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Chiral *Ansa* Zirconocene Compounds with [Me$_2$Si] and [Me$_4$Si$_2$] Bridges and with *tert*-Butyl Ring Substituents: Synthesis and Structural Characterization of the *Racemo* Complexes *rac*-[Me$_2$Si(C$_5$H$_2$-2,4-Bu^t$_2$)$_2$]ZrCl$_2$ and *rac*-[Me$_4$Si$_2$(C$_5$H$_2$-2,4-Bu^t$_2$)$_2$]ZrCl$_2$

Cary E. Zachmanoglou, Jonathan G. Melnick, Brian M. Bridgewater, David G. Churchill, and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027

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A series of chiral *ansa* zirconocene compounds that feature (i) [Me$_2$Si] and [Me$_4$Si$_2$] bridges and (ii) two *tert*-butyl substituents on each cyclopentadienyl ring, namely, *rac*-[Me$_2$Si(Cp$^{\mathrm{Bu^t_2}}$)$_2$]ZrCl$_2$, *rac*-[Me$_2$Si(Cp$^{\mathrm{Bu^t_2}}$)$_2$]Zr(Ph)Cl, *rac*-[Me$_2$Si(Cp$^{\mathrm{Bu^t_2}}$)$_2$]ZrMe$_2$, *rac*-[Me$_2$Si(Cp$^{\mathrm{Bu^t_2}}$)$_2$]Zr(CO)$_2$, *rac*-[Me$_4$Si$_2$(Cp$^{\mathrm{Bu^t_2}}$)$_2$]ZrCl$_2$, and *rac*-[Me$_4$Si$_2$(Cp$^{\mathrm{Bu^t_2}}$)$_2$]Zr(CO)$_2$, has been synthesized. In each case, the complex exists as the *racemo* isomer due to inter-ring steric interactions between the Bu^t substituents proximal to the *ansa* bridge that destabilize the *meso* isomer. *rac*-[Me$_4$Si$_2$(Cp$^{\mathrm{Bu^t_2}}$)$_2$]ZrCl$_2$ is the first structurally characterized *ansa* zirconocene complex with a [Me$_4$Si$_2$] bridge that adopts a *racemo* geometry. IR spectroscopic studies on the dicarbonyl complexes (Cp$^{\mathrm{1,3-Bu^t_2}}$)$_2$Zr(CO)$_2$, *rac*-[Me$_2$Si(Cp$^{\mathrm{Bu^t_2}}$)$_2$]Zr(CO)$_2$, and *rac*-[Me$_4$Si$_2$(Cp$^{\mathrm{Bu^t_2}}$)$_2$]Zr(CO)$_2$ demonstrate that the [Me$_2$Si] and [Me$_4$Si$_2$] *ansa* bridges have opposite electronic influences in this system, with the [Me$_2$Si] bridge exerting an electron-withdrawing effect and the [Me$_4$Si$_2$] bridge exerting an electron-donating effect. The [Me$_2$Si] and [Me$_4$Si$_2$] bridges also exert a different influence with respect to olefin polymerization, with {*rac*-[Me$_2$Si(Cp$^{\mathrm{Bu^t_2}}$)$_2$]ZrCl$_2$/MAO} being a more active catalyst system for polymerization of ethylene than is either {(Cp$^{\mathrm{1,3-Bu^t_2}}$)$_2$ZrCl$_2$/MAO} or {*rac*-[Me$_4$Si$_2$(Cp$^{\mathrm{Bu^t_2}}$)$_2$]ZrCl$_2$/MAO}.

Introduction

Zirconocene complexes have important applications as catalysts for olefin polymerization[1] and as reagents for organic synthesis.[2,3] The widespread use of zirconocene complexes derives, in large part, from the fact that modification of the ring substituents may be readily achieved and the resulting steric and electronic changes may have a significant impact on the chemistry of the system.[4,5] Substituents that link the two cyclopentadienyl groups together, i.e., *ansa* bridges, are of special importance since they exert a profound influence resulting from (i) an increase in configurational stability of the zirconocene fragment and (ii) the displacement of the cyclopentadienyl groups from their natural positions.[4,6] C_2-symmetric *racemo ansa* metallocenes, in particular, are of considerable interest because of their ability to serve as catalysts for the synthesis of highly isotactic polypropylene, whereas the *meso* isomers produce atactic polypropylene.[1] The isolation of pure *racemo* zirconocene complexes, however, is commonly thwarted by the presence of the *meso* isomer.[1] In this paper, we

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[4] Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525−9546.

[5] See, for example: Janiak, C. In *Metallocenes, Volume 2; Synthesis, Reactivity, Applications*; Togni, A., Halterman, R., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 576−577.

[6] See, for example: (a) Churchill, D. G.; Bridgewater, B. M.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 178−179. (b) Churchill, D.; Shin, J. H.; Hascall, T.; Hahn, J. M.; Bridgewater, B. M.; Parkin, G. *Organometallics* **1999**, *18*, 2403−2406. (c) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255−3256. (d) Shin, J. H.; Parkin, G. *Chem. Commun.* **1999**, 887−888. (e) Lee, H.; Bonanno, J. B.; Hascall, T.; Cordaro, J.; Hahn, J. M.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1999**, 1365−1368. (f) Labella, L.; Chernega, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 395−402. (g) Chernega, A.; Cook, J.; Green, M. L. H.; Labella, L.; Simpson, S. J.; Souter, J.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3225−3243. (h) Conway, S. L. J.; Dijkstra, T.; Doerrer, L. H.; Green, J. C.; Green, M. L. H.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1998**, 2689−2695. (i) Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65−75. (j) Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159−167. (k) Dorer, B.; Diebold, J.; Weyand, O.; Brintzinger, H. H. *J. Organomet. Chem.* **1992**, *427*, 245−255. (l) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828−1838.

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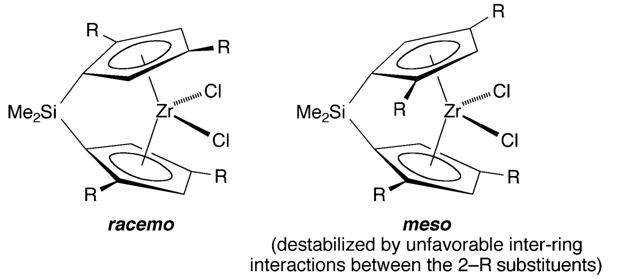

Figure 1. *Racemo* and *meso* isomers. Steric interactions between 2-R substituents destabilize the *meso* isomer.

report the synthesis and structural characterization of C_2-symmetric *racemo*-zirconocene complexes that feature two *tert*-butyl substituents on each cyclopentadienyl ring and $[Me_2Si]$ and $[Me_4Si_2]$ *ansa* bridges.

Results and Discussion

Although simple zirconocene complexes that feature *tert*-butyl substituents on the cyclopentadienyl rings are long known, as illustrated by $(Cp^{Bu^t})_2ZrCl_2$,[7] $(Cp^{1,2-Bu^t_2})_2ZrCl_2$,[8] and $(Cp^{1,3-Bu^t_2})_2ZrCl_2$,[9,10] *ansa*-zircononcene counterparts have not been widely studied. For example, while $[Me_2Si(Cp^{Bu^t})_2]ZrCl_2$ ($[Me_2Si(Cp^{Bu^t})_2] = [Me_2Si(C_5H_3\text{-}3\text{-}Bu^t)_2]$) has been synthesized[11,12] and studied as an olefin polymerization catalyst,[13] the more heavily substituted counterpart $[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ ($[Me_2Si(Cp^{Bu^t_2})_2] = [Me_2Si(C_5H_2\text{-}2,4\text{-}Bu^t_2)_2]$) was unknown. Ring substituents may exert significant effects on the chemistry of a system, and so we viewed $[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ to be an important synthetic target, especially because the presence of the *tert*-butyl ligand in the 2-position of the cyclopentadienyl ring should strongly favor the desired *racemo* isomer on the basis of Bercaw's synthesis of *rac*-$[Me_2Si(C_5H_2\text{-}2\text{-}TMS\text{-}4\text{-}Bu^t)_2]ZrCl_2$.[14,15] Specifically, Bercaw established that bulky Me_3Si substituents in the 2-position on the cyclopentadienyl rings of an *ansa* metallocene derivative provide an effective means to favor the C_2-symmetric *racemo* isomer over the C_s-symmetric *meso* isomer (cf. Figure 1); the origin of this selectivity is inter-ring repulsion between the 2-substituents that destabilizes the *meso* isomer.[16] By analogy, we rationalized that 2-Bu^t substituents should likewise promote the formation of *racemo* isomers in *ansa* zirconocene compounds that feature $[Me_2Si]$ and $[Me_4Si_2]$ bridges.

Synthesis and Characterization of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$, *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(Ph)Cl$, *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrMe_2$, and *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$. The *ansa* ligand $[Me_2Si(Cp^{Bu^t_2})_2]Li_2$ ($Cp^{Bu^t_2} = C_5H_2\text{-}2,4\text{-}Bu^t_2$) may be obtained by a conventional procedure involving (i) reaction of Me_2SiCl_2 with $(Cp^{1,3-Bu^t_2})Li$ followed by (ii) deprotonation with Bu^nLi, from which the zirconocene complex *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ may be obtained by reaction with $ZrCl_4$ (Scheme 1).[17] Although the yield of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ is moderate (35%), it is higher than those reported for the related complexes *rac*-$[Me_2Si(C_5H_2\text{-}2\text{-}TMS\text{-}4\text{-}Bu^t)_2]ZrCl_2$ (4−15%)[14] and $[Me_2Si(C_5H_2\text{-}2,4\text{-}TMS_2)_2]ZrCl_2$ (22%),[18,19] which feature a 2-Me_3Si substituent rather than 2-Bu^t substituent on the cyclopentadienyl rings. The molecular structure of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ has been determined by X-ray diffraction (Figure 2), thereby confirming that the complex exists as the *racemo* isomer. The facile isolation of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ is in marked contrast to the ability to isolate the *racemo* isomer for $[Me_2Si(Cp^{Bu^t})_2]ZrCl_2$, which possesses a single *tert*-butyl group on each cyclopentadienyl ligand. Thus, $[Me_2Si(Cp^{Bu^t})_2]ZrCl_2$ is obtained as a 1:1 *racemo/meso* mixture via the reaction of $\{[Me_2Si(C_5H_3\text{-}3\text{-}Bu^t)_2]\}^{2-}$ derivatives with $ZrCl_4$,[11,12] and considerable modifications of the synthetic procedure are required to obtain the pure *rac*-$[Me_2Si(Cp^{Bu^t})_2]ZrCl_2$ isomer.[20] Furthermore, the incorporation of a methyl group in the 2-position results in the *racemo/meso* mixture of only 2:1 for $[Me_2Si(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]ZrCl_2$,[11a] and thus, as noted by Bercaw,[14] a 2-*tert*-butyl substituent is very effective at enforcing a *racemo* geometry.

As observed for *rac*-$[Me_2Si(C_5H_2\text{-}2\text{-}TMS\text{-}4\text{-}Bu^t)_2]ZrCl_2$,[14] the structure of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ is reduced from that of an idealized metallocene geometry with the Cl−Zr−Cl and Me−Si−Me planes being twisted relative to each other (Figure 3) in order to minimize steric interactions between both (i) the 4-Bu^t substituents and the Cl ligands and (ii) the 2-Bu^t substituents and the methyl groups of the *ansa* bridge. The twisting of the Cl−Zr−Cl and Me-Si−Me planes for *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ (20°) is, however, substantially greater than that for *rac*-$[Me_2Si(C_5H_2\text{-}2\text{-}TMS\text{-}4\text{-}Bu^t)_2]ZrCl_2$ (11°) and is presumably due to the shorter C−C versus Si−C bond lengths, resulting in greater steric interactions between the 2-Bu^t substituents and the *ansa* bridge.

rac-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ is a precursor for a variety of other derivatives, e.g., *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(Ph)Cl$, *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrMe_2$, and *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$, as illustrated in Scheme 1. It is worth noting that

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[14] Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171−180.

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[16] Another approach to enforce the formation of *racemo* zirconocenes involves the use of a biphenyl linker. See: Huttenloch, M. E.; Diebold, J.; Rief, U.; Brintzinger, H. H.; Gilbert, A. M.; Katz, T. J. *Organometallics* **1992**, *11*, 3600−3607.

[17] Other derivatives of $[Me_2Si(Cp^{Bu^t_2})_2]$ have recently been obtained, namely, $[Me_2Si(Cp^{Bu^t_2})_2]Mg$, $[Me_2Si(Cp^{Bu^t_2})_2]Fe$, $[Me_2Si(Cp^{Bu^t_2})_2]Yb(OEt_2)$, $[Me_2Si(Cp^{Bu^t_2})_2]Yb(CNXyl)_2$, and $[Me_2Si(Cp^{Bu^t_2})_2]Yb(bipy)$. See: Schultz, M.; Sofield, C. D.; Walter, M. D.; Andersen, R. A. Submitted.

[18] Langmaier, J.; Samec, Z.; Varga, V.; Horacek, M.; Choukroun, R.; Mach, K. *J. Organomet. Chem.* **1999**, *584*, 323−328.

[19] Isomeric *meso*-$[Me_2Si(C_5H_2\text{-}3,4\text{-}TMS_2)_2]ZrCl_2$ is also known. See: Douziech, B.; Choukroun, R.; Lorber, C.; Donnadieu, B. *J. Organomet. Chem.* **2002**, *649*, 15−20.

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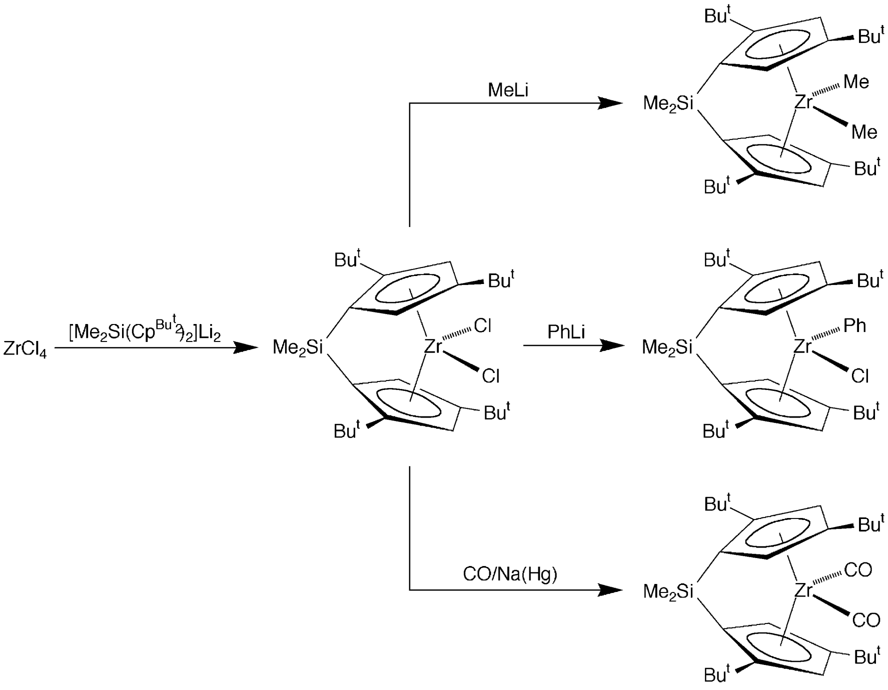
Scheme 1



the synthesis of *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]ZrMe_2}$ via treatment of *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2}$ with MeLi in benzene requires heating at 80 °C, which is in contrast to the syntheses of many other zirconocene dimethyl compounds that proceed readily at room temperature. For example, $\mathrm{Cp_2ZrCl_2}$ and $[\mathrm{Me_2Si(C_5H_4)_2]ZrCl_2}$ react rapidly with MeLi in benzene to give the corresponding dimethyl derivatives within 30 min at room temperature, as monitored by ^{1}H NMR spectroscopy.[21] The lower activity of *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2}$ towards methylation is presumably a consequence of increased steric demands resulting from the incorporation of *tert*-butyl substituents.

The molecular structures of *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]Zr(Ph)Cl}$ and *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2}$ have also been determined by X-ray diffraction (Figures 4 and 5), and the coordination geometries are similar to that for *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2}$, as summarized in Table 1. Furthermore, the twisting of the X−Zr−X and Me−Si−Me planes relative to each other are also similar: *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2}$ (20°), *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]Zr(Ph)Cl}$ (22°), and *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2}$ (20°). Although the structure of *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]ZrMe_2}$ has not been determined by X-ray diffraction, the compound is readily assigned a *racemo* structure by virtue of the fact that ^{1}H NMR spectroscopy indicates that the methyl groups attached to silicon are chemically equivalent, as are the methyl groups attached to zirconium; for a *meso* structure, both pairs of methyl groups are diastereotopic.

Synthesis and Characterization of *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2}$ and *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2]Zr(CO)_2}$. By comparison to the $[\mathrm{Me_2Si}]$ bridge, the longer $[\mathrm{Me_4Si_2}]$ linker has not been used extensively in *ansa*-zirconocene chemistry and the number of derivatives is rather limited, viz., $[\mathrm{Me_4Si_2(C_5H_4)_2]ZrCl_2}$,[22] [$\mathrm{Me_4Si_2(C_5H_3}$-3-

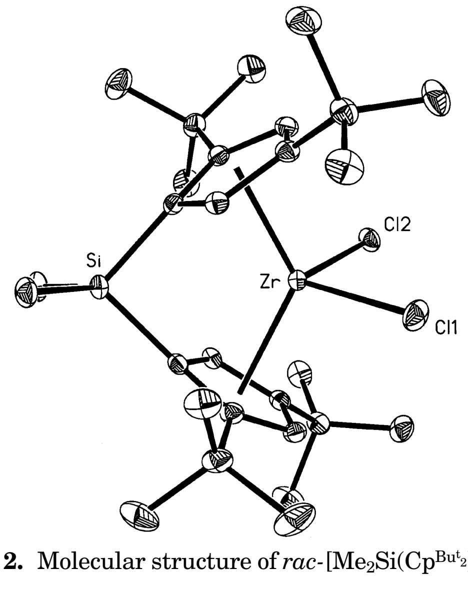


Figure 2. Molecular structure of *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2}$.

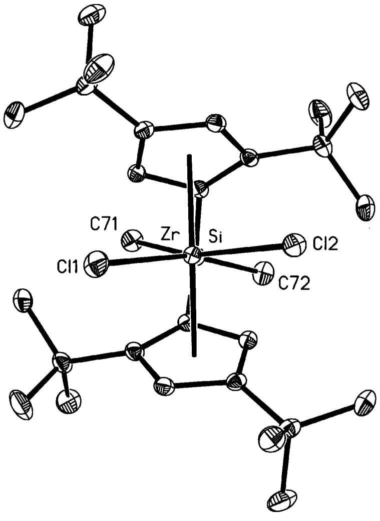


Figure 3. View of *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2}$ emphasizing the twisting of the $[\mathrm{Me_2Si}]$ and $[\mathrm{ZrCl_2}]$ planes.

Table 1. Geometrical Data for Selected $(Cp^R)_2ZrCl_2$ Derivatives

	α/deg	β/deg	γ/deg	τ/deg	φ/deg	Δ(d_{Zr-C})/Å	ref
$(Cp^{1,2-Bu^t_2})_2ZrCl_2$	61.4	118.6	128.7	5.1		0.198	*a*
$(Cp^{1,3-Bu^t_2})_2ZrCl_2$	48.6	131.4	133.3	1.0		0.063	*b*
rac-$[Me_2Si(C_5H_2\text{-}2\text{-}TMS\text{-}4\text{-}Bu^t)_2]ZrCl_2$	62.6	117.4	126.7	4.7	15.8	0.179	*c*
rac-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$	62.7	117.3	126.5	4.6	15.4	0.146	this work
rac-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(Ph)Cl$	62.3	117.7	126.3	4.3	14.9	0.168	this work
rac-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$	57.7	122.3	133.2	5.5	19.8	0.193	this work
rac-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$	56.5	123.5	131.6	4.1	−10.4	0.160	this work
rac-$[Me_4Si_2(Cp^{Bu^t_2})_2]Zr(CO)_2$	39.0	141.0	148.2	3.7	−1.7	0.132	this work

[a] Hughes, R. P.; Lomprey, J. R.; Rheingold, A. L.; Haggerty, B. S.; Yap, G. P. A. *J. Organomet. Chem.* **1996**, *517*, 89−99. [b] (a) Urazowski, I. F.; Ponomaryev, V. I.; Nifant'ev, I. E.; Lemenovskii, D. A. *J. Organomet. Chem.* **1989**, *368*, 287−294. (b) Böhme, U.; Langhof, H. *Z. Kristall.* **1993**, *206*, 281−283. [c] Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171−180.

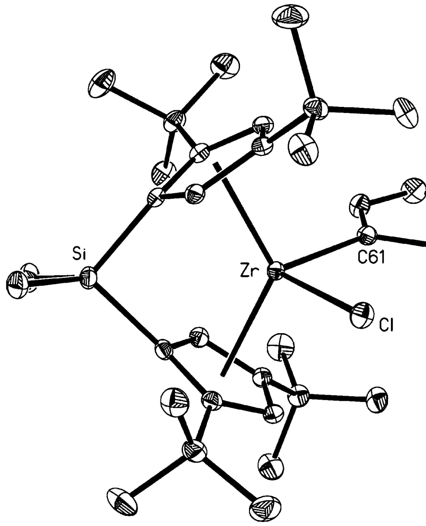


Figure 4. Molecular structure of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(Ph)Cl$.

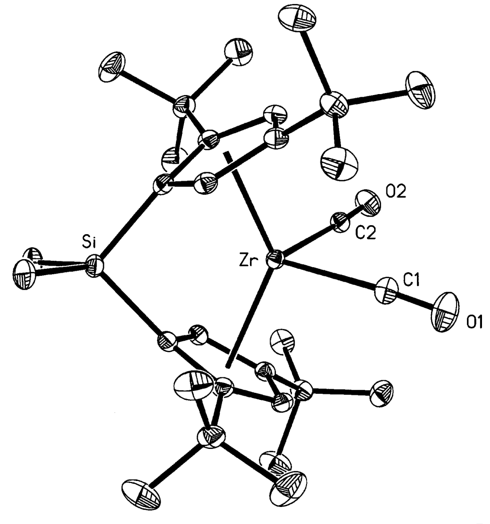
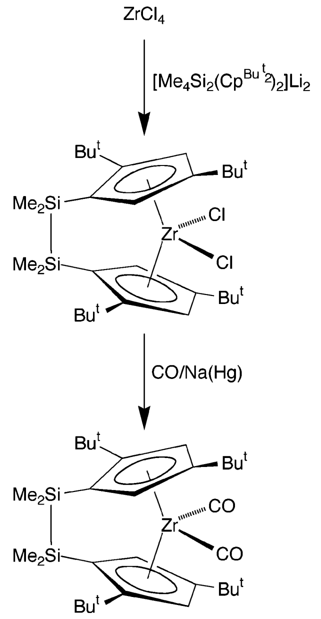


Figure 5. Molecular structure of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$.

$Bu^t)_2]ZrCl_2$,[23] $[Me_4Si_2(Ind^R)_2]ZrCl_2$ (Ind^R = Ind, 2-MeInd, 3-TMSInd, and $IndH_4$),[22,24,25] $[Me_4Si_2(Flu)_2]ZrCl_2$,[26] and $[Me_4Si_2(AzuH_5)_2]ZrCl_2$.[27,28] To complement this series, we sought to synthesize *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$; furthermore, comparison with *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ would provide a means to demonstrate how the different $[Me_2Si]$ and $[Me_4Si_2]$ linkers modify the structure and reactivity of the zirconocene center.

Scheme 2



In a manner analogous to the synthesis of $[Me_2Si(Cp^{Bu^t_2})_2]Li_2$, the related ligand $[Me_4Si_2(Cp^{Bu^t_2})_2]Li_2$ with a $[Me_4Si_2]$ *ansa* bridge may be obtained by a sequence involving (i) reaction of $[Me_2SiCl]_2$ with $(Cp^{1,3-Bu^t_2})Li$ followed by (ii) deprotonation with Bu^nLi, from which the *ansa* zirconocene complex *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ may be obtained by treatment with $ZrCl_4$ (Scheme 2). The molecular structure of *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ has been determined by X-ray diffraction (Figures 6 and 7), thereby demonstrating that the compound also exists as a *racemo* isomer. This observation is significant in view of the report that related zirconocene complexes with a $[Me_4Si_2]$ bridge exist primarily as a *meso* isomer, with no *rac*-$[Me_4Si_2(Cp^R)_2]ZrCl_2$ derivative having been structurally characterized by X-ray diffraction. For example, $[Me_4Si_2(C_5H_3\text{-}3\text{-}Bu^t)_2]ZrCl_2$ exists exclusively as a *meso* isomer,[23] which is also the favored isomer for a series of indenyl complexes, namely, *meso*-$[Me_4Si_2(Ind^R)_2]ZrCl_2$ (Ind^R = Ind, 2-MeInd, 3-TMSInd, and

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(21) Tian, G.; Wang, B.; Xu, S.; Zhang, Y.; Zhou, X. *J. Organomet. Chem.* **1999**, *579*, 24−29.

(22) Also see: (a) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571. (b) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9,* 301−308.

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(28) Abbreviations: Ind = indenyl, Flu = fluorenyl, Azu = azulenyl.

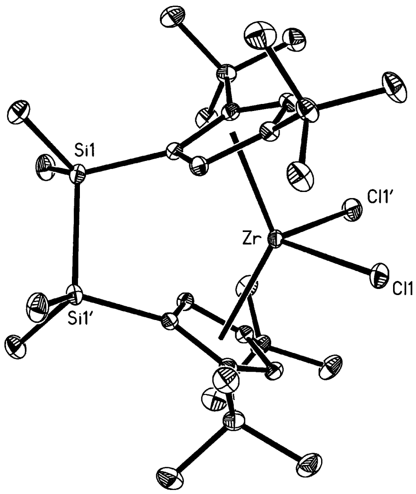

Figure 6. Molecular structure of *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$.

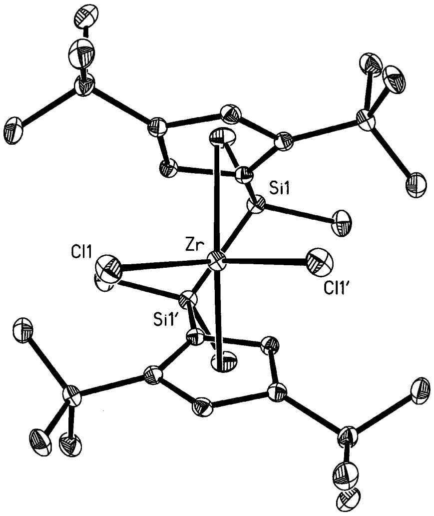

Figure 7. Orthogonal view of *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$.

$\mathrm{IndH_4}$).[25,29] Of the indenyl complexes, however, the 2-MeInd derivative exists as a 1:1 *meso*:*racemo* mixture, thereby re-emphasizing the role that a 2-substituent on the cyclopentadienyl ring plays in favoring the *racemo* isomer. Thus, even though the 2-$\mathrm{Bu^t}$ substituents within *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ are separated by a greater distance than those in *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$, the inter-ring interaction is still sufficient to favor the *racemo* isomer. The dicarbonyl derivative *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$, obtained by reduction of *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ with Na(Hg) in the presence of CO (Scheme 2), likewise possesses a *racemo* structure, as judged by the chemical equivalence of the two CO ligands in the ^{13}C NMR spectrum. The molecular structure of *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$ has also been determined by X-ray diffraction (Figures 8 and 9). Comparison of Figures 7 and 9 indicates that the $[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]$ ligand in *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ and *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$ adopts a very different conformation with respect to a twisting of the Si−Si vector relative to the $\mathrm{Cp_{cent}}$−$\mathrm{Cp_{cent}}$ vector. Thus, whereas the dihedral angle between the Si−Zr−Si and $\mathrm{Cp_{cent}}$−Zr−$\mathrm{Cp_{cent}}$ planes is negligible for the dicarbonyl complex *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$ (0.2°), it is quite substantial for the dichloride derivative *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ (37.2°); a plausible explanation for this conformational difference resides with the cylindrically smaller carbonyl ligand exerting less steric interaction with the cyclopentadienyl substituents (see below).

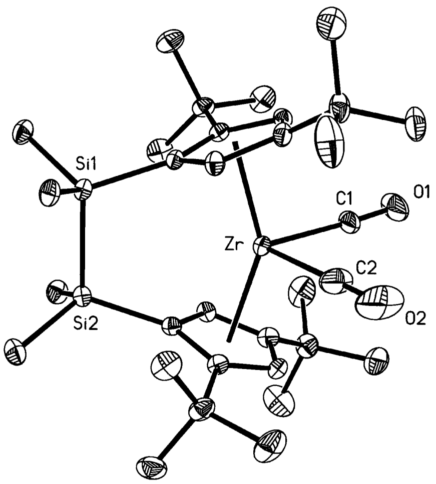

Figure 8. Molecular structure of *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$.

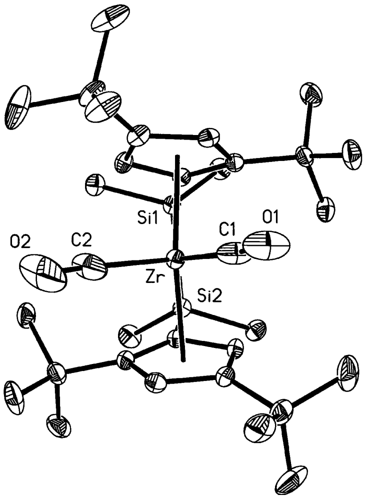

Figure 9. Orthogonal view of *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$.

Structural and Electronic Consequences of [$\mathrm{Me_2Si}$] and [$\mathrm{Me_4Si_2}$] *ansa* Bridges. An important aspect of the series of zirconocene compounds $(\mathrm{Cp^{1,3-Bu^t_2}})_2\mathrm{ZrCl_2}$, *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$, and *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ pertains to how the [$\mathrm{Me_2Si}$] and [$\mathrm{Me_4Si_2}$] *ansa* bridges influence the nature of the zirconocene center, both structurally and electronically. With respect to coordination geometry, the structures of bent metallocenes with idealized C_{2v} geometry may be defined by the angular parameters illustrated in Figure 10, of which α = interplanar-ring angle; β = $\mathrm{Cp_{norm}}$−$\mathrm{Cp_{norm}}$ angle ($\alpha + \beta = 180°$); γ = $\mathrm{Cp_{cent}}$−M−$\mathrm{Cp_{cent}}$ angle; and $\tau = 0.5(\gamma - \beta)$ = tilt angle (the angle between the M−$\mathrm{Cp_{cent}}$ vector and the ring normal).[4] Although it must be emphasized that this representation pertains specifically to metallocenes with a strict C_{2v} geometry, the derived values for distorted metallocenes still provide a useful simple means to assess structural variations. Comparison of the data listed in Table 1 indicates that

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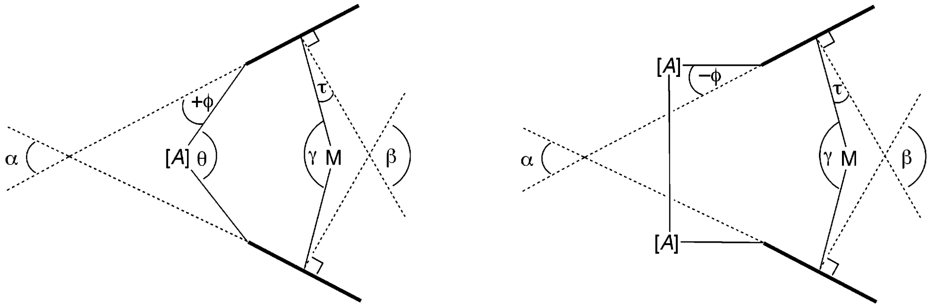
(29) Although $[\mathrm{Me_4Si_2(Ind)_2}]\mathrm{ZrCl_2}$ has been reported to exist exclusively as a *meso* isomer (ref 24), there are also reports that provide evidence for the existence of a *racemo* isomer (refs 22 and 24).



$$\alpha = 180 - \beta;\ \alpha = 2\tau - \gamma + 180;\ \tau = 0.5(\gamma - \beta)$$

Figure 10. Parameters to define single and double atom bridged metallocene geometries.

Table 2. IR Spectroscopic Data for $(Cp^{R})_2Zr(CO)_2$ Derivatives

	$\nu(CO)_{sym}$/cm^{-1}	$\nu(CO)_{asym}$/cm^{-1}	$\nu(CO)_{av}$/cm^{-1}	ref
$(Cp^{1,3-Bu^t_2})_2Zr(CO)_2$	1958	1868	1913.0	*a*
rac-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$	1962	1878	1920.0	this work
rac-$[Me_4Si_2(Cp^{Bu^t_2})_2]Zr(CO)_2$	1954	1865	1909.5	this work

[a] Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525−9546.

incorporation of the $[Me_2Si]$ bridge reduces the Cp_{cent}−Zr−Cp_{cent} angle (γ) from 133.3° for $(Cp^{1,3-Bu^t_2})_2ZrCl_2$ to 126.5° for *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$. This change is accompanied by an increase in the tilt angle (τ) from 1.0° for $(Cp^{1,3-Bu^t_2})_2ZrCl_2$ to 4.6° for *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ and a corresponding increase in the variation of Zr−C bond lengths (Δd_{Zr-C}). As such, the $[Me_2Si]$ *ansa* bridge causes a shift in coordination of the cyclopentadienyl rings towards η^3-coordination. Increasing the length of the *ansa* bridge to that of $[Me_4Si_2]$ results in an increase in Cp_{cent}−Zr−Cp_{cent} angle (γ) from 126.5° for *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ to 131.6° for *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$, a value that is comparable to that for unbridged $(Cp^{1,3-Bu^t_2})_2ZrCl_2$ (133.3°). In addition to the difference in Cp_{cent}−Zr−Cp_{cent} angles, another significant difference between *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ and *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ is that the angle between A−C_{ipso} vector and the Cp mean plane (ϕ) is positive for *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ (15.4°) but negative for *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ (−10.4°). The negative value of ϕ indicates that the $[Me_4Si_2]$ bridge is attempting to force the cyclopentadienyl rings to become more parallel; such closure, however, is prevented by interactions between the ring Bu^t substituents and the chloride ligands. In this regard, the cylindrically less sterically demanding carbonyl ligands allow the cyclopentadienyl ligands to become more parallel and the Cp_{cent}−Zr−Cp_{cent} angle (γ) for *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]Zr(CO)_2$ expands to 148.2°. Furthermore, the magnitude of ϕ is reduced from −10.4° for *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ to −1.7° for *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]Zr(CO)_2$, indicating that the Si−C_{ipso} vector lies close to the Cp plane for the dicarbonyl.

The electronic impact of the $[Me_2Si]$ and $[Me_4Si_2]$ bridges on the zirconium center may be readily probed by the variation of the ν(CO) stretching frequencies of the dicarbonyl compexes, as has been previously demonstrated for a large variety of other $(Cp^R)_2Zr(CO)_2$ derivatives.[4] Examination of the ν(CO) values listed in Table 2 indicates that incorporation of a $[Me_2Si]$ bridge causes an increase in ν(CO) stretching frequency, with $\nu(CO)_{av}$ of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$ (1920 cm^{-1}) being greater than that for $(Cp^{1,3-Bu^t_2})_2Zr(CO)_2$ (1913 cm^{-1}). This variation of ν(CO) stretching frequency indicates that the $[Me_2Si]$ *ansa* bridge exerts an electron-withdrawing effect in this system. A similar conclusion is obtained by consideration of the reduction potentials of $(Cp^{1,3-Bu^t_2})_2ZrCl_2$ (−34 mV) and *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ (142 mV),[4,30] which indicate that it is easier to reduce the *ansa*-bridged complex, and thus the $[Me_2Si]$ acts as an electron-withdrawing substituent. The $[Me_2Si]$ bridge has also been shown to exert an electron-withdrawing influence in other zirconocene systems, an observation that has been rationalized in terms of the displacement of the cyclopentadienyl rings from their natural positions in the unbridged system.[4]

In contrast to the electron-withdrawing effect of a $[Me_2Si]$ *ansa* bridge, the longer $[Me_4Si_2]$ linker exerts an electron-donating effect, as judged by comparison of the $\nu(CO)_{av}$ values of *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]Zr(CO)_2$ (1909.5 cm^{-1}), $(Cp^{1,3-Bu^t_2})_2Zr(CO)_2$ (1913.0 cm^{-1}), and *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$ (1920.0 cm^{-1}). Since the Cp_{cent}−Zr−Cp_{cent} angle (γ) of *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]Zr(CO)_2$ (131.6°) is comparable to that of $(Cp^{1,3-Bu^t_2})_2ZrCl_2$ (133.3°), the displacement of the cyclopentadienyl rings from their natural positions is no longer the dominant factor responsible for modifying $\nu(CO)_{av}$; rather, the inductive effect of the $[Me_4Si_2]$ group is now responsible for determining the electronic impact at the zirconium center. In support of this notion, a single Me_3Si substituent is observed to exert an electron-donating effect in non-*ansa* zirconocene complexes as judged by the $\nu(CO)_{av}$ values for $(Cp^{TMS})_2Zr(CO)_2$ (1929 cm^{-1}) and $Cp_2Zr(CO)_2$ (1932 cm^{-1}).[4,31]

Influence of $[Me_2Si]$ and $[Me_4Si_2]$ *ansa* Bridges on the Activity of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ and *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ as Olefin Polymerization Catalysts. The influence of $[Me_2Si]$ and $[Me_4Si_2]$ *ansa* bridges on the ability of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ and *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ to serve as catalysts for

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(30) Values relative to $E°\{[Cp_2ZrCl_2/[Cp_2ZrCl_2]^-\} = 0$ V. $E°\{[Cp_2ZrCl_2/[Cp_2ZrCl_2]^-\}$ is −2.040 V relative to Ag^+/Ag and −2.253 V relative to $[Cp_2Fe]^+/Cp_2Fe$. See ref 4.

(31) It should be noted, however, that inferences pertaining to electron-donating characteristics of substituents is dependent upon the probe method (e.g., ν(CO) versus $E°$ values). See ref 4.

ethylene polymerization, in the presence of methylalumoxane (MAO), has been addressed by comparison with $(\mathrm{Cp^{Bu^t_2}})_2\mathrm{ZrCl_2}$. Under identical conditions, the activity of *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ (106 g PE [mmol Zr]$^{-1}$ [h]$^{-1}$ [atm $\mathrm{C_2H_4}$]$^{-1}$) is a factor of ~3 greater than those of both *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ (35 g PE [mmol Zr]$^{-1}$ [h]$^{-1}$ [atm $\mathrm{C_2H_4}$]$^{-1}$) and $(\mathrm{Cp^{Bu^t_2}})_2\mathrm{ZrCl_2}$ (37 g PE [mmol Zr]$^{-1}$ [h]$^{-1}$ [atm $\mathrm{C_2H_4}$]$^{-1}$). The greater activity of the *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$/MAO catalyst is presumably a result of the reduced steric demands in the front of the metallocene wedge resulting from the constraints of the $[\mathrm{Me_2Si}]$ *ansa* bridge. In this regard, the $\mathrm{Cp_{cent}{-}Zr{-}Cp_{cent}}$ angle (γ) is much smaller for *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ (126.5°) than for both $(\mathrm{Cp^{1,3-Bu^t_2}})_2\mathrm{ZrCl_2}$ (133.3°) and *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ (131.6°). In addition to steric considerations, electronic factors may also influence activity although not necessarily in a straightforward manner. For example, a more electrophilic metal center would be expected to facilitate coordination of the olefin, but would also increase anion binding and thus possibly decrease activity.

Conclusions

In summary, a series of chiral *ansa* zirconocene compounds that feature (i) $[\mathrm{Me_2Si}]$ and $[\mathrm{Me_4Si_2}]$ bridges and (ii) two *tert*-butyl substituents on each cyclopentadienyl ring, namely, *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$, *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{Zr(Ph)Cl}$, *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{ZrMe_2}$, *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$, *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$, and *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$, has been synthesized. In each case, the complex exists as the *racemo* isomer due to inter-ring steric interactions between the $\mathrm{Bu^t}$ substituents proximal to the *ansa* bridge that destabilize the *meso* isomer. The inter-ring interaction for the *meso* isomer is sufficiently strong that the *racemo* isomer is also favored for $[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ with a longer linker and *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2}$ is the first structurally characterized *racemo ansa* zirconocene complex with a $[\mathrm{Me_4Si_2}]$ bridge. The electronic impact of the $[\mathrm{Me_2Si}]$ and $[\mathrm{Me_4Si_2}]$ bridges has been probed by IR spectroscopic studies on the dicarbonyl complexes *rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$ (1920.0 cm^{-1}), $(\mathrm{Cp^{1,3-Bu^t_2}})_2\mathrm{Zr(CO)_2}$ (1913.0 cm^{-1}), and *rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{Zr(CO)_2}$ (1909.5 cm^{-1}), with the variation in ν(CO) stretching frequencies demonstrating that the $[\mathrm{Me_2Si}]$ and $[\mathrm{Me_4Si_2}]$ *ansa* bridges have opposite electronic influences; thus, the $[\mathrm{Me_2Si}]$ bridge exerts an electron-withdrawing effect, while the $[\mathrm{Me_4Si_2}]$ bridge exerts an electron-donating effect. The electron-withdrawing effect of the $[\mathrm{Me_2Si}]$ bridge is attributed to the displacement of the cyclopentadienyl ligands from their natural positions, while the electron-donating effect of the $[\mathrm{Me_4Si_2}]$ bridge is attributed to a simple inductive effect. Finally, the $[\mathrm{Me_2Si}]$ and $[\mathrm{Me_4Si_2}]$ bridges exert a different influence with respect to olefin polymerization activity. Specifically, comparison of $\{(\mathrm{Cp^{1,3-Bu^t_2}})_2\mathrm{ZrCl_2/MAO/C_2H_4}\}$ and $\{$*rac*-$[\mathrm{Me_4Si_2(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2/MAO/C_2H_4}\}$ systems indicates that the $[\mathrm{Me_4Si_2}]$ bridge has little effect on the catalytic activity, whereas consideration of $\{$*rac*-$[\mathrm{Me_2Si(Cp^{Bu^t_2})_2}]\mathrm{ZrCl_2/MAO/C_2H_4}\}$ demonstrates that the shorter $[\mathrm{Me_2Si}]$ bridge results in a 3-fold increase in activity. The greater activity of the $[\mathrm{Me_2Si}]$-bridged system may be rationalized in terms of a reduced $\mathrm{Cp_{cent}{-}Zr{-}Cp_{cent}}$ angle, which results in a more open metallocene geometry.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques under a nitrogen or argon atmosphere, except where otherwise stated. Solvents were purified and degassed by standard procedures. ^{1}H and ^{13}C NMR spectra were measured on Bruker 300 DRX and Bruker Avance 500 DMX spectrometers. Chemical shifts are reported in ppm relative to $\mathrm{SiMe_4}$ (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ 7.15 for $\mathrm{C_6D_5H}$ and δ 7.26 for $\mathrm{CHCl_3}$) and ^{13}C resonances (δ 128.0 for $\mathrm{C_6D_6}$ and δ 77.0 for $\mathrm{CDCl_3}$). Coupling constants are given in hertz. IR spectra were recorded as pentane solutions in sealed KBr cells on a Perkin-Elmer Paragon 1000 spectrometer, and the data are reported in reciprocal centimeters. Elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer. $\mathrm{(CpH)_2}$, $\mathrm{Bu^tBr}$, dibenzo-18-crown-6 ether, $\mathrm{Bu^nLi}$ (2.5 M in hexanes), $\mathrm{Me_2SiCl_2}$, PhLi (1.8 M in CyH/$\mathrm{Et_2O}$, 70/30), methylalumoxane (10 wt % solution in toluene), and anhydrous DME were obtained from Aldrich. Sodium hydride was obtained from Aldrich as 60% dispersion in mineral oil and washed with pentane before use. MeLi was obtained from Aldrich as a 1.4 M solution in $\mathrm{Et_2O}$ but was used as a solid after removal of the solvent in vacuo. 1,2-Dichloro-1,1,2,2-tetramethyldisilane was purchased from Gelest and used without further purification.

Synthesis of Di-*tert*-butylcyclopentadiene. Di-*tert*-butylcyclopentadiene (as a mixture of 1,3- and 1,4-isomers) was prepared using a modification of a literature preparation of 1,3,5-tri-*tert*-butylcyclopentadiene.[32,33] A mixture of NaH (37.2 g, 1.55 mol) and dibenzo-18-crown-6 ether (9.0 g, 25 mmol) under a $\mathrm{N_2}$ atmosphere was cooled to −78°C and treated with THF (50 mL). The mixture was maintained at −78 °C and treated sequentially with $\mathrm{Bu^tBr}$ (144 mL, 1.25 mol) and a solution of freshly cracked CpH (41.2 mL, 0.50 mol) in THF (50 mL). The mixture was stirred at −78 °C for 12 h and then at 0 °C for a further 12 h. Finally the mixture was refluxed for 12 h. ***CAUTION!*** Care must be exercised in carrying out this reaction by allowing the reaction to warm slowly to prevent thermal runaway. After refluxing for 12 h, the reaction mixture was allowed to cool to room temperature and then placed in an ice bath and quenched slowly with water (200 mL). Pentane (200 mL) was added, and the organic layer was separated from the aqueous layer. The aqueous layer was washed with pentane (3 × 100 mL), and the combined organic layers were washed with brine. The volatile components were removed by means of a Rotovap, yielding a mixture of mono-, di-, and tri-*tert*-butylcyclopentadienes. A ca. 3:1 mixture of 1,3-di-*tert*-butylcyclopentadiene and 1,4-di-*tert*-butylcyclopentadiene isomers was obtained as a clear pale yellow oil by vacuum fractional distillation using a 12 in. Vigreux column (bp 50 °C at 180 mTorr). Yield: 51.1 g (57%). ^{1}H NMR of 1,3-di-*tert*-butylcyclopentadiene ($\mathrm{C_6D_6}$): 6.34 [t, J = 2, 1H], 5.83 [t, J = 2, 1H], 2.80 [t, J = 2, 2H], 1.20 [s, 9H], 1.12 [s, 9H]. ^{1}H NMR of 1,4-di-*tert*-butylcyclopentadiene ($\mathrm{C_6D_6}$): 6.07 [t, J = 2, 2H], 2.87 [t, J = 2, 2H], 1.13 [s, 18H].

Synthesis of $(\mathrm{Cp^{1,3-Bu^t_2}})\mathrm{Li}$. A mixture of 1,3- and 1,4-di-*tert*-butyl cyclopentadiene (20.85 g, 0.117 mol) in pentane (200 mL) at −78 °C was treated slowly with $\mathrm{Bu^nLi}$ (2.5 M in hexanes, 47 mL, 0.118 mol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h, gradually becoming a clear pale yellow gel. Approximately 80% of the pentane was removed under reduced pressure, and the product was precipitated as a white solid by addition of $\mathrm{Et_2O}$ (200 mL).

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(32) Dehmlow, E. V.; Bollmann, C. *Z. Naturforsch.* **1993**, *48b*, 457−460.

(33) For other syntheses of di-*tert*-butylcyclopentadiene, see: (a) Venier, C. G.; Casserly, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 2808−2809. (b) Schönholzer, S.; Slongo, M.; Rentsch, C.; Neuenschwander, M. *Makromol. Chem.* **1980**, *181*, 37−45.

The mixture was filtered, and the precipitate of $(Cp^{1,3-Bu^t_2})Li$ was washed with pentane and dried in vacuo. Yield: 17.0 g (79%).

Synthesis of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$. (a) A solution of $(Cp^{1,3-Bu^t_2})Li$ (7.20 g, 39.1 mmol) in THF (40 mL) was treated with a solution of Me_2SiCl_2 (2.13 mL, 17.6 mmol) in THF (20 mL). The mixture was stirred and heated at 90 °C in a glass ampule for 2 days, resulting in the gradual formation of a white precipitate (***Caution*****:** a protective screen must be employed since the temperature of the reaction is above the boiling point of the solvent). The volatile components were removed in vacuo, and residual THF was removed by triturating in pentane followed by removal in vacuo. The product was extracted into pentane (250 mL), and the pentane was removed under reduced pressure, yielding $[Me_2Si(Cp^{Bu^t_2})_2]H_2$ as a clear yellow oil (7.1 g, 97%) composed of a mixture of isomers.

(b) A solution of $[Me_2Si(Cp^{Bu^t_2})_2]H_2$ (7.26 g, 17.6 mmol) in toluene (20 mL) was treated with Bu^nLi (2.5 M in hexanes, 14.0 mL, 35.0 mmol) at room temperature under argon. The mixture was refluxed for 2 days, and a suspension of $ZrCl_4$ (4.10 g, 17.6 mmol) in toluene (20 mL) was added at room temperature. The mixture was refluxed for 5 days. After this period, the volatile components were removed in vacuo and the product was extracted into CH_2Cl_2 (300 mL). The mixture was filtered, and the filtrate was concentrated to ca. 15 mL. *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ was precipitated as a bright yellow powder by addition of pentane (200 mL) and was isolated by filtration and dried in vacuo. *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ was purified by recrystallization from toluene. Yield: 3.48 g (35%). Crystals suitable for X-ray diffraction were obtained from a benzene solution. Anal. Calcd for *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ ($C_{28}H_{46}SiZrCl_2$): C, 58.7; H, 8.1. Found: C, 58.8; H, 7.9. ^1H NMR (C_6D_6): δ 6.89 [d, J = 3, 2H], 5.98 [d, J = 3, 2H], 1.39 [s, 18H], 1.32 [s, 18H], 0.70 [s, 6H]. ^1H NMR ($CDCl_3$): δ 6.71 [d, J = 3, 2H], 5.84 [d, J = 3, 2H], 1.30 [s, 18H], 1.29 [s, 18H], 0.97 [s, 6H]. ^{13}C NMR ($CDCl_3$): δ 153.2 [s, Cp], 148.5 [s, Cp], 125.6 [dd, $^1J_{C-H}$ = 170, $^3J_{C-H}$ = 7, Cp], 111.4 [dd, $^1J_{C-H}$ = 167, $^3J_{C-H}$ = 9, Cp], 101.9 [s, *ipso* Cp], 35.4 [s, *C*Me$_3$], 34.1 [s, *C*Me$_3$], 33.2 [q, $^1J_{C-H}$ = 126, C(CH$_3$)$_3$)], 29.9 [q, $^1J_{C-H}$ = 126, C(CH$_3$)$_3$], 3.7 [q, $^1J_{C-H}$ = 121, Si(CH$_3$)$_2$].

Synthesis of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$. A mixture of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ (0.50 g, 0.87 mmol) and Na(Hg) amalgam (Na, 60 mg, 2.6 mmol; Hg, 2 mL) in THF (20 mL) in a glass ampule was cooled to −78 °C and treated with CO (ca. 1 atm). The mixture was allowed to warm to room temperature and stirred for 12 h. After this period, the volatile components were removed in vacuo, and the product was extracted into pentane (3 × 15 mL). The filtrate was concentrated and cooled to −78 °C, giving *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(CO)_2$ as a green powder, which was isolated by filtration and dried in vacuo. Yield: 0.21 g (43%). Greenish-black crystals suitable for X-ray diffraction were obtained from pentane. ^1H NMR (C_6D_6): δ 5.39 [d, J = 3, 2H], 5.13 [d, J = 3, 2H], 1.26 [s, 18H], 1.18 [s, 18H], 0.54 [s, 6H]. IR (pentane, cm^{-1}): 1962 (ν_{sym}) and 1878 (ν_{asym}). ^{13}C NMR (C_6D_6): δ 269.1 [s, Zr(CO)$_2$], 138.5 [s, Cp], 129.5 [s, Cp], 101.0 [dd, $^1J_{C-H}$ = 166, $^3J_{C-H}$ = 9, Cp], 94.6 [dd, $^1J_{C-H}$ = 168, $^3J_{C-H}$ = 9, Cp], 71.0 [s, *ipso*-Cp], 35.0 [q, $^1J_{C-H}$ = 126, C(CH$_3$)$_3$], 33.8 [s, *C*Me$_3$], 32.0 [s, *C*Me$_3$], 31.6 [q, $^1J_{C-H}$ = 126, C(CH$_3$)$_3$], 3.3 [q, $^1J_{C-H}$ = 120, Si(CH$_3$)$_2$].

Synthesis of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrMe_2$. A suspension of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ (0.20 g, 0.35 mmol) and MeLi (31 mg, 1.40 mmol) in toluene (25 mL) was heated in an ampule at 80 °C for 1 day. After this period, the mixture was filtered and the filtrate was concentrated and cooled to −78 °C, giving *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrMe_2$ as an off-white powder, which was isolated by filtration and dried in vacuo. Yield: 0.09 g (48%). Anal. Calcd for *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrMe_2$ ($C_{30}H_{52}SiZr$): C, 67.7; H, 9.9. Found: C, 68.6; H, 9.3. ^1H NMR (C_6D_6): δ 6.84 [d, J = 3, 2H], 5.79 [d, J = 3, 2H], 1.37 [s, 18H, 2Bu^t], 1.28 [s, 18H, 2Bu^t], 0.66 [s, 6H, SiMe$_2$], 0.33 [s, 6H, ZrMe$_2$]. ^{13}C NMR (C_6D_6): δ 144.8 [s, Cp], 144.5 [s, Cp], 120.1 [dd, $^1J_{C-H}$ = 165, $^4J_{C-H}$ = 8, Cp], 110.8 [dd, $^1J_{C-H}$ = 165, $^4J_{C-H}$ = 8, Cp], 95.7 [s, *ipso* Cp], 34.7 [s, *C*Me$_3$], 34.0 [q, $^1J_{C-H}$=116, Zr(CH$_3$)$_2$], 33.9 [s, *C*Me$_3$], 33.6 [q, $^1J_{C-H}$ = 126, C(CH$_3$)$_3$], 30.9 [q, $^1J_{C-H}$ = 126, C(CH$_3$)$_3$], 3.8 [q, $^1J_{C-H}$ = 121, Si(CH$_3$)$_2$].

Synthesis of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(Ph)Cl$. A suspension of *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]ZrCl_2$ (0.50 g, 0.87 mmol) in Et_2O (15 mL) was treated with PhLi (1.8 M in CyH/Et_2O, 70/30, 1 mL, 1.80 mmol) and stirred for 1 day at room temperature. The volatile components were removed in vacuo, and residual Et_2O was removed by triturating in pentane followed by removal in vacuo. The product was extracted into pentane, and the filtrate was concentrated and cooled to −78 °C to give *rac*-$[Me_2Si(Cp^{Bu^t_2})_2]Zr(Ph)Cl$ as a bright yellow powder, which was isolated by filtration and dried in vacuo. Yield: 0.29 g (54%). Crystals suitable for X-ray diffraction were obtained from pentane. ^1H NMR (C_6D_6): δ 7.93 [d, J = 7, 2H, *ortho*-Ph], 7.15 [t, J = 7, 2H, *meta*-Ph], 7.07 [t, J = 7, 1H, *para*-Ph], 6.80 [d, J = 3, 1H], 6.77 [d, J = 3, 1H], 5.98 [d, J = 3, 1H], 5.91 [d, J = 3, 1H], 1.40 [s, 9H], 1.37 [s, 9H], 1.31 [s, 9H], 0.97 [s, 9H], 0.75 [s, 6H, Si(CH_3)$_2$, coincidental]. ^{13}C NMR (C_6D_6): δ 182.9 [s, *ipso*-Ph], 152.9 [s, Cp], 152.8 [s, Cp], 147.9 [s, Cp], 147.1 [s, Cp], 141.3 [d, $^1J_{C-H}$ = 156, *ortho*-Ph], 126.3 [d, $^1J_{C-H}$ = 157, *para*-Ph], 126.2 [d, $^1J_{C-H}$ = 157, *meta*-Ph], 125.3 [dd, $^1J_{C-H}$ = 169, $^3J_{C-H}$ = 7, Cp], 122.0 [dd, $^1J_{C-H}$ = 169, $^3J_{C-H}$ = 7, Cp], 113.5 [dd, $^1J_{C-H}$ = 166, $^3J_{C-H}$ = 9, Cp], 110.1 [dd, $^1J_{C-H}$ = 166, $^3J_{C-H}$ = 9, Cp], 99.9 [s, *ipso*-Cp], 95.9 [s, *ipso*-Cp], 35.9 [s, *C*Me$_3$], 35.6 [s, *C*Me$_3$], 34.2 [s, *C*Me$_3$], 34.1 [s, *C*Me$_3$], 33.8 [q, $^1J_{C-H}$ = 126, C(CH$_3$)$_3$], 33.4 [q, $^1J_{C-H}$ = 126, C(CH$_3$)$_3$], 30.7 [q, $^1J_{C-H}$ = 128, C(CH$_3$)$_3$], 30.5 [q, $^1J_{C-H}$ = 128, C(CH$_3$)$_3$], 4.7 [q, $^1J_{C-H}$ = 120, Si(CH$_3$)$_2$], 3.8 [q, $^1J_{C-H}$ = 121, Si(CH$_3$)$_2$].

Synthesis of *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$. (a) A solution of $(Cp^{1,3-Bu^t_2})Li$ (10.0 g, 54.3 mmol) in THF (200 mL) was treated slowly with a solution of tetramethyl-1,2-dichlorodisilane (4.55 mL, 24.4 mmol) in THF (30 mL) at room temperature and then refluxed under argon for 6 days. After this period, the volatile components were removed in vacuo and the product was extracted into pentane (50 mL). The mixture was filtered, and the pentane was removed in vacuo to give $[Me_4Si_2(Cp^{Bu^t_2})_2]H_2$ as an oil. The oil was dissolved in toluene (100 mL) and then treated with Bu^nLi (2.5 M in hexanes, 21.7 mL, 54.3 mmol) at room temperature. The mixture was refluxed under argon for 18 h. The volatile components were removed in vacuo, and pentane (50 mL) was added, resulting in a gelatinous suspension, which was treated with Et_2O (100 mL) to deposit $[Me_4Si_2(Cp^{Bu^t_2})_2]Li_2$ as a light yellow powder, which was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 4.28 g (36%).

(b) A solution of $[Me_4Si_2(Cp^{Bu^t_2})_2]Li_2$ (1.59 g, 3.30 mmol) in DME (15 mL) at −78 °C was treated with a suspension of $ZrCl_4$ (0.77 g, 3.30 mmol) in DME (15 mL) at −78 °C (obtained by addition of cold DME to cold $ZrCl_4$). The mixture was allowed to warm to room temperature and then heated at 95 °C for 3 days. The volatile components were removed in vacuo. The residue was extracted into CH_2Cl_2 (200 mL) and the mixture filtered. The filtrate was concentrated to ca. 5 mL, and *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ was precipitated by addition of pentane. The mixture was filtered, and the precipitate was washed with pentane and dried in vacuo. *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ was purified by extraction into toluene (3 × 10 mL), followed by concentrating to ca. 5 mL and precipitation with pentane (15 mL). The precipitate was isolated by filtration, washed with pentane, and dried in vacuo, giving *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ as an off-white powder. Yield: 0.29 g (14%). Crystals suitable for X-ray diffraction were obtained from chloroform. Anal. Calcd for *rac*-$[Me_4Si_2(Cp^{Bu^t_2})_2]ZrCl_2$ ($C_{30}H_{52}Si_2ZrCl_2$): C, 57.1; H, 8.3. Found: C, 56.9; H, 8.4. ^1H NMR (C_6D_6): δ 6.66 [d, J = 3, 2H], 5.91 [d, J = 3, 2H], 1.33 [s, 18H], 1.31 [s, 18H], 0.68 [s, 6H], 0.26 [s, 6H]. ^1H NMR ($CDCl_3$): 6.49 [d, J = 3, 2H], 5.88 [d, J = 3, 2H], 1.26 [s, 18H], 1.23 [s, 18H], 0.82 [s, 6H], 0.35 [s, 6H]. ^{13}C NMR ($CDCl_3$): 159.0 [s, Cp], 156.6 [s, Cp], 120.8 [s, *ipso*-Cp], 116.3 [dd, $^1J_{C-H}$ = 169, $^3J_{C-H}$ = 9, Cp], 108.3 [dd,

Table 3. Crystal, Intensity Collection, and Refinement Data

	rac-[$Me_2Si(Cp^{Bu^t_2})_2$]-$ZrCl_2$	*rac*-[$Me_2Si(Cp^{Bu^t_2})_2$]-Zr(Ph)Cl	*rac*-[$Me_2Si(Cp^{Bu^t_2})_2$]-$Zr(CO)_2$	*rac*-[$Me_4Si_2(Cp^{Bu^t_2})_2$]-$ZrCl_2$	*rac*-[$Me_4Si_2(Cp^{Bu^t_2})_2$]-$Zr(CO)_2$
lattice	monoclinic	monoclinic	monoclinic	tetragonal	monoclinic
formula	$C_{28}H_{46}Cl_2SiZr$	$C_{34}H_{51}ClSiZr$	$C_{30}H_{46}O_2SiZr$	$C_{30}H_{52}Cl_2Si_2Zr$	$C_{32}H_{52}O_2Si_2Zr$
fw	572.86	614.51	557.98	631.02	616.14
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$I4_1cd$	Pn
a, Å	15.002(2)	10.148(1)	15.027(1)	18.519(1)	12.2632(7)
b, Å	12.949(1)	17.056(1)	12.901(1)	18.519(1)	10.4353(6)
c, Å	16.357(2)	19.392(1)	16.508(1)	19.423(1)	13.2677(7)
α, deg	90	90	90	90	90
β, deg	108.309(2)	90.570(1)	108.586(1)	90	94.028(1)
γ, deg	90	90	90	90	90
V, $Å^3$	3016.5(6)	3356.4(3)	3033.3(4)	6661.4(6)	1693.7(1)
Z	4	4	4	8	2
temp, K	233	243	233	243	243
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ(calcd), g cm^{-3}	1.261	1.216	1.222	1.258	1.208
μ(Mo Kα), mm^{-1}	0.595	0.462	0.424	0.579	0.420
θ max, deg	28.2	28.3	28.3	28.3	28.3
no. of data	6799	7598	6877	2531	4390
no. of params	304	335	322	161	236
R_1	0.0230	0.0300	0.0256	0.0207	0.0246
wR_2	0.0602	0.0769	0.0689	0.0531	0.0665
GOF	1.051	1.036	1.029	1.003	1.118

$^1J_{C-H}$ = 165, $^3J_{C-H}$ = 9, Cp], 35.3 [s, *C*Me_3], 35.1 [s, *C*Me_3], 32.2 [q, $^1J_{C-H}$ = 126, C(CH_3)$_3$], 30.2 [q, $^1J_{C-H}$ = 126, C(CH_3)$_3$], 2.6 [q, $^1J_{C-H}$ = 122, Si(CH_3)$_2$], 1.6 [q, $^1J_{C-H}$ = 121, Si(CH_3)$_2$].

Synthesis of *rac*-[$Me_4Si_2(Cp^{Bu^t_2})_2$]$Zr(CO)_2$. A mixture of *rac*-[$Me_4Si_2(Cp^{Bu^t_2})_2$]$ZrCl_2$ (63 mg, 0.10 mmol) and Na(Hg) amalgam (Na, 10 mg, 0.4 mmol; Hg, 2 mL) in THF (15 mL) in an ampule was cooled to −78 °C and treated with CO (ca. 1 atm). The mixture was allowed to warm to room temperature and stirred for 24 h. After this period, the volatile components were removed in vacuo, and the product was extracted into pentane (2 × 10 mL). The volatile components were removed from the filtrate in vacuo, and the residue was dissolved in benzene (10 mL) and lyophilized to give *rac*-[$Me_4Si_2(Cp^{Bu^t_2})_2$]$Zr(CO)_2$ as a green-brown powder. Yield: 30 mg (48%). ^{1}H NMR (C_6D_6): δ 5.91 [d, J = 3, 2H], 5.12 [d, J = 3, 2H], 1.42 [s, 18H], 1.23 [s, 18H], 0.41 [s, 6H], 0.40 [s, 6H]. IR (pentane, cm^{-1}): 1954 (ν_{sym}) and 1865 (ν_{asym}). ^{13}C NMR (C_6D_6): δ 274.5 [s, Zr(*C*O)$_2$]; 134.4 [s, Cp], 134.0 [s, Cp]; 105.0 [s, *ipso*-Cp], 98.3 [dd, $^1J_{C-H}$ = 166, $^3J_{C-H}$ = 6, Cp], 97.8 [dd, $^1J_{C-H}$ = 168, $^3J_{C-H}$ = 8, Cp], 34.2 [q, $^1J_{C-H}$ = 126, C(CH_3)$_3$], 33.5 [s, *C*Me_3], 32.1 [s, *C*Me_3], 31.5 [q, $^1J_{C-H}$ = 126, C(CH_3)$_3$], 3.8 [q, $^1J_{C-H}$ = 120, Si(CH_3)], 1.3 [q, $^1J_{C-H}$ = 121, Si(CH_3)].

Ethylene Polymerization by $(Cp^R)_2ZrCl_2$/MAO. A stock solution of zirconocene catalyst was prepared by treating a solution of $(Cp^R)_2ZrCl_2$ (0.046 mmol) in toluene (5 mL) with MAO (10 mL of 10 wt % solution in toluene), corresponding to an Al:Zr ratio of 328:1. The catalyst solution (5 mL) was added to a stirred saturated solution of ethylene in toluene (25 mL) at 0 °C. The ethylene pressure was maintained at 1 atm during the course of the polymerization. The reaction mixture was quenched after 15 min by addition of methanol (10 mL), and the polyethylene was isolated by filtration, washed with methanol, and dried. Each polymerization run was performed twice to obtain the average activity: $(Cp^{Bu^t_2})_2ZrCl_2$ (37 g PE [mmol Zr]$^{-1}$ [h]$^{-1}$ [atm C_2H_4]$^{-1}$), *rac*-[$Me_2Si(Cp^{Bu^t_2})_2$]$ZrCl_2$ (106 g PE [mmol Zr]$^{-1}$ [h]$^{-1}$ [atm C_2H_4]$^{-1}$), *rac*-[$Me_4Si_2(Cp^{Bu^t_2})_2$]$ZrCl_2$ (35 g PE [mmol Zr]$^{-1}$ [h]$^{-1}$ [atm C_2H_4]$^{-1}$).

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector, and crystal data, data collection, and refinement parameters are summarized in Table 3. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 5.03).[34]

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Supporting Information Available: Crystallographic data in CIF format for *rac*-[$Me_2Si(Cp^{Bu^t_2})_2$]$ZrCl_2$, *rac*-[$Me_2Si(Cp^{Bu^t_2})_2$]Zr(Ph)Cl, *rac*-[$Me_2Si(Cp^{Bu^t_2})_2$]$Zr(CO)_2$, *rac*-[$Me_4Si_2(Cp^{Bu^t_2})_2$]$ZrCl_2$, and *rac*-[$Me_4Si_2(Cp^{Bu^t_2})_2$]$Zr(CO)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049273J

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