at 4.28 ppm to the *racemic-*isomer follow the arguments given in Section 4.6.2. for the titanium analogue. ^{1}H NMR (CDCl₃): 7.16–6.90 (m, 20H), 5.90 (t, 4H), 5.85–5.70 (m, 4H), 4.91 (s, 1H), 4.28 (s, 1H). ^{13}C NMR (CDCl₃): 141.6, 139.8, 135.6, 129.5, 129.0, 128.7, 127.8, 127.6, 127.0, 113.5, 113.3, 110.7, 106.1, 54.4, 51.3.

4.7.4. From 6-(1-naphthyl)fulvene (29)

In a similar procedure, a solution of 6-(1-naphthyl)fulvene (**29**, 352 mg, 1.72 mmol) in 30 mL of toluene was heated at reflux with ZrCl₂ (**17**, 0.86 mmol) for 4 h. The reaction mixture was filtered and the filter cake washed repeatedly with toluene. The solvent was removed from the combined filtrate and washings in vacuo to give 369 mg (75%) of off-white *meso-ansa-*(**29b**) and *racemic-ansa-*(**29a**) isomers. The spectral evidence for the presence of both *meso-* and *racemic-*isomers is: (1) the presence of 30 sp²-C signals; and (2) the presence of 2 sp³-C signals and of 2 ^{1}H methine singlets. The ratio of the *meso:racemic-*isomers can be obtained by integrating the ^{1}H methine singlets at 6.20 and 6.28 ppm and obtaining a ratio of 6.20:6.28 signals of 17:83. Noting that the *racemic* methine H should be more shielded (Section 4.6.2), we can conclude that the *racemic-ansa-*isomer (**29a**) is the major isomer. Upon recrystallization of mixture **29a** and **29b** from a toluene–hexane pair a colorless product was recovered; its ^{1}H NMR spectrum now lacked the singlet at 6.20 ppm and its ^{13}C NMR spectrum had no signal at 45.5. Hence, the recrystallized product consisted of essentially the *racemic-ansa-*isomer. Crystal samples submitted thus far to Professor A.L. Rheingold (then of the University of Delaware and now of the University of California at San Diego) for single-crystal X-ray determination have led to the unambiguous determination that this isomer has the *racemic* structure (**29a**). However, better crystals will be required, in order to refine the data to attain *R* < 10%.

^{1}H NMR (CDCl₃): 8.56 (d, 4H), 7.99 (d, 2H), 7.79–7.66 (m, 6H), 7.52–7.18 (m, 8H), 6.85 (m, 4H), 6.52

(m, 4H), 6.44 (s, 2H), 6.20–6.28 (2s, total of 2H). ^{13}C NMR (CDCl$_3$): 136.58, 136.12, 134.94, 134.57, 133.87, 131.63, 129.21, 129.13, 128.98, 128.17, 128.05, 127.86, 127.51, 127.21, 126.40, 125.72, 125.64, 125.55, 125.50, 125.25, 124.46, 1223.13, 123.02, 122.16, 121.52, 120.00, 113.43, 113.24, 110.28, 106.66, 48.30, 45.46.

4.7.5. From 6-(9-anthryl)fulvene (30)

A solution of 6-(9anthryl)fulvene (30, 2.23 g, 8.8 mmol) in 30 mL of toluene was stirred with a suspension of ZrCl$_2$ (14.4 mol) and LiCl in 20 mL of toluene at RT for 12 h and then at reflux for 6 h. The cooled reaction mixture was filtered and the filtrate cake washed thrice with 20-mL portions of toluene. The combined filtrate and washings were freed of solvent in vacuo to give 1.92 g (65%) of light brown *racemic*-1,2-(di-9-anthryl)ethylene-bis(cyclopentadienyl)zirconium dichloride (30a). Recrystallization from a toluene–hexane gave colorless, air- and moisture-sensitive 30a. ^{1}H NMR (CDCl$_3$): 7.95 (d, 2H), 7.74 (d, 4H), 7.65 (d, 2H), 7.44–7.15 (m, 10H), 6.81 (m, 4H), 6.47 (m, 2H), 6.40 (s, 2H), 6.16 (s, 2H). ^{13}C NMR (CDCl$_3$): 137.8, 136.1, 134.6, 133.9, 131.7, 129.2, 129.0, 128.2, 128.1, 127.6, 126.4, 125.9, 125.6, 125.3, 124.5, 123.1 spectrum (6.16) and in the ^{13}C spectrum (48.4) are consonant with only one *ansa*-isomer. Steric control decisively supports the *racemic* structure (30a) for that single isomer.

4.8. ansa-Metallocene dichlorides of hafnium

4.8.1. From 6,6-dimethylfulvene (15)

A mixture of 6,6-dimethylfulvene (15, 1.00 mL, 8.7 mmol) and a suspension of HfCl$_2$ (11.6 mmol) and LiCl in 60 mL of toluene was heated at reflux for 12 h. The cooled reaction mixture was freed of solvent in vacuo and the residue subjected to Soxhlet extraction with 10% chloroform in hexane to yield 1.83 g (90%) of colorless, air- and moisture-sensitive tetramethylene-bis(cyclopentadienyl)hafnium dichloride (21). ^{1}H NMR (CDCl$_3$): 6.57 (t, 4H), 6.02 (t, 4H), 1.46 (s, 12H). ^{13}C NMR (CDCl$_3$): 141.6, 121.7, 106.7, 44.7, 28.5.

4.9. Hydrometallations of fulvenes

4.9.1. Hydrotitanation of 6,6-dimethylfulvene (15), (attempted)

Attempts to generate di-*n*-butyltitanium dichloride (22) at −78 °C just before adding 6,6-dimethylfulvene (15) to such a reagent failed because of the instability of 22 even at such low temperatures. Thus to a solution of TiCl$_4$ (4.0 mL, 4.0 mmol) in 30 mL of toluene at −78 °C were slowly added 2 equiv. of *n*-butyllithium (5.0 mL of 1.6 M in hexane, 8.0 mmol). During 30 min the progression of a colorless reaction mixture to yellow to green to brown and then to black signaled decomposition of 22 to TiCl$_2$ (16). Addition of 2 equiv. of 6,6-dim-

ethylfulvene and warming to RT and finally 65 °C led to the formation of a mixture of tetramethylethylene-bis(cyclopentadienyl)titanium dichloride (19) (NMR spectral data in Section 4.6.1) and bis(isopropylcyclopentadienyl)titanium dichloride (25), readily identifiable by a 12H doublet at 1.45 and a 2H septet at 3.25 ppm.

4.9.2. Hydrozirconation of 6,6-dimethylfulvene (15)

To a white suspension of ZiCl$_4$ (2.12 g, 9.1 mmol) in 50 mL of toluene at −78 °C were slowly added 2 equiv. of *n*-butyllithium (18.2 mmol, 11.4 mL of 1.6 M), whereupon the solution turned light brown as it was warmed to RT. After 6 h 6,6-dimethylfulvene (15, 1.97 g, 18.6 mmol) was added and the reaction continued for 1 h at RT and 6 h at 65 °C. Filtration of the cooled reaction mixture and removal of volatiles in vacuo gave the light-brown bis(isopropylcyclopentadienyl)zirconium dichloride (26) consistently in >90% yield. Extraction with hexane in a Soxhlet apparatus over 1 h gave colorless 26 in 75% yield. ^{1}H NMR (CDCl$_3$): 6.60 (t, 4H), 6.45 (t, 4H), 3.25 (septet, 2H), 1.45 (d, 12H). ^{13}C NMR (CDCl$_3$): 142.0, 114.6, 112.0, 28.3, 23.2.

4.9.3. Hydrozirconation of 6-phenylfulvene (28)

A mixture of 6-phenylfulvene (28, 860 mg, 5.6 mmol) and di-*n*-butylzirconium dichloride (23, 2.8 mmol, cf. Section 4.9.2) in 40 mL of toluene was allowed to react at RT for 1 h and at reflux for 2 h. Solvent removal in vacuo and the solid washed well with pentane to remove any residual 28. The residue was slurried again with toluene and the LiCl filtered off. The filtrate was freed of volatiles in vacuo to give 282 mg (95%) of light brown bis(benzylcyclopentadienyl)zirconium dichloride (28c). Further purification by Soxhlet extraction gave 75% of colorless 28c. ^{1}H NMR (C$_6$D$_6$): 715–6.99 (m, 10H), 5.89 (t, 4H), 5.69 (t, 4H), 3.98 (s, 4H). ^{13}C NMR (CDCl$_3$): 140.71, 133.81, 129.59, 129.16, 127.03, 117.51, 112.96, 36.07.

4.9.4. Hydrozirconation of 6-(1-naphthyl)fulvene (29)

A mixture of 6-(1-naphthyl)fulvene (29, 1.9 g, 9.2 mmol) and Bu$^n_2$ZrCl$_2$ (23, 4.6 mmol) in 40 mL of toluene was allowed to react for 1 h at RT and 3 h at 65 °C. The cooled mixture was filtered to remove the LiCl. The filtrate was freed of solvent in vacuo and the residue was extracted with methylene chloride in a Soxhlet apparatus. In this way a 55% yield of almost colorless bis(1-naphthylmethyl(cyclopentadienyl))zirconium dichloride (29c) was obtained. ^{1}H NMR (CDCl$_3$): 8.05 (m, 3H), 7.88 (m, 4H), 7.76 (m, 3H), 7.44 (m, 4H), 6.21 (m, 4H), 6.16 (m, 4H), 4.52 (s, 4H). ^{13}C NMR (CDCl$_3$): 142.5, 136.0, 133.9, 128.8, 127.4, 127.0, 126.1, 125.9, 125.7, 124.7, 124.0, 117.5, 112.4, 47.7.

4.9.5. Hydrozirconation of 6,6-diphenylfulvene (31)

A mixture of 6,6-diphenylfulvene (31, 202 g, 8.84 mmol) and Bu$^n_2$ZrCl$_2$ (23, 4.42 mmol) in 40 mL of

toluene was allowed to react for 1 h at RT and 3 h at 65 °C. The cooled reaction mixture was freed of solvent in vacuo and the residue extracted with methylene chloride in a Soxhlet apparatus. The filtrate was freed of volatiles to give a light brown residue of bis(diphenylmethyl(cyclopentadienyl))zirconium dichloride (**31c**) (65% yield). Washing with pentane gave an off-white sample of **31c**, whose ^1H and ^{13}C NMR spectra were identical with the product obtained in Section 4.7.2.

4.9.6. Hydrohafniation of 6,6-dimethylfulvene (**15**)

A mixture of 6,6-dimethylfulvene (**15**, 1.7 mL, 14.2 mmol) and $Bu^n_2HfCl_2$ (**24**, 7.1 mmol, made analogous to $Bu^n_2ZrCl_2$ from $HfCl_4$ and 2 equiv. of *n*-butyllithium) in 40 mL of toluene was allowed to react for at RT for 1 h and at 65–70 °C for 4 h. The toluene was removed from the reaction mixture and the residue extracted with hexane in a Soxhlet apparatus. The hexane yielded 2.44 g (73%) of red-brown bis(isopropylcyclopentadienyl)hafnium dichloride (**27**). ^1H NMR ($CDCl_3$): 6.30 (t, 3H), 6.12 (t, 4H), 3.14 (septet, 2H), 1.14 (d, 12H). ^{13}C NMR ($CDCl_3$): 141.3, 113.1, 110.7, 27.0, 22.6.

4.10. Comparative polymerizations of ethylene with metallocene catalysts

4.10.1. Typical polymerization run for tetramethylethylene-bis(cyclopentadienyl)titanium dichloride (**19**)

Polymerizations were conducted in 250 mL resin-coated glass pressure (Fisher-Porter) bottle 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 pro-catalysts, tetramethylethylene-bis(cyclopentadienyl)titanium dichloride (**19**, 0.560 mmol), in 100 mL of predried and deoxygenated toluene was treated with 28 mmol of MAO in toluene (Al:Ti = 50:1) 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 10 min. Usual quench with aqueous HCl and filtration with a methanol-wash allow the polyethylene to be isolated. In this case the polymerization activity (PA) in grams of polyethylene (PE) per gram of Ti, per atmosphere was calculated as 2640. Such polyethylene generally melted over 135 °C.

4.10.2. Analogous polymerization with bis(cyclopentadienyl)titanium dichloride

An analogous polymerization of ethylene using 0.53 mmol of titanocene dichloride and 28 mmol (50 equiv.) of MAO for 10 min gave a PA = 1100 g PE/g Ti h atm.

4.10.3. Analogous polymerization with bis(isopropylcyclopentadienyl)hafnium dichloride (**27**)

A parallel polymerization of ethylene using 1.02 mmol of **27** and 50 equiv. of MAO for 30 min gave a PA = 182 g PE/g Hf h atm.

4.10.4. Analogous polymerization with bis(benzylcyclopentadienyl)zirconium dichloride (**28c**)

With 0.85 mmol of **28c** and 50 equiv. of MAO for 15 min of ethylene purge, a PA of 242 g PE/g Zr h atm was obtained.

4.10.5. Analogous polymerization with bis(diphenyl-methyl(cyclopentadienyl))zirconium dichloride (**31c**)

With 0.18 mmol of **31c** and 50 equiv. of MAO for 10 min of ethylene purge, a PA of 62 g PE/g Zr h atm was obtained.

4.10.6. Analogous polymerization with bis(1-naphthyl-methyl(cyclopentadienyl))zirconium dichloride (**29c**)

With 0.79 mmol of **29c** and 50 equiv. of MAO for 15 min of ethylene purge, a PA of 126 g PE/g Zr h atm was obtained.

4.10.7. Analogous polymerization with 1:1 racemic- and meso-1,2-diphenylethylene-bis(cyclopentadienyl) titanium dichloride

With 0.45 mmol of this metallocene and 50 equiv. of MAO for 10 min of ethylene purge, a PA of 3170 g PE/g Zr h atm was obtained.

4.10.8. Analogous polymerization with racemic- and meso-1,2-di(1-naphthyl)ethylene-bis(cyclopentadienyl)-titanium dichloride

With 0.20 mmol of this catalyst and 50 equiv. of MAO for 10 min of ethylene purge, a PA of 313 g PE/g Zr h atm was obtained.

4.10.9. Analogous polymerization with 1:1 racemic- and meso-1,2-diphenylethylene-bis(cyclopentadienyl)-zirconium dichloride (**28a** and **28b**)

With 0.75 mmol of this catalyst and 50 equiv. of MAO for 10 min of ethylene purge, a PA of 360 g PE/g Zr h atm was obtained.

4.10.10. Analogous polymerization with 83:17 mixture of racemic- and meso-1,2-di(1-naphthyl)ethylene-bis(cyclopentadienyl)zirconium dichloride (**29a** and **29b**)

With 0.22 mmol of this mixture and 50 equiv. of MAO for 15 min of ethylene purge, a PA of 52 g PE/g Zr h atm was obtained.

4.11. Reductive dimerizations of N-benzylideneaniline (**9**)

4.11.1. With titanium dichloride

To 15 mmol of $TiCl_2$ (**16**) in 40 mL of toluene (free of $Bu^n_2TiCl_2$, Eq. (2)) but containing the LiCl by-product

was added 5.40 g (30 mmol) of *N*-benzylideneaniline (**9**) at 25 °C. The mixture was heated at reflux for 2 h to form a dark khaki-colored suspension. Hydrolysis with 1 N aqueous HCl and separation of the organic layer, which was dried over $MgSO_4$ and freed of solvent in vacuo, provided 5.10 g (94% recovery) of products, which by ^{1}H NMR spectroscopy and comparison with spectral data of authentic samples to consist of 15% of *N*-phenylbenzylamine (**39**, but without D atoms) and 85% of *racemic*-1,2-dianilino-1,2-diphenylethane. After exchange with D_2O, the *racemic*-isomer showed a sharp C–H peak at 4.6 ppm. The corresponding CH peak for the *meso*-isomer at 5.0 ppm was absent [29].

When an identical reaction run was worked up with DCl in D_2O, the *N*-phenylbenzylamine (**39**) was mono-deuteriated in the methylene group (^{1}H NMR peak at 4.29 and the N–H peak at 3.97 ppm was absent), the changes of which are consistent with the structure, Ph–CHD–ND–Ph (**39**).

4.11.2. With zirconium dichloride (17)

Similar to the foregoing, a mixture of *N*-benzylideneaniline (**9**) (6.00 g, 33 mmol) and freshly prepared $ZrCl_2$ (**17**, 16.3 mmol) free of $Bu^n_2ZrCl_2$ but containing LiCl was heated to reflux for 4 h. Hydrolytic work-up gave a 90% conversion to a mixture of *N*-phenylbenzylamine (20%) and an 80:20 mixture of *racemic*-1,2-dianilinoethane and *meso*-1,2-dianilinoethane (85%). The proportion of *racemic* to *meso*-isomers was determined by integration of C–H proton peaks at 4.6 and 5.0 ppm.

4.11.3. With di-n-butylzirconium dichloride (23)

N-Benzylideneaniline (**9**, 2.1 g, 11.4 mmol) and a slurry of $Bu^n_2ZrCl_2$ (**23**, 5.7 mmol) and LiCl in 40 mL were mixed at 25 °C to form a dark brown suspension in an exothermic reaction. After being stirred for 1 h at RT the reaction mixture was heated at reflux for 2 h and then subjected to the usual hydrolytic work-up. In 85% recovery, the reaction products consisted of *N*-phenylbenzylaniline (49%) and an 80:20 mixture of *racemic*-and *meso*-1,2-dianilino-1,2-diphenylethane (51%). Although the *N*-phenylbenzylaniline could have resulted either from transfer-hydrozirconation or epizirconation, formation of the *racemic*- and *meso*-1,2-dianilinoethanes require epizirconation, either directly by $ZrCl_2$ or by transfer (cf. discussion in Section 3.1).

4.11.4. With zirconium dichloride (17) and the isolation of the mixture of racemic- and meso-1,1-dichloro-2,3,4,5-tetraphenyl-2,5-diazaazirconacyclopentanes (10 and 11 with M = Zr)

The experiment described in Section 4.11.2 but instead of a hydrolytic work-up the reaction mixture was cooled to RT and filtered to remove the LiCl. The filtrate was freed of toluene in vacuo and the dark tan washed repeatedly to give a mixture of *racemic*- and *meso*-iso-

mers **10** and **11**, calculated to be a 70% yield and present in a 80:20 ratio. This product could be recrystallized from a toluene–hexane pair. ^{1}H NMR (THF-d_8) of **10** and **11**: 7.60–7.00 (m), 6.93–6.88 (m), 6.56–6.46 (m), 4.90 (s, *meso*-CH), 4.55 (s, *racemic*-CH); ^{13}C NMR (THF-d_8): 65.3 (*racemic*-CH), 63.3 (*meso*-CH).

4.11.5. Polymerization with the mixture of racemic- and meso-1,1-dichloro-2,3,4,5-tetraphenyl-2,5-diazazirconacyclopentanes (10 and 11 with M = Zr)

Analogous to the foregoing polymerizations a mixture of **10** and **11** (160 mg, 0.29 mmol) in 100 mL of toluene was treated with 28 mmol (50 equiv.) of MAO was treated with ethylene at 40 psi for 15 min. Usual work-up gave 9.45 g of polyethylene for a PA = 129 PE/g Zr h atm.

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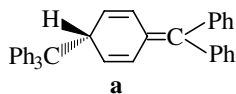
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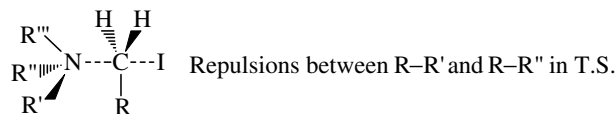
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