chloride ion. Complex $[IrHCl(o\text{-}Ph_2PC_6H_4NHR)_2]Cl$ (**12**, **13**) does not react with carbon monoxide, an observation which is consistent with its observed formation during the carbonylation reaction of $IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR)$. Indeed, if the carbonylation is carried out in the presence of added DABCO, the quantity of complex **12** or **13** formed is considerably reduced. The reaction of carbon monoxide with the neutral iridium(III) amide complexes **10** and **11**, but not with the cationic iridium(III) amine complexes **12** and **13**, reflects the greater electron density imparted to the iridium center by the anionic amide ligand. Carbon disulfide shows analogous reactivity to carbon monoxide, but these neutral complexes **10** and **11** do not react with ethylene or hydrogen.

Rhodium Complexes. The kinetic lability of rhodium complexes causes them to be less stable than their iridium counterparts. We have, nevertheless, prepared unstable solutions of the rhodium(I) analogues and investigated their reaction chemistry with carbon monoxide. When $[Rh(\mu\text{-}Cl)(C_8H_{14})]_2$ is reacted with 4 equiv of $o\text{-}Ph_2PC_6H_4NHCH_2Ph$ in dichloromethane solvent, a solution containing the air-sensitive complex $[Rh(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl$ (**16**) is formed. No upfield ^1H NMR resonances indicative of a rhodium hydride are observed, and the doublet $^{31}P\{^1H\}$ NMR resonance at δ 53.7 ($^1J(RhP)$ = 176 Hz) supports the formulation as a rhodium(I) complex.[17] Addition of carbon monoxide to the solution yields the rhodium(I) carbonyl complex $RhCl(CO)(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2$ (**17**) (eq 10). Complex **17**

$$\tfrac{1}{2}[Rh(\mu\text{-}Cl)(C_8H_{14})_2]_2 + 2o\text{-}Ph_2PC_6H_4NHCH_2Ph \longrightarrow [Rh(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl + C_8H_{14} \quad (10)$$

$$\downarrow CO$$

$$RhCl(CO)(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2$$

17

is characterized by IR and both ^1H and $^{31}P\{^1H\}$ NMR spectroscopy: ν(NH) 3210 cm^{-1}, ν(CO) 1963 cm^{-1}; δ 6.47 (br, 2 H, N*H*), 4.26 (d, 4 H, CH_2), 19.8 (d, $^1J(RhP)$ = 118 Hz). These results show that the intramolecular addition of an N–H bond is more favorable for iridium(I) than it is for rhodium(I), in agreement with previous experimental results on oxidative addition reactions.[18]

Acknowledgment. We thank both the graduate school of Tulane University and the Louisiana Board of Regents for financial support. We thank the Office of Naval Research for funds to purchase the FTIR spectrometer.

Supplementary Material Available: Tables of bond distances, bond angles, general displacement parameter expressions (U's), root-mean-square amplitudes of anisotropic displacement, and torsion angles (17 pages); a listing of values of F_o and F_c (62 pages). Ordering information is given on any current masthead page.

(17) By comparison, ^1J(RhP) = 133 Hz in $[Rh(dppe)_2]Cl$ (Miller, J. S.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97* 1067–1073), and ^1J(RhP) = 124 Hz in *trans*-$RhCl(CO)(PPh_3)_2$ (Tolman, C. A.; Meakin, P. R.; Lindner, D. L.; Jesson, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 2762–2774).

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Analysis of the π-Facial Preference for Complexation of a Camphor-Derived, Enantiomerically Pure Cyclopentadienyl Ligand to $CpMCl_2$ Fragments (M = Ti and Zr)[1]

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Optically pure (+)-(1*R*,7*S*)-1,10,10-trimethyltricyclo[5.2.1.0^{2,6}]deca-2,5-diene (**3**) has been synthesized and its lithium salt condensed with $TiCl_3$·3THF, $CpTiCl_3$, $ZrCl_4$, $CpZrCl_3$, and $Cp''ZrCl_3$. In each instance, a pair of stereoisomeric complexes was isolated. Relative to the behavior of the parent isodicyclopentadienide anion where exo complexation increases in importance relative to the steric demands of the second ligand, the present camphor-derived anion invariably prefers endo coordination. This change in π-facial response is attributed to the presence of the apical syn-methyl group in **3**, which serves to more closely equalize the available space above- and below-plane. The end result is a synergistic driving force from both electronic and steric contributions to achieve endo coordination to the extent possible.

In the preceding paper,[1] we have established the limits to complexation of the isodicyclopentadienide anion from its two distinctive faces with cyclopentadienyltitanium dichloride reagents. At −78 °C, reaction occurs with $RCpTiCl_3$ under kinetic control to deliver **1** exclusively. When the same process is carried out at room temperature, thermodynamic factors appear to override more subtle electronic influences and exo complexes such as **2** are formed stereoselectively.

Herein, attention is given to preparation of the optically active camphor-derived diene **3** and to elucidation of the

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(1) Paper 44 in the series dealing with isodicyclopentadienes and related molecules. For 43, see: Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Sornay, C.; Rogers, R. D.; Rheingold, A. *Organometallics*, in press.

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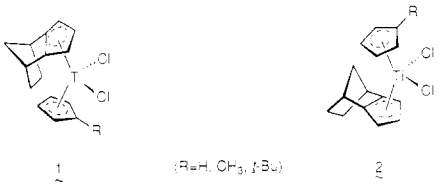


1 (R=H, CH_3, *t*-Bu) 2

level and direction of stereochemical control that operates during its coordination to various titanium and zirconium reagents.[2,3] The availability of this enantiomerically pure hydrocarbon holds special interest for several reasons. Attractive possibilities are offered by **3** for elaborating organometallic complexes potentially useful for inducing asymmetry in a number of organic reactions. Bicycloannulation of the cyclopentadienide anion as in **4** provides

3 4

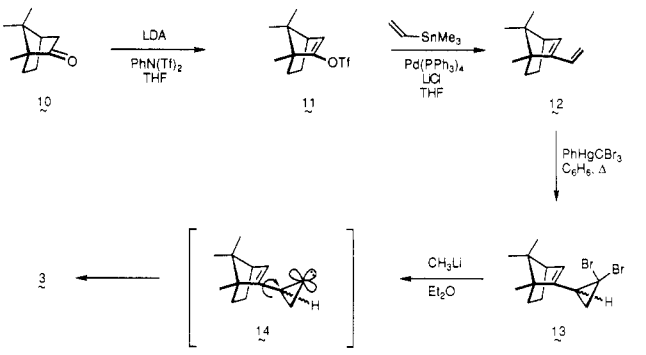
for a more rigid system than the majority of previous examples where the chiral substituent has been attached merely by a single σ bond.[4,5] The generally disappointing response of the latter group of organometallic complexes in realizing chirality transfer can be traced in part to the lack of conformational rigidity.

From an electronic perspective, methyl substitution of the isolated methano group and a bridgehead site in isodicyclopentadiene had earlier been recognized computationally not to provide an avenue for additional interaction with the key norbornyl framework orbitals. No amelioration of their influence on the cyclopentadienyl π system was thereby anticipated. However, the appreciable steric contribution of the syn-10-methyl group was certain to be important in modulating overall π-facial stereoselectivity.

Synthetic Considerations

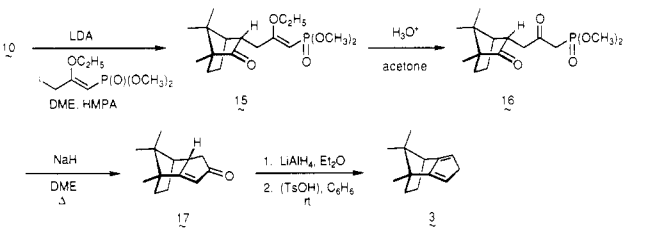
Two approaches have been developed to arrive at **3**. The conceptual basis for the first synthetic entry originated from previous experience showing that diene **5**[6] and related systems[7] can be efficiently cyclopentannulated by means

Scheme I



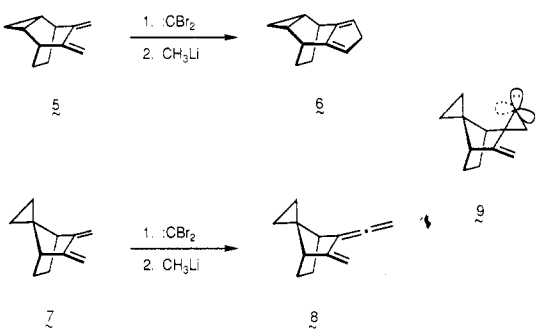
10 11 12 13 14 3

Scheme II



10 15 16 17 3

of the Skattebøl reaction.[8] Failure of the procedure when the ring system is further strained as in **7** (only allene formation materializes)[9,10] was attributed to an inability of the torsionally constrained emply carbene p orbital as in **9** to interact with the flanking double bond.[11] This geometric restriction does not apply when the cyclopropylcarbene is situated completely external to the norbornene ring (see **14**).



5 6 9 7 8

To evaluate the effects of enhanced conformational maneuverability of this type, diene **12** was prepared (Scheme I). The enol triflate **11** of (1*R*)-(+)-camphor (**10**), accessed by condensation of the lithium enolate with *N*-phenyltrifluoromethanesulfonimide,[12] underwent smooth coupling with vinyltrimethylstannane when heated in the presence of 5 mol % $Pd(PPh_3)_4$ and 4 equiv of lithium chloride in tetrahydrofuran.[13] Exposure of **12** to dibromocarbene, as generated from 1 equiv of phenyl(tribromomethyl)mercury in hot benzene,[14] was anticipated to result in regiospecific cyclopropanation of the external

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(5) Exceptions may be found in ref 2 and 3 and: (a) Paquette, L. A.; Gugelchuk, M.; McLaughlin, M. L. *J. Org. Chem.* **1987**, *52*, 4732. (b) Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E.; Blaser, D.; Boese, R. *J. Am. Chem. Soc.* **1987**, *109*, 8105.

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Table I. Comparative 300-MHz ^{1}H NMR Spectral Data (δ Values, $CDCl_3$ Solution)

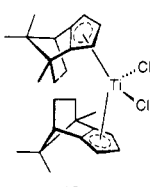
compd	central CCp (1 H)	peripheral CCp (2 H)	RCp (5 H)	bridgehead (1 H)	exo-ethano bridge (1 H)	endo-ethano bridge (1 H)	methyl substituents (3 H each)
				A. Titanium Series			
18	5.92 (dd, J = 2.7, 2.7 Hz)	6.47 (d, J = 2.7 Hz)		2.75 (d, J = 4 Hz)	2.0–1.4 (m)		1.23 (s), 0.92 (s), 0.27 (s)
19			obscured by absorptions of **18**				1.41 (s), 1.25 (s), 1.13 (s), 0.93 (s), 0.91 (s), 0.85 (s)
20	6.23 (m)	6.40 (m)	6.56 (m)	2.77 (d, J = 4 Hz)	1.80 (m)	2.02 (m), 1.65 (m)	1.24 (s), 0.93 (s), 0.26 (s)
21	6.55 (m)	6.30 (m)	6.59 (s)	3.06 (d, J = 4 Hz)	1.65 (m)	0.74 (m)	1.42 (s), 0.90 (s), 0.63 (s)
				B. Zirconium Series			
22	5.98 (t, J = 3 Hz)	6.21 (dm, J = 3 Hz)		2.70 (d, J = 4 Hz)	2.60 (m)	1.85 (m)	1.20 (s), 0.91 (s), 0.21 (s)
23	6.16–6.33 (m)			3.00 (d, J = 4 Hz)	1.65 (m)	0.67 (m)	1.40 (s), 1.25 (s), 1.20 (s), 0.91 (s), 0.80 (s), 0.20 (s)
24	6.19 (m)	6.15 (m)	6.45 (s)	2.72 (d, J = 4 Hz)	2.00 (m)	1.88 (m)	1.21 (s), 0.91 (s), 0.80 (s)
25	6.19 (m)	6.05 (m)	6.48 (s)	3.01 (d, J = 4 Hz)	1.83 (m), 1.64 (m)	0.69 (m)	1.39 (s), 0.92 (s), 0.80 (s)
26	5.45 (m)	6.01 and 5.76 (t, J = 3 Hz)		2.68 (d, J = 4 Hz)	2.70–0.66 (m)		1.39 (s), 1.15 (s), 0.15 (s)
27	5.61 (m)	5.61 (m)		2.99 (d, J = 4 Hz)			0.98 (s), 0.90 (s), 0.89 (s)

double bond for obvious steric reasons. In line with this expectation, attack at the internal double bond was not seen and **13** was isolated in 73% yield as an approximately equal mixture of two diastereomers. Both of these dibromides appear to converge to **3** when exposed to 4 equiv of methyllithium in ether at room temperature, since **3** was isolated in 79% efficiency.[15] Evidently, both stereoisomers of carbene **14** find it possible to attain proper stereoelectronic alignment for electrocyclization.

Despite the efficiency of this route to **3**, the considerable expense associated with several reagents deterred its full-scale implementation for the preparation of large amounts of diene. The alternative pathway developed in Scheme II was therefore developed. Following alkylation of the enolate anion of (1*R*)-(+)-camphor with (3-iodo-2-ethoxypropenyl)phosphonate[16] to give **15** and aqueous acidic hydrolysis of this intermediate to diketo phosphonate **16**, the process converges with that originally devised by Halterman and Vollhardt.[3] All five steps can be conveniently scaled up. Hence, this manner of crafting **3** from camphor qualifies as the more utilitarian.

Complexation to Group 4 Transition Metals

Diene **3** was transformed into its lithium salt by heating with *n*-butyllithium in hexane. Exposure of this salt (CCpLi) to titanium trichloride tris(tetrahydrofuran) complex[17] in 1,2-dimethoxyethane at the reflux temperature led to the formation of a 9:1 mixture of isomers (^{1}H NMR analysis). Recrystallization from toluene afforded the major complex (**18**) as purple red crystals (43%) exhibiting $[\alpha]^{20}_D$ +107° (*c* 2.8, toluene). Its C_2 symmetric nature was spectroscopically apparent. That below-plane complexation had occurred on both ligands was revealed by appearance of the two peripheral Cp olefinic protons (δ 6.47 (d, J = 2.7 Hz)) *downfield* of the lone central proton (δ 4.92 (t, J = 2.7 Hz)).[1] Furthermore, the methano bridge carbon shift of 70.0 ppm shows it to be deshielded, an indication of its remoteness to the titanium atom.[1] Finally, the locations of the three methyl singlets (δ 1.22, 0.91, and 0.26) also constitute important stereochemical identifiers.



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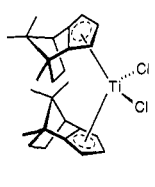
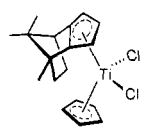


19

The minor isomer, which was not further purified, was recognized to be unsymmetrical on the basis of the six methyl singlets evident in its ^{1}H NMR spectrum. Its formulation as **19** could thereby be made.

When CCpLi was stirred with $CpTiCl_3$ in dry tetrahydrofuran solution at room temperature for 18 h, a crude product was obtained whose ^{1}H NMR spectrum showed it to consist of a 7:1 mixture of **20** and **21**. Slow crystallization from a solvent system comprised of dichloromethane and hexane gave **20** in 58% yield. This substance was clearly a member of the endo series. Its spectral properties (Table I), in particular the relative position of the CCp olefinic protons (peripheral at δ 6.40 versus central at δ 6.23) and the wide spacing of the methyl singlets (δ 1.24, 0.93, and 0.26), are again stereochemically revealing. As in other members of this series, the metal atom exerts a strong deshielding effect on the endo ethano protons which are seen at δ 1.65.



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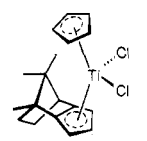

21

This long-range anisotropy is evident in the requisite reversed sense in **21**. In this instance, the proximity of the titanium center to the methano bridge induces marked alterations in the resonances of at least two of the methyl substituents (δ 1.42, 0.90, 0.63). Furthermore, the endo ethano protons return to their normally shielded position (δ 0.74) and the peripheral CCp protons (δ 6.30) appear upfield of that bonded to the central carbon (δ 6.55).

Attempts to condense CCpLi and CCpTl with $Cp''TiCl_3$[18] under a variety of conditions failed to give rise to characterizable amounts of mixed complex. Mixtures were produced in which the desired dichloride was indeed a constituent. However, the enhanced solubility imparted

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(16) Piers, E.; Abeysekera, B. *Can. J. Chem.* **1982**, *60*, 1114.
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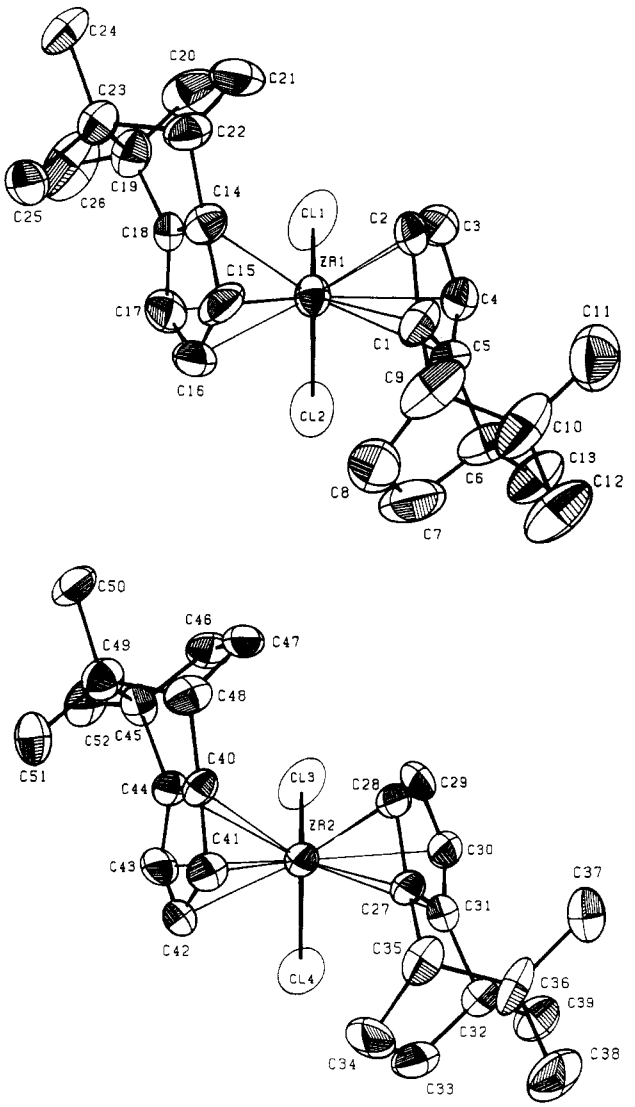
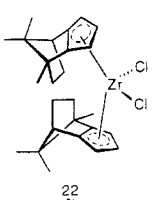


Figure 1. Crystallographic determined molecular structure of **22** showing both molecules in the asymmetric unit as drawn with 50% thermal ellipsoids.

to this substance by the pentamethylcyclopentadienyl ligand did not allow for effective selective crystallization to be accomplished.

This complication did not carry over to the zirconocene series. The lithium salt of camphorCp reacted with freshly sublimed zirconium tetrachloride in refluxing 1,2-dimethoxyethane to deliver a 13:1 mixture of **22** and **23** in 50% yield after 72 h. The degree of stereofacial differentiation is more highly accentuated in this instance relative to **18** and **19**, although in the same direction.



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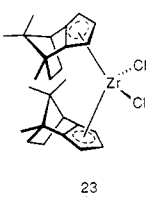
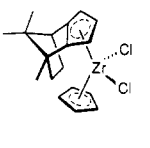


23

The three-dimensional features of **22**, obtained pure by slow evaporation from toluene, were suggested by its ^{1}H NMR spectrum (Table I). X-ray crystallographic analysis showed the two molecules in the asymmetric unit to be essentially identical (Figure 1). The groups attached to the coordinating five-membered rings of the camphor ligands average 0.42 Å out-of-plane away from the zirconium atom. Worthy of note is the fact that the methyl-substituted bridgehead carbons [C(6) and C(19) in Figure 1; C(32) and C(45)] are bent further out of the C_5 plane (0.46 Å) than are the other bridehead carbons [C(9), C(22); C(35), C(48)] at 0.38 Å. In addition, the Cp carbons attached to C(6), C(19) and C(32), C(45) exhibit the longest Zr–C separations, which at Δ = 0.25 Å are seen to vary widely (2.42–2.67 Å). The carbon atoms that comprise the two Cp rings are almost perfectly eclipsed, but with the bicyclic subunits oriented away from each other. The closest intramolecular contacts between the chlorine atoms and carbons not in the five-membered rings are Cl(1)···C(20) at 3.45 (2) Å, Cl(2)···C(7) at 3.55 (2) Å, Cl(3)···C(46) at 3.39 (1) Å, and Cl(4)···C(33) at 3.45 (1) Å.

In order to gain some measure of insight into the relative steric demands of other Cp components, CCpLi was also condensed with $CpZrCl_3 \cdot 2THF$[19] and $Cp''ZrCl_3$.[18] In the first instance, stirring in dry tetrahydrofuran solution at 20 °C for 24 h was adequate to deliver a 2:1 mixture of **24** and **25** in 58% isolated yield. For bonding to the pentamethylCp reaction partner to proceed at a reasonable rate, the reagents had to be heated at reflux in toluene for 48 h. Under these conditions, a 1.4:1 mixture of **26** and **27** was produced.



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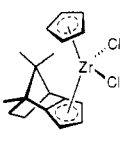

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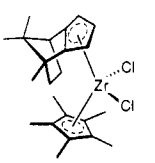
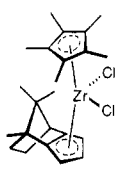


26



27

With the structural assignment to **22** firmly established, it proved to be an easy matter to relate the spectroscopic properties of **24–27** directly to those of the C_2 symmetric species. As revealed in Table I, the stereochemistry of the individual mixed zirconium complexes cannot now be judged reliably by the sequence in which the peripheral and central CCp olefinic protons make their appearance. Fortunately, the methyl absorptions provide important configurational information. Furthermore, the very close identity of the ^{13}C NMR shifts within the camphor frameworks of **22**, **24**, and **26** (see Experimental Section) suggests a common sensitivity to the relative location of the zirconium atom.

Discussion

Previously, **3** had been studied only in connection with its π-facial stereoselectivity toward three reactive dienophiles.[20] The strong tendency exhibited by the parent isodicyclopentadiene (isodiCp) hydrocarbon for kinetically preferred below-plane bonding[21] was expected to persist, since the addition of three methyl groups in CCp was seen to exert no net change of any magnitude on the level of σ–π norbornyl–cyclopentadiene electronic interaction.[22]

(19) Erker, G.; Berg, K.; Treschanke, L.; Engel, K. *Inorg. Chem.* **1982**, *21*, 1277.
(20) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3148.
(21) (a) Paquette, L. A. In *Stereochemistry and Reactivity of Pi Systems*; Watson, W. H.; Ed.; Verlag Chemie: Deerfield Beach, FL, 1983; pp 41–73. (b) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328.

Indeed, maleic anhydride, *N*-phenylmaleimide, and dimethyl acetylenedicarboxylate add to **3** to furnish *syn*-sesquinorbornene products exclusively.[20]

Consequently, to the extent that the same effects contribute to the ability of its conjugate anion **4** to capture electrophiles stereoselectively,[1,23] formation of the mixed titanocene and zirconocene complexes should also be biased toward the endo face. Although this stereochemical course is clearly preferred throughout all the examples studied, there has surfaced an enhancement of the level of below-plane π-facial coordination relative to isodicyclopentadiene. Nonetheless, none of the present processes were *totally stereoselective*.

With a major steric contribution stemming from the apical syn-methyl substituent in **4**, the explanation for its reluctance to coordinate from the exo direction to $CpZrCl_3$ and $Cp''ZrCl_3$ can be linked to this significant nonbonded interaction. It is instructive to recall that the isodicyclopentadienide anion complexes to this pair of reagents *exclusively* from the exo direction.[1] This stereochemical preference is believed to be dictated by the considerably reduced level of steric congestion that exists above-plane. By contrast, the apical syn-methyl group in **4** plays the important role of much more closely equalizing the available space extant on its two π surfaces. The ratios associated with the formation of **24**/**25** (2:1) and **26**/**27** (1.4:1) are ascribed in part to this phenomenon. The other findings indicate these ratios not to be stereorandom, however. The kinetic preference for, and continued dominance of, below-plane complexation persists and is believed to be of stereoselectronic origin. The orbital tilting phenomenon discussed elsewhere[1,23] may only be worth several hundred calories per mole in the relevant transition states but is adequate not to escape detection in the product mixtures.

The formation of small amounts of **19** and **23** during condensation with $TiCl_3$·3THF and $ZrCl_4$ can be rationalized analogously. The isodiCp and camphorCp ligands are sterically bulky structural building blocks. Where isodiCp is concerned, reaction of its anion with the tri- and tetrachloride salts of the group 4 transition metals delivers the symmetrical exo,exo complexes with complete stereoselectivity.[24] In these examples, the customary electronically drived predilection for reaction below-plane has been totally overridden by steric factors. The CCp ligand is yet more bulky and the switch to above-plane coordination should be more dramatic in this series, but it is not. In our view, the transition states for endo complexation in both series are closely comparable in their associated energy costs. Here the similarity stops. Where exo complexation is concerned, the transition state associated with the CCp series is considerably more energy demanding because of the presence of methyl groups on the methano bridge, the steric consequences of which cannot be ignored by the in-bound metal.[25] Consequently, both reactions in question are sterically controlled because of ligand size. For isodiCp, however, this translates to $k_{exo} \gg k_{endo}$, while for CCp k_{endo} is favored over k_{exo} by a smaller margin.

We conclude that **4** shares with its parent isodiCp anion a kinetic preference for the formation of below-plane complexes. This π-facial stereoselectivity is accentuated for CCp, particularly when the second ligand is also sterically bulky, because the endo surface in this instance is less congested.

(22) Gleiter, R., personal communication.
(23) (a) Hsu, L.-Y.; Hathaway, S. J.; Paquette, L. A. *Tetrahedron Lett.* **1984**, 259. (b) Paquette, L. A.; Schirch, P. F. T.; Hathaway, S. J.; Hsu, L.-Y.; Gallucci, J. C. *Organometallics* **1986**, *5*, 490.
(24) Gallucci, J. C.; Gautheron, B.; Gugelchuk, M.; Meunier, P.; Paquette, L. A. *Organometallics* **1987**, *6*, 15.
(25) Brown, F. K.; Houk, K. N. *J. Am. Chem. Soc.* **1986**, *107*, 1971.

Experimental Section

(−)-(1*R*)-1,7,7-Trimethyl-2-vinylbicyclo[2.2.1]hept-2-ene (12). To a cold (0 °C), magnetically stirred solution of lithium diisopropylamide (7.2 mmol) in dry tetrahydrofuran was added (1*R*)-(+)-camphor (1.0 g, 6.5 mmol) in 5 mL of the same solvent. The reaction mixture was stirred for 1 h before a solution of *N*-phenyltriflimide (2.57 g, 7.2 mmol) in tetrahydrofuran (5 mL) was introduced by syringe. The solution was allowed to warm slowly to room temperature, stirred for 4 h, and freed of solvent in vacuo. The residue was purified by silica gel chromatography (hexane elution) to give **11** (1.50 g, 81%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (d, J = 3.8 Hz, 1 H), 2.43 (m, 1 H), 1.90 (m, 1 H), 1.60 (m, 1 H), 1.25 (m, 1 H), 1.14 (m, 1 H), 1.01 (s, 3 H), 0.90 (s, 3 H), 0.77 (s, 3 H).

Tetrakis(triphenylphosphine)palladium (1.28 g, 1.11 mmol) and lithium chloride (3.76 g, 88.7 mmol) were transferred to the reaction flask under argon. Following the introduction of anhydrous tetrahydrofuran (80 mL), a solution of **11** (6.96 g, 22.16 mmol) in the same solvent (20 mL) was added via syringe, to be followed by vinyltrimethylstannane (4.28 g, 22.16 mmol). The reaction mixture was slowly warmed to reflux and maintained at that temperature for 1 h prior to cooling. Water and a 1:1 mixture of pentane and ether were added, and the organic phase was washed extensively with water and dried. Solvent evaporation and chromatography of the residual oil (silica gel, pentane elution) afforded 3.38 g of **12** as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (dd, J = 11.2, 17.8 Hz, 1 H), 6.18 (d, J = 3.2 Hz, 1 H), 5.32 (dd, J = 1.9, 17.8 Hz, 1 H), 4.92 (dd, J = 1.9, 11.2 Hz, 1 H), 2.28 (br t, J = 3.5 Hz, 1 H), 1.90–1.82 (m, 1 H), 1.57–1.36 (m, 3 H), 1.11 (s, 3 H), 0.79 (s, 3 H), 0.77 (s, 3 H); MS m/z (M^+) calcd 162.1408, obsd 162.1402; $[\alpha]^{20}_D$ −159° (*c* 4.29, hexane).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.76; H, 11.20.

(+)-(1*R*,7*S*)-1,10,10-Trimethyltricyclo[5.2.1.0^{2,6}]deca-2,5-diene (3). A magnetically stirred mixture of phenyl(tribromomethyl)mercury (9.8 g, 18.5 mmole and **12** (3.0 g, 18.5 mmol) in 65 mL of benzene was heated at the reflux temperature for 4.5 h. After cooling, the reaction mixture was filtered through Celite, concentrated, redissolved in pentane, and chromatographed on neutral alumina (pentane elution). Solvent evaporation in vacuo yielded 4.60 g (75%) of **13** which was utilized directly in the next step.

A solution of **13** (2.82 g, 8.45 mmol) in ether (5 mL) was treated at room temperature with ethereal methyllithium (22.5 mL of 1.5 M, 4 equiv) and stirred overnight. The reaction mixture was cooled to 0 °C and quenched carefully with water. The organic phase was washed several times with saturated ammonium chloride solution and water prior to drying. Chromatography of the concentrate on neutral alumina (pentane elution) gave 1.10 g (75%) of **3** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (br s, 1 H), 5.63 (s, 1 H), 3.18 (d, J = 22.9 Hz, 1 H), 3.06 (d, J = 22.9 Hz, 1 H), 2.51 (d, J = 4.3 Hz, 1 H), 2.00 (dddd, J = 11.2, 10.9, 3.8, 3.4 Hz, 1 H), 1.80 (ddd, J = 11.2, 10.4, 2.7 Hz, 1 H), 1.37 (ddd, J = 11.2, 9.5, 2.7 Hz, 1 H), 1.28 (ddd, J = 10.4, 9.5, 3.8 Hz, 1 H), 1.13 (s, 3 H), 0.98 (s, 3 H), 0.71 (s, 3 H); $[\alpha]^{26}_D$ +5.1° (*c* 0.31, hexane). The ^{1}H NMR spectrum compares very closely to that recorded previously at 250 MHz[3] and at 60 MHz.[15]

(1*R*,3*S*,4*R*)-3-[3-(Dimethylphosphono)-2-propanon-1-yl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (16). (1*R*)-(+)-Camphor (10.0 g, 66 mmol) dissolved in dry 1,2-dimethoxyethane (50 mL) was added during 30 min to a cold (−78 °C), magnetically stirred solution of lithium diisopropylamide (66 mmol) in tetrahydrofuran (50 mL). The reaction mixture was allowed to warm to −20 °C during 1 h and recooled to −78 °C, at which point dry hexamethylphosphoramide (11.83 g, 66 mmol) was introduced. After 20 min, a solution of dimethyl (3-bromo-2-ethoxypropenyl)phosphonate (18.03 g, 66 mmol) and anhydrous sodium iodide (200 °C, 0.01 Torr, 1 h) (14.84 g, 99 mmol) in dry 1,2-dimethoxyethane (45 mL) was added during 30 min. The reaction mixture was allowed to warm to room temperature, stirred for 12 h, and poured into water. The product was extracted into dichloromethane (3 × 100 mL) and the combined organic layers

were washed with brine and water prior to drying.

The solvent was removed under reduced pressure, and the resulting oil (15) was directly dissolved in acetone (50 mL) and treated with 1 N hydrochloric acid (2 mL). This solution was stirred for 1.5 h, neutralized with solid potassium carbonate, filtered, and evaporated under reduced pressure. The residue was dissolved in dichloromethane (50 mL), washed with sodium bicarbonate solution and water, dried, and freed of solvent. The oil was added to a silica gel column. Elution with 20% ethyl acetate in petroleum ether removed unreacted camphor, whereas elution with ethyl acetate gave **16** as a colorless oil (13.15 g, 63%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (d, J = 11.2 Hz, 3 H), 3.79 (d, J = 11.2 Hz, 3 H), 3.2–2.9 (m, 4 H), 2.70 (dd, J = 19, 9 Hz, 1 H), 2.19 (s, 1 H), 1.9–1.55 (m, 2 H), 1.43 (m, 1 H), 1.23 (m, 1 H), 1.00 (s, 3 H), 0.93 (s, 3 H), 0.91 (s, 3 H). This spectrum is identical with that reported earlier.[3]

(1*R*,6*S*,7*R*)-1,10,10-Trimethyltricyclo[5.2.1.0^{2,6}]dec-2-en-4-one (17). To pentane-washed sodium hydride (760 mg, 32 mmol) in dry 1,2-dimethoxyethane under argon was added 10.0 g (32 mmol) of **16**. The reaction mixture was heated at reflux for 24 h, cooled, and quenched with saturated sodium bisulfate solution. After drying, the solution was evaporated and the residue was purified by silica gel chromatography (elution with 20% ethyl acetate in petroleum ether) to afford pure **17** as a clear, colorless oil (4.87 g, 80%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (d, J = 2.5 Hz, 1 H), 3.35 (s, 1 H), 2.47 (dd, J = 16.6, 5.9 Hz, 1 H), 2.23 (dd, J = 16.6, 4.6 Hz, 1 H), 1.98 (dd, J = 4.0, 3.8 Hz, 1 H), 1.86 (m, 1 H), 1.67 (m, 1 H), 1.18 (m, 2 H), 1.01 (s, 6 H). This spectrum is identical with that described elsewhere.[3]

Alternate Preparation of 3. A solution of **17** (4.00 g, 21 mmol) in anhydrous ether (100 mL) was added dropwise to a slurry of lithium aluminum hydride (800 mg, 21 mmol) in the same solvent (100 mL). Stirring was continued for 30 min, and water was introduced dropwise under nitrogen. The reaction mixture was acidified with 1 N hydrochloric acid, and the organic layer was separated. The aqueous phase was extracted with ether (3 × 100 mL), and the combined organic solutions were dried and concentrated.

The residual oil was dissolved in benzene (50 mL), treated with *p*-toluenesulfonic acid (362 mg), and stirred at room temperature for 24 h. Following neutralization with solid potassium carbonate, the reaction mixture was dried and concentrated. Chromatography of the residue (neutral alumina, pentane elution) gave 2.74 g (75%) of **3**, identical in all respects with the diene described above.

{(1*R*,7*S*)-1,10,10-Trimethyltricyclo[5.2.1.0^{2,6}]deca-2,5-dienyl}lithium. To a solution of **3** (5.0 g, 29 mmol) in dry hexane (100 mL) under argon was added *n*-butyllithium (18 mL of 1.6 M, 29 mmol) via syringe. The resulting mixture was heated at reflux for 24 h, cooled, and concentrated in vacuo to ca. 25 mL. The solution was cooled to 0 °C for 2 h, and the white air-sensitive solid was collected by filtration under argon. This solid was washed with dry hexane (2 × 25 mL) at 0 °C and dried under high vacuum. The yield was 70%.

(+)-Bis(η^5-(1*R*,7*S*)-1,10,10-trimethyltricyclo[5.2.1.0^{2,6}]-deca-3,5-dien-2-yl)dichlorotitanium (18). A solution of the titanium trichloride tris(tetrahydrofuran complex (244 mg, 0.7 mmol) in dry 1,2-dimethoxyethane (20 mL) was prepared under argon at −78 °C and added via cannula to a dimethoxyethane solution (50 mL) of the preceding lithium salt (238 mg, 1.3 mmol). The reaction mixture was warmed to room temperature, subsequently heated at reflux for 48 h, and concentrated under reduced pressure. The residue was taken up in ether, cooled to −78 °C, and maintained at this temperature while dry hydrogen chloride was bubbled in for 15 min. The solution was next stirred at room temperature for 2 h, chloroform (100 mL) was added, and the resulting solution was poured into 6 N hydrochloric acid (50 mL). The separated aqueous layer was extracted with chloroform (2 × 50 mL) and the combined organic phases were dried and evaporated. Following solvent removal, the residue was placed in a Soxhlet cup. After initial extraction with HCl-saturated pentane, the dichlorides were extracted into HCl-saturated carbon tetrachloride. Following evaporation of the carbon tetrachloride, recrystallization from toluene afforded 140 mg (43%) of **18** as purple-red crystals: mp 179–180 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 122.1, 113.5, 113.0, 70.0, 54.3, 51.6, 32.2, 25.4, 21.1, 19.9, 12.8 (quaternary Cp carbons not observed); $[\alpha]^{20}_D$ +107° (*c* 2.8, toluene).

Table II. Experimental Crystallographic Data for 22

mol wt	508.7
space group	$P2_12_12_1$
temp, °C	20
cell constants	
a, Å	12.308 (3)
b, Å	13.700 (3)
c, Å	28.809 (9)
cell vol, Å^3	4857.8
formula units/unit cell	8
D_{calc}, g cm^{-3}	1.39
μ_{calc}, cm^{-1}	6.0
diffractometer/scan	Enraf-Nonius CAD-4/θ–2θ
radiatn, graphite monochromator	Mo Kα (λ = 0.710 73 Å)
max cryst dimens, mm	0.30 × 0.35 × 0.35
scan width	0.80 + 0.35 tan θ
std reflctns	600; 060; 0,0,16
decay of stds	±2%
reflctns measd	4228
2θ range, deg	2 ≤ 2θ ≤ 48
range of *h*,*k*,*l*	+14,+15,+32
reflctns obsd [$F_o \geq 5\sigma(F_o)$][b]	3090
computer programs[c]	SHELX[26a]
struct soln	MULTAN[26b]
no. of parameters varied	523
weights	$[\sigma(F_o)^2]^{-1}$
GOF	4.8
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.051
R_w	0.055
R inverse configuration	0.052
largest feature final diff map, e Å^{-3}	0.9

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 20°$). [b] Corrections: Lorentz–polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref 27.

These spectral data are identical with those reported in ref 3.

(η^5-Cyclopentadienyl){η^5-(1*R*,7*S*)-1,1,10-trimethyltricyclo[5.2.1.0^{2,6}]deca-3,5-dien-2-yl}dichlorotitanium (20 and 21). To magnetically stirred solution of $CpTiCl_3$ (640 mg, 2.9 mmol) in dry tetrahydrofuran (50 mL) under argon was added via cannula during 20 min a solution of **4**-Li (530 mg, 2.9 mmol) in 20 mL of the same solvent. After 18 h at room temperature, the solvent was removed under reduced pressure and the residue was taken up in chloroform. Concentrated hydrochloric acid (12 mL) was added, the mixture was stirred for 1 h, the organic layer was separated, and the aqueous phase was extracted with chloroform (2 × 25 mL). The combined organic layers were dried, filtered, and evaporated to leave a residue which was transferred to a Soxhlet apparatus. After initial extraction with HCl-saturated pentane for 12 h, the product was extracted into HCl-saturated chloroform during 12 h. ^{1}H NMR analysis showed the **20**/**21** isomer ratio to be 7:1. Recrystallization of this material from dichloromethanehexane gave 5.96 mg (58%) of a red solid: mp 181–182 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 181.76, 153,58, 149.13, 117.75, 115.90, 109.71, 100.95, 78.30, 53.98, 51.76, 51.01, 37.46, 32.30, 29.53, 25.73, 23.65, 21.03, 20.08, 19.80, 12.83, 11.08; MS *m*/*z* (M$^+$) calcd 356.0578, obsd 356.0596.

Anal. Calcd for $C_{18}H_{22}Cl_2Ti$: C, 60.51; H, 6.21. Found: C, 59.93, H, 6.23.

Bis{η^5-(1*R*,7*S*)-1,10,10-trimethyltricyclo[5.2.1.0^{2,6}]deca-3,5-dien-2-yl}dichlorozirconium (22 and 23). To a cold (−78 °C), magnetically stirred slurry of **4**-Li (3.50 g, 0.019 mol) in 100 mL of dry 1,2-dimethoxyethane was added sublimed zirconium tetrachloride (2.16 g, 0.009 mol). The reaction mixture was warmed to the reflux temperature, heated for 72 h, recooled to −78 °C, and treated with gaseous hydrogen chloride for 15 min. This solution was warmed to room temperature and stirred for 2 h. The solvent was removed under reduced pressure, and the residue was sublimed (170–175 °C at 10^{-3} Torr) to give 2.3 g (50%) of a 13:1 mixture of **22** and **23**. Slow evaporation of a solution of this material from toluene afforded pure **22** as yellow crystals: mp 199–201 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 153.64, 149.33, 114.86, 110.09, 109.00, 70.02, 53.49, 51.18, 32.20, 25.21, 20.97, 19.82, 12.77; MS *m*/*z* (M$^+$) calcd 508.1051, obsd

Table III. Bond Distances (Å) and Angles (deg) for 22

Bond Distances			
Zr(1)–Cl(1)	2.425 (4)	Zr(1)–Cl(2)	2.425 (4)
Zr(1)–C(1)	2.59 (1)	Zr(1)–C(2)	2.49 (1)
Zr(1)–C(3)	2.43 (1)	Zr(1)–C(4)	2.54 (1)
Zr(1)–C(5)	2.62 (1)	Zr(1)–C(14)	2.60 (1)
Zr(1)–C(15)	2.51 (1)	Zr(1)–C(16)	2.42 (1)
Zr(1)–C(17)	2.52 (1)	Zr(1)–C(18)	2.67 (1)
Zr(2)–Cl(3)	2.434 (4)	Zr(2)–Cl(4)	2.431 (4)
Zr(1)–C(27)	2.57 (1)	Zr(2)–C(28)	2.52 (1)
Zr(2)–C(29)	2.44 (1)	Zr(2)–C(30)	2.54 (1)
Zr(2)–C(31)	2.65 (1)	Zr(2)–C(40)	2.59 (1)
Zr(2)–C(41)	2.54 (1)	Zr(2)–C(42)	2.45 (1)
Zr(2)–C(43)	2.50 (1)	Zr(2)–C(44)	2.58 (1)
Zr(1)–Cent1	2.22	Zr(1)–Cent2	2.23
Zr(2)–Cent3	2.23	Zr(2)–Cent4	2.22

Bond Angles			
Cl(1)–Zr(1)–Cl(2)	91.3 (1)	Cl(3)–Zr(3)–Cl(4)	90.6 (1)
Cent1–Zr(1)–Cent2	129.5	Cent1–Zr(1)–Cl(1)	106.6
Cent1–Zr(1)–Cl(2)	105.8	Cent2–Zr(1)–Cl(1)	109.0
Cent2–Zr(1)–Cl(2)	108.0	Cent4–Zr(2)–Cl(1)	107.1
Cent4–Zr(2)–Cl(2)	108.5	Cent3–Zr(2)–Cent4	129.0
Cent3–Zr(2)–Cl(3)	106.2	Cent3–Zr(2)–Cl(4)	108.5

508.1024; $[\alpha]^{21}_D$ +170° (*c* 2.0, toluene).

Anal. Calcd for $C_{26}H_{34}Cl_2Zr$: C, 61.38; H, 6.74. Found: C, 61.22; H, 6.81.

X-ray Crystallographic Analysis of 22.[26] A yellow single crystal of the title complex was mounted on a pin and transferred to a goniometer. The space group was determined to be the acentric $P2_12_12_1$ from the systematic absences. A summary of data collection parameters is given in Table II.

Least-squares refinement with isotropic thermal parameters led to $R = 0.090$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The remaining hydrogen atoms were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.051$ and $R_w = 0.055$. The final values of the positional parameters are given in the supplementary material.

(26) The package of programs utilized included: (a) Sheldrick, G. M. SHELX, a system of computer programs for X-ray structure determination as locally modified, 1976. (b) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A.* **1971**, *A27*, 368.

(27) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1972; Vol. IV, pp 72, 99, 149.

(η^5-Cyclopentadienyl){η^5-(1*R*,7*S*)-1,10,10-trimethyltricyclo[5.2.1.0^{2,6}]deca-3,5-dien-2-yl}dichlorozirconium (24 and 25). A solution of **4**-Li (500 mg, 2.8 mmol) in dry tetrahydrofuran was transferred via cannula during 20 min to a magnetically stirred solution of (η^5-cyclopentadienyl)trichlorozirconium bis(tetrahydrofuran) (640 mg, 2.9 mmol) in the same solvent (20 mL). The reaction mixture was stirred at room temperature for 24 h and evaporated under reduced pressure. The residue was dissolved in chloroform (20 min), cooled to −78 °C, and treated with gaseous hydrogen chloride. After 1 h at room temperature, the solution was poured into 50 mL of 6 N hydrochloric acid and the organic phase was dried and evaporated. The residue was sublimed (150 °C, 10^{-3} Torr) and washed with cold pentane to yield 660 mg (58%) of a 2:1 mixture of **24** and **25** as a yellow solid: mp 178–179 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 181.76, 153.58, 149.13, 117.75, 115.90, 109.71, 100.95, 78.30, 53.98, 51.76, 51.01, 37.46, 32.30, 29.53, 25.73, 23.65, 21.03, 20.08, 19.80, 12.83, 11.08; MS *m/z* (M^+) calcd 399.0219, obsd 399.0178.

Anal. Calcd for $C_{18}H_{22}Cl_2Zr$: C, 54.11; H, 5.55. Found: C, 54.00; H, 5.70.

(η^5-Pentamethylcyclopentadienyl){η^5-(1*R*,7*S*)-1,10,10-trimethyltricyclo[5.2.1.0^{2,6}]deca-3,5-dien-2-yl}dichlorozirconium (26 and 27). Solid **4**-Li (540 mg, 3.0 mmol) was added to dry toluene (50 mL) at room temperature, to be followed by 1.00 g (3.0 mmol) of solid (η^5-pentamethylcyclopentadienyl)trichorozirconium. The reaction mixture was heated at reflux for 48 h, cooled, and concentrated. The residue was taken up in chloroform (20 mL), treated with 20 mL of 4 N hydrochloric acid, and stirred for 1 h. The organic phase was dried and evaporated to leave a solid which proved to be a 1.4:1 mixture of **26** and **27**. Recrystallization of this material from dichloromethane–hexane afforded 850 mg (60%) of yellow crystals: mp 171–172 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 156,89, 152.18, 150.58, 124.54, 124.22, 123.64, 122.43, 112.04, 107.91, 107.66, 68.87, 54.39, 53.75, 51.26, 37.84, 31.14, 29.05, 24.61, 24.10, 20.63, 20.32, 19.83, 12.90, 12.69, 12.52, 11.95, 10.61; MS *m/z* (M^+) calcd 469.0816, obsd 469.0872.

Anal. Calcd for $C_{23}H_{32}Cl_2Zr$: C, 58.69; H, 6.85. Found: C, 58.55; H, 6.87.

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Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, least-squares planes, and thermal parameters for **22** (9 pages); a listing of observed and calculated structure factors for **22** (6 pages). Ordering information is given on any current masthead page.