1512 *Organometallics* 1989, *8*, 1512-1517

Stereoselective Formation from a (1*S*,5*S*)-(−)-Verbenone-Derived Cyclopentadiene of Dimeric and Mixed Titanium and Zirconium Dichloride Complexes[1]

Kevin J. Moriarty, Robin D. Rogers,[2] and Leo A. Paquette*

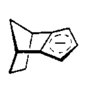
Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, and the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received November 22, 1988

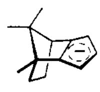
The optically active cyclopentadienide anion 4 undergoes reaction with $TiCl_3{\cdot}3THF$, $CpTiCl_3$, $ZrCl_4$, and Cp^*ZrCl_3 to form a single complex in each instance. That coordination occurs above plane in 4, its less sterically congested surface, was established by ^1H and ^{13}C NMR correlations and by X-ray crystallographic analysis of 12, which is monoclinic, $P2_1$, with a = 12.128 (9) Å, b = 7.536 (8) Å, c = 13.970 (8) Å, β = 99.64 (5)°, and D_{calcd} = 1.30 g cm^{-3} for Z = 2. When $CpZrCl_3$ is the coreactant, a 1:1 mixture of both possible stereoisomeric complexes results. Thus, 4 is a more facially discriminating species than is 3, a finding that provides some mechanistic insight into the electronic character and mode of reaction of cyclopentadienide anions grafted to plane-nonsymmetric bicyclic frameworks.

The addition of a cyclopentadienide anion to a transition-metal halide constitutes one of the more important organometallic reactions. Recently, some effort has been made to develop an understanding of the π-facial stereoselectivity that materializes when the Cp rings involved in such processes are fused to various plane-nonsymmetric bicyclic frameworks.[1,3,4] The importance of steric factors is generally accepted, but the relevance of electronic interactions in guiding the coordination process is, by its nature, more difficult to establish.

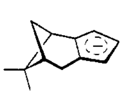
Examples culled from our recent comprehensive analysis of the impact of structural modification in the Cp ligand on the stereoselectivity of capture of $CpMCl_3$ reagents (M = Ti and Zr) illustrate the fundamental questions at issue. Thus, the isodicyclopentadienide anion (1) reacts with (η^5-cyclopentadienyl)titanium trichloride in tetrahydrofuran solution at room temperature to give the above-plane complex exclusively.[3c,d] The camphor-derived anion 2,



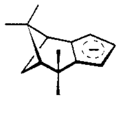
1



2



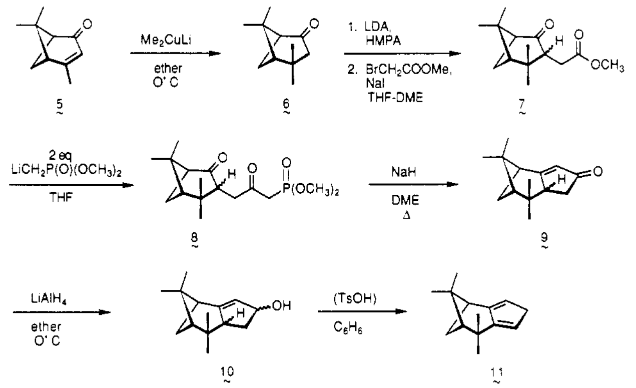
3



4

which carries an appreciably larger steric bias on its exo surface, reacts under the same conditions to give a 1:7 mixture rich in the below-plane stereoisomer.[3e] Intuition would suggest that this stereochemical reversal is the direct consequence of the apical syn-methyl substituent in 2. This hypothesis has received X-ray crystallographic support. On the other hand, the exceptionally clean formation of the stereoisomeric below-plane titanocene dichloride when 1 and $CpTiCl_3$ are allowed to condense at −78 °C has been attributed to a stereoelectronic origin.[3c,d] Intriguing as well is the finding that 3 bonds to $CpTiCl_3$ at low temperature predominantly (5:1) from that direction syn to the dimethyl-substituted bridge.[1]

Scheme I



We report here our findings with 4, an optically active cyclopentadienide prepared by chemical modification of commercially available (1*S*,5*S*)-(−)-verbenone (5). This new ligand differs from 3 in absolute configuration and in having a sterically demanding (although not facially discriminating) pair of geminal methyl groups immediately adjacent to the anionic five-membered ring. Will the anticipated kinetic retardation result in similar stereodirectionality being drawn from the remainder of the carbocyclic superstructure? Clarification of this issue would provide substance to predictability considerations involving bicyclo[3.3.1]heptanes 3 and 4 and possibly constitute an indirect probe of the role of long-range σ–π interaction within the norbornyl systems 1 and 2.

Synthetic Considerations

Exposure of 5 to lithium dimethylcuprate in ether at 0 °C resulted in conjugate addition of a methyl group. When attempted alkylation of 6 with 3-bromo-2-ethoxypropenylphosphonate[3e,5] was found to proceed very inef-

---

[1] Paper 46 in the series dealing with isodicyclopentadienes and related molecules. For part 45, see: Paquette, L. A.; Moriarty, K. J.; Rogers, R. D. *Organometallics*, preceding paper in this issue.

[2] Author to whom queries concerning the X-ray crystallographic analysis should be addressed.

(3) (a) McLaughlin, M. L.; McKinney, J. A.; Paquette, L. A. *Tetrahedron Lett.* **1986**, 5595. (b) Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Ibid.* **1986**, 5599. (c) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Crocq, V. *Organometallics* **1988**, *7*, 1873. (d) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Sornay, C.; Rogers, R. D.; Rheingold, A. L., submitted for publication. (e) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D., submitted for publication. (f) Paquette, L. A.; Gugelchuk, M.; McLaughlin, M. L. *J. Org. Chem.* **1987**, *52*, 4732.

(4) (a) Halterman, R. L.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1986**, 1461; *Organometallics* **1988**, *7*, 883. (b) See also Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1987**, *109*, 8105.

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

0276-7333/89/2308-1512$01.50/0 © 1989 American Chemical Society

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

	VCp				methano		apical	
compd	central	peripheral	RCp	bridgehead	anti	syn	syn-methyl	other methyls
				A. Titanium Series				
12	6.50 (t, J = 2.5 Hz)	6.21 (t, J = 2.5 Hz) 6.01 (t, J = 2.5 Hz)		2.87 (t, J = 5 Hz) 1.66 (m)	2.52	1.97 (d, J = 11 Hz)	0.44 (s)	1.40, 1.39, 1.33
13	6.44 (t, J = 3 Hz)	6.21 (d, J = 3 Hz)	6.57 (s)	2.91 (t, J = 5 Hz) 1.67 (t, J = 5 Hz)	2.56 (m)	1.91 (d, J = 11 Hz)	0.44 (s)	1.41, 1.37, 1.30
				B. Zirconium Series				
14	6.29 (t, J = 2.5 Hz)	6.14 (t, J = 2.5 Hz) 5.94 (t, J = 2.5 Hz)		2.77 (t, J = 10 Hz) 1.69 (t, J = 5 Hz)	2.56 (m)	2.10 (t, J = 11 Hz)	0.40 (s)	1.40, 1.39, 1.28
15	6.29 (m)	6.24 (m)	6.47 (s)	2.80 (t, J = 5 Hz) 1.72 (m)	2.59 (m)	2.03 (d, J = 11 Hz)	0.40 (s)	1.40, 1.37, 1.23
16	6.24 (t, J = 3 Hz)	3.38 (t, J = 3 Hz) 6.04 (t, J = 3 Hz)	6.46 (s) 1.72 (m)	3.00 (t, J = 5 Hz)	2.67 (m)	0.95 (d, J = 10 Hz)	1.06 (s)[a]	1.57, 1.43, 1.08[a]
17	5.97 (t, J = 3 Hz)	5.83 (t, J = 3 Hz) 5.23 (t, J = 3 Hz)		2.60 (t, J = 5 Hz) 1.66 (t, J = 6 Hz)	2.51 (m)	2.67 (d, J = 10 Hz)	0.37 (s)	1.45, 1.37, 1.23

[a] These signals may be interchanged.

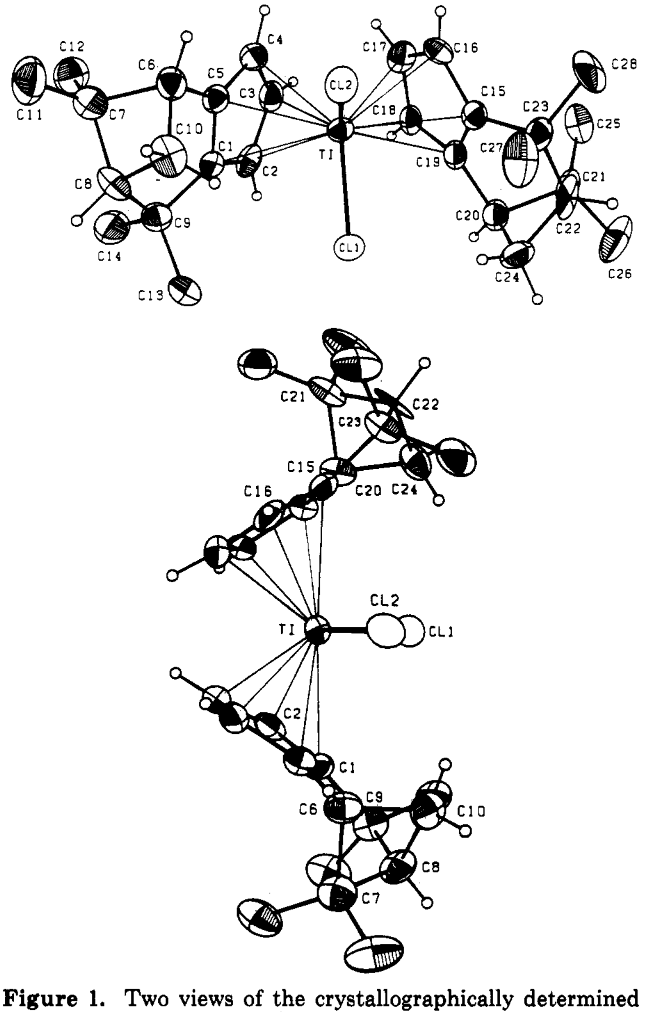


Figure 1. Two views of the crystallographically determined molecular structure of 12 as drawn with 50% probability ellipsoids.

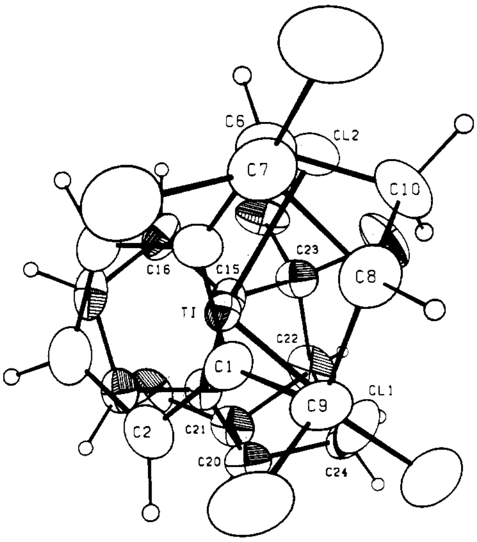


Figure 2. Projection of 12 showing the mutual orientation of the tricyclic ligands.

ficiently because of the neopentyl nature of the enolate carbon, recourse was made instead to methyl bromoacetate, a smaller electrophile. Following deprotonation with lithium diisopropylamine in HMPA, C–C bond formation was conducted in a tetrahydrofuran–1,2-dimethoxyethane solvent system containing sodium iodide. These conditions furnished 7 in 60% yield and made possible the efficient recovery of unreacted 6. Reaction of 7 with 2 equiv of the lithium salt of dimethyl methylphosphonate effected the desired chain lenghtening to give diketo phosphonate 8 (62%).

Intramolecular cycloannulation within 8 was accomplished by heating with sodium hydride in 1,2-dimethoxyethane to give 9.[4a,6] Following lithium aluminum hydride reduction of 9 in ether at room temperature, the unstable allylic alcohol was immediately dissolved in benzene and stirred overnight at 20 °C in the presence of a catalytic quantity of *p*-toluenesulfonic acid. Diene 11 is the double bond isomer expected on thermodynamic grounds.[3b,7]

For the conversion of 11 to 4, the diene was dissolved in dry ether under argon and treated with 1.1 equiv of *n*-butyllithium. After 12 h at the reflux temperature, cooling to 20 °C induced precipitation of the lithium salt. Further purification by washing with fresh ether was followed by drying under high vacuum and storage in a Schlenk tube under argon prior to use.

Complexation to Group 4 Transition Metals

The lithium salt of 4 was heated with 0.5 equiv of the titanium trichloride tris(tetrahydrofuran) complex[8] in dry 1,2-dimethoxyethane at the reflux temperature for 3 days. Following Soxhlet extraction of the residue and recrystallization from dichloromethane–hexane, purple-brown

---

(6) An alternative base strongly recommended for this type of cyclization of potassium carbonate and 18-crown-6 in toluene: Aristoff, P. A. *Synth. Commun.* **1983**, *13*, 145.

(7) (a) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218. (b) Bartlett, P. D.; Wu, C. *Ibid.* **1983**, *105*, 100.

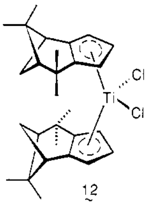
(8) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 137.

Table II. Experimental Crystallographic Data for 12[14]

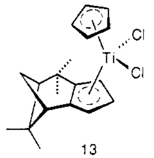
mol wt	493.4
space group	$P2_1$
temp, °C	20
cell constants[a]	
a, Å	12.128 (9)
b, Å	7.536 (8)
c, Å	13.970 (8)
β, deg	99.64 (5)
cell vol, Å^3	1259
formula units/unit cell	2
D_{calcd}, g cm^{-3}	1.30
μ_{calcd}, cm^{-1}	5.1
diffractometer/scan	Enraf-Nonius CAD-4/θ-2θ
radiatn, graphite monochromator	Mo Kα (λ = 0.71073 Å)
max cryst dimens, mm	0.08 × 0.13 × 0.35
scan width	0.80 + 0.35 tan θ
std reflctns	500; 040; 005
decay of stds	±1%
reflctions measd	2465
2θ range, deg	$2 \leq 2\theta \leq 50$
range of h, k, l	+14,+8,±16
reflctions obsd [$F_o \geq 5\sigma(F_o)$][b]	1734
computer programs[c]	SHELX[14a]
struct soln	heavy-atom techniques
no. of parameters varied	279
weights	unit
GOF	1.60
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.058
R_w	0.065
R inverse configuratn	0.058
largest feature final diff map, e/Å^3	0.3

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 reflections ($\theta < 19°$). [b] Corrections: Lorentz-polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref 14b.

parallelepiped crystals of a titanocene dichloride were isolated in 45% yield. Subsequent to growing well-defined single crystals of 12, structural confirmation was gained by means of X-ray crystallography (Table II, Figure 1). As reflected in the ORTEP diagrams, a single rotamer resides in the crystal.



12



13

Relevantly, the mutual orientation of the tricyclic ligands appears to be the only one readily attainable on steric grounds (Figure 2). Despite adoption of this arrangement, rather severe effects are to be noted on the usually symmetric Ti–C η^5-separations (Table III). For example, the unsubstituted Cp carbon atoms C(3) and C(17) are seen to have short Ti–C distances of 2.33 (1) and 2.31 (1) Å, respectively. Of the remaining Cp ring atoms, those adjacent to the position carrying the CMe$_2$ fragment exhibit farther approaches (Ti–C(2) = 2.48 (1) and Ti–C(16) = 2.447 (9) Å) than the other two (Ti–C(4) = 2.319 (9) and Ti–C(18) = 2.36 (1) Å). The carbon atoms bonded to the CMe$_2$ fragments show very long separations: Ti–C(1) = 2.63 (1) and Ti–C(15) = 2.626 (9) Å, followed by Ti–C(5) = 2.499 (9) and Ti–C(19) = 2.58 (1) Å. Most unusually, the Ti–C η^5-separations show a range of 0.32 Å!

A priori, this phenomenon might be attributed to severe steric repulsions stemming from the CMe$_2$ fragments, C(9) and C(23). The closest C···Cl contacts are compiled in Table IV. The closest Cl(1) contact at 2.57 Å is to a hydrogen on C(24), with the methyl protons from C(13) and C(14) (the latter from a different molecule) being next.

Table III. Bond Distances (Å) and Angles (deg) for 12

Bond Distances			
Ti–Cl(1)	2.286 (3)	Ti–Cl(2)	2.353 (3)
Ti–C(1)	2.63 (1)	Ti–C(2)	2.46 (1)
Ti–C(3)	2.32 (1)	Ti–C(4)	2.314 (9)
Ti–C(5)	2.502 (9)	Ti–C(15)	2.626 (9)
Ti–C(16)	2.449 (8)	Ti–C(17)	2.30 (1)
Ti–C(18)	2.34 (1)	Ti–C(19)	2.57 (1)
C(1)–C(2)	1.40 (1)	C(1)–C(5)	1.40 (1)
C(1)–C(9)	1.53 (1)	C(2)–C(3)	1.41 (1)
C(3)–C(4)	1.39 (2)	C(4)–C(5)	1.42 (1)
C(5)–C(6)	1.48 (1)	C(6)–C(7)	1.60 (1)
C(6)–C(10)	1.56 (2)	C(7)–C(8)	1.57 (2)
C(7)–C(11)	1.53 (2)	C(7)–C(12)	1.50 (2)
C(8)–C(9)	1.53 (2)	C(8)–C(10)	1.55 (1)
C(9)–C(13)	1.55 (1)	C(9)–C(14)	1.56 (2)
C(15)–C(16)	1.43 (1)	C(15)–C(19)	1.38 (2)
C(15)–C(23)	1.53 (1)	C(16)–C(17)	1.39 (2)
C(17)–C(18)	1.41 (1)	C(18)–C(19)	1.40 (1)
C(19)–C(20)	1.50 (1)	C(20)–C(21)	1.57 (1)
C(20)–C(22)	2.04 (2)	C(20)–C(24)	1.52 (2)
C(21)–C(26)	1.56 (2)	C(21)–C(25)	1.50 (2)
C(21)–C(26)	1.57 (2)	C(22)–C(23)	1.55 (1)
C(22)–C(24)	1.48 (1)	C(23)–C(27)	1.51 (2)
C(23)–C(28)	1.49 (2)	Cent1–Ti	2.11
Cent2–Ti	2.12		
Bond Angles			
Cl(1)–Ti–Cl(2)	99.2 (1)	C(2)–C(1)–C(5)	107.5 (9)
C(2)–C(1)–C(9)	131 (1)	C(5)–C(1)–C(9)	119.6 (9)
C(1)–C(2)–C(3)	108 (1)	C(2)–C(3)–C(4)	108 (1)
C(3)–C(4)–C(5)	107.4 (9)	C(1)–C(5)–C(4)	108.5 (9)
C(1)–C(5)–C(6)	118.2 (9)	C(4)–C(5)–C(6)	132.7 (9)
C(5)–C(6)–C(7)	106.5 (9)	C(5)–C(6)–C(10)	108.4 (9)
C(7)–C(6)–C(10)	86.2 (8)	C(6)–C(7)–C(8)	84.4 (8)
C(6)–C(7)–C(11)	112 (1)	C(8)–C(7)–C(11)	108 (1)
C(6)–C(7)–C(12)	116 (1)	C(8)–C(7)–C(12)	124 (1)
C(11)–C(7)–C(12)	110 (1)	C(7)–C(8)–C(9)	117 (1)
C(7)–C(8)–C(10)	87.8 (8)	C(9)–C(8)–C(10)	109.9 (9)
C(8)–C(9)–C(13)	110 (1)	C(1)–C(9)–C(14)	107 (1)
C(8)–C(9)–C(14)	112.6 (8)	C(13)–C(9)–C(14)	107.0 (9)
C(6)–C(10)–C(8)	86.0 (8)	C(16)–C(15)–C(19)	108 (1)
C(16)–C(15)–C(23)	129 (1)	C(19)–C(15)–C(23)	121.7 (9)
C(15)–C(16)–C(17)	107 (1)	C(16)–C(17)–C(18)	108.3 (9)
C(17)–C(18)–C(19)	107.6 (9)	C(15)–C(19)–C(18)	109.0 (9)
C(15)–C(19)–C(20)	117.5 (9)	C(18)–C(19)–C(20)	132 (1)
C(21)–C(20)–C(22)	49.3 (7)	C(19)–C(20)–C(24)	110 (1)
C(21)–C(20)–C(24)	88.3 (8)	C(22)–C(20)–C(24)	46.4 (6)
C(20)–C(21)–C(22)	81.0 (9)	C(20)–C(21)–C(25)	120.4 (9)
C(22)–C(21)–C(25)	125 (1)	C(20)–C(21)–C(26)	112 (1)
C(22)–C(21)–C(26)	109 (1)	C(25)–C(21)–C(26)	108 (1)
C(20)–C(22)–C(21)	49.7 (6)	C(20)–C(22)–C(23)	106.0 (7)
C(21)–C(22)–C(23)	117.5 (8)	C(20)–C(22)–C(24)	48.2 (6)
C(21)–C(22)–C(24)	90.3 (9)	C(23)–C(22)–C(24)	113.4 (8)
C(15)–C(23)–C(22)	101.2 (9)	C(15)–C(23)–C(27)	113.1 (9)
C(22)–C(23)–C(27)	110 (1)	C(15)–C(23)–C(28)	110.7 (9)
C(22)–C(23)–C(28)	114.6 (9)	C(27)–C(23)–C(28)	108 (1)
C(20)–C(24)–C(22)	85.4 (8)	Cent1–Ti–Cent2	131.9
Cent1–Ti–Cl(1)	105.2	Cent1–Ti–Cl(2)	106.0
Cent2–Ti–Cl(1)	105.9	Cent2–Ti–Cl(2)	104.2

These effects may be responsible for the inequivalence in Ti–Cl distances and in the fact that there are two long Ti–C distances for ring 2 [C(15), C(19)] and only one for ring 1 [C(1)].

Metalation of 4-Li with (η^5-cyclopentadienyl)titanium trichloride in tetrahydrofuran solution at room temperature for 24 h, followed by addition of hydrochloric acid according to standard practice,[9] furnished the titanocene dichloride 13 (45%). The identical result was achieved at −78 °C. Its stereochemistry was again indicated by ^{1}H NMR spectroscopy (Table I). The central VCp vinyl proton appears as a triplet at δ 6.44, substantially deshielded relative to the peripheral Cp protons flanking it (δ 6.21), and the syn-endo-methyl group at δ 0.44 is clearly

---

[9] Smith, J. A.; Brintzinger, H. H. J. Organomet. Chem. 1981, 218, 159.

Table IV. Closest C• • •Cl Contacts in 12 (Values in Å)[a]

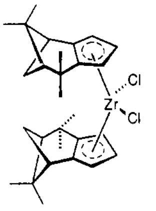
chlorine atom	carbon atom	position	dist
Cl(1)	C(19)	Cp ring	3.10 (1)
	C(1)	Cp ring	3.192 (9)
	C(2)	Cp ring	3.22 (1)
	C(13)	methyl	3.25 (1)
	C(24)	CH_2 bridge	3.30 (1)
	C(20)		3.46 (1)
	C(15)	Cp ring	3.52 (1)
Cl(2)	C(16)	Cp ring	3.04 (1)
	C(5)	Cp ring	3.07 (1)
	C(6)		3.19 (1)
	C(4)	Cp ring	3.34 (1)
	C(10)	CH_2 bridge	3.34 (1)
	C(15)	Cp ring	3.38 (1)
	C(27)		3.48 (1)

[a] For atomic numbering, see Figure 1.

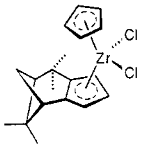
distal to the transition-metal center which in turn strongly influences the chemical shift of the syn-methano bridge proton (δ 2.56).

An attempt to condense the lithium salt of 4 with Cp^*TiCl_3[10] under analogous conditions, but at more elevated temperatures, did not afford characterizable amounts of mixed complex, perhaps as a consequence of excessive steric congestion.

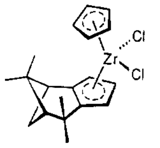
Exposure of cyclopentadienide 4 to freshly sublimed zirconium tetrachloride in dry 1,2-dimethoxyethane and subsequent heating of the reaction mixture at the reflux temperature for 3 days provided **14** in 65% yield. As with **12**, this zirconocene dichloride exhibited a stereochemically diagnostic ^1H NMR spectrum (Table I). The question of stereofacial differentiation is convincingly resolved by the chemical shift of the endo apical methyl substituent (singlets at δ 0.41 and 0.40), which because of its remoteness from the metal center is not subject to its diagnostically intense deshielding influence.[3d-f]



14



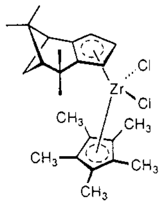
15



16

The condensation of 4-Li with $CpZrCl_3{\cdot}2THF$[11] was performed in toluene solution and required 3 days at the reflux temperature to proceed to completion. Under these conditions, an inseparable 1:1 mixture of **15** and **16** was obtained. Since **16** happened to be the first example of transition-metal coordination by 4 syn to its dimethyl-substituted methano bridge, brief comparison of certain key ^1H NMR features of these diastereomerically related complexes is warranted. The structural details of **15** and **16** happen to be most clearly defined by the chemical shifts of the pairs of hydrogen atoms and methyl groups on the one-carbon bridges. As in related molecules,[3] the zirconium atom exerts a demonstrably intense deshielding effect on the nearby syn, endo substituent. In **15**, the presumed closest nonbonded contact is to a bridge hydrogen atom. This proximity is reflected in the appearance of this proton at low field (δ 2.59) while the syn-methyl signal is seen in its normal location in the spectrum (δ 0.40). The situation is, of course, reversed in **16**, where the syn-methyl group is subject to the long-range anisotropic contributions of the metal (δ 1.06 or 1.08). These trends are considered to be reliably diagnostic of the π-facial stereochemistry adopted by the VCp ligand.

Reaction of 4-Li with Cp^*ZrCl_3,[10] carried out in entirely similar fashion, gave an isomerically homogeneous product consisting exclusively of **17**. The three-dimensional features of this yellow crystalline solid were again determined to be as illustrated by ^1H NMR analysis (Table I). The strong tendency for complexation to the less sterically congested surface of 4 with increasing bulkiness of the second ligand was once more made evident.



17

Discussion

Complexation of 4 to the several titanium and zirconium chloride reagents proceeds exclusively from the below-plane direction except where $CpZrCl_3$ is involved. In this instance, a statistical distribution of the two possible stereoisomeric complexes is produced. Because 4 is a sterically bulky reagent, its rate of reaction with group 4 metal halides is qualitatively slower than comparable processes involving **1**–**3**. Consequently, it did not prove practical in most cases to perform the above reactions at various temperatures. The exception was $CpTiCl_3$; however, this reagent gave no evidence of change in π-facial selectivity over the range of −78 to +20 °C.

Clearly, 4 exhibits a strong predilection for coordination to Ti and Zr from its less sterically congested π-surface. The departure of $CpZrCl_3$ from the norm may stem from a combination of two factors: the VCp and Cp centroid–Zr distances are appreciably longer than their Ti counterparts, and the companion Cp ligand is the least sterically demanding of the set. Consequently, above-plane coordination as in **16** now becomes possible without the development of excessive steric congestion.

It has proven difficult to find a clear rationale for certain stereoselectivities exhibited by the pinane-derived anion **3**.[1] The capability of its gem-dimethyl-substituted bridge to exert dipole, polarizability, and π-anisotropic effects favoring syn complexation has been offered as a possible explanation.[1] σ/π interactions of similar type are known[12] and may be related in origin to the sometimes contrasteric behavior of **3**. To the extent that these subtle electronic effects are present in **3**, they should operate as well in **4** since the bicyclic components are almost identical. The added pair of geminal methyl groups immediately proximal to the cyclopentadienide moiety have no capacity for facial discrimination. However, these substituents are sterically demanding and therein resides the probable underlying cause of the differing stereoselective responses of **3** and **4**.

The contrasteric capacity of **3** surfaces most noticeably in its reactions at −78 °C. At this low temperature, rates are sufficiently slowed that reaction trajectories can (and presumably do) proceed via transition states that are

---

[10] Blenkers, J.; DeLiefde, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

[11] Erker, G.; Berg, K.; Treschanke, L.; Engel, K. *Inorg. Chem.* **1982**, *21*, 1277.

[12] Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328.

reactantlike. Under such circumstances, the electronic differences that distinguish the two stereodistinctive π surfaces in **3**, small as they are, find it possible to exert some modicum of control over the direction of complexation. With increases in reaction temperature, the transition states appear to take on productlike characteristics and therefore to be sensitive to the steric effects that are relevant to each specific example. For obvious reasons, this translates into heightened complexation away from the methyl-substituted methano bridge.

The data described herein suggest that the very substantive steric bulk of **4** is adequate for the majority of reactions to pass over transition states that are productlike. The resulting sensitivity to nonbonded steric congestion would, of course, mask any intrinsic electronic preference for π-facial stereoselectivity, since these effects are rather small. In general, however, any attendant increase in activation energy can be expected to shift the selectivity criterion in the direction of steric control.

The preceding relationship is an important one and may well impact also on the reactivity of the metal center in **12**–**17**, and especially its capability for engaging in highly stereocontrolled chemical reactions. This phenomenon, which is presently under active investigation, may be of appreciable utility in synthesis when properly optimized and understood.

Experimental Section

(1*S*,5*S*)-(−)-4,4,6,6-Tetramethylbicyclo[3.1.1]heptan-2-one (6).[13] Anhydrous copper(I) iodide (25.23 g, 0.135 mol; recrystallized from saturated aqueous potassium iodide solution, extracted with tetrahydrofuran in a Soxhlet apparatus, and dried at 100 °C/0.01 Torr for 6 h) was slurried in dry ether (200 mL) at 0 °C under argon. Methyllithium (174 mL of 1.5 M in ether, 0.265 mol) was introduced dropwise via canula during 30 min. After 15 min of stirring at 0 °C, (1*S*,5*S*)-(−)-verbenone (20.28 g, 0.135 mol) in 100 mL of dry ether was added over 30 min under argon. The reaction mixture was stirred for 1 h at 0 °C prior to being quenched with 100 mL of saturated ammonium chloride solution. After arrival at room temperature, ammonium hydroxide was added until the copper salts dissolved. The separated aqueous layer was extracted with ether (3 × 200 mL), and the combined organic phases were washed twice with brine, dried, and evaporated. The residual oil was purified by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) to give 14.0 g (62%) of **6** as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.51 (t, J = 5 Hz, 1 H), 2.47 (m, 1 H), 2.33 (d, J = 3 Hz, 2 H), 1.84 (t, J = 5 Hz, 1 H), 1.60 (d, J = 10 Hz, 1 H), 1.32 (s, 3 H), 1.15 (s, 3 H), 1.05 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 212.86, 57.77, 53.36, 47.90, 40.72, 31.76, 31.50, 28.74, 26.95, 25.38, 25.03; MS *m/z* (M$^+$) calcd 166.1358, obsd 166.1347; $[\alpha]^{23}_{\mathrm{D}}$ −22.5° (*c* 18.5, ethanol).

(1*S*,5*R*)-3-((Methoxycarbonyl)methyl)-4,4,6,6-tetramethylbicyclo[3.1.1]heptan-2-one (7). To diisopropylamine (34.40 g, 0.34 mol) in a cold (−78 °C) mixture (1:5) of tetrahydrofuran and 1,2-dimethoxyethane (100 mL) was added *n*-butyllithium in hexanes (0.34 mol). After 2 h, a solution of **6** (56.60 g, 0.34 mol) in 50 mL of dry 1,2-dimethoxyethane (DME) was introduced during 30 min at −78 °C. At this point, HMPA (60.93 g, 0.34 mol) was added, the mixture was stirred for an additional 30 min, and a solution of methyl bromoacetate (104.0 g, 0.68 mol) and sodium iodide (122.3 g, 0.68 mol) in 100 mL of dry DME was introduced rapidly. The reaction mixture was kept at −78 °C for an additional hour and at room temperature for 12 h prior to being poured into water (300 mL). The separated aqueous phase was extracted with ether (3 × 200 mL), and the combined organic layers were dried and evaporated. Distillation of the residue gave 49.1 g (61%) of **7** as a colorless oily mixture of epimers, bp 115–117 °C at 0.01 Torr. The epimers were separated chromatographically.

For the 3*S* epimer: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.71 (s, 3 H), 3.03 (t, J = 7 Hz, 1 H), 2.74 (d, J = 5 Hz, 1 H), 2.60 (d, J = 6 Hz, 2 H), 2.50 (t, J = 17 Hz, 1 H), 1.50 (t, J = 6 Hz, 1 H), 1.48 (d, J = 10 Hz, 1 H), 1.37 (s, 3 H), 1.24 (s, 3 H), 1.17 (s, 3 H), 0.93 (s, 3 H).

For the 3*R* epimer: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.70 (s, 3 H), 3.02 (t, J = 7 Hz, 1 H), 2.80 (d, J = 5 Hz, 1 H), 2.59 (d, J = 6 Hz, 2 H), 2.47 (t, J = 17 Hz, 1 H), 1.48 (d, J = 6 Hz, 1 H), 1.47 (t, J = 10 Hz, 1 H), 1.36 (s, 3 H), 1.23 (s, 3 H), 1.16 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 212.68, 173.36, 57.78, 55.01, 51.40, 50.67, 39.26, 35.73, 32.75, 29.06, 27.31, 26.75, 25.80, 25.04; MS *m/z* (M$^+$) calcd 238.1578, obsd 238.1568.

Anal. Calcd for $C_{18}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.38; H, 9.40.

(1*S*,5*R*)-3-(3-(Dimethylphosphono)-2-oxoprop-1-yl)-4,4,6,6-tetramethylbicyclo[3.1.1]heptan-2-one (8). Keto ester **7** (49.10 g, 0.21 mol) dissolved in 100 mL of dry tetrahydrofuran was added to a solution of the lithium salt of dimethyl methylphosphonate (50.87 g, 0.41 mol) in tetrahydrofuran (500 mL) at −78 °C over 20 min. The reaction mixture was stirred at −78 °C for 1 h, then warmed to room temperature, and stirred for an additional hour before being poured into water. The aqueous phase was extracted with dichloromethane (3 × 300 mL), and the combined organic layers were dried, filtered, and evaporated. The remaining yellow oil was placed atop a column of silica gel. Following elution with 20% ethyl acetate in petroleum ether to remove unreacted **7**, the product was eluted with ethyl acetate as a viscous colorless oil (43.0 g, 62%).

For the 3*S* epimer: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.770 (s, 3 H), 3.743 (s, 3 H), 3.19 (m, 4 H), 2.97 (m, 3 H), 1.85 (m, 2 H), 1.31 (s, 3 H), 1.09 (s, 3 H), 0.99 (s, 3 H), 0.82 (s, 3 H).

For the 3*R* epimer: colorless solid; mp 109–110 °C (from pentane–ether); ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.773 (s, 3 H), 3.740 (s, 3 H), 3.19 (m, 4 H), 2.97 (m, 3 H), 1.85 (m, 2 H), 1.32 (s, 3 H), 1.19 (s, 3 H), 1.13 (s, 3 H), 0.86 (s, 3 H).

For the mixture: ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 214.75, 200.94, 200.87, 58.01, 57.25, 55.32, 55.06, 53.05, 52.96, 52.83, 52.74, 51.18, 43.09, 42.85, 42.46, 42.30, 41.15, 40.76, 39.46, 35.99, 35.50, 31.46, 29.08, 27.89, 27.59, 27.41, 26.36, 25.83, 25.27, 24.79, 24.12; MS *m/z* (M$^+$) calcd 330.1596, obsd 330.1622.

Anal. Calcd for $C_{16}H_{27}O_5P$: C, 58.17; H, 8.24. Found: C, 58.34; H, 8.47.

(1*R*,8*R*)-7,7,9,9-Tetramethyltricyclo[6.1.1.0^{2,6}]dec-2-en-4-one (9). A solution of **8** (23.3 g, 0.071 mol) in 100 mL of dry 1,2-dimethoxyethane was added at room temperature via canula to a slurry of sodium hydride (1.69 g, 0.071 mol) in 800 mL of the same solvent. The reaction mixture was heated at reflux for 18 h, cooled, and poured into water. The separated aqueous phase was extracted with ether (3 × 250 mL), and the combined organic layers were dried and evaporated. The residual oil was purified by chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether) to give 7.8 g (51%) of **9** as a pale yellow oil. Crystallization from pentane gave the major epimer as a colorless solid: mp 52–53 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.69 (d, J = 2 Hz, 1 H), 3.41 (m, 1 H), 3.04 (t, J = 4 Hz, 1 H), 2.67 (m, 1 H), 2.37 (m, 3 H), 1.83 (t, J = 6 Hz, 1 H), 1.39 (s, 3 H), 1.20 (s, 3 H), 1.15 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 208.25, 204.74, 123.23, 56.28, 49.22, 40.72, 39.02, 36.61, 34.15, 29.72, 28.47, 25.74, 25.16; MS *m/z* (M$^+$) calcd 204.1514, obsd 204.1513.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.07; H, 9.93.

(1*R*,8*R*)-7,7,9,9-Tetramethyltricyclo[6.1.1.0^{2,6}]deca-2,5-diene (11). To a magnetically stirred slurry of lithium aluminum hydride (1.44 g, 0.038 mol) in dry ether (150 mL) was added a solution of **9** (7.80 g, 0.038 mol) in the same solvent (50 mL) during 30 min. After 1 h, the reaction mixture was cooled to 0 °C, quenched with water, and treated with 150 mL of 1 N hydrochloric acid. The separated aqueous phase was extracted four times with ether, and the combined organic layers were dried and evaporated to give **10** as an oil.

This material was directly dissolved in dry benzene (50 mL), *p*-toluenesulfonic acid (720 mg, 0.0038 mol) was introduced, and the solution was stirred for 24 h. Anhydrous potassium carbonate was added followed by anhydrous magnesium sulfate. After being left standing for 2 h with intermittent swirling, the solution was filtered and evaporated. The residual oil was purified by chro-

---

(13) Sempuku, K. *Jpn. Kokai Tokyo Koho Jp*, Appl 79/164,558, Dec 18, 1979; *Chem. Abstr.* **1982**, *96*, 69022.

matography on neutral alumina (elution with pentane). There was isolated 4.50 g (63%) of 11 as a light yellowish oil: $[\alpha]^{21}{}_D$ +22.2° (*c* 5.8, hexane); ^{1}H NMR (300 MHz, C_6D_6) δ 6.00 (m, 1 H), 5.79 (m, 1 H), 2.89 (d, J = 0.6 Hz, 2 H), 2.66 (t, J = 5 Hz, 1 H), 2.39 (m, 1 H), 1.61 (t, J = 6 Hz, 1 H), 1.47 (d, J = 10 Hz, 1 H), 1.39 (s, 3 H), 1.26 (s, 3 H), 1.19 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 153.13, 152.00, 123.89, 120.13, 54.11, 44.70, 42.77, 40.83, 37.21, 31.63, 31.00, 29.23, 27.76, 25.21; MS *m/z* (M^+) calcd 188.1565, obsd 188.1516.

((1*R*,8*R*)-7,7,9,9-Tetramethyltricyclo[6.1.1.0^{2,6}]deca-2,5-dienyl)lithium (4-Li). Diene 11 (4.5 g, 24 mmol) was dissolved in dry ether (100 mL) and treated with *n*-butyllithium (15.6 mL of 1.6 M, 25 mmol) via syringe at room temperature. The reaction mixture was heated at reflux for 24 h, cooled, and concentrated to a volume of 50 mL. After being cooled to 0 °C for 1 h, the colorless solid lithium salt precipitated. The residual ether was removed via cannula, fresh ether was added, and the mixture was recooled to 0 °C for 1 h. The ether was again removed via cannula, and the solid was dried under high vacuum and transferred under argon to a Schlenk tube. The air- and moisture-sensitive solid weighed 3.03 g (65%).

Bis(η^5-(1*R*,8*R*)-7,7,9,9-tetramethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorotitanium (12). To a magnetically stirred slurry of 4-Li (660 mg, 3.4 mmol) in dry 1,2-dimethoxyethane at −78 °C under argon was added solid $TiCl_3\cdot 3THF$ (630 mg, 1.7 mmol). The reaction mixture was then brought to room temperature and heated at the reflux temperature for 3 days. The solvent was subsequently evaporated, the residue was taken up in chloroform, and 20 mL of concentrated hydrochloric acid was added. After 20 min of stirring, the organic layer was separated and the aqueous phase was extracted with chloroform (2 × 50 mL). The combined organic solutions were dried, filtered, and evaporated. The residue was transferred to a Soxhlet thimble and extracted with hydrogen chloride saturated pentane. Removal of the product was next achieved with HCl-saturated chloroform. Recrystallization from dichloromethane–hexane afforded 440 mg of a 2.3:1 mixture of 12 and $VCpTiCl_3$. Pure 12 was isolated as a purple-brown solid: mp 198–200 °C (from dichloromethane–hexane); 217 mg (45%); ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.77, 152.77, 142.59, 140.42, 116.73, 116.35, 115.59, 115.10, 111.22, 54.53, 54.45, 45.55, 45.39, 45.03, 44.91, 40.51, 40.19, 31.35, 31.09, 29.95, 29.74, 27.62, 24.35; MS *m/z* (M^+ − Cl) calcd 457.2141, obsd 457.2163; $[\alpha]^{21}{}_D$ +491° (*c* 2, toluene).

Anal. Calcd for $C_{28}H_{38}Cl_2Ti$: C, 68.18; H, 7.71. Found: C, 68.20; H, 7.89.

X-ray Crystallographic Analysis of 12. A purple-brown single crystal of 12 was mounted on a pin and transferred to the goniometer. The space group was determined to be either the centric $P2_1/m$ or acentric $P2_1$ from the systematic absences. Statistical tests indicated that the space group was centric; however, the subsequent solution and successful refinement of the structure was carried out in the acentric space group $P2_1$. A summary of data collection parameters is given in Table II.

The geometrically constrained hydrogen atoms were placed in calculated position 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5 Å^2). Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of R = 0.058 and R_w = 0.065. The final values of the positional parameters are given in Table VIII (supplementary material).

(η^5-Cyclopentadienyl)(η^5-(1*R*,8*R*)-7,7,9,9-tetramethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorotitanium (13). A solution of 4-Li (260 mg, 1.3 mmol) and $CpTiCl_3$ (290 mg, 1.3 mmol) in dry tetrahydrofuran (150 mL) was stirred at room temperature under an argon atmosphere for 24 h. The solvent was removed under reduced pressure, the residue was taken up in chloroform (50 mL), and concentrated hydrochloric acid (20 mL) was added. This mixture was stirred for 20 min, and the separated aqueous phase was extracted with chloroform (2 × 50 mL). The combined organic layers were dried and evaporated to leave a residue that was placed in a Soxhlet thimble and extracted with hydrogen chloride–saturated pentane for 12 h. Following this, the product was extracted into HCl–saturated chloroform during 12 h. The solvent was removed in vacuo, and the solid was recrystallized from dichloromethane–hexane to give 217 mg (45%) of 13 as purple-brown crystals: mp 201–202 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 151.35, 142.59, 119.77, 119.39, 117.01, 114.53, 54.48, 45.43, 45.24, 40.39, 30.99, 30.19, 29.88, 27.59, 24.30; MS *m/z* (M^+ − Cl) calcd 335.1046, obsd 335.1057; $[\alpha]^{21}{}_D$ +204.6° (*c* 0.044, toluene).

Anal. Calcd for $C_{19}H_{24}Cl_2Ti$: C, 61.46; H, 6.52. Found: C, 61.20; H, 6.53.

Bis(η^5-(1*R*,8*R*)-7,7,9,9-tetramethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorozirconium (14). The lithium salt of 4 (570 mg, 2.9 mmol) was dissolved in dry 1,2-dimethoxyethane (50 mL), and the solution was cooled to −78 °C under argon. Sublimed zirconium tetrachloride (340 mg, 1.5 mmol) was introduced, and the reaction mixture was warmed to room temperature then heated at reflux for 3 days. Following the predescribed workup, the residue was transferred to a sublimator and the product was sublimed at 150–160 °C and 0.001 Torr. There was isolated 520 mg (65%) of 14 as yellow crystals: mp 201–202 °C (from dichloromethane–heptane); ^{1}H NMR (see Table I); MS *m/z* (M^+) calcd 534.1393, obsd 534.1376; $[\alpha]^{21}{}_D$ +274° (*c* 0.18, toluene).

Anal. Calcd for $C_{28}H_{38}Cl_2Zr$: C, 62.25; H, 7.14. Found: C, 62.59; H, 7.28.

(η^5-Cyclopentadienyl)(η^5-(1*R*,8*R*)-7,7,9,9-tetramethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorozirconium (15 and 16). A mixture of 4-Li (450 mg, 2.3 mmol) and $CpZrCl_3\cdot 2THF$ (940 mg, 2.3 mmol) in dry toluene (75 mL) was heated at the reflux temperature for 3 days. Product isolation was performed in the predescribed manner. Following sublimation of the residue at 150–160 °C and 0.001 Torr, there was isolated an inseparable 1:1 mixture of 15 and 16 as yellow crystals: mp 161–162 °C (600 mg, 63%); ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, C_6D_6, ppm) 144.94, 120.46, 115.91, 115.71, 113.82, 113.70, 110.79, 107.70, 106.44, 54.91, 54.72, 45.54, 44.91, 44.77, 40.86, 39.75, 35.84, 34.23, 31.54, 31.03, 29.83, 28.86, 27.58, 27.39, 25.79, 24.39; MS *m/z* (M^+) calcd 412.0298, obsd 412.0317.

Anal. Calcd for $C_{19}H_{24}Cl_2Zr$: C, 55.04; H, 5.83. Found: C, 54.90;, H, 5.94.

(η^5-Pentamethylcyclopentadienyl)(η^5-(1*R*,8*R*)-7,7,9,9-tetramethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorozirconium (17). A mixture of 4-Li (550 mg, 2.8 mmol) and $Cp''ZrCl_3$ (940 mg, 2.8 mmol) in dry toluene (75 mL) was heated at the reflux temperature for 3 days. Product isolation was achieved as before to give after sublimation 700 mg (55%) of 17 as yellow crystals: mp 184–185 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 147.09, 139.87, 123.64, 116.16, 109.53, 104.67, 54.34, 45.83, 44.48, 39.87, 30.27, 30.06, 29.90, 27.60, 24.23, 12.44; MS *m/z* calcd 482.1080, obsd 482.1044; $[\alpha]^{21}{}_D$ +86.4° (*c* 0.22, toluene).

Anal. Calcd for $C_{24}H_{34}Cl_2Zr$: C, 59.47; H, 7.07. Found: C, 59.14; H, 7.15.

Acknowledgment. The Ohio State group thanks the National Cancer Institute (Grant CA-12115) for their financial support of this research program.

Supplementary Material Available: Tables of least-squares planes, thermal parameters, final fractional coordinates, and thermal parameters for 12 (4 pages); a listing of observed and calculated structure factors for 12 (4 pages). Ordering information is given on any current masthead page.

---

(14) 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) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1972; Vol. IV, pp 72, 99, 149. (c) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, *A27*, 368.