$(CF_3)_3AuPMe_3$ (13). In the glovebox, $(CF_3)_2AuI(PMe_3)$ (0.45 g, 0.84 mmol) and $Cd(CF_3)_2{\cdot}DME$ (0.58 g, 1.70 mmol) were added to the 25-mL heavy-walled reaction vessel described in the preparation of 11, method A. It was necessary to remove the Teflon needle valve to allow addition of the solids. The needle valve was replaced, and the reaction vessel was removed from the glovebox. CH_2Cl_2 (15 mL) was frozen into the vessel on a vacuum line, and CF_3I (5.5 mmol) was measured into a calibrated volume and transferred to the reactor with liquid nitrogen cooling. The Teflon needle valve was closed, and the reaction mixture was heated at 60 °C for 12 h; the color of the solution remained pale yellow throughout the thermolysis. The reaction mixture was withdrawn via syringe and filtered. The solvent was removed from the filtrate in vacuo, and the solid residue was extracted with several portions of diethyl ether. This ether solution was taken to dryness, and the residue (0.36 g) was transferred to a sublimator where sublimation (75 °C, 10^{-4} Torr) onto a water-cooled probe gave 0.32 g (0.67 mmol) of white crystalline 13, 80% yield based on $(CF_3)_2AuI(PMe_3)$. MS: *m/e* (relative intensity) 461 (1.4), $(CF_3)_2(CF_2)AuPMe_3$; 411 (13), $(CF_3)_2AuPMe_3$; 323 (5.4), CF_2AuPMe_3; 273 (100), $AuPMe_3$. Anal. Calcd for $C_6H_9F_9PAu$: C, 15.01; H, 1.89; F, 35.62; P, 6.45. Found: C, 15.08; H, 1.83; F, 35.33; P, 6.36.

$(CF_3)_2AuI(PMe_3)$ and $Cd(CF_3)_2{\cdot}DME$. In an NMR tube reaction, $(CF_3)_2AuI(PMe_3)$ (12 mg, 0.022 mmol), $Cd(CF_3)_2{\cdot}DME$ (11 mg, 0.032 mmol), and 0.5 mL of CH_2Cl_2 were sealed under an argon atmosphere. The sample was heated overnight at 35 °C; the predominant products observed in the ^{19}F NMR spectrum were 1, 13, and CF_3I.

$(CF_3)_2AuI(PMe_3)$ and CF_3AuPMe_3. CF_3AuPMe_3 (25 mg, 0.046 mmol) and $(CF_3)_2AuI(PMe_3)$ (20 mg, 0.058 mmol) were added to an NMR tube sealed to a ground glass joint. On the vacuum line, 0.5 mL of CH_2Cl_2 was distilled into the mixture and the tube was flame sealed under argon. The sample was heated for 12 h at 40 °C and examined by ^{19}F NMR: The major resonances were due to the 1 and 11 starting materials; no evidence was seen for 13.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. We appreciate the assistance of Dr. James A. Happe and Dr. Raymond L. Ward in obtaining the NMR spectra.

Registry No. 1, 59963-16-5; **2**, 119970-84-2; **3**, 60898-04-6; **4t**, 119970-85-3; **4c**, 120052-42-8; **5t**, 119970-86-4; **5c**, 120052-43-9; **6t**, 119970-87-5; **7t**, 119970-88-6; **7c**, 120052-44-0; **8t**, 119970-89-7; **8c**, 120052-45-1; **9c**, 119970-90-0; **9t**, 120052-46-2; **10c**, 119970-91-1; **10t**, 120052-47-3; **11c**, 119970-92-2; **11t**, 120052-48-4; **12c**, 119970-93-3; **12t**, 120052-49-5; **13**, 107546-93-0; CF_3I, 2314-97-8; CH_3I, 74-88-4; $ClAuPMe_3$, 15278-97-4; $ClAuPEt_3$, 15529-90-5; $ClAuPPh_3$, 14243-64-2; $Cd(CF_3)_2 \cdot DME$, 76256-47-8; $Hg(CF_3)_2$, 371-76-6; $MeAuPMe_3$, 32407-79-7; Br_3AuPMe_3, 59110-29-1; $IAuPMe_3$, 25892-35-7; I_3AuPMe_3, 119970-94-4; CF_3Br, 75-63-8; Cl_3AuPEt_3, 56213-22-0; O_3AuPPh_3, 83971-98-6; $ClAuI_2(PMe_3)$, 119970-95-5; $ClAuBr_2(PPh_3)$, 32425-13-1.

(1*R*)-(−)-Nopol as the Source of an Optically Pure Fused Cyclopentadienyl Ligand. Stereochemical Course of Complexation to Cyclopentadienyltitanium and -zirconium Dichloride Fragments[1]

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Received November 14, 1988

The optically active pinane-related cyclopentadienide anion 4 has been complexed with $TiCl_3{\cdot}3THF$, $CpTiCl_3$, $ZrCl_4$, $CpZrCl_3$, and Cp^*ZrCl_3 for the purpose of assessing the level of π-facial stereoselectivity capable of being attained by this rather unusual ligand. In the homocomplexation experiments, the less hindered surface of 4 is utilized almost exclusively. At room temperature and above, the less sterically demanding Cp and Cp* ligands also exhibit a preference for coordination from above plane, although respectable levels of below-plane complexation now make their appearance. The dominance of above-plane reactivity ceases to persist when 4 is reacted with $CpTiCl_3$ and $CpZrCl_3$ at −78 °C. Under these circumstances, the proportion of 6 increases to 83% and 10 becomes the exclusive product. X-ray crystallographic data are provided for zirconocene 10.

Interest in optically active titanocene and zirconocene dichlorides has increased significantly in recent years in concert with a growing awareness of their ability to achieve stereodifferentiation in selected organic transformations.[3–5] Our thrust in this area has been to fuse a cyclopentadienyl

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[1] Paper 45 in the series dealing with isodicyclopentadienes and related molecules. For 44, see: Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D., submitted for publication.

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

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

(4) Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Tetrahedron Lett.* **1986**, 5599.

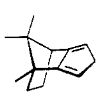
0276-7333/89/2308-1506$01.50/0

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

	PCp				methano		
compd	central	peripheral	RCp	bridgehead	ring	bridging	methyls
5	5.95 (m)	6.13 (m)		2.81 (t, *J* = 6.4 Hz)	3.39 (dd, *J* = 17.3, 2.7 Hz)	2.79 (m)	1.36 (s)
				2.09 (m)	2.44 (m)	1.12 (d, *J* = 9.8 Hz)	0.49 (s)
6	6.28 (m)	6.36 (m)	6.53 (s)	3.10 (t, *J* = 9 Hz)	3.15 (dd, *J* = 14, 2 Hz)	2.75 (m)	1.34 (s)
		6.18 (m)		2.17 (m)	2.93 (dd, *J* = 14, 4 Hz)	0.78 (d, *J* = 10 Hz)	0.74 (s)
7	6.31 (t, *J* = 3 Hz)	6.11 (m)	6.50 (s)	2.82 (m)	3.42 (dd, *J* = 14, 3 Hz)	2.74 (m)	1.37 (s)
		6.00 (m)		2.15 (m)	2.82 (m)	1.30 (d, *J* = 10 Hz)	0.50 (s)
8	6.19 (t, *J* = 3 Hz)	5.91 (dm, *J* = 3 Hz)		2.74 (t, *J* = 5 Hz)	3.30 (dd, *J* = 14, 3 Hz)	2.74 (m)	1.37 (s)
		5.84 (m)		2.17 (m)	2.76 (dd, *J* = 14, 3 Hz)	1.39 (d, *J* = 9 Hz)	0.48 (s)
10	6.31 (t, *J* = 3 Hz)	6.04 (dm, *J* = 3 Hz)	6.43 (s)	3.00 (t, *J* = 5 Hz)	3.03 (dd, *J* = 14, 2 Hz)	2.71 (m)	1.34 (s)
				2.19 (m)	2.85 (dd, *J* = 14, 4 Hz)	0.74 (d, *J* = 9 Hz)	0.93 (s)
11	5.95 (t, *J* = 3 Hz)	5.27 (t, *J* = 3 Hz)		2.93 (t, *J* = 5 Hz)	3.14 (dd, *J* = 15, 2 Hz)	2.50 (m)	1.85 (s)
		5.24 (t, *J* = 3 Hz)		2.16 (m)	2.74 (dd, *J* = 12, 4 Hz)	0.74 (d, *J* = 9 Hz)	1.10 (s)
							[2.04 (s)]
12	5.96 (t, *J* = 3 Hz)	5.41 (t, *J* = 3 Hz)		2.72 (t, *J* = 5 Hz)	3.29 (dd, *J* = 14, 3 Hz)	2.50 (m)	1.35 (s)
		5.22 (t, *J* = 3 Hz)		2.16 (m)	2.68 (dd, *J* = 14, 3 Hz)	1.84 (d, *J* = 10 Hz)	0.47 (s)
							[2.05 (s)]

ring to an enantiomerically homogeneous bicyclic structural unit. The camphor-derived diene 1 is one example.[1,3a,b,4,6] Since molecules having these characteristics necessarily cause the π-surfaces of the ligand to be topologically distinctive, a necessary first step to the development of their complexes as potential asymmetric catalysts is a detailed understanding of the face selectivity exercised during coordination of these chiral dienes to transition metals.[7]

Herein, we examine the stereochemical course followed by the optically pure pinane-fused cyclopentadiene 2 in its reactions with cyclopentadienyltitanium and -zirconium trichlorides. The accompanying paper[8] deals with the response of the verbenone-derived system 3 toward a similar array of reagents.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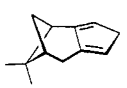
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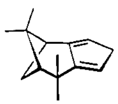
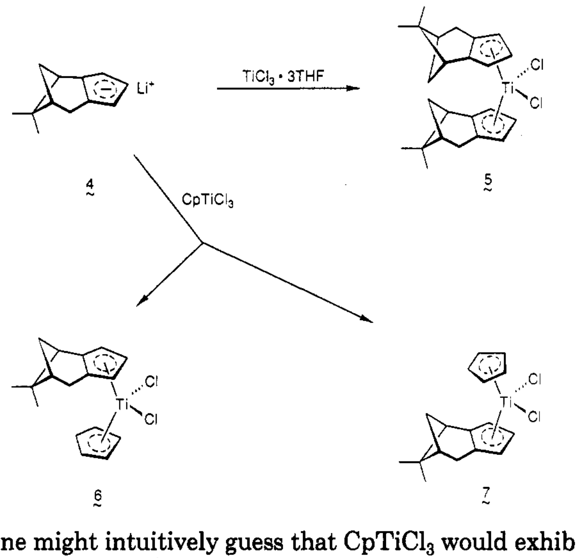

3

Attention is called to a fundamental distinction between 1 and the 2/3 pair. The norbornyl framework present in 1 is conformationally rigid. As a consequence, its syn-10-methyl substituent discourages (but does not totally inhibit) above-plane complexation.[1] Progression from a bicyclo[2.2.1]heptyl chiral auxiliary to one of the bicyclo[3.1.1]heptyl type as found in 2 and 3 is accompanied by a modulation of the prevailing steric congestion, particularly on one face of the five-membered ring. In other words, steric contributions from the syn-methyl group in the latter two dienes differ from those found in 1. The impact of these changes on kinetically controlled π-facial complexation could be substantial and was deemed worthy of investigation.

Results

The synthesis of 2 (PCp) described earlier[9] was adopted without change. The optically active hydrocarbon was transformed into 4 by conventional reaction with *n*-butyllithium in ether. McLaughlin had earlier reacted 4 with titanium tetrachloride at 0–20 °C to produce 5 in 39% yield.[9a] The three-dimensional features of this deep red solid were established unequivocally at that time by X-ray crystal structure analysis. When this transformation was repeated presently with the titanium trichloride tris(tetrahydrofuran) complex[10] in refluxing 1,2-dimethoxyethane for 48 h, the identical metallocene was isolated as the only observable product in improved (71%) yield. In this example, a strong tendency for above-plane complexation to the ligand (as drawn) is clearly in evidence.



4
5
6
7

One might intuitively guess that $CpTiCl_3$ would exhibit entirely comparable face selectively in its bonding to PCpLi (4). However, exposure of 4 to (η^5-cyclopentadienyl)titanium trichloride in tetrahydrofuran solution at −78 °C, followed by slow warming to room temperature during 18 h, resulted in smooth conversion to a 5:1 mixture of two stereoisomeric titanocene dichlorides. Following purification of the major constituent, it was clear

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(5) (a) Le Moigne, F.; Dormond, A.; Leblanc, J.-C.; Moise, C.; Tirouflet, J. *J. Organomet. Chem.* **1973**, *54*, C13. (b) Tirouflet, J.; Dormond, A.; Leblanc, J.-C.; Le Moigne, F. *Tetrahedron Lett.* **1973**, 257. (c) Leblanc, J.-C.; Moise, C.; Bounthakna, T. *Co. R. Seances Acad. Sci., Ser.* **1974**, *278C*, 973. (d) Bounthakna, T.; Leblanc, J.-C.; Moise, C. *Ibid.* **1975**, *280C*, 1431. (e) Dormond, A.; Tirouflet, J.; Le Moigne, F. *J. Organomet. Chem.* **1975**, *101*, 71. (f) Leblanc, J.-C.; Moise, C. *Ibid.* **1976**, *120*, 65. (g) Lebanc, J.-C.; Moise, C. *Ibid.* **1977**, *131*, 35. (h) Leblanc, J.-C.; Moise, C.; Tirouflet, J. *Nouv. J. Chim.* **1977**, *211*. (i) Cesarotti, E.; Kagan, H. B.; Goddard, R.; Kruger, C. *J. Organomet. Chem.* **1978**, *162*, 297. (j) Dormond, A.; Kolavudh, T.; Tirouflet, J. *Ibid.* **1979**, *177*, 181. (l) Cesarotti, E.; Ugo, R.; Kagan, H. B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 779. (m) Couturier, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *195*, 291. (n) Cesarotti, E.; Ugo, R.; Vitiello, L. *J. Mol. Catal.* **1981**, *12*, 63. (o) Dormond, A.; El Bouadili, A.; Moise, C. *Tetrahedron Lett.* **1983**, 3087.

(6) (a) McLaughlin, M. L.; McKinney, J. A.; Paquette, L. A. *Tetrahedron Lett.* **1986**, 5595. (b) Burgstahler, A. W.; Boger, D. L.; Naik, N. C. *Tetrahedron* **1976**, *32*, 309.

(7) The two cyclopentadienyl faces do, of course, become equivalent when the ligand possesses C_2 symmetry. See ref 3c.

(8) Moriarty, K. J.; Rogers, R. D.; Paquette, L. A. *Organometallics*, following paper in this issue.

(9) (a) Paquette, L. A.; Gugelchuk, M.; McLaughlin, M. L. *J. Org. Chem.* **1987**, *52*, 4732. (b) Paquette, L. A.; McLaughlin, M. L. *Org. Synth.*, in press.

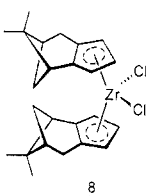
(10) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 137.

from its ^{1}H NMR spectrum that a reversal in the direction of complexation had materialized. As in related molecules, the metal center exerts a demonstrably strong shielding influence on the proximal syn, endo substituent. For example, the appearance of the endo-methyl singlet in **5** at δ 0.49 is very telling, especially in relation to the more normal location of its exo-methyl (δ 1.36) and syn-methano proton absorption (δ 1.12, Table I). The situation is reversed for **6** where the endo-methyl singlet is clearly displaced to lower field (δ 0.74). In **7**, the long-range anisotropy once again influences in diagnostic fashion the endo-methyl chemical shift (δ 0.50).

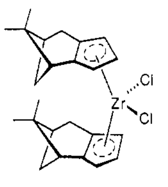
Although the stereochemical crossover is pronounced, the reaction temperatures utilized for forming **5** and **6**/**7** are also disparate. Since an interdependence of temperature and product distribution has previously been noted in the camphor series,[1,11] **4** and $CpTiCl_3$ were also brought into reaction at room temperature and at the reflux point of the solvent (THF). In both of these latter experiments, the **6**/**7** ratio was skewed in favor of **7** (1:3).

No indication could be obtained to demonstrate that these stereoisomeric complexes experienced interconversion under the reaction conditions. The control experiments that were applied to test this issue were very similar to those utilized earlier.[11] However, both **6** and **7** proved stable to all starting materials, intermediates, and side or decomposition products that might be somehow involved in modulating π-facial selectivity. Consequently, by all indicators the product distributions recorded above appear to be the result of kinetically controlled coordination to the two available faces of **4**.

When attempted reaction of **4** with Cp^*TiCl_3[12] failed to give rise to well-defined products, attention was directed in turn to zirconium reagents. Following the admixture of **4** with freshly sublimed $ZrCl_4$ in cold 1,2-dimethoxyethane and subsequent heating at the reflux temperature for 72 h, the symmetrical complex **8** was isolated as a 45:1 mixture with an unsymmetrical isomer believed to be **9**. Although crystals of the major substance could not be obtained in a form suitable for X-ray analysis, its formulation as **8** could be arrived at with confidence by direct comparison of its ^{1}H NMR spectrum with that of **5** (Table I). Once again, the upfield regions are especially typical for those systems in which the zirconium atom occupies that surface of the PCp ligand remote from the gem-dimethyl substituents.



8



9

Minor product **9** was present in concentration levels sufficiently low that its extensive purification and detailed spectral characterization was not pursued. However, its lack of C_2 symmetry was clearly apparent.

Anion **4** could be effectively condensed with $CpZrCl_3\cdot 2THF$[13] and Cp^*ZrCl_3[12] in toluene solution heated at reflux for prolonged time periods (48 and 72 h, respectively). In the first instance, a single complex resulted when the

Table II. Experimental Crystallographic Data for 10[20]

mol wt	386.5
space group	$P2_12_12_1$
temp, °C	20
cell constants[a]	
a, Å	7.005 (4)
b, Å	9.171 (2)
c, Å	25.131 (5)
cell vol, Å^3	1615
formula units/unit cell	4
D_{calcd}, g cm^{-3}	1.59
μ_{calcd}, cm^{-1}	8.96
diffractometer/scan	Enraf-Nonius CAD4/θ-2θ
range of rel transmission factors, %	93.3/100
radiatn, graphite monochromator	Mo Kα (λ = 0.71073 Å)
max cryst dimens, mm	0.05 × 0.15 × 0.35
scan width	0.80 + 0.35 tan θ
std reflctns	600; 080; 0,0,20
decay of stds	±2%
reflctns measd	1681
2θ range, deg	$2 \le 2\theta \le 50$
range of *h*, *k*, *l*	+8,+10,+29
reflctns obsd [$F_0 \ge 5\sigma(F_o)$][b]	1406
computer programs[c]	SHELX[20a]
struct soln	heavy-atom techniques
no. of parameters varied	181
weights	$[\sigma(F_o)^2 + 0.00001F_o^2]^{-1}$
GOF	1.43
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.030
R_w	0.030
R inverse configuratn	0.029
largest feature final diff map, e/Å^3	0.3

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

Table III. Bond Distances (Å) and Angles (deg) for 10

	Bond Distances		
Zr–Cl(1)	2.448 (2)	Zr–Cl(2)	2.422 (2)
Zr–C(1)	2.462 (6)	Zr–C(2)	2.501 (6)
Zr–C(3)	2.519 (5)	Zr–C(4)	2.519 (6)
Zr–C(5)	2.484 (6)	Zr–C(6)	2.581 (6)
Zr–C(7)	2.490 (6)	Zr–C(8)	2.433 (6)
Zr–C(9)	2.495 (5)	Zr–C(10)	2.602 (5)
C(1)–C(2)	1.389 (8)	C(1)–C(5)	1.412 (9)
C(2)–C(3)	1.405 (9)	C(3)–C(4)	1.391 (9)
C(4)–C(5)	1.403 (9)	C(6)–C(7)	1.417 (8)
C(6)–C(10)	1.38 (1)	C(6)–C(14)	1.513 (8)
C(7)–C(8)	1.386 (9)	C(8)–C(9)	1.395 (9)
C(9)–C(10)	1.423 (8)	C(10)–C(11)	1.514 (8)
C(11)–C(12)	1.537 (9)	C(12)–C(13)	1.54 (1)
C(12)–C(15)	1.556 (8)	C(13)–C(14)	1.572 (8)
C(14)–C(15)	1.564 (8)	C(15)–C(16)	1.516 (8)
C(15)–C(17)	1.528 (9)		
Zr–Cent1	2.19	Zr–Cent2	2.21
	Bond Angles		
Cl(1)–Zr–Cl(2)	93.60 (7)	C(2–)C(1)–C(5)	107.8 (6)
C(1)–C(2)–C(3)	108.2 (6)	C(2)–C(3)–C(4)	108.2 (6)
C(3)–C(4)–C(5)	108.0 (6)	C(1)–C(5)–C(4)	107.7 (6)
C(7)–C(6)–C(10)	108.4 (6)	C(7)–C(6)–C(14)	130.3 (6)
C(10)–C(6)–C(14)	117.4 (6)	C(6)–C(7)–C(8)	107.7 (6)
C(7)–C(8)–C(9)	108.8 (6)	C(8)–C(9)–C(10)	107.5 (6)
C(6)–C(10)–C(9)	107.6 (6)	C(6)–C(10)–C(11)	119.0 (6)
C(9)–C(10)–C(11)	132.5 (6)	C(10)–C(11)–C(12)	107.6 (6)
C(11)–C(12)–C(13)	111.5 (6)	C(11)–C(12)–C(15)	111.8 (5)
C(13)–C(12)–C(15)	87.7 (5)	C(12)–C(13)–C(14)	85.8 (5)
C(6)–C(14)–C(13)	101.7 (5)	C(6)–C(14)–C(15)	113.2 (5)
C(13)–C(14)–C(15)	86.3 (5)	C(12)–C(15)–C(14)	85.4 (5)
C(12)–C(15)–C(16)	119.3 (6)	C(14)–C(15)–C(16)	120.8 (5)
C(12)–C(15)C(17)	111.8 (5)	C(14)–C(15)–C(17)	111.6 (6)
C(16)–C(15)–C(17)	106.9 (6)		
Cent1–Zr–Cl(1)	105.7	Cent1–Zr–Cl(2)	107.3
Cent2–Zr–Cl(1)	106.6	Cent2–Zr–Cl(2)	106.8
Cent1–Zr–Cent2	130.7		

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(11) (a) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Crocq, V. *Organometallics* **1988**, *7*, 1873. (b) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Sornay, C.; Rogers, R. D.; Rheingold, A. L., submitted for publication.

(12) Blenkers, J.; DeLiefde, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

(13) Erker, G.; Berg, K.; Treschanke, L.; Engel, K. *Inorg. Chem.* **1982**, *21*, 1277.

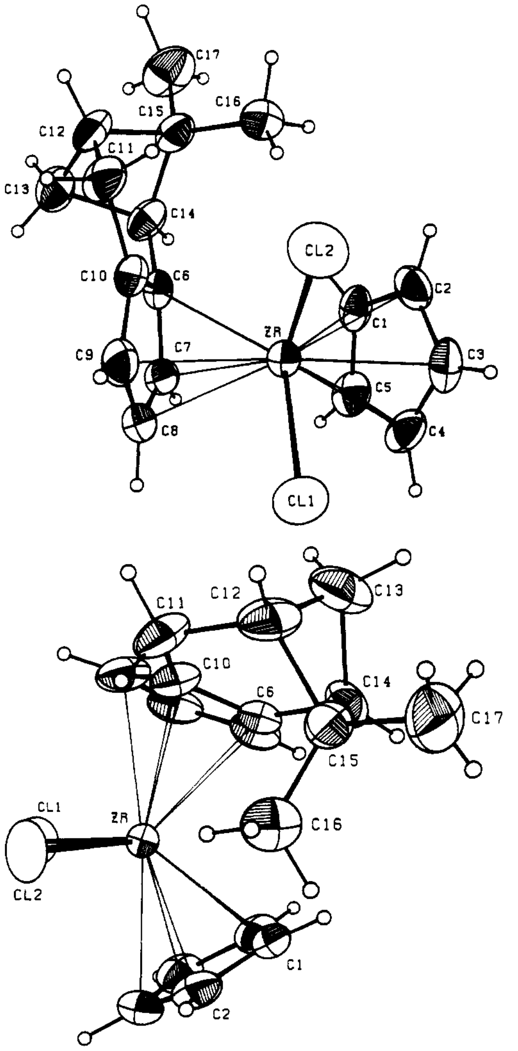
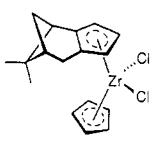
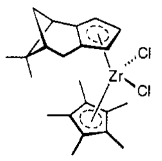


Figure 1. Two views of the crystallographically determined molecular structure of **10** as drawn with 50% probability ellipsoids.

reagents were initially mixed at −78 °C prior to attaining the more elevated temperatures. Although the spectral features of the product (Table I) indicated it to be **10**, confirmation of the below-plane stereochemical arrangement was sought by means of X-ray crystallography. As seen in Figure 1 and Tables II and III, the complex is indeed the result of coordination syn to the methyl groups. Both of its cyclopentadiene rings are essentially planar within experimental error. The dihedral angle between the least-squares plane defined by the C(6), C(10), C(11), and C(14) atoms and that containing atoms C(6)–C(10) inclusively generates an *upward* tilting of 15.3° about the central portion of the pinene ligand. The disposition of the C(16) methyl group relative to the most proximal atoms of the Cp ring, i.e. C(1) and C(2), is such that the nonbonded distances are 3.448(9) and 3.539(9) Å, respectively. The C(16)–Zr distance of 3.881 (6) Å shows it to be longer still. Additionally, chlorine atom Cl(2) is clearly seen to lie 2.74 Å away from the nearest hydrogen atom on C(16). At 93.60°, the Cl–Zr–Cl angle is within the expected range.[14] The distances between the zirconium atom and the centroids of the Cp and PCp ligands (Table III) show them to be closely comparable (differences of 0.02 Å). The inference that can be drawn is that the pinene segment is not exerting a level of steric compression adequate to force an increase in its distance from the metal atom. There exists, of course, the usual tilting of the substituted Cp ring in that direction where the more highly substituted C(6) and C(10) are somewhat further removed from Zr than those that carry only a hydrogen atom.



10



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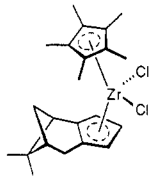
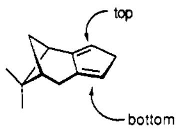


12

Table IV. Product Distribution Summary



reagent	reaction conditions	product ratio,[a] % top	bottom
$TiCl_4$	DME, Δ	>98	<2
$TiCl_3·3THF$	DME, Δ	>98	<2
$CpTiCl_3$	THF, −78 to 20 °C	1	5
	THF, RT	3	1
	THF, Δ	3	1
$ZrCl_4$	DME, Δ	45	1[b]
$CpZrCl_3·2THF$	toluene, mix at −78 °C; Δ	<2	>98
	toluene, mix at RT; Δ	3.5	1
Cp^*ZrCl_3	toluene, mix at −78 °C, Δ	2	1
	toluene, mix at RT, Δ	2	1

[a] Product analysis by 300 MHz ^1H NMR. [b] For one of the PCp ligands only. [c] RT = room temperature.

When the $CpZrCl_3·2THF$ and **4** were premixed in toluene at room temperature before being heated at reflux, a two-component product mixture resulted consisting of **10** and its π-facial stereoisomer in a 1:3.5 ratio (300 MHz, ^1H NMR analysis). Under either set of conditions (Table IV), the reaction of **4** with Cp^*ZrCl_3 in toluene gave rise to a 1:2 mixture of **11** and **12**. Although these stereoisomers could not be separated, the chemical shifts of the individual pairs of methyl groups (Table I) were convincingly diagnostic of the assigned stereochemistries.

Discussion

While facial stereoselectivity is indeed exhibited by cyclopentadienide anion **4**, the range of observed product distributions (Table IV) is somewhat broader than anticipated. Since selected PCp complexes were shown not to experience π-facial equilibration under the reaction conditions or when individually heated, the indication is that the observed ratios reflect kinetic control of the complexation process. The pronounced tendency for above-plane coordination noted in the conversion of **5** to **8** can be understood in terms of simple steric considerations. The PCp ligand is relatively bulky and dual coordination to a Group 4 metal from the below-plane direction syn to its methyl groups is strongly deterred because maximum congestion materializes under these circumstances. In addition, the experimental results indicate that mixed top/bottom complexation as in **9** becomes marginally operational only when the metal is zirconium. In general, cyclopentadienide centroid–zirconium distances are 0.15 Å longer than those in related titanocenes.[15] Accordingly,

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[14] Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -hafnium Compounds*; Chichester (W. Sussex): E. Horwood, NY, 1986.

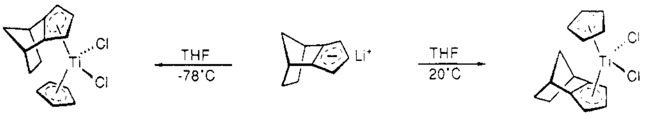
[15] Gallucci, J. C.; Gautheron, B.; Gugelchuk, M.; Meunier, P.; Paquette, L. A. *Organometallics* **1987**, *6*, 15 and relevant references cited therein.

the very modest levels of π-complexation as in **9** (2% of the product mixture) may be linked directly to this increase in intraannular space.

As the steric demands of the second ligand are reduced, the extent of above-plane coordination should moderate, and this is indeed the case. In those examples involving the coordination of **4** to $CpTiCl_3$, $CpZrCl_3$, and Cp^*ZrCl_3 *at room temperature and above*, the preference for π-bonding from the top surface is seen to persist (Table IV). However, below-plane stereoselection is also in evidence and its level is now far more equitable than in the homocomplexation experiments. In spite of this reasonable trend, these data appear to have ramifications that go beyond the purely steric realm. For example, it is well recognized that pentamethylcyclopentadienide (Cp*) has appreciably greater steric demands than does the unsubstituted Cp ring.[16] Notwithstanding, Cp^*ZrCl_3 exhibits a somewhat greater tendency to react with **4** from its more crowded bottom surface than does $CpZrCl_3$.

This departure from the norm spurred us to assess the magnitude of the facial preference at lower temperatures. If Cp^*ZrCl_3 was premixed with **4** in toluene at −78 °C prior to the usual reflux period, the ratios of **11** to **12** was left unchanged at 1:2. However, the product distribution from analogous condensations with $CpTiCl_3$ and $CpZrCl_3$ were dramatically altered. The −78 °C complexation reactions proved highly conducive to heightened coordination from the more congested face of **4**. The proportion of **6** increased from 25% to 83%, while **10** now became the only detectable product!

Similar variations in product distribution with temperature have been noted earlier in the reactions of isodicyclopentadienide anion (**13**) with $CpTiCl_3$ and $RCpTiCl_3$ ($R = CH_3$, *t*-Bu).[11] *At the lower temperature, kinetically controlled complexation materializes as well on the more hindered surface of the norbornyl-fused ligand.* There is therefore a parallel correlation. In the case of **13**, σ/π interactions have been proposed as the possible source of the kinetic factor. As already mentioned, this is unlikely for **4**. Furthermore, the behavior of **4** is *not* mirrored by the anion of **3**, a simple dimethyl derivative which enters into π-complexation almost universally from the above-plane direction.



14 13 15

The crystal structure of **10** (Figure 1) indicates that the planar Cp ring fused to the bicyclo[2.1.1]hexyl unit adopts a significant folding angle of 15.3° at the seam. The end result of this deformation is to position the second ligand more remote from the C(16) methyl group. This increase in distance is adequate to place all atoms beyond usual van der Waals contact. Complexation from the other face induces comparable folding in the opposite direction.[8] Consequently, this does not appear to be a factor for distinguishing the two π surfaces in PCp.

Several other mechanisms might operate to influence the directionality of complexation to **4**. First, the lithium counterion might already have a predilection for residing below plane, thereby distorting the geometry of the PCp ligand in an upward direction prior to reaction with the transition metal reagent. Adoption of this working hypothesis, however, would require rationalization of the underlying cause of preferred Li^+ coordination and go contrary to the recognized fact that lithium cyclopentadienides are customarily highly dissociated entities in solution.[17,18] On the other hand, the gem-dimethyl-substituted bridge could be acting so as to introduce differential dipole and polarizability effects[19] that become most apparent at the lower reaction temperatures. The changes in stereoselectivity may come about at more elevated temperatures as a result of the overriding of these subtle electronic contributions (and perhaps accompanying π-anisotropy effects) by steric considerations. Finally, the possibility exists that the exothermicity differences for the two competing complexation reactions in any given instance have something to do with the relative stabilities of the transition states. We hypothesize that phenomena of this type, which distort the reactant and thus alter the ease of reaching a particular transition state, are significant in influencing π-facial stereoselectivity.

Experimental Section

((1*S*,8*R*)-9,9-Dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-dienyl)lithium (4). A solution of **2** (2.84 g, 0.018 mol) in dry ether (50 mL) was treated via syringe with 11.25 mL of 1.6 M *n*-butyllithium in hexanes (0.018 mol) and heated at the reflux temperature for 12 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. This solution was cooled at 0 °C for 2 h, and the white, air-sensitive solid was collected by filtration under argon. The solid was washed with cold hexane (2 × 50 mL) and dried under high vacuum; yield 2.0 g (67%).

Bis(η^5-(1*S*,9*R*)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorotitanium (5). A solution of $TiCl_3 \cdot 3THF$ (1.07 g, 2.9 mmol) in 50 mL of dry 1,2-dimethoxyethane was cooled to −78 °C, blanketed with argon, and treated via canula with a solution of **4** (960 mg, 5.8 mmol) in the same solvent. The reaction mixture was warmed to room temperature, heated at reflux for 48 h, and concentrated in vacuo. The residual solid was taken up in ether, cooled to −78 °C, and treated with concentrated HCl for 15 min. The solution was stirred at room temperature for 2 h, chloroform (100 mL) was added, and the organic phase was poured into 50 mL of 6 N hydrochloric acid. The chloroform layer was separated, and the aqueous phase was extracted with this solvent (2 × 50 mL). Following drying and evaporation of the combined organic solutions, the residue was transferred to a Soxhlet cup and extracted first with HCl-saturated pentane. Subsequent extraction with HCl-saturated carbon tetrachloride gave **5** which was recrystallized from dichloromethane–hexane (900 mg, 71%). The spectral properties of this substance were identical with those previously reported.[9a]

(η^5-Cyclopentadienyl)(η^5-(1*S*,8*R*)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorotitanium (6 and 7). A cold (−78 °C), magnetically stirred solution of $CpTiCl_3$ (380 mg, 1.7 mmol) in 50 mL of anhydrous tetrahydrofuran was treated during 20 min via canula with a solution of **4** (330 mg, 2.0 mmol) in the same solvent (20 mL) under argon. Upon completion of the addition, the reaction mixture was slowly warmed to room temperature and stirred for 18 h prior to solvent evaporation. The residue was dissolved in chloroform (20 mL), concentrated hydrochloric acid (12 mL) was added, and stirring was resumed at room temperature for 1 h. The separated aqueous phase was extracted with chloroform (2 × 25 mL), and the combined organic layers were dried and evaporated. The solid was subjected to

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[16] (a) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (b) Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1980**, *13*, 121 and relevant references cited in these reviews.

[17] (a) Maciel, G. E.; Hancock, L. F.; Lafferty, L. F.; Mueller, P. A.; Musker, W. K. *Inorg. Chem.* **1966**, *5*, 554. (b) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307. (c) Cox, R. H.; Terry, H. W., Jr.; Harrison, L. W. *Ibid.* **1971**, *93*, 3297. (d) Wagner, B. O.; Ebel, H. F. *Tetrahedron* **1970**, *26*, 5155.

[18] For a detailed summary of theoretical calculations on cyclopentadienyllithium, see: Alexandrates, S.; Streitwieser, A., Jr.; Schaefer, H. F. III *J. Am. Chem. Soc.* **1976**, *98*, 7959.

[19] Vogel, P. In *Stereochemistry and Reactivity of Pi Systems*; Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983; pp 147–195.

extraction with HCl-saturated pentane in a Soxhlet apparatus. Subsequent extraction with HCl-saturated carbon tetrachloride removed some of **6** and all of **7**. Final extraction with HCl-saturated chloroform afforded pure **6** (264 mg, 45%). The combined yield of the last two extractions was 55%, with **7** constituting 9% of the total.

For **6**: mp 201–202 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 125.09, 119.73, 119.65, 119.12, 118.20, 109.96, 45.46, 41.08, 41.00, 36.67, 29.96, 27.83, 23.59; $[\alpha]^{21}{}_D$ −1613.7° (*c* 0.044, toluene).

Anal. Calcd for $C_{17}H_{20}Tl_2Ti$: C, 59.49; H, 5.87. Found: C, 59.74; H, 5.97. For **7**: ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 142.18, 140.93, 120.20, 119.14, 113.90, 112.42, 43.62, 42.37, 40.38, 31.29, 29.13, 26.02, 21.14; MS *m/z* ($M^+ - Cl$) calcd 307.0733, obsd. 307.0756.

A second set of reactions was performed analogously, but initially at room temperature. Isolated in 45–50% yield was a 1:3 mixture of **6** and **7**.

Finally, the reagents were mixed at the reflux temperature over a 20-min period. In this instance, the **6**/**7** ratio was found again to be 1:3.

Bis(η^5-(1*S*,8*R*)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorozirconium (8). A cold (−78 °C) solution of **4** (4.90 g, 0.30 mol) in dry 1,2-dimethoxyethane (100 mL) was treated with sublimed zirconium tetrachloride (2.90 g, 0.013 mol), warmed to room temperature, and heated at reflux for 72 h. Following solvent evaporation, dichloromethane (50 mL) and 4 N hydrochloric acid (10 mL) were introduced and the mixture was stirred at room temperature for 1 h. The aqueous phase was extracted with dichloromethane (2 × 25 mL), and the combined organic layers were dried and concentrated in vacuo. Sublimation of the residue at 150–160 °C and 10^{-3} Torr afforded the zirconocene dichlorides as a yellow, air-stable solid (4.1 g, 67%). ^{1}H NMR showed the ratio of **8** to **9** to be 45:1: mp 179–181 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$ ppm) 137.01, 134.09, 115.44, 109.90, 108.88, 42.94, 42.47, 40.87, 32.51, 28.60, 26.18, 21.15; MS *m/z* (M^+) calcd 480.0737, obsd 480.0796; $[\alpha]_D{}^{21}$ −76.0° (*c* 0.55, toluene).

Anal. Calcd for $C_{24}H_{30}HCl_2Zr$: C, 59.98; H, 6.29. Found: C, 59.87; H, 6.38.

(η^5-Cyclopentadienyl)(η^5-(1*S*,8*R*)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)dichlorozirconium (10). A. Low-Temperature Conditions. (η^5-Cyclopentadienyl)trichlorozirconium bis(tetrahydrofuran) (1.00 g, 2.5 mmol) was added to dry toluene (100 mL), and this solution was cooled to −78 °C while solid **4** (410 mg, 2.5 mmol) was introduced. The reaction mixture was heated at reflux for 48 h, cooled, and concentrated. The residue was dissolved in chloroform (20 mL), and 4 N hydrochloric acid (20 mL) was added. After being stirred for 1 h, this mixture was poured into water, the separated aqueous phase was extracted with chloroform (2 × 25 mL), and the combined organic layers were dried and evaporated. Sublimation of the residue at 150 °C and 10^{-4} Torr gave 600 mg (66%) of **10** as yellow crystals: mp 134–135 °C; ^{1}H NMR (see Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 138.86, 134.23, 119.41, 115.80, 109.22, 107.19, 44.83, 41.10, 36.38, 29.12, 27.68, 24.79, 21.10; MS *m/z* (M^+) calcd 383.9985, obsd 384.0016; $[\alpha]^{21}{}_D$ −66.4° (*c* 0.25, toluene).

Anal. Calcd for $C_{17}H_{20}Cl_2Zr$: C, 52.82; H, 5.22. Found: C, 52.81; H, 5.25.

B. At Room Temperature. (η^5-Cyclopentadienyl)trichlorozirconium bis(tetrahydrofuran) (1.30 g, 3.2 mmol) was dissolved in dry toluene under argon. Solid **4** (0.58 g, 0.0035 mmol) was added at room temperature, and the mixture was stirred for 1 h at room temperature prior to heating at reflux for 3 days. The cooled solution was freed of toluene under reduced pressure. The residue was dissolved in chloroform (30 mL) and 15 mL of concentrated hydrochloric acid was added. The solution was stirred for 20 min at room temperature. The organic layer was separated, and the aqueous phase was extracted twice with 50 mL of chloroform. The combined organic layers were dried, filtered, and evaporated. The residue was transferred to a sublimator, and the product was sublimed at 160–170 °C (0.001 Torr). There was isolated 0.69 g (56%) of a 1:3.5 mixture of **10** and its π-facial diastereomer. For the latter stereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.43 (s, 1 H), 6.31 (t, J = 3 Hz, 1 H), 6.00 (m, 1 H), 5.85 (br s, 1 H), 3.30 (dd, J = 14, 3 Hz, 1 H), 2.78 (m, 2 H), 2.45 (m, 1 H), 2.18 (br s, 1 H), 1.42 (d, J = 10 Hz, 1 H), 1.37 (s, 3 H), 0.48 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 138.86, 134.23, 119.41, 115.80, 115.40, 115.35, 109.22, 109.01, 107.19, 44.83, 42.77, 42.47, 41.10, 40.76, 36.38, 32.41, 29.12, 28.60, 27.68, 26.10, 25.79, 21.10; MS *m/z* (M^+) calcd 383.9985, obsd 383.9985.

(η^5-(1*S*,8*R*)-9,9-Dimethyltricyclo[6.1.1.0^{2,6}]deca-3,5-dien-2-yl)(η^5-pentamethylcyclopentadienyl)dichlorozirconium (11 and 12). A mixture of **4** (1.11 g, 7.0 mmol) and (η^5-pentamethylcyclopentadienyl)trichlorozirconium (2.22 g, 7.0 mmol) in dry toluene (100 mL) was slurried at room temperature, heated at the reflux temperature for 72 h under argon, and worked up in the predescribed manner. The residual solid was recrystallized from dichloromethane–hexane to give 2.1 g (69%) of a 1:2 mixture of **11** and **12** as a yellow solid: mp 181–182 °C; ^{1}H NMR (see Table I); MS *m/z* calcd 456.0795, obsd 456.0767.

Anal. Calcd for $C_{22}H_{30}Cl_2Zr$: C, 57.86; H, 6.62. Found: C, 57.97; H, 6.55.

X-ray Crystallographic Analysis of 10.[20] A transparent single crystal of the complex was mounted on a pin and transferred to the goniometer. The space group was determined to be acentric $P2_12_12_1$ from the systematic absences. A summary of data collection parameters is given in Table II.[21]

Least-squares refinement with isotropic thermal parameters led to R = 0.069. 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 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 = 0.030 and R_w = 0.030. The final values of the positional parameters are given in the supplementary material. The absolute configuration shown was chosen since it was known.

Acknowledgment. We thank the National Cancer Institute (Grant CA-12115) for their financial support of this research program.

Supplementary Material Available: Tables of the final fractional coordinates, thermal parameters, and least-squares for **10** (4 pages); a listing of observed and calculated structure factors for **10** (3 pages). Ordering information is given on any current masthead page.

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[20] The package of programs and crystallographic constants 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.

[21] For a comparison of structural parameters, see: Antinolo, A.; Lappert, M. F.; Singh, A.; Winterborn, D. J. W.; Engelhardt, L. M.; Raston, C. L.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans.* 1987, 1463.