Reductive Coupling of an Indenylidene with Calcium To Form Bis(indenyl) *ansa*-Metallocenes: Molecular Structures of *trans*-$Ph_2C_2H_2$-*rac*-(η^5-4,7-$Me_2C_9H_4)_2Ca(THF)_2$ and *trans*-$Ph_2C_2H_2$-*rac*-(η^5-4,7-$Me_2C_9H_4)_2Fe$

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Received December 7, 1998

1-*E*-benzylidene-4,7-dimethylindene (**1**) is reductively coupled by activated calcium to form two isomers, *trans*-$Ph_2C_2H_2$-*rac*-(η^5-4,7-$Me_2-C_9H_4)_2Ca(THF)_2$ (*trans-rac*-**2**) and *cis*-$Ph_2C_2H_2$-*meso*-(η^5-4,7-$Me_2-C_9H_4)_2Ca(THF)_2$ (*cis-meso*-**2**) in an approximately 1:1 ratio. Reaction of the calcium species with $FeCl_2$ produces a mixture of the corresponding trans-rac and cis-meso ferrocenophane species (**3**) along with another ferrocenophane isomer that is presumed to be either the trans-meso or cis-rac isomer. Thus, the relative geometry of the indenyl rings is not retained entirely during the transfer of the ligand framework from calcium to iron. A complete scrambling of the indenyl ring geometry appears to occur upon transfer of the ligand framework from calcium to zirconium. The results of X-ray crystal structure determinations of 1-*E*-benzylidene-4,7-dimethylindene, *trans*-$Ph_2C_2H_2$-*rac*-(η^5-4,7-$Me_2-C_9H_4)_2Ca(THF)_2$, and *trans*-$Ph_2C_2H_2$-*rac*-(η^5-4,7-$Me_2-C_9H_4)_2Fe$ are described.

Introduction

We reported recently the facile reductive coupling of phenylfulvene with activated calcium to yield a mixture of *ansa*-calcocenes with *cis*- and *trans*-diphenylethano bridges.[1] The predominant trans isomer was isolated by fractional recrystallization, and its structure was confirmed by X-ray crystallography. This new calcocene has been shown to be a versatile precursor for the preparation of C_2-symmetric metallocenes of iron,[1] chromium,[2] and zirconium.[1] An elegant and even more direct application of fulvene coupling to the synthesis of group 4 *ansa*-metallocene dichlorides was also recently reported by Eisch and co-workers.[3] In this case the reductive coupling is accomplished by the divalent group 4 transition metal dihalides themselves.

The formation of 1,1′-(1,2-*trans*-diphenylethanediyl)-calcocene as the major isomer in the coupling of phenylfulvene by activated calcium led us to investigate the possibility of preparing a single C_2-symmetric product selectively. Our initial efforts were directed at increasing the steric bulk of the 6-aryl group of the fulvene in order to promote formation of the trans-coupling product, but this met with only limited success. As a result, we turned to an indenyl fulvene analogue that we hoped would impose additional steric limitations on the stereochemistry of the coupling reaction, in addition to meeting the limitation discovered in our previous work: that the fulvene must be devoid of abstractable hydrogens. Described herein are the preparation and molecular structures of 1-*E*-benzylidene-4,7-dimethylindene, its calcocene coupling product, and a ferrocene complex derived therefrom.

Results

Synthesis and Structure of 1-*E*-Benzylidene-4,7-dimethylindene. There are four calcocene diastereomers that could arise from the coupling of a benzylideneindene by calcium since either a cis or trans stereochemistry within the 1,2-diphenylethano bridge can be combined with either a meso or rac orientation of the indenyl rings (Scheme 1). We sought to limit the number of isomers which could form by introducing methyl substituents at the 4- and 7-benzenoid positions of the indenyl molecule in order to block isomerization of the benzylideneindene from an *E* to a *Z* geometry during the reductive coupling reaction. Our limited knowledge of the mechanistic details of the fulvene coupling notwithstanding, our subsequent attempts to couple the simpler 1-*E*-benzylideneindene with activated cacium resulted in an ill-defined mixture of products, the ^1H NMR spectrum of which could not be attributed solely to the trans-rac and cis-meso isomers.

Using a modification of the method reported by Friguelli et al. for the synthesis of 1-*E*-benzylideneindene,[4] we synthesized 1-*E*-benzylidene-4,7-dimethylindene (**1**) from 4,7-dimethylindene. Although the preparation of this compound has been mentioned previously,[5,6]

(1) Kane, K. M.; Shapiro, P. J.; Cubbon, R.; Vij, A.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4567.
(2) Matare, G. J.; Foo, D. M.; Kane, K. M.; Wagener, M.; Shapiro, P. J.; Concolino, T.; Rheingold, A. L. Manuscript in preparation.
(3) Eisch, J. J.; Shi, X.; Owuor, F. A. *Organometallics* **1998**, *17*, 5219.
(4) Fringuelli, F.; Pani, G.; Pizzo, F. *Tetrahedron* **1994**, *50*, 11499.
(5) Herz, W. *J. Am. Chem. Soc.* **1953**, *75*, 73.
(6) Riedel, M.; Erker, G.; Bosch, B.; Bertuleit, A. Ger. Patent DE 19632919 A1 980219, 1996.

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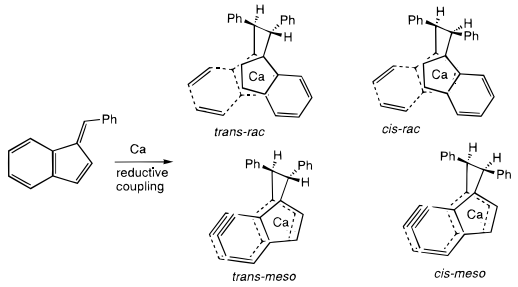
Publication on Web 07/24/1999

Scheme 1. Four Possible Isomers from the Reductive Coupling of Benzylideneindene with Calcium



its synthesis and characterization have not yet been fully described.

The fulvene is a yellow, crystalline compound that can be recrystallized from hot ethanol or purified by sublimation in yields approaching 60%. The ^{1}H and ^{13}C NMR assignments for **1** were determined from a combination of HETCOR and COSY experiments. Whereas Fringuelli et al. determined the orientation of the phenyl group in 1-*E*-benzylideneindene using NOE experiments,[4] we were able to isolate an X-ray quality crystal of **1** that confirms the *E*-configuration of the phenyl moiety. There are four independent molecules in the unit cell. This is a consequence of the crystal packing, in which two independent chains of molecules having no true symmetry relation stack parallel to the [100] direction. In each chain, the normals to the fused rings make an angle of approximately 45° with the [100] direction. However, in each chain, the normals to the phenyl groups are alternately parallel and perpendicular to [100]. Thus, with two crystallographically independent molecules per chain, and two independent chains, a $Z = 4$ is obtained. An ORTEP drawing of the four molecules is shown in Figure 1 alongside a packing diagram of the crystal. Crystallographic data for **1** are given in Table 1 and selected bond lengths and angles for one of the indenylidene molecules, C1−C18, are presented Table 2.

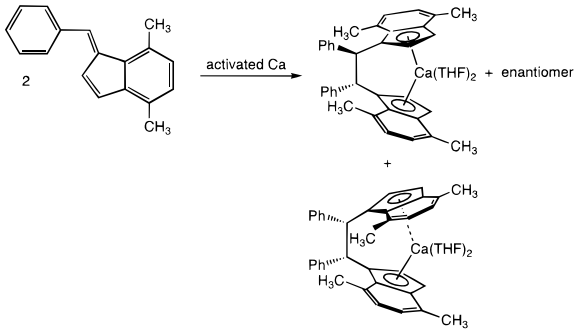
Examples of crystallographically characterized indenylidenes are few.[7−9] The molecular structure of **1** is most comparable to that of *trans*-1,1′-bis(indenylidene),[7] which differs from **1** by the absence of methyl substituents at the 4,7-positions of the indene rings and by the constrained coplanarity of the substituents about the fulvene double bond. The exocyclic fulvene bond lengths for the two molecules are similar (1.340(5) Å for **1** and 1.342(4) Å for the bis(indenylidene). The pattern of C−C double and single bonds within the indene rings of the two molecules are also similar. In both molecules, the π-electrons of the benzenoid portion of the indene rings are delocalized, as revealed by the fairly uniform lengths of their C−C bonds.

The features of the molecular structure of **1** most relevant to the chemistry described herein are the nonbonded distances between C(11) and C(12) (3.246 Å) and between C(12) and C(16) (4.259 Å). The greater span of the C(12)−C(16) distance indicates that rotation about the C(9)−C(12) bond would be significantly hindered by the methyl group at C(5).

^{1}H and ^{13}C NMR assignments for **1** (Experimental Section) were based on a combination of HETCOR, COSY, and APT experiments and by comparison with spectral data for dimethylindene and earlier assignments for *E*-1-benzylidene-1*H*-indene.[4]

Preparation and NMR Characterization of *ansa*-Calcocene and *ansa*-Ferrocene Complexes. The reaction of **1** with activated calcium takes several hours, which contrasts with the reductive coupling of phenylfulvene (complete in 45 min).[1] The *ansa*-calcocene **2** is isolated as a tan powder which is stable in the solid state under a nitrogen atmosphere if stored at −25 °C. At room temperature the solid darkens to brown over days. In this respect, **2** is less stable than its biscyclopentadienyl analogue, which undergoes a similar discoloration much more slowly, over months of storage at room temperature.

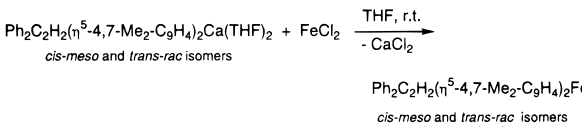
Although a crystal structure determination of **2** revealed only the trans-rac isomer (vide infra), the ^{1}H NMR spectrum of the isolated product indicated that another isomer, the cis-meso isomer, was also present since a total of four distinct methyl resonances were observed (eq 1).



(1)

The presence of either the trans-meso and cis-rac isomers could be eliminated since each individual isomer would have contributed four methyl peaks to the spectrum. A roughly 50:50 ratio of the trans-rac and cis-meso isomers was indicated by the relative intensities of the methyl resonances at δ 3.04, 2.95, 2.32, 2.30 in the ^{1}H NMR spectrum of the mixture in benzene-d_6.

The reaction of **2** with $FeCl_2$ produces a variable mixture of isomers of the ferrocenophane complex **3** (eq 2).



(2)

Two isomers are formed predominantly, and we assign these as the trans-rac and cis-meso isomers based on the number of distinct methyl peaks in the ^{1}H NMR spectrum of the mixture in benzene-d_6 (two singlets for the trans-rac isomer at δ 2.71, 2.22 and two singlets for the cis-meso isomer at δ 2.53, 1.92) and on the number of peaks corresponding to hydrogens on the cyclopentadienyl portion of the indenyl ring (two doublets for the trans-rac isomer at δ 5.06, 3.97 and two doublets for the cis-meso isomer at δ 4.68, 4.47). Our assignment

(7) Capparelli, M. V.; Machado, R.; de Sanctis, Y.; Arce, A. J. *Acta Crystallogr.* **1996**, *C52*, 947.
(8) Erhardt, W. D.; Ammon, H. L. *Tetrahedron Lett.* **1975**, 3997.
(9) Fernández-G., J. M.; Solorzano-Maldonado, K.; Rodríguez-Romero, A.; Soriano-García, M. *Acta Crystallogr.* **1996**, *C52*, 460.

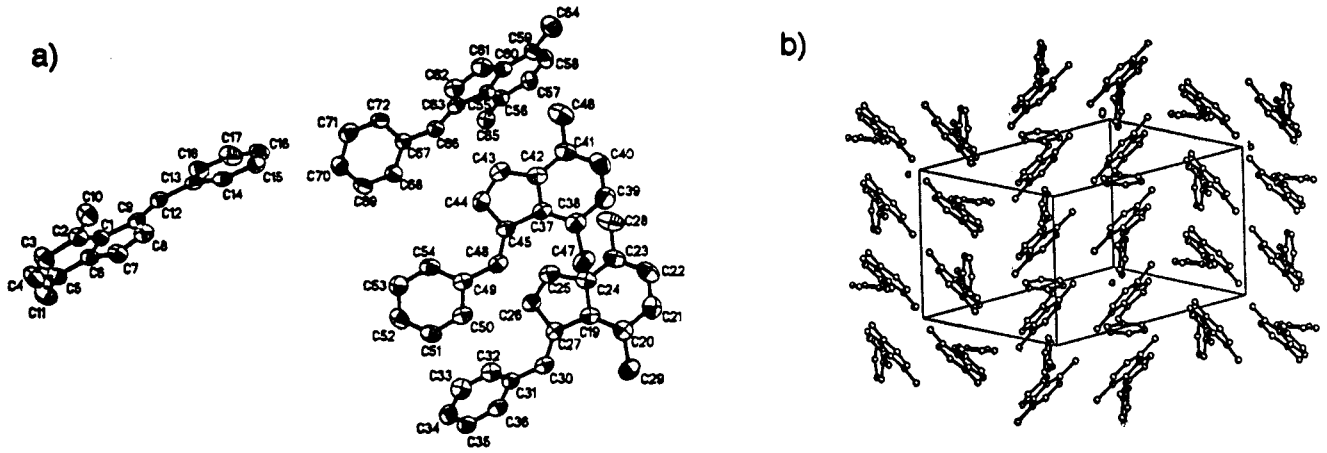


Figure 1. (a) Molecular structures of four independent molecules in the crystal of **1** with atom labelings. Thermal ellipsoids are plotted at 50% probability. (b) Crystal packing diagram.

Table 1. Crystallographic Data for 1 and *trans-rac*-3

	1	*trans-rac*-**3**
formula	$C_{18}H_{16}$	$C_{36}H_{32}Fe$
mol wt	232.31	520.47
cryst syst	triclinic	orthorhombic
space group	*P*1	*Pbca*
a (Å)	10.0013(2)	12.9203(4)
b (Å)	15.0257(3)	17.2732(4)
c (Å)	18.4490(2)	23.6686(7)
α (deg)	82.371(1)	90
β (deg)	78.313(1)	90
γ (deg)	78.958(1)	90
V (Å^3)	2651.95(8)	5282.2(3)
Z	4	8
T (K)	213(2)	213(2)
λ (Å)	0.701 73 (Mo Kα)	0.701 73 (Mo Kα)
ρ_{calcd} (g/cm^3)	1.164	1.309
μ (mm^{-1})	0.065	0.594
F_{000}	992	2192
cryst size	0.10 × 0.10 × 0.05	0.10 × 0.10 × 0.05 mm
θ range (deg)	1.38−23.28	1.72−25.00
hkl limits	−11/10; −16/16; −20/15	−14/16; −17/22; −31/29
no. reflcns collected	11 106	23 031
no. indep reflcns	7087 (R_{int} = 0.0502)	4642 (R_{int} = 0.2051)
data/restraints/ param	7084/0/650	2075/317/335
GOF	1.049	1.229
R(F_o)[a]	0.0800 ($F > 2\sigma(F)$)	0.0856 ($F > 2\sigma(F)$)
wR(F_o^2)[b]	0.1918	0.1440
largest diff peak/ hole (e Å^{-3})	0.413/−0.352	0.379/−0.309

[a] $R = \sum|F_o - F_c|/\sum|F_o|$. [b] $wR = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$; $w = 1/\sigma^2(F_o)^2 + (xP)^2 + (yP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

C(1)−C(9)	1.490(5)	C(6)−C(7)	1.471(6)
C(1)−C(6)	1.405(5)	C(7)−C(8)	1.332(6)
C(1)−C(2)	1.398(5)	C(8)−C(9)	1.483(5)
C(2)−C(3)	1.394(6)	C(9)−C(12)	1.340(5)
C(3)−C(4)	1.383(6)	C(12)−C(13)	1.465(5)
C(4)−C(5)	1.394(6)		
C(1)−C(2)−C(10)	124.4(4)	C(5)−C(6)−C(7)	129.1(4)
C(3)−C(2)−C(10)	119.6(4)	C(1)−C(9)−C(12)	128.8(3)
C(3)−C(2)−C(1)	116.0(4)	C(1)−C(9)−C(8)	104.2(3)
C(4)−C(5)−C(6)	116.0(4)	C(8)−C(9)−C(12)	126.9(4)
C(6)−C(5)−C(11)	121.9(4)	C(9)−C(12)−C(13)	128.6(4)
C(4)−C(5)−C(11)	122.1(4)	C(2)−C(1)−C(9)	131.7(4)

of peaks for the two isomers is based on the assumption that the trans-rac species is the predominant of the two and is the isomer that is enriched upon recrystallization of the isomer mixture. We base this assumption on our experience with *trans*- and *cis*-$Ph_2C_2H_2(\eta^5\text{-}C_5H_4)_2Ca(THF)_2$.[1] On occasion, additional peaks due to another isomer of **3** appear in the methyl and indenyl regions of the ^{1}H NMR spectrum of the ferrocenophane product. We tentatively assign this isomer as either the trans-meso or the cis-rac form of **3** based on the pattern of four distinct methyl resonances in the benzene-d_6 ^{1}H NMR spectrum at δ 2.85, 2.57, 2.11, 2.03. This additional isomer has appeared in some preparations in amounts approaching that of the cis-meso isomer. As with the calcocene complex, the crystal of the ferrocene complex selected for X-ray analysis contained only the trans-rac isomer (vide infra).

Compound **3** is isolated as a purple precipitate upon addition of petroleum ether to a toluene solution of the compound. The compound is extremely air-sensitive as compared with the other [2]ferrocenophanes,[10−18] turning light brown immediately upon exposure to air in either the solid state or in solution. The compound appears to be light-sensitive as well, decomposing from a purple benzene-soluble solid to an insoluble brown solid, even upon storage in a nitrogen atmosphere, if it is not protected from light. The exceptional instability of this compound can probably be attributed to the propensity of the indenyl ring toward ($\eta^5-\eta^3$) slippage in combination with the strain imposed by the interannular bridge.

X-ray Structures of *trans*-$Ph_2C_2H_2$-*rac*-(η^5-4,7-$Me_2C_9H_4)_2Ca(THF)_2$ and *trans*-$Ph_2C_2H_2$-*rac*-(η^5-4,7-$Me_2C_9H_4)_2Fe$. Two unique calcocene molecules and a free molecule of THF were found in the unit cell of the crystal of **2** that was characterized. Both calcocene molecules exhibit a trans-rac stereochemistry. The X-ray

(10) Yasufuku, K.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1997**, *16*, 6624.
(11) Aggarwal, V. K.; Jones, D.; Turner, M. L.; Adams, H. *J. Organomet. Chem.* **1996**, *524*, 263.
(12) Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993**, *115*, 7035.
(13) Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1971**, *27*, 4343.
(14) Tan, T. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Chem. Soc. Chem. Commun.* **1975**, 771.
(15) Vyacheslav V.; Dement'ev, F. C.-L.; Parkanyi, L.; Sharma H.; Pannell, K. H.; Nguyen, M. T.; Diaz, A. *Organometallics* **1993**, *12*, 1983.
(16) Finckh, W.; Tang, B.-Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993**, *12*, 823.
(17) Laing, M. B.; Trueblood, K. N. *Acta Crystallogr.* **1965**, *19*, 373.
(18) Heberhold, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1837.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans-rac*-2 and *trans-rac*-3

	trans-rac-**2** (M = Ca, L = OC_5H_8)		*trans-rac*-**3**
	molecule 1	molecule 2	(M = Fe, L = none)
	Average Bond Distance (Å)		
M−L	2.339(5)	2.346(20)	- - -
M-Cp(centroid)	2.452(3)	2.458(14)	1.64(4)
	Bond Angle (deg)		
L−M−L	90.2(2)	93.2(2)	- - -
cent−M−cent (δ)	118.5	118.8	164.2°
Cp−Cp bend(α)	66.4(3)	66.0(3)	22.9(4)
Ph−Ph twist	47.2(3)	86.5(2)	71.0(2)
	Torsion Angle (deg)		
Ph-C−C−Ph[b]	50.4(9)	54.7(8)	66(1)
Ind-C−C−Ind[c]	56.7(8)	47.5(8)	39.5(9)

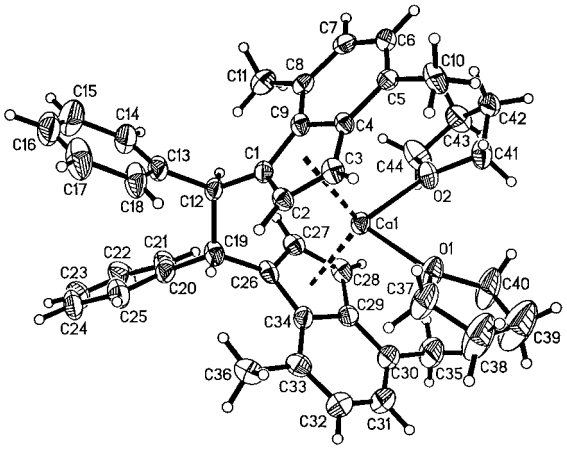


Figure 2. Molecular structure of one of the trans-rac-calcocene molecules in the crystal of **2**. Thermal ellipsoids are plotted at 50% probability.

crystal structure has not yet been completely refined[19] due to our inability to identify and refine a long chain molecule that is also present in the crystal. Nevertheless, the core structures show definitive atom connectivity and reasonable bond lengths and angles. An ORTEP drawing of one of the calcocene molecules (molecule 1) is shown in Figure 1. Selected bond distances and angles for both molecules are listed in Table 3 (All crystallographic details available up to the writing of this manuscript are in the Supporting Information).

The indenyl rings in *trans-rac*-**2** (Figure 2) adopt a more open bent-sandwich structure as compared with the structure of the cyclopentadienyl analogue, *trans*-$Ph_2C_2H_2(\eta^5\text{-}C_5H_4)_2Ca(THF)_2$.[1] This is reflected in the narrower cent−Ca−cent angles (118.5°and 118.8° as compared to 119.9°) and the larger angles between the indenyl ring planes (66.4°and 66.0° as compared to 58.0°). The average Ca−Cp(centroid) distance of 2.45 Å is comparable to the 2.42 Å distance found in the cyclopentadienyl analogue. The Ca−O distances are comparable to those of *trans*-$Ph_2C_2H_2(\eta^5\text{-}C_5H_4)_2Ca(THF)_2$. The greater bending angle between the indenyl rings of **2** is accompanied by wider O−Ca−O angles (90.2°and 93.2° as compared to 84.7°). This allows the two tetrahydrofuran (THF) molecules in the equatorial wedge to adopt more of a mutually coplanar arrangement as opposed to the mutually perperpendicular orientation encountered in the cyclopentadienyl analogue. The planar nature of one of the coordinated THF molecules in molecule 1 (O(1), C(37)−C(40)) and its relatively large thermal ellipsoids indicate that it is positionally disordered.

The molecular structure of *trans-rac*-**3** is shown in Figure 3. Crystallographic data and selected bond distances and angles are listed in Tables 1 and 3, respectively. In contrast to [*m*]ferrocenophanes, there are few reported structures of bridged bis(indenyl)iron complexes.[20,21,27,28] Distortions in ferrocenophanes are typically described by the tilt angle α, between the ring planes, and by the angle fomed by the metal and the ring centroids, δ. The values for α and δ for *trans-rac*-**3**, 22.9° and 164.4°, respectively, are comparable with those exhibited by other carbon bridged [2]ferrocenophanes.[10,11,17,18] The average Fe−Cp(centroid) distance of 1.64 Å is also normal. Nevertheless, some ring slippage is evident from the large variation in distances between the iron and the coordinated carbons of the indenyl rings. In general, the benzenoid carbons (C(1), C(5), C(26), C(30)) are slipped farthest from the iron center with distances of 2.079(9)−2.119(9) Å; however, C(4) and C(29), at 2.045(9) and 2.072(8) Å, are also somewhat distant from the iron center as compared with C(2), C(3), C(27), and C(28), which range from 1.961(9) Å to 2.022(9) Å. This additional slippage can be attributed to the strain imposed by the two-carbon bridge on the metallocene structure, which is also evident from the large deviations of C(2) and C(27), the bridgehead carbons, from the mean planes of the indenyl rings by 0.030(5) and 0.033(5) Å, respectively. The Ind−C−C−Ind torsion angle of 39.5° is quite large when compared to that of 1,1′-tetramethyleneferrocene,[16] in which the corresponding Cp-C−C−Cp torsion angle is 25°. Consequently, the C_5 rings *trans-rac*-**3** are more staggered (Figure 3b), by approximately 18° as compared to the 9−10° angle of staggering in 1,1′-tetramethyleneferrocene.

Discussion and Conclusion

Although the reductive coupling of 1-*E*-benzylidene-4,7-dimethylindene with activated calcium to form an *ansa*-bis(indenyl)calcium complex is stereoselective, forming only two of four possible diastereomers through a retention of the *E* geometry about the fulvene C−C bond, we were disappointed by the lack of selectivity of the coupling for the C_2-symmetric trans-rac isomer. Surprisingly, formation of the trans isomer is less favored in this case than in the synthesis of $Ph_2C_2H_2(\eta^5\text{-}C_5H_4)_2Ca(THF)_2$.

Poor rac:meso ratios have generally been obtained in the kinetic products of the synthesis of group 4 *ansa*-metallocene complexes from dianions of bridged, symmetrically substituted dicyclopentadiene ligands and bridged bis(indene) ligands. Brintzinger has attributed these poor stereoselectivities to the formation of intermediates with one η^1-bonded ring, in which there would

(19) Crystal data for **2**: space group $P2_1/n$; monoclinic; a = 23.1634(4) Å; b = 15.0033(3) Å; c = 28.3090(2) Å; β = 104.836(1)°; V = 9510.2(3) Å^3; Z = 12; R indices at current level of refinement [$I > 2\sigma(I)$, R_1 = 0.0932, wR_2 = 0.2342 for 13 431 independent reflections; GOF = 1.051. The structure will be submitted for publication to Cambridge Crystal Structure Data Base upon completion.

(20) Scott, P.; Rief, U.; Diebold, J.; Brintzinger, H. H. *Organometallics* **1993**, *12*, 3094.

(21) Dewan, J. C. *Organometallics* **1983**, *2*, 83.

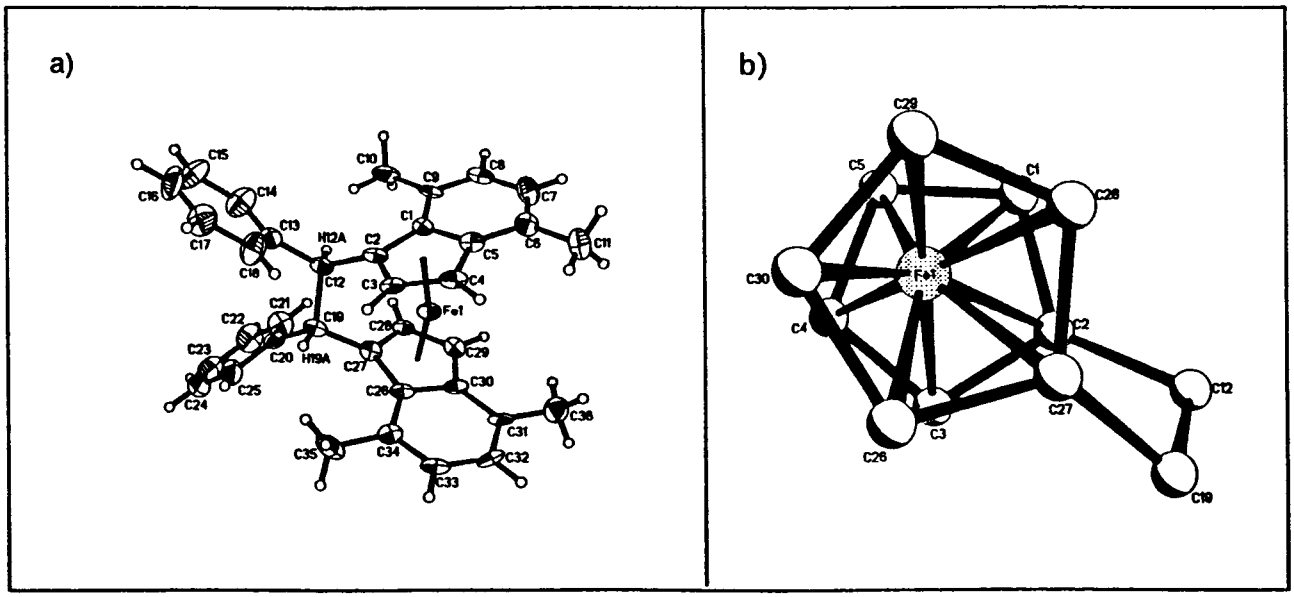


Figure 3. (a) Side view of molecular structure of *trans-rac*-**3**. (b) Top view of a partial structure showing the staggered conformation of the metallocene rings and the degree of twist in the two-carbon bridge. Thermal ellipsoids are plotted at 50% probability.

be negligible steric interaction between the substituents on the rings.[22] Although the fulvene reductive coupling probably involves a different mechanism of ligand assembly about the metal, this method offered no real improvement in diastereolectivity in the synthesis of the title calcocene complex. Eisch likewise obtained a 1:1 mixture of *meso*- and *rac*-benzometallocene isomers in the coupling of 1′,1′-dimethylbenzofulvene with zirconium chloride. Nevertheless, his employment of the transition metal itself as the template for fulvene coupling is preferable to having an additional transmetalation step, not only because it is more direct but also because we have found that the transmetalation results in additional loss of stereochemistry.

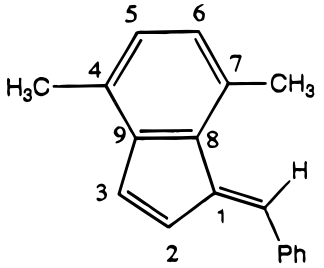
Transfer of the bis-indenyl ligand framework from calcium to iron occurs with some loss of stereochemistry, since a third isomer besides the trans-rac and cis-meso ferrocenophane isomers appears in the reaction product. An even greater loss of stereochemistry was encountered upon transferring the ligand framework from calcium to either $ZrCl_4(SMe_2)_2$ or $ZrCl_4(THF)_2$. Both reactions produced a complex mixture of products which could not be distinguished by their peaks in the ^{1}H NMR spectrum and which could not be separated or even enriched in one species by crystallization. Thus, achieving a diastereochemically pure racemic form of an *ansa*-bis(indenyl)calcium complex (either through the stereoselective reductive coupling of indenylfulvenes with activated calcium or the separation of a isomeric mixture) does not guarantee that this stereochemistry is retained upon transfer of the ligand framework from the calcium center to a transition metal. Complete retention of meso or rac stereochemistry upon transmetalation is guaranteed only with stannyl or silyl derivatives of the ligand framework.[23,24]

(22) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H.-H. *J. Organomet. Chem.* **1989**, *369*, 359.
(23) Hüttenhofer, M.; Schaper, F.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1998**, *110*, 2378.
(24) Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Ziegler, R. *Organometallics* **1996**, *15*, 5046.

Experimental Section

General Procedures. All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques. All solvents were distilled under nitrogen over sodium benzophenone ketyl (tetrahydrofuran, toluene, methylcyclohexane) or CaH_2 (petroleum ether). The solvents were then stored in line-pots from which they were either vacuum-transferred from sodium benzophenone ketyl or cannulated directly. NMR solvents (Isotech): Benzene-d_6 and $CDCl_3$ were dried over activated 4 Å molecular sieves. Argon was purified by passage over oxy tower BASF catalyst (Aldrich) and 4 Å molecular sieves. 4,7-Dimethylindene was prepared as described by Erker et al..[25] Cetylammonium bromide (Aesar), calcium granules (Strem), $HgCl_2$ (Aldrich), and $FeCl_2$ (Aldrich), were used as received from the supplier. NMR spectra were recorded on an IBM NR-300 (300 MHz ^{1}H, 75 MHz ^{13}C) an IBM NR-200 (200 MHz ^{1}H, 50 MHz ^{13}C), and a Varian Gemini 300 (300 MHz ^{1}H, 75 MHz ^{13}C).

Preparation of *E*-1-benzylidene-1*H*-4,7-dimethylindene, 1. Using a modification of the method reported by



Fringuelli et al.,[4] dimethylindene (23.5 g, 0.16 mol) was added slowly to a mixture of 0.61 g of cetyltriethylammonium bromide in 250 mL of 0.25 M NaOH. After stirring rapidly for 10 min, benzaldehyde (17.3 g, 0.16 mol) was added dropwise to the mixture over a 3 h period. The mixture was stirred overnight, and the resultant yellow solid was isolated by filtration. The product was washed with water several times, allowed to air-dry, and then crystallized from hot ethanol to give bright yellow needles. A second crop was obtained by

(25) Erker, G.; Psiorz, C.; Fröhlich, R.; Grehl, M.; Krüger, C.; Nolte, M. *Tetrahedron* **1995**, *51*, 4347.

concentrating the filtrate and cooling: total yield, 22.4 g (60%); mp, 58−59 °C. ^{1}H NMR ($CDCl_3$): δ 7.68 (s, 1H, fulvenyl-H); 7.54−7.64 (m, 2 H, $H_{2'}$, $H_{6'}$); 7.41−7.50 (m, 2H, $H_{3'}$, $H_{5'}$), 7.32−7.40 (m, 1H, $H_{4'}$), 7.10 (dd, 1H, H_5 or H_6), 6.88−7.2 (m, 3H, H_2, H_3, and H_5 or H_6), 2.68, 2.45 (s, each 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 143.1, 141.6, 137.7, 133.0, 130.4, 128.1 (C_1, C_4, C_7, C_8, C_9, and $C_{1'}$), 133.0 (*C*HPh), 130.4 ($C_{2'}$ and $C_{6'}$), 128.9 (C_2 or C_3), 131.5 (C_2 or C_3), 126.3 (C_5 or C_6), 128.4 ($C_{3'}$ and $C_{5'}$), 127.8($C_{4'}$), 21.4, 18.0 (*C*H$_3$). Anal. Calcd for $C_{18}H_{16}$: C, 93.0; H, 6.7. Found: C, 93.0; H, 6.9.

Preparation of $Ph_2C_2H_2$-(η^5-4,7-$Me_2C_9H_4$)$_2$Ca(THF)$_2$, 2. Calcium granules (0.65 g, 16 mmol) were activated with $HgCl_2$ (0.047 g, 0.17 mmol) by combining the two solids in 150 mL THF, letting the mixture sit undisturbed for 1 h, under a blanket of argon, and then rapidly stirring the mixture for 1 h. The fulvene **1** (1.7 g, 7.3 mmol) was added to the solution at room temperature with stirring. On addition of the fulvene the solution initially turned green then grayish-brown. The mixture was stirred at room temperture for 8 h. The excess calcium was removed by filtration, and the filtrate was evaporated to dryness to yield a beige foam that was washed twice with hexane. The solid was resuspended in diethyl ether, cooled at −78 °C, and filtered cold to afford **2** as a white, flocculent solid (yield, 1.3 g, 55%). ^{1}H NMR (C_6D_6); mixture of isomers): δ 7.83 (d,$^3J_{HH}$ = 7.1 Hz, Ph-*H*); 7.59 (d, $^3J_{HH}$ = 6.9 Hz, Ph-*H*); 7.29 (d, $^3J_{HH}$ = 3.4 Hz, H_5 and H_6); 7.13−6.94 (m, H_5 or H_6 and Ph-*H*); 6.82 (s, PhC*H*Cp), 6.59−6.43 (m, H_2 and H_3 and Ph-*H*); 6.11, 5.98 (d, $^3J_{HH}$ = 3.4 Hz, H_2 and H_3); 6.03 (s, PhC*H*Cp); 3.04, 2.95, 2.32, 2.30 (s, 4,7-C*H*$_3$); 2.88, 1.15 (br, THF). ^{13}C NMR (C_6D_6; mixture of isomers): δ 130.3, 129.6 (C_5 and C_6); 126.4, 126.2, 125.4, 125.0, 124.8, 120.5, 120.0, 119.8, 118.0 (C_1, C_4, C_5, C_6, C_8, C_9 and phenyl carbons); 117.0, 114.5, 95.1, 94.0 (C_2 and C_3); 68.5, 24.8 (THF); 55.0, 50.5 (Ph*C*HCp); 22.8, 21.6, 19.2 (4,7-*C*H$_3$). Anal. Calcd for $C_{44}H_{48}O_2Ca$: C, 81.44; H, 7.45. Found: C, 81.07; H, 7.12.

Preparation of $Ph_2C_2H_2$-(η^5-4,7-$Me_2C_9H_4$)$_2$Fe, 3. THF (50 mL) was vacuum-transferred onto a mixture of $FeCl_2$ (0.20 g, 1.5 mmol) and **2** (1.0 g, 1.5 mmol) at −78 °C, and the reaction mixture was warmed to room temperature and stirred overnight with the entire reaction vessel wrapped in aluminum foil to exclude light. The resulting deep purple solution was dried under vacuum, and the product was redissolved in 50 mL of toluene and filtered to remove the $CaCl_2$ byproduct. The $CaCl_2$ was washed repeatedly with toluene, and the combined filtrate and washings were concentrated to 10 mL and cooled to −78 °C to precipitate **3** as a purple solid: yield, 0.31 g, 40%. ^{1}H NMR (C_6D_6; trans-rac and *cis-meso* isomers): δ 7.42, 6.91−7.18 (m, phenyl-*H*). ^{1}H NMR (C_6D_6; trans-rac isomer): δ 6.85, 6.59 (d, $^3J_{H-H}$ = 6.3 Hz, H_5 and H_6), 6.04 (s, PhC*H*Cp), 5.06, 3.97 (d, $^3J_{H-H}$ = 2.5 Hz, H_2 and H_3), 2.71, 2.22 (s, 4,7-C*H*$_3$). ^{1}H NMR (C_6D_6; cis-meso isomer): δ 6.67, 6.37 (d, $^3J_{H-H}$ = 6.5 Hz, H_5 and H_6), 6.59 (s, PhC*H*Cp), 4.68, 4.47 (d, $^3J_{H-H}$ = 2.6 Hz, H_2 and H_3), 2.53, 1.92 (s, 4,7-C*H*$_3$). ^{1}H NMR (C_6D_6; third, minor isomer (trans-meso or cis-rac): δ 5.09 (s, PhC*H*Cp), 2.85, 2.57, 2.11, 2.03 (s, 4,7-C*H*$_3$). ^{13}C NMR (C_6D_6-d_6): δ 129.2, 128.4, 128.2, 126.7 (Ph−*C*). ^{13}C NMR (trans-rac isomer): δ 126.3, 121.4 (C_5 and C_6), 75.2, 68.2 (C_2, C_3), 58.7 (Ph*C*HCp), 22.3, 18.3 (4,7-*C*H$_3$). ^{13}C NMR (cis-meso isomer): δ 124.8, 119.0 (C_5 and C_6), 73.6, 59.0 (C_2, C_3), 54.8 (Ph*C*HCp) 21.1, 17.8 (4,7-*C*H$_3$). Anal. Calcd for $C_{36}H_{32}Fe$: C, 83.07; H, 6.20. Found: C, 83.49; H, 6.51.

X-ray Crystal Structure Determinations. For compound **1**, a suitable crystal chosen from a batch grown from hot ethanol was mounted on a pin with silicon grease, and the pin was mounted on a goniometer head. Crystals of **2** were grown by slow diffusion of petroleum ether into a THF solution of the compound. A suitable crystal was mounted in a glass capillary under a nitrogen atmosphere. Crystals of **3** were grown from a concentrated benzene solution that was cooled at 5 °C for several days. After the benzene was decanted from the crystals, they were coated with mineral oil. A suitable crystal was mounted on a pin with silicon grease, and the pin was mounted on a goniometer head and immediately placed under a nitrogen stream.

Data were collected using a Siemens (Bruker) SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating around −54 °C. A total of 1271 frames of data were collected using ω scans with a scan width of 0.3° per frame for 30 s. Additional parameters are available in the cif file. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software (V. 4.050, Bruker Analytical X-ray Systems, Madison, WI, 1995) and refined using SAINT (V. 4.050, Bruker Analytical X-ray Systems, Madison, WI, 1995) on all observed reflections. Data reduction was performed using the SAINT software which corrects for Lp and decay. Absorption corrections were applied using SADABS (Program for absorption corrections using Siemens CCD based on the method of Robert Blessing[26]). The structures were solved by the direct method using the SHELXS-97 program (Sheldrick, G. M., University of Göttingen, Germany, 1997) and refined by the least-squares method on F^2 using SHELXL-97, which is incorporated in SHELXTL-PC V 5.10 (PC/UNIX-Version, Bruker Analytical X-ray Systems, Madison, WI, 1995). All non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated by geometrical methods and refined as a Riding model. In each case, the crystals used for the diffraction studies showed no decomposition during data collection.

Acknowledgment. P.J.S. is grateful to the National Science Foundation for a CAREER grant (No. CHE-9502739) in support of this work. The establishment of the Single-Crystal X-ray Dirffraction Laboratory at the University of Idaho was supported by the NSF-Idaho EPSCoR Program, the National Science Foundation, and the M. J. Murdock Charitable Trust of Vancouver, WA. We thank Prof. Roger Willett (Washington State University) and Dr. Roland Fröhlich (Westfälischen Wilhelms Universität, Münster) for examining and commenting on the validity of the X-ray crystal structure of compound **1**. We also thank Dr. Gary Knerr (University of Idaho) for his assistance in acquiring NMR data.

Supporting Information Available: Details of the structure determinations for **1**, *trans-rac*-**2**, and *trans-rac*-**3**, including tables listing atomic coordinates, thermal parameters, and bond distances and angles, figures showing structures, and text giving details of the packing analysis. This material is available free of charge via the Internet at http://pubs/acs.org.

OM980990L

(26) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.
(27) Alías, F. M.; Barlow, S.; Tudor, J. S.; O'Hare, D.; Perry, R. T.; Nelson, J. M.; Manners, I. *J. Organomet. Chem.* **1997**, *528*, 47.
(28) Tudor, J.; Barlow, S.; Payne, B. R.; O'Hare, D.; Nguyen, P.; Evans, C. E. B.; Manners, I. *Organometallics* **1999**, *18*, 2281.