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Stereochemical Course of π-Face Coordination to Isodicyclopentadiene during Formation of Mixed Titanocene and Zirconocene Dichloride Complexes[1]

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Reaction of the isodicyclopentadienide anion with RCpTiCl$_3$ (R = H, CH$_3$, *t*-Bu) and Cp″TiCl$_3$ in tetrahydrofuran solution at −78 °C is shown to proceed stereoselectively with formation of endo titanocene dichloride complexes. When the same reactions are performed at 20 °C up to the reflux temperature of the solvent, the stereoisomeric exo complexes are cleanly formed instead. Control experiments have not led to the interconversion of these isomer pairs. Comparable reaction of isodiCpLi with CpZrCl$_3$ and Cp″ZrCl$_3$ in boiling tetrahydrofuran also delivered only exo complexes. The structural parameters of several products, as defined by X-ray crystallographic analysis, are discussed. The endo complexes appear to be more sterically constrained than the exo isomers. Their formation at low temperatures is thought to be kinetically controlled and to stem from electronic features imparted to the Cp anion portion of the isodicyclopentadienyl ligand by its fused norbornyl framework.

Titanocene and zirconocene dichloride complexes have played a key role in the evolution of structural,[2] synthetic,[3] and catalytic organometallic chemistry.[4] Recently, the simple dicyclopentadienyl members of group 4 have been recognized as potential drugs in the treatment of certain types of cancer.[5] In particular, these dichlorides have shown significant inhibitory activity against Ehrlich ascite tumor cells,[6] human colon carcinoma,[7] and lymphocytic leukemia.[8]

Notwithstanding these exciting developments, little prior attention has been given to examination of cyclopentadienyl ligands whose π faces are topologically distinct. While the most commonly encountered structural units are the plane-symmetric η^5-cyclopentadienyl and η^5-pentamethylcyclopentadienyl rings, there have been several examples where optically active side chains were appended to a η^5-cyclopentadienyl ring.[9] However, these were freely rotating substituents and did not result in topological differences between the two faces of the Cp ligand. During the past several years, the Vollhardt group at Berkeley[10] and ours at Ohio State[11] have been engaged in the preparation of annulated, optically active cyclopentadienes with a long-range view to the utilization of their TiCl$_2$ and ZrCl$_2$ complexes in asymmetric synthesis.

Proper twofold conjoining of a Cp ring to a carbobicyclic system generates a structural ensemble of pπ orbitals intrinsically capable of bifacial stereoselectivity in bonding to a metal.[12] The isodicyclopentadiene molecule (1) is a case in point. X-ray analyses of derivatives of 1[13] clearly establish that its endo surface is the more sterically congested, a conclusion that has received theoretical support.[14] Notwithstanding, dienophiles prefer to capture 1 from below-plane,[15] except when steric factors are overriding.[16] The isodicyclopentadienide anion likewise exhibits a strong kinetic preference for endo capture of electrophiles to deliver C_s-symmetric products.[17] These stereochemical proclivities have been rationalized in terms of disrotatory tilting of the pπ orbitals within the unsaturated ring[12a,b]

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(1) Paper 43 in the series dealing with isodicyclopentadienes and related molecules. For Part 42, see: Gugelchuk, M.; Paquette, L. A., submitted for publication. For Part 41: Paquette, L. A.; Vanucci, C.; Rogers, R. D., submitted for publication.

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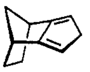
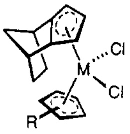
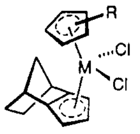
as well as on steric grounds.[14]



1



2 (M=Ti, Zr)

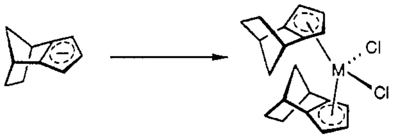


3

The unique orbital construction presumed to be present in the isodiCp anion (4) has prompted us to initiate an investigation designed to elucidate the level of stereoelectronic control that operates during mixed complexation to reagents of the type (RCp)$TiCl_3$[18] and (RCp)$ZrCl_3$. The acquisition of 2 and 3 would not only permit direct comparison of the structural consequences of above- and below-plane complexation but also provide compounds of interest in the previously described bioassays. Furthermore, the stereochemical results realized in this study were expected to serve as important reference points for those product-determinative options that are operative in structurally more elaborate, optically active examples.[19]

Results

In a previous report,[12d] we disclosed that 4 reacts with tri- and tetrachloride salts of the group 4 transition metals to deliver the symmetrical complexes 5 (M = Ti, Zr, Hf) in highly stereoselective fashion. Relevantly, both isodiCp ligands in 5 are complexed from their exo surfaces. Although this stereochemical outcome goes contrary to experience garnered from reactions involving simpler electrophiles,[17] the isodiCp ligand is recognized to be relatively large. Its size is therefore better accommodated by exo complexation. One might properly inquire whether this thermodynamic bias had overridden an intrinsic, electronically driven kinetic preference from below-plane coordination. In order to assess whether 4 is subject to an unprecedented balance between electronic and steric effects, its mixed complexation to more classically substituted cyclopentadienyls has now been investigated.[18]



4 5

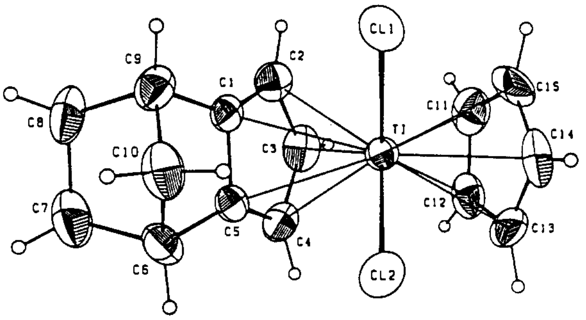
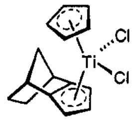


Figure 1. Crystallographically determined molecular structure of 6 as drawn with 50% thermal ellipsoids.

Isodicyclopentadiene reacts with *n*-butyllithium to give the reactive isodiCpLi, which can be used in situ or isolated as an air- and moisture-sensitive solid. Either form has provided the same stereochemical results. Reaction of 1 with thallous ethoxide in dry hexane gives rise to the thallium salt of 4, the preservation of which can best be achieved by storage in the dark at −20 °C.

Condensation of either form of 4-Li with commercially available $CpTiCl_3$ in tetrahydrofuran solution at *room temperature* resulted in the formation of 6 as the only characterizable product (40% isolated). This complex exhibits a particularly distinctive pair of signals for the isodiCp vinyl protons. Specifically, the lone central proton appears as a triplet (δ 6.43, J = 2.8 Hz) downfield of the doublet (δ 6.15, J = 2.8 Hz) due to the two peripheral protons (Table I). The identical substance was produced when 4-Tl was heated with $CpTiCl_3$ for several hours.

In striking contrast, admixing of isodiCpLi with $CpTiCl_3$ in tetrahydrofuran at −78 °C followed by slow warming to room temperature provided no spectral indication for the formation of 6. Instead, a stereoisomeric complex (7) was generated that exhibits a reversal in the ordering of the isodiCp vinyl protons. In this instance, the two peripheral protons happen to be more deshielded than their central counterpart (Table I).



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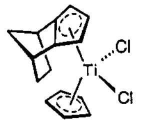

7

Proper stereochemical distinction between 6 and 7 was achieved by X-ray crystallographic analysis (Table II) of 6, the molecular structure of which is shown in Figure 1. The final bond lengths and angles for 6 are listed in Table III. In line with precedent,[2] its titanium atom possesses pseudotetrahedral geometry, the tetrahedron being defined by the pair of chlorine atoms and the centroids of the two approximately planar five-membered rings. At 2.349–2.362 Å, the Ti–Cl bonds are strikingly similar to those en-

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

compd	central isodiCp	peripheral isodiCp	RCp	bridgehead	exo-ethano bridge	endo-ethano bridge	methano bridge
6	6.43 (t, J = 2.8 Hz)	6.15 (d, J = 2.8 Hz)	6.53 (s)	3.35 (s)	1.89 (dm, J = 9.3 Hz)	1.07 (dm, J = 9.3 Hz)	1.41 (d, J = 9.4 Hz) 1.11 (dd, J = 9.4, 2.3 Hz)
7	6.13 (t, J = 2.6 Hz)	6.35 (d, J = 2.6 Hz)	6.53 (s)	3.36 (s)		1.90–1.76 (m)	
8	6.38 (t, J = 2.8 Hz)	6.11 (d, J = 2.8 Hz)	6.38 (t, J = 2.6 Hz) 6.20 (t, J = 2.6 Hz)	3.35 (s)	1.88 (d, J = 7.5 Hz)	1.11 (d, J = 7.5 Hz)	1.34 (d, J = 9.0 Hz)
9	6.06 (t, J = 2.8 Hz)	6.33 (d, J = 2.8 Hz)	6.38 (t, J = 2.6 Hz) 6.17 (t, J = 2.6 Hz)	3.36 (s)		2.00–1.80 (m)	
10	6.12 (t, J = 2.8 Hz)	6.36 (d, J = 2.8 Hz)	6.36 (m)	3.34 (s)		1.90–1.80 (m)	
11	6.35 (t, J = 3.0 Hz)	6.07 (d, J = 3.0 Hz)	6.48 (t, J = 2.6 Hz) 6.35 (t, J = 2.6 Hz)	3.34 (s)	1.88 (d, J = 7.4 Hz)	1.09 (d, J = 7.4 Hz)	1.35 (d, J = 9.0 Hz)
12	6.11 (t, J = 2.6 Hz)	5.14 (d, J = 2.6 Hz)		3.33 (s)	1.88 (dm, J = 7.5 Hz)	1.06 (dm, J = 7.5 Hz)	2.29 (d, J = 8.5 Hz) 1.50 (dd, J = 8.5, 2.3 Hz)
13	6.41 (t, J = 3.0 Hz)	5.96 (d, J = 3.0 Hz)	6.45 (s)	3.36 (s)		1.86–1.05 (m)	
14	5.70 (t, J = 3.0 Hz)	5.11 (d, J = 3.0 Hz)		3.34 (s)		1.83–0.94 (m)	

Table II. Experimental Crystallographic Data for 6, 9, 12, and 14

	6	**9**	**12**	**14**
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	16.129 (5)[a]	6.836 (3)	13.020 (9)	13.269 (7)
b, Å	7.378 (5)	13.878 (5)	12.556 (9)	12.651 (9)
c, Å	12.071 (3)	16.011 (8)	11.164 (7)	11.400 (6)
α, deg		89.03 (3)		
β, deg	108.19 (3)	79.92 (3)	101.13 (7)	101.88 (5)
γ, deg		85.76 (3)		
V, Å^3	1365	1491 (1)	1790.9	1872.7
Z	4	4	4	4
mol wt	315.1	329.1	385.2	428.6
D_{calcd}, g cm^{-3}	1.53	1.47	1.43	1.52
μ, cm^{-1}	9.2	9.3	7.09	7.76
diffractometer/scan	Enraf-Nonius CAD4/θ–2θ	Nicolet R3m/Ω	Enraf-Nonius CAD4/θ–2θ	Enraf-Nonius CAD4/θ–2θ
rdtn, graphite monochromator	Mo Kα (λ = 0.71073 Å)		Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
cryst size	0.05 × 0.08 × 0.23	0.21 × 0.27 × 0.31	0.25 × 0.30 × 0.30	0.25 × 0.55 × 0.95
T, °C	20	22	20	20
2θ limits	$2° \le 2\theta \le 44°$	$4° \le 2\theta \le 50°$	$2° \le 2\theta \le 40°$	$2° \le 2\theta \le 44°$
range of h, k, l	±16,+7,+12	±8,±16,+19	±12,+12,+10	±14,+13,+12
reflctns obsd [$F_o \ge 5\sigma(F_o)$][b]	1150	4197	1320	2179
GOF	0.89	1.132	5.50	3.50
$R(F)$[c]	0.040	0.040	0.119	0.027
$R_w(F)$[d]	0.041	0.048	0.141	0.031
no. parameters varied	163		203	208
weights	$[\sigma(F_o)^2]^{-1}$		unit	$[\sigma(F_o)^2]^{-1}$

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 19°$ (6), 24 reflections 17° (12), 25 reflections, 20° (14). [b] Corrections: Lorentz, polarization, and absorption (empirical, psi scan). [c] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w(F) = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ with $w = 1/\sigma^2(F_o)$.

countered in related compounds.[12d] However, the Cl–Ti–Cl angle (97.0°) is larger than that normally encountered (92.5–96.1°).[12d] The metal-ring carbon distances reveal the metal-ring interactions to be asymmetric. For the Cp ring, the Ti–C distances are in the range 2.359–2.403 Å; the gaps relative to the isodiCp ligand are somewhat more disparate (2.355–2.447 Å). As expected on steric grounds alone, C-3 lies closest to the metal while C-1 and C-5 are the most distant.

It follows that 7 should be the below-plane complex. In fact, its ^{1}H NMR parameters compare very favorably with those of 9 (see below) whose structure has been independently confirmed by crystallographic means. The inversion of chemical shifts associated with its isodicyclopentadienyl vinyl protons has been alluded to above. In addition, the methano and ethano bridge protons of the norbornyl group in 7 are not at all as well differentiated as they are in 6 but appear very close to each other as a rather nondescript multiplet near δ 1.85 at 300 MHz (Table I). The ^{13}C NMR absorptions of the methano bridge carbons in 6 and 7 offer additional interesting contrast. Whereas the signal in 6 (47.84 ppm) compares closely to that reported for 5 (M = Ti, 47.71 ppm),[12d] deshielding on the order of 12 ppm is seen in 7 (59.28 ppm). This effect constitutes another useful diagnostic tool for stereochemical assignment since, as will develop below, it is linked directly to which isodiCp face happens to be involved in complexation.

At this point, several control experiments were performed in order to demonstrate convincingly that 7 cannot transform to 6 under the reaction conditions. To this end, isodiCpLi was condensed with $CpTiCl_3$ at 20 °C and at the reflux temperature of tetrahydrofuran in the presence of a 10-fold excess of 7. In both instances, a 20:1 mixture of 7 and 6 (the latter resulting from direct complexation) was produced.

In a complementary study, 1 was reacted with sodium in methanol-O-d to effect essentially complete H/D exchange of its cyclopentadiene ring. The extent of isotopic labeling was ascertained by conversion to 7-d_3 and ^{1}H/^{2}H NMR analysis of this complex. Its deuterium atoms were seen as two broad singlets at δ 6.38 and 6.17 in a 2:1 ratio. When 7-d_3 was admixed with an equimolar amount of 6 in tetrahydrofuran and maintained either at room temperature (18 h) or at reflux (18 h), no crossover was seen. The ^{2}H NMR spectrum of reisolated 6 was totally devoid of signals! Admixture of 4-d_3 with $CpTiCl_3$ and 7 as described above again showed that no intermediate, side, or decomposition product is involved in converting one material into the other.

Table III. Bond Distances (Å) and Angles (deg) for 6

	Bond Distances		
Ti–Cl(1)	2.349 (2)	Ti–Cl(2)	2.362 (2)
Ti–C(1)	2.447 (6)	Ti–C(2)	2.376 (6)
Ti–C(3)	2.355 (6)	Ti–C(4)	2.357 (6)
Ti–C(5)	2.434 (5)	Ti–C(11)	2.359 (6)
Ti–C(12)	2.363 (6)	Ti–C(13)	2.395 (6)
Ti–C(14)	2.400 (6)	Ti–C(15)	2.403 (6)
C(1)–C(2)	1.428 (8)	C(1)–C(5)	1.390 (8)
C(1)–C(9)	1.493 (8)	C(2)–C(3)	1.399 (9)
C(3)–C(4)	1.404 (8)	C(4)–C(5)	1.418 (8)
C(5)–C(6)	1.525 (8)	C(6)–C(7)	1.558 (9)
C(6)–C(10)	1.537 (8)	C(7)–C(8)	1.550 (9)
C(8)–C(9)	1.547 (8)	C(9)–C(10)	1.542 (8)
C(11)–C(12)	1.398 (9)	C(11)–C(15)	1.375 (9)
C(12)–C(13)	1.386 (9)	C(13)–C(14)	1.379 (9)
C(14)–C(15)	1.360 (9)	Cent1–Ti	2.07
Cent2–Ti	2.07		
	Bond Angles		
Cl(1)–Ti–Cl(2)	96.97 (7)	C(2)–C(1)–C(5)	107.8 (5)
C(2)–C(1)–C(9)	142.8 (6)	C(5)–C(1)–C(9)	107.8 (5)
C(1)–C(2)–C(3)	107.3 (6)	C(2)–C(3)–C(4)	109.0 (6)
C(3)–C(4)–C(5)	107.0 (6)	C(1)–C(5)–C(4)	108.7 (5)
C(1)–C(5)–C(6)	106.6 (5)	C(4)–C(5)–C(6)	143.1 (6)
C(5)–C(6)–C(7)	103.4 (5)	C(5)–C(6)–C(10)	99.9 (4)
C(7)–C(6)–C(10)	100.2 (5)	C(6)–C(7)–C(8)	103.4 (5)
C(7)–C(8)–C(9)	103.9 (5)	C(1)–C(9)–C(8)	103.8 (5)
C(1)–C(9)–C(10)	100.4 (5)	C(8)–C(9)–C(10)	100.2 (5)
C(6)–C(10)–C(9)	95.7 (5)	C(12)–C(11)–C(15)	107.9 (7)
C(11)–C(12)–C(13)	107.1 (6)	C(12)–C(13)–C(14)	107.7 (6)
C(13)–C(14)–C(15)	108.9 (6)	C(11)–C(15)–C(14)	108.3 (7)
Cent1–Ti–Cent2	130.5	Cent1–Ti–Cl(1)	105.9
Cent1–Ti–Cl(2)	106.5	Cent2–Ti–Cl(1)	106.3
Cent2–Ti–Cl(2)	105.8		

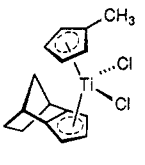
Table IV. Selected Bond Distances (Å) and Angles (deg) for 9

	molecule	
	A	B
(a) Bond Distances		
Ti–Cl(1)	2.338 (1)	2.344 (1)
Ti–Cl(2)	2.391 (1)	2.402 (1)
Ti–C(1)	2.448 (3)	2.435 (3)
Ti–C(2)	2.384 (3)	2.402 (3)
Ti–C(3)	2.334 (3)	2.344 (4)
Ti–C(4)	2.347 (3)	2.353 (4)
Ti–C(5)	2.414 (3)	2.404 (4)
Ti–C(7)	2.474 (3)	2.472 (3)
Ti–C(8)	2.388 (4)	2.372 (4)
Ti–C(9)	2.311 (3)	2.316 (3)
Ti–C(10)	2.368 (3)	2.393 (4)
Ti–C(11)	2.494 (3)	2.516 (3)
C(1)–C(2)	1.410 (4)	1.404 (5)
C(1)–C(5)	1.393 (5)	1.403 (5)
C(1)–C(6)	1.498 (5)	1.503 (5)
C(2)–C(3)	1.391 (5)	1.398 (5)
C(3)–C(4)	1.405 (6)	1.394 (6)
C(4)–C(5)	1.390 (5)	1.417 (5)
C(7)–C(8)	1.405 (5)	1.418 (5)
C(7)–C(11)	1.411 (4)	1.402 (5)
C(7)–C(14)	1.506 (5)	1.524 (4)
C(8)–C(9)	1.400 (5)	1.373 (5)
C(9)–C(10)	1.414 (5)	1.408 (5)
C(10)–C(11)	1.399 (4)	1.386 (4)
C(11)–C(12)	1.508 (4)	1.528 (4)
C(12)–C(13)	1.601 (10)	1.569 (5)
C(12)–C(16)	1.474 (5)	1.515 (5)
C(13)–C(14)	1.615 (7)	1.579 (5)
C(14)–C(15)	1.475 (7)	1.526 (5)
C(15)–C(16)	1.450 (8)	1.511 (6)
Ti–CNT1	2.068 (3)	2.068 (3)
Ti–CNT2	2.090 (3)	2.102 (3)
(b) Bond Angles		
Cl(1)–Ti–Cl(2)	91.9 (1)	92.5 (1)
Cl(1)–Ti–CNT(1)	106.4 (1)	106.1 (1)
Cl(1)–Ti–CNT(2)	106.5 (1)	107.3 (1)
Cl(2)–Ti–CNT(1)	106.1 (1)	105.5 (1)
Cl(2)–Ti–CNT(2)	106.8 (1)	105.9 (1)
CNT(1)–Ti–CNT(2)	131.9 (1)	132.3 (1)
C(2)–C(1)–C(5)	106.6 (3)	107.2 (3)
C(2)–C(1)–C(6)	127.2 (3)	125.7 (3)
C(5)–C(1)–C(6)	126.2 (3)	127.1 (3)
C(1)–C(2)–C(3)	108.5 (3)	108.8 (3)
C(2)–C(3)–C(4)	108.1 (3)	108.1 (3)
C(3)–C(4)–C(5)	107.2 (4)	107.7 (3)
C(1)–C(5)–C(4)	109.6 (3)	108.2 (3)
C(8)–C(7)–C(11)	108.3 (3)	107.6 (3)
C(8)–C(7)–C(14)	142.2 (3)	142.8 (3)
C(11)–C(7)–C(14)	106.0 (3)	106.4 (3)
C(7)–C(8)–C(9)	107.2 (3)	107.2 (3)
C(8)–C(9)–C(10)	108.9 (3)	109.5 (3)
C(9)–C(10)–C(11)	107.2 (3)	107.2 (3)
C(7)–C(11)–C(10)	108.2 (3)	108.5 (3)
C(7)–C(11)–C(12)	106.8 (2)	107.3 (3)
C(10)–C(11)–C(12)	142.7 (3)	142.0 (3)
C(11)–C(12)–C(13)	99.1 (3)	97.5 (3)
C(11)–C(12)–C(16)	113.3 (3)	111.9 (3)
C(13)–C(12)–C(16)	96.8 (3)	99.0 (3)
C(12)–C(13)–C(14)	89.5 (4)	93.2 (2)
C(7)–C(14)–C(13)	99.4 (3)	98.0 (3)
C(7)–C(14)–C(15)	111.9 (3)	109.4 (3)
C(13)–C(14)–C(15)	97.7 (4)	98.8 (3)
C(14)–C(15)–C(16)	105.5 (3)	105.6 (3)
C(12)–C(16)–C(15)	106.6 (4)	103.8 (3)

Consequently, the bifacial complexation so clearly exhibited by **4** does not appear to stem from some isomerization process induced at the more elevated temperatures. Rather, all indicators point to operation of two different kinetically controlled processes which are stereochemically exclusive at the −78 and 25 °C temperature limits.

In order to assess the impact of steric factors on stereoselectivity, the unadorned Cp was incrementally substituted. The first stage of this effort focused on $H_3CCpTiCl_3$, synthesized by proper adaptation of Cardoso's method.[20] Thus, condensation of H_3CCpLi with chlorotrimethylsilane gave a mixture of $H_3CCpSi(CH_3)_3$ isomers, which without purification was condensed with titanium tetrachloride. An 80% overall yield was realized from methylcyclopentadiene.[21]

As in the unsubstituted example, the stereoselectivity of the condensation of **4**-Li with $H_3CCpTiCl_3$ was linked directly to temperature. At 20 °C, a 40:60 mixture of **8** and **9** was formed. On the other hand, heating of the reactants in boiling tetrahydrofuran gave **8** in 40% yield with only a trace of **9** detectable by ^1H NMR. Its spectral features provided unequivocal indication of above-plane stereochemistry (Table I). When the reaction was performed instead at −78 → 20 °C, complex **9** was isolated (65%). In this instance, a trace of the symmetrical complex **5** (M = Ti) was detected by ^{13}C NMR to be the only byproduct. The efficiency of these complexation reactions



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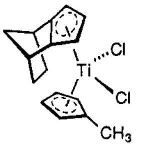

9

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(20) (a) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156. (b) See also: Llinas, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37.

(21) This methodology offers significantly greater convenience than those reported heretofore: (a) Dvoryantseva, G. G.; Sheintrer, Yu. N.; Nesmeyanov, A. N.; Nogina, O. V.; Lazareova, N. A.; Dubovitskii, V. A. *Dokl. Chem.* (*Engl. Transl.*) **1965**, *161*, 303. (b) Verkouw, H. T.; Van Oven, H. O. *J. Organomet. Chem.* **1973**, *59*, 259. (c) Nesmeyanov, A. N.; Nogina, O. V.; Lazareva, N. A.; Dubovitskii, V. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1967**, 777.

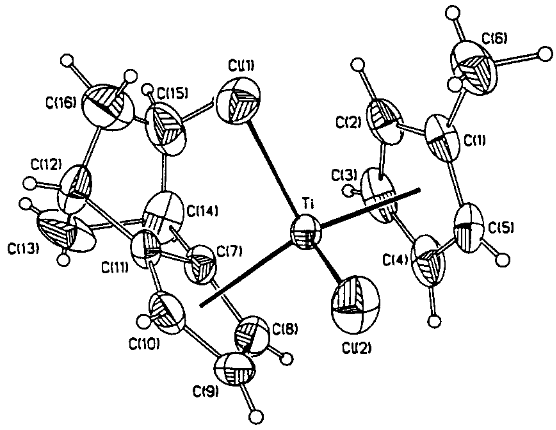
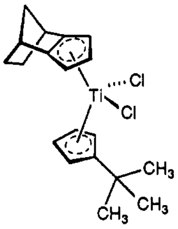


Figure 2. Molecular structure of one of two similar molecules comprising the crystallographic asymmetric unit of **9** as drawn with 50% thermal ellipsoids.

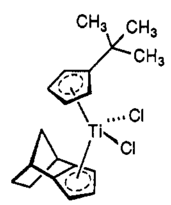
is particularly noteworthy since disproportionation is often recognized to be troublesome for processes of this type.[22]

The structural assignment to **9** was substantiated by X-ray crystallographic analysis (Tables II and IV, Figure 2). In this instance, the asymmetric unit consists of two crystallographically independent but very similar molecules. The Ti–Cl bond lengths (2.338 and 2.391 Å; 2.344 and 2.402 Å) in **9** are somewhat more extreme than those in **6**, but otherwise within normal limits.[2,12b] On the other hand, the average Cl–Ti–Cl angle (92.2°) is smaller than that customarily observed. As in **6**, the Cp rings are asymmetrically disposed about the titanium atom. However, the canting is more severe in **9**. The Ti–Cl distances to the H_3CCp ring fall in the range 2.334–2.447 Å. Since the largest gap is to methyl-substituted carbon 1, the more pronounced tilting appears to arise from steric decompression. For the isodiCp ligand, the Ti–C distances fall in the 2.312–2.515 Å range, with C-9 residing most proximate to the metal.

When the identical reaction conditions (−78 → 20 °C) were applied to *t*-BuCpTiCl$_3$, **10** and **11** were isolated in a 10:90 ratio. A mixture was also obtained when the lithium isodicyclopentadienide solution was added at room temperature. However, when a temperature of −78 °C was maintained throughout the reaction period, **10** could be produced exclusively. In contrast, heating of the reactants in tetrahydrofuran as before delivered **11** alongside a trace of **10**. The ^1H (Table I) and ^{13}C NMR spectra of this pair of complexes serve as unmistakable indicators of their endo and exo nature, respectively.



10



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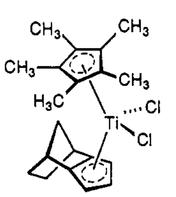

12

When recourse was next made to (η^5-pentamethylcyclopentadienyl)trichlorotitanium,[23] two modifications in the reaction conditions were found necessary. Use of isodiCpLi in this instance resulted in the onset of considerable degradation of the organometallic reagent. While smooth condensation did result with **4**-Tl, refluxing benzene temperatures were needed for complex formation to proceed at a reasonable rate. As anticipated from the earlier observations, only **12** was obtained (50%). X-ray analysis (Tables II and V, Figure 3) confirmed that complexation had occurred above-plane, in agreement with the low-field ^1H NMR signals (δ 6.11, 1 H; 5.14, 2 H) and the shielded nature of the methano carbon (49.14 ppm).

The metrical differences between **6** and **12** can be attributed to the cumulative effect of the five methyl groups about the periphery of the Cp ring. In this instance, the Ti–Cl bond lengths are essentially identical (2.339 and 2.341 Å) and the Me$_5$Cp ring is almost perfectly disposed in a symmetric sense about the metal. The isodiCp ligand is again tilted in the usual direction (2.35–2.48 Å) and the

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

	Bond Distances		
Ti–Cl(1)	2.341 (6)	Ti–Cl(2)	2.339 (7)
Ti–C(1)	2.40 (2)	Ti–C(2)	2.42 (2)
Ti–C(3)	2.48 (2)	Ti–C(4)	2.38 (2)
Ti–C(5)	2.44 (2)	Ti–C(11)	2.47 (2)
Ti–C(12)	2.42 (2)	Ti–C(13)	2.35 (2)
Ti–C(14)	2.36 (2)	Ti–C(15)	2.48 (2)
C(1)–C(2)	1.39 (3)	C(1)–C(5)	1.51 (3)
C(1)–C(6)	1.53 (3)	C(2)–C(3)	1.41 (3)
C(2)–C(7)	1.51 (3)	C(3)–C(4)	1.45 (3)
C(3)–C(8)	1.47 (3)	C(4)–C(5)	1.40 (3)
C(4)–C(9)	1.54 (3)	C(5)–C(10)	1.49 (3)
C(11)–C(12)	1.43 (3)	C(11)–C(15)	1.37 (3)
C(11)–C(19)	1.46 (3)	C(12)–C(13)	1.44 (3)
C(13)–C(14)	1.39 (3)	C(14)–C(15)	1.40 (3)
C(15)–C(16)	1.52 (3)	C(16)–C(17)	1.60 (3)
C(16)–C(20)	1.52 (3)	C(17)–C(18)	1.58 (3)
C(18)–C(19)	1.57 (3)	C(19)–C(20)	1.56 (3)
Ti–Cent1	2.10	Ti–Cent2	2.09
	Bond Angles		
Cl(1)–Ti–Cl(2)	95.1 (2)	C(2)–C(1)–C(5)	106 (2)
C(2)–C(1)–C(6)	132 (2)	C(5)–C(1)–C(6)	121 (2)
C(1)–C(2)–C(3)	112 (2)	C(1)C(2)–C(7)	123 (2)
C(3)–C(2)–C(7)	123 (2)	C(2)–C(3)–C(4)	106 (2)
C(2)–C(3)–C(8)	128 (2)	C(4)–C(3)–C(8)	127 (2)
C(3)–C(4)–C(5)	110 (2)	C(3)–C(4)–C(9)	125 (2)
C(5)–C(4)–C(9)	124 (2)	C(1)–C(5)–C(4)	106 (2)
C(1)–C(5)–C(10)	125 (2)	C(4)–C(5)–C(10)	130 (2)
C(12)–C(11)–C(15)	110 (2)	C(12)–C(11)–C(19)	140 (2)
C(15)–C(11)–C(19)	109 (2)	C(11)–C(12)–C(13)	104 (2)
C(12)–C(13)–C(14)	110 (2)	C(13)–C(14)–C(15)	107 (2)
C(11)–C(15)–C(14)	110 (2)	C(11)–C(15)–C(16)	107 (2)
C(14)–C(15)–C(16)	143 (2)	C(15)–C(16)–C(17)	101 (2)
C(15)–C(16)–C(20)	102 (2)	C(17)–C(16)–C(20)	98 (2)
C(16)–C(17)–C(18)	103 (2)	C(17)–C(18)–C(19)	103 (2)
C(11)–C(19)–C(18)	105 (2)	C(11)–C(19)–C(20)	101 (1)
C(18)–C(19)–C(20)	99 (2)	C(16)–C(20)–C(19)	96 (2)
Cent1–Ti–Cent2	131.9	Cent1–Ti–Cl(1)	106.4
Cent1–Ti–Cl(2)	107.2	Cent2–Ti–Cl(1)	106.2
Cent2–Ti–Cl(2)	104.0		

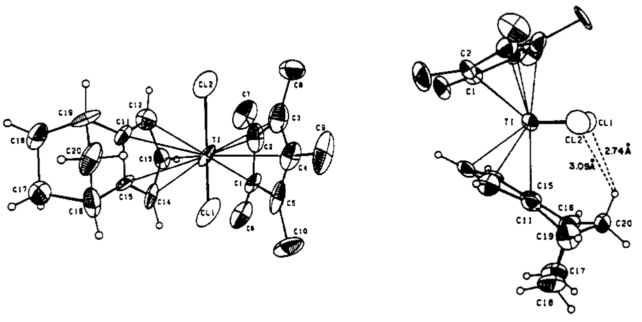

Figure 3. Two views of the crystallographically determined molecular structure of **12** as drawn with 50% thermal ellipsoids.

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(22) (a) Lee, J. G.; Brubaker, C. H. *J. Organomet. Chem.* **1977**, *135*, 115. (b) Dormond, A.; Ou-Khan; Tirouflet, J. *C. R. Hebd. Seances Ser. C Acad. Sci., Paris* **1974**, *278C*, 1207. (c) Dormond, A.; Ou-Khan; Tirouflet, J. *Ibid.* **1975**, *280C*, 389.

(23) Blenkers, J.; De Liefde, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

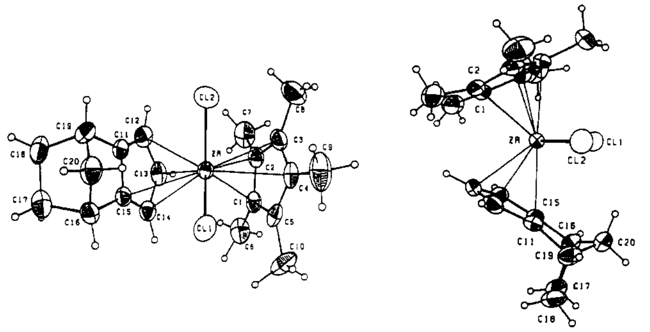
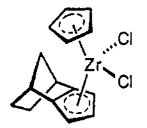


Figure 4. Two views of the crystallographically determined molecular structure of 14 as drawn with 50% thermal ellipsoids.

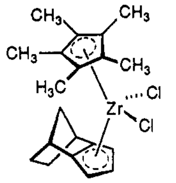
Cl–Ti–Cl angle is quite normal (95.1°).

Two significant pieces of information can be gleaned from the ORTEP diagrams depicted in Figures 1–3: (a) *having the methano bridge directed between the Cl–Ti–Cl group is appreciably more favorable from a steric vantage point* (see Figure 3) *then the alternative option of a syn-oriented ethano bridge, particularly when the required geometry of the syn H–C–C–H is considered*; (b) while complexation from the exo surface distorts the cyclopentadienyl ring of the isodiCp ligand in the preferred[24] endo direction, Figure 2 shows that *deformation in the exo direction is also possible. The specific extent of upward folding in **9** amounts to 14.5°.*

The ready availability of $CpZrCl_3 \cdot 2THF$[25] and $Cp''ZrCl_3$[23] prompted examination of the stereoselectivity associated their mixed complexation to **4**-Li. As a consequence of the lower solubility and lessened reactivity of these zirconium reagents, substantive modification of the reaction conditions earlier employed was in order. In an attempt to capitalize on the coordinative properties of 1,2-dimethoxyethane, **4**-Li and $CpZrCl_3 \cdot 2THF$ were heated together in this solvent for 100 h. These conditions afforded **13** in poor yield (5%). When recourse was made instead to toluene and reflux was maintained for 3 days, efficient condensation materialized to deliver both **13** and **14** (65% and 55%, respectively).



13



14

Since heating was required to drive these reactions, we were not surprised to find that both products belonged to the exo series. These conclusions were initially founded on the ^1H (Table I) and ^{13}C NMR characteristics of these complexes and later substantiated by X-ray crystallographic analysis of **14** (Table II and VI, Figure 4). Both Zr–Cl bonds in **14** are equivalent and the average Zr–Cp″ and Zr–isodiCp distances are 2.528 (9) and 2.52 (5) Å, respectively. Once again, the furthest approach belongs to those two isodiCp carbons linked to the norbornane ring: C(11), 2.589 (3) Å, and C(15), 2.549 (3) Å. The closest Cl(1)···C contacts not to a ligand ring atom belong to C(10) at 3.224 (4) Å followed by C(16) at 3.350 (4) Å. For Cl(2), C(8) at 3.267 (5) Å and C(19) at 3.594 (4) Å are most proximal. These data suggest an orientation of the isodiCp ligand having a substituent group closer to Cl(1).

Table VI. Bond Distances (Å) and Angles (deg) for 14

Bond Distances			
Zr–Cl(1)	2.4400 (9)	Zr–Cl(2)	2.4389 (9)
Zr–C(1)	2.524 (3)	Zr–C(2)	2.515 (3)
Zr–C(3)	2.543 (3)	Zr–C(4)	2.526 (3)
Zr–C(5)	2.530 (3)	Zr–C(11)	2.589 (3)
Zr–C(12)	2.532 (3)	Zr–C(13)	2.457 (3)
Zr–C(14)	2.469 (3)	Zr–C(15)	2.549 (3)
C(1)–C(2)	1.414 (4)	C(1)–C(5)	1.420 (5)
C(1)–C(6)	1.482 (5)	C(2)–C(3)	1.396 (5)
C(2)–C(7)	1.498 (5)	C(3)–C(4)	1.421 (5)
C(3)–C(8)	1.491 (5)	C(4)–C(5)	1.415 (5)
C(4)–C(9)	1.499 (5)	C(5)–C(10)	1.485 (5)
C(11)–C(12)	1.413 (5)	C(11)–C(15)	1.396 (4)
C(11)–C(19)	1.503 (5)	C(12)–C(13)	1.406 (5)
C(13)–C(14)	1.405 (4)	C(14)–C(15)	1.414 (5)
C(15)–C(16)	1.507 (4)	C(16)–C(17)	1.546 (5)
C(16)–C(20)	1.533 (5)	C(17)–C(18)	1.555 (5)
C(18)–C(19)	1.539 (5)	C(19)–C(20)	1.544 (5)
Zr–Cent1	2.22	Zr–Cent2	2.21

Bond Angles			
Cl(1)–Zr–Cl(2)	97.76 (3)	C(2)–C(1)–C(5)	107.7 (3)
C(2)–C(1)–C(6)	127.2 (3)	C(5)–C(1)–C(6)	124.4 (3)
C(1)–C(2)–C(3)	108.7 (3)	C(1)–C(2)–C(7)	125.6 (3)
C(3)–C(2)–C(7)	124.8 (3)	C(2)–C(3)–C(4)	107.9 (3)
C(2)–C(3)–C(8)	125.8 (4)	C(4)–C(3)–C(8)	125.9 (4)
C(3)–C(4)–C(5)	108.0 (3)	C(3)–C(4)–C(9)	126.0 (4)
C(5)–C(4)–C(9)	125.9 (4)	C(1)–C(5)–C(4)	107.6 (3)
C(1)–C(5)–C(10)	124.5 (3)	C(4)–C(5)–C(10)	127.6 (3)
C(12)–C(11)–C(15)	108.2 (3)	C(12)–C(11)–C(19)	143.1 (3)
C(15)–C(11)–C(19)	107.2 (3)	C(11)–C(12)–C(13)	106.8 (3)
C(12)–C(13)–C(14)	109.6 (3)	C(13)–C(14)–C(15)	106.4 (3)
C(11)–C(15)–C(14)	109.0 (3)	C(11)–C(15)–C(16)	106.7 (3)
C(14)–C(15)–C(16)	143.1 (3)	C(15)–C(16)–C(17)	104.7 (3)
C(15)–C(16)–C(20)	101.3 (3)	C(17)–C(16)–C(20)	99.5 (3)
C(16)–C(17)–C(18)	103.0 (3)	C(17)–C(18)–C(19)	103.9 (3)
C(11)–C(19)–C(18)	103.8 (3)	C(11)–C(19)–C(20)	100.7 (3)
C(18)–C(19)–C(20)	99.8 (3)	C(16)–C(20)–C(19)	95.2 (3)
Cent1–Zr–Cent2	130.4	Cent1–Zr–Cl(1)	105.6
Cent1–Zr–Cl(2)	107.7	Cent2–Zr–Cl(1)	105.8
Cent2–Zr–Cl(2)	104.9		

Discussion

The observation that reaction of isodiCpLi with $RCpTiCl_3$ proceeds with high facial selectivity depending upon temperature holds considerable interest. As usual, there is a possibility that small amounts (≤3%) of the stereoisomeric complex could have formed and escaped detection. Nevertheless, the stereoselection is most impressive. Since it is clear from examination of the three-dimensional structural characteristics of **6**, **9**, and **12** (Figure 1–3) that below-plane complexation brings into play more severe nonbonded interactions, we are led to the conclusion that exo stereochemistry is more thermodynamically rewarding. Since equilibration between the isomeric complexes has not proven possible, the only available facts stem from crystallographic data. Nevertheless, the exclusive formation of **6**, **8**, and **11**–**14** at the more elevated temperatures is consistent with this proposal.

Should the preceding analysis be correct, then it is logical to conclude that the below-plane adducts **7**, **9**, and **10** arise from kinetically controlled processes. The orbital construct in **4** may indeed be sufficiently unique to foster contrathermodynamic complexation. Some time ago, we gave consideration to the consequences of mixing between the high-lying norbornyl σ orbitals in this anion with its flanking π orbitals.[12a,b] In short, the relatively substantive σ/π mixing induces a modicum of disrotatory tilting toward the methano bridge in ψ_1, as shown in **15**.[26] If d_σ

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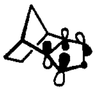
(24) Consult the many pertinent references cited in ref 16a.

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

(metal)-ψ_1 (ligand) interactions were to surface as those of greatest import, then exo complexation should be overwhelmingly preferred. However, this is unlikely. Rather, attention needs to be focused on the customarily greater relevance of d_π-ψ_2 interactions. The isodicyclopentadienide ψ_2, illustrated in **16**, assumes that the π lobes remain sufficiently tilted to render the two π faces easily distinguishable to a metal ion. Under these circumstances, a metal with diffuse d_π orbitals should be better able to engage in overlap on the endo face as in **17**.

15



16

17

In principle, this conclusion is capable of experimental test. In particular, it should be possible to modulate the extent of σ donation and/or steric interference from the norbornenyl moiety to the fused cyclopentadienide ring. The consequences of positioning a pair of methyl groups on the methano bridge are presented in the subsequent paper.[19a] Alternatively, one can reduce the level of strain within the bicyclic unit; in so doing, the energies of the σ orbitals drop and can no longer impact as effectively on the higher lying π orbitals so important to the reacting metal species. As is documented elsewhere,[19b,c] the end result of such structural manipulations is a much stricter adherence to steric control.

The above discussion is largely based on frontier orbital considerations and ignores several additional parameters that most certainly play an important role. Should σ complexation be initially involved, with the titanium center complexed by tetrahydrofuran, then the low temperature results could be rationalized on the basis of more rapid ligand loss (THF) compared to σ complex reversion. The opposite would need to be true at higher temperatures. Evidence for or against this mechanistic crossover hypothesis has been difficult to acquire, and the issue remains open.

On the other hand, a study of the stereochemical dependence of the Li^+ counterion is capable of providing important information and work along these lines is in progress.[27] Once these facts are established, it will be necessary to define as precisely as possible the role of the counterion in terms of its chemical nature and locus.

Finally, some additional comments on the spectral properties of the product complexes are in order. While the assigned molecular structures are fully confirmed by their mass spectral fragmentation patterns, no differences of any measurable significance surface during cleavage of the endo and exo stereoisomers. As concerns ultraviolet absorption, it has previously been recognized[28] that the maximum wavelength exhibited by such complexes is linked directly to the electronic contributions and steric bulkiness of the cyclopentadiene ring substituents. Thus, the greater the electron-donating capacity and steric size, the larger the bathochromic shift. For the stereoisomeric isodicyclopentadiene complexes prepared in the present study, those of the endo type exhibit a bathochromic displacement relative to their exo counterparts. These findings are in agreement with the greater steric compression that exists when the metal is coordinated syn to the ethano bridge of the isodiCp ligand. Also of interest is the similar position of the absorption maximum exhibited by **11** and $(t\text{-BuCp})_2TiCl_2$. On this basis, the norbornyl and *tert*-butyl substituents would appear to exert closely comparable electronic and steric influences.

Experimental Section

Isodicyclopentadienyllithium (4-Li). Isodicyclopentadiene (1.0 g, 0.008 mol) was dissolved in ether (50 mL) under argon and cooled to −78 °C. To the cold solution was added 1 equiv of *n*-butyllithium (1.6 M) via syringe, and the mixture was warmed to room temperature, stirred for 1 h, and heated at the reflux temperature for 12 h. A white solid formed. The reaction mixture was returned to room temperature, concentrated to approximately 20 mL in vacuo, and cooled to 0 °C for 2 h. The remaining ether was carefully removed by cannula from the solid, which was washed with cold (−20 °C) ether (2 × 20 mL) and dried under high vacuum for 6 h. The white salt (780 mg, 75%) is an air- and moisture-sensitive solid.

Isodicyclopentadienylthallium (4-Tl). Isocyclopentadiene (1.0 g, 0.008 mol) was dissolved in dry hexane under argon and cooled to 0 °C. Thallium ethoxide (2.00 g, 0.007 mol) was introduced via syringe, and the reaction mixture was stirred at 0 °C for 2 h and at room temperature for 12 h. The hexane was removed under vacuum to leave a waxy yellow solid. This material was dissolved in a minimum amount of ether and cooled to 0 °C for 2 h. The ether was decanted, and the residual yellow solid was dried under high vacuum. There was isolated 1.2 g (45%) of **4-Tl**. This salt is air- and light-sensitive and is best stored in the dark at −20 °C.

***exo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-cyclopentadienyl)titanium (6). A. From 4-Li.** A solution of **4-Li** (0.30 g, 0.002 mol) in dry tetrahydrofuran (20 mL) was prepared under argon at room temperature. In a second flask, cyclopentadienyltitanium trichloride (480 mg, 0.002 mol) in the same solvent (30 mL) was analogously prepared. The lithium salt solution was slowly transferred via cannula into the trichloride solution over a 20-min period. The reaction mixture was stirred for 12 h and freed of solvent in vacuo. The residue was dissolved in HCl-saturated chloroform, stirred for 20 min, and again freed of solvent. Following transfer to a Soxhlet extractor, the product was extracted in turn with HCl-saturated pentane (12 h) and HCl-saturated chloroform (12 h), and recrystallized from dichloromethane–hexane. There was isolated 250 mg (40%) of **6**: mp 172–173 °C; ^1H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 146.10, 129.69, 119.24, 107.50, 47.84, 41.40, 27.99; MS *m/z* (M^+) calcd 314.0125, obsd 314.0134.

Anal. Calcd for $C_{14}H_{16}Cl_2Ti$: C, 57.16; H, 5.12. Found: C, 56.87; H, 5.20.

B. From 4-Tl. Cyclopentadienyltitanium trichloride (540 mg, 0.0024 mol) and **4-Tl** (820 mg, 0.0024 mol) were dissolved in dry benzene under argon at room temperature. The reaction mixture was stirred at room temperature for 1 h, heated at reflux for 12 h, and cooled. Following filtration through a Celite pad, the pad was washed with dichloromethane (100 mL). The solvent was removed in vacuo and the red solid was washed with cold pentane. The product was recrystallized from dichloromethane/hexane to give 340 mg (45%) of **6**, spectroscopically identical with the material isolated in part A.

***endo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-cyclopentadienyl)titanium (7).** Isodicyclopentadiene (500 mg, 0.004 mol) was dissolved in tetrahydrofuran (30 mL) under argon, cooled to −78 °C, and treated with *n*-butyllithium via syringe. This solution was slowly warmed to room temperature, stirred for 30 min, and transferred via cannula to a cold (−78 °C), magnetically stirred solution of cyclopentadienyltitanium trichloride (890 mg, 0.004 mol) in tetrahydrofuran (50 mL) during 30 min. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvent was removed, the residue was dissolved in chloroform (20 mL), and concentrated hydrochloric acid (20 mL) was added. After 20 min of stirring, the organic layer was dried and concentrated. The residue was transferred to a Soxhlet extractor and extracted with HCl-saturated pentane (12 h) and HCl-saturated chloroform (12 h). Solvent evaporation and re-

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(26) Böhm, M. C.; Gleiter, R., private communication.

(27) Work along these lines is currently being undertaken collaboratively with Professor P. von R. Schleyer (Erlangen).

(28) Fauconet, M. Thèse de 3e Cycle, University of Dijon, 1984.

crystallization from dichloromethane–hexane afforded 260 mg (21%) of **7**: mp 141–142 °C; ^{1}H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 155.00, 124.66, 119.49, 112.81, 59.28, 42.48, 27.03; MS *m/z* (M^+) calcd 304.0125, obsd 304.0139.

Anal. Calcd for $C_{14}H_{16}Cl_2Ti$: C, 57.16; H, 5.12. Found: C, 56.93; H, 5.21.

Isodicyclopentadiene-*d*$_4$. Sodium metal (87 mg, 3.8 mmol) was slowly added at 0 °C under argon to methanol-*O*-*d* (8.13 g, 0.246 mol) with vigorous stirring. The solution was warmed to room temperature and stirred for 30 min prior to the addition of **1** (500 mg, 3.8 mmol). The mixture was stirred at 20 °C for 12 h, poured into water (50 mL), and extracted three times with pentane. The combined pentane extracts were dried, filtered, and evaporated at 30 Torr. The residual oil was added to a column of neutral alumina and eluted with pentane (200 mL). The solvent was removed to leave a colorless oil (450 mg, 88%), which was used without further purification.

***endo*-Dichloro(η^5-isodicyclopentadienyl-*d*$_3$)(η^5-cyclopentadienyl)titanium (7-*d*$_3$).** Reaction of isodiCp-*d*$_4$ (150 mg, 1.1 mmol) with *n*-butyllithium (1 equiv) and $CpTiCl_3$ (241 mg, 1.1 mmol) in dry tetrahydrofuran (70 mL) in the predescribed manner afforded **7**-*d*$_3$ in 24% yield: ^{2}H NMR ($CDCl_3$) showed two broad singlets at δ 6.38 and 6.17 in a 2:1 ratio.

Prototypical Control Experiments. A. Attempted Equilibration of 7. A solution of **7** (100 mg, 0.32 mmol) and $CpTiCl_3$ (7 mg, 0.032 mmol) in dry tetrahydrofuran (50 mL) was blanketed with argon and treated with a solution of **4**-Li (0.032 mmol) in the same solvent (10 mL) during 20 min at room temperature. After 18 h of continued stirring, workup furnished 98 mg (97%) of solid product. ^{1}H NMR analysis at 300 MHz showed the material to consist of a 20:1 mixture of **7** and **6**. Repetition of the reaction at the reflux temperature gave identical results.

B. Attempted Crossover Experiment. A solution of **4-Li-*d*$_3$** (0.1 mmol) and **6** (30 mg, 1.0 mmol) in dry tetrahydrofuran (25 mL) under argon was stirred at room temperature for 18 h. Workup in the usual manner afforded 28 mg (89%) of recovered **6**, ^{2}H NMR analysis of which showed it to completely lack isotopic label. Repetition of this reaction at the reflux temperature gave entirely similar negative results.

***exo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-methylcyclopentadienyl)titanium (8).** A solution of isodicyclopentadienyllithium (260 mg, 1.88 mmol) in dry tetrahydrofuran (45 mL) was added dropwise to a refluxing solution of $H_3CCpTiCl_3$ (440 mg, 1.88 mmol) in the same solvent (25 mL). After 3 h of heating, the reaction mixture was poured into 8 mL of concentrated hydrochloric acid. The aqueous layer was extracted three times with chloroform. The combined organic layers were washed with water, dried, and evaporated. Recrystallization of the brown residue from dichloromethane saturated with hydrogen chloride and hexane afforded 245 mg (40%) of **8** as black crystals: mp 177 °C; ^{1}H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 144.13, 127.55, 122.25, 113.03, 106.06, 48.25, 41.94, 28.80, 17.38 (quarternary C not observed).

Anal. Calcd for $C_{16}H_{18}Cl_2Ti$: C, 58.39; H, 5.51; Cl, 21.54; Ti, 14.55. Found: C, 58.17; H, 5.60; Cl, 21.78; Ti, 14.31.

***endo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-methylcyclopentadienyl)titanium (9).** A solution of isodicyclopentadiene (650 mg, 0.005 mol) in dry tetrahydrofuran (5 mL) was treated dropwise at −78 °C with *n*-butyllithium in hexane (6 mL, 5.4 mmol). The mixture was allowed to warm gradually to 25 °C and stirred for 30 min. This solution was added dropwise to a solution of $H_3CCpTiCl_3$ (1.16 g, 0.005 mol) in cold (−78 °C) tetrahydrofuran, stirred for 14 h at room temperature, and poured into 20 mL of concentrated hydrochloric acid. The aqueous layer was extracted with dichloromethane (3×), and the combined organic phases were dried and evaporated. The red solid was crystallized from HCl-saturated dichloromethane/hexane to give 1.07 g (65%) of **9**: mp 151 °C; ^{1}H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 152.23, 122.598, 112.43, 110.05, 59.46, 43.34, 27.94, 17.50; MS *m/z* (M^+) calcd 328, obsd 328.

Anal. Calcd for $C_{16}H_{18}Cl_2Ti$: C, 58.39; H, 5.51; Cl, 21.54; Ti, 14.55. Found: C, 58.52; H, 5.43; Cl, 21.23; Ti, 14.78.

***endo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-*tert*-butylcyclopentadienyl)titanium (10).** This complex was synthesized by using the method described for **9**, except for the fact that the reaction mixture obtained after addition of **4**-Li to *t*-$BuCpTiCl_3$ was stirred at −78 °C for 5 h before being allowed to warm to room temperature. There isolated in 45% yield red crystals of **10**: mp 169 °C; ^{1}H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 153.16, 147.81, 122.73, 121.30, 111.26, 110.26, 59.33, 46.42, 31.27, 27.99 (quaternary *t*-butyl C not observed).

Anal. Calcd for $C_{19}H_{24}Cl_2Ti$: C, 61.47; H, 6.51; Cl, 19.10; Ti, 12.90. Found: C, 61.70; H, 6.17; Cl, 19.32; H, 13.01.

***exo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-*tert*-butylcyclopentadienyl)titanium (11).** This complex was prepared in the manner described for **8** and obtained in 55% yield as red crystals: mp 191 °C; ^{1}H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 147.24, 144.78, 127.60, 119.05, 113.75, 106.25, 47.71, 41.84, 35.01, 31.72, 28.80.

Anal. Calcd for $C_{19}H_{24}Cl_2Ti$: C, 61.47; H, 6.51; Cl, 19.10; Ti, 12.90. Found: C, 61.03; H, 6.83; Cl, 19.43; Ti, 12.45.

***exo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-pentamethylcyclopentadienyl)titanium (12).** (Pentamethylcyclopentadienyl)titanium trichloride (1.03 g, 3.1 mmol) was dissolved in dry benzene (50 mL), treated with isodicyclopentadienylthallium (880 mg, 3.1 mmol), stirred at room temperature for 1 h, and heated at reflux for 12 h. The cooled reaction mixture was filtered through a Celite pad, and the latter was washed with dichloromethane (100 mL). The combined filtrates were evaporated under reduced pressure, and the red solid was washed with cold pentane and placed in a Soxhlet extractor. Extraction in the predescribed manner followed by recrystallization from dichloromethane/hexane provided 600 mg (50%) of **12**: mp 185–186 °C dec; ^{1}H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 150.04, 129.11, 121.78, 104.82, 49.14, 41.02, 28.09, 13.42.

Anal. Calcd for $C_{20}H_{26}Cl_2Ti$: C, 62.34; H, 6.80. Found: C, 62.08; H, 6.81.

Prototypical Control Reaction. A solution of **7** (100 mg, 0.32 mmol) and $CpTiCl_3$ (7 mg, 0.032 mmol) in dry tetrahydrofuran (30 mL) under argon was treated with freshly prepared isodicyclopentadienyllithium (0.032 mmol) and stirred at room temperature for 18 h. The solvent was removed under reduced pressure, and the residue was dissolved in chloroform (20 mL), treated with concentrated hydrochloric acid (20 mL), and stirred for 20 min. The aqueous phase was extracted with chloroform (2 × 25 mL), and the combined organic layers were dried, filtered, and evaporated. The residue (98 mg, 97%) exhibited an ^{1}H NMR spectrum showing **7** to predominate overwhelmingly over a trace amount of **6**.

***exo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-cyclopentadienyl)zirconium (13).** Isodicyclopentadienyllithium (160 mg, 1.2 mmol) was slurried in dry toluene (50 mL) at −78 °C under argon. Following the addition of solid $CpZrCl_3 \cdot 2THF$ (470 mg, 1.2 mmol), the mixture was warmed to room temperature, stirred for 1 h, and heated at the reflux temperature for 72 h. Following solvent evaporation, the residue was dissolved in chloroform (25 mL), concentrated hydrochloric acid (20 mL) was added, and the mixture was stirred for 20 min. After the usual workup, the residue was sublimed at 160–165 °C and 0.01 Torr to give 210 mg (49%) of **13**, mp 153–155 °C; ^{1}H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 142.78, 115.42, 103.31, 48.99, 40.92, 28.32; MS *m/z* (M^+) calcd 357.9642, obsd 357.9683.

Anal. Calcd for $C_{14}H_{16}Cl_2Zr$: C, 50.62; H, 4.71. Found: C, 50.25; H, 4.50.

***exo*-Dichloro(η^5-isodicyclopentadienyl)(η^5-pentamethylcyclopentadienyl)zirconium (14).** Condensation of isodicyclopentadienylzirconium trichloride (290 mg, 0.9 mmol) in dry toluene (75 mL) according to the predescribed procedure afforded 220 mg (55%) of **14** after sublimation at 150–160 °C and 0.01 Torr: mp 246–248 °C; ^{1}H NMR (Table I); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 145.08, 124.02, 102.66, 49.50, 40.50, 28.39, 12.44; MS *m/z* (M^+) calcd 428.0425, obsd 428.0472.

Anal. Calcd for $C_{20}H_{26}Cl_2Zr$: C, 56.04; H, 6.11. Found: C, 55.77; H, 6.13.

X-ray Data Collection, Structure Determination, and Refinement. Single crystals of **6**, **9**, **12**, and **14** were mounted on pins and transferred to the goniometer. The space groups were determined for **6**, **12**, and **14** from the systematic absences. A summary of data collection parameters is given in Table II.

Only poor quality, very irregular crystals of **12** could be isolated and were available for this study. As a result standard deviations are poor, the *R* factors and GOF are high, and fine details of the structure are obscured. Few data above $2\theta = 40°$ were usable. The limited data set available was, however, sufficient to determine the gross overall structure and important nonbonded contacts.

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 final fractional coordinates, least-squares planes, and thermal parameters for **6**, **9**, **12**, and **14** (18 pages); listings of observed and calculated factors for **6**, **9**, **12**, and **14** (36 pages). Ordering information is given on any current masthead page.

Stereochemically Uniform Mode of Iron Carbonyl Complexation to Spirocyclic Isodicyclopentadienes[1]

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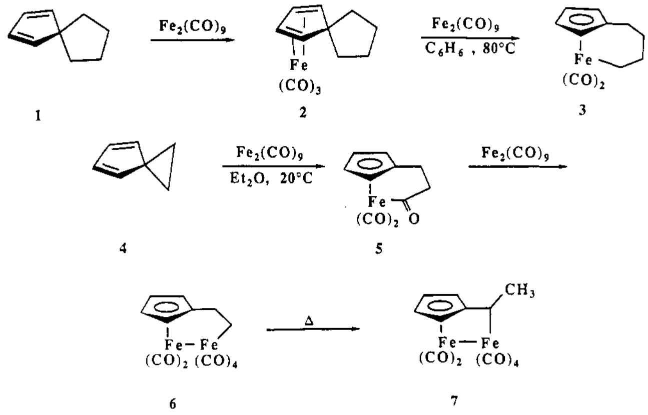
The ligands **14** and **15** derived by suitable spiroalkylation of isodicyclopentadiene were reacted with various iron carbonyl reagents in order to assess π-facial stereoselectivity and other reactivity differences. In contrast to the behavior of these dienes in Diels–Alder reactions, complexation occurred only above-plane. The less strained spiro[4.4]nonadiene **15** reacts with $Fe_2(CO)_9$ to form the η^4-complex **16**, the three-dimensional features of which were established by crystallographic analysis. The results of heating **15** with $(BDA)Fe(CO)_3$ in benzene were bond fission and formation of the σ-allyl π-isodicyclopentadienyl complex **17**. The latter substance could not be made to undergo carbonyl insertion. For **14**, heating with $(BDA)Fe(CO)_3$ led directly to the σ-acyl system **20** for which X-ray data were also obtained. Use of $Fe_2(CO)_9$ delivered a mixture of **20** and the fulvene complex **21**. The uniform mode of iron carbonyl complexation throughout this series is attributed to steric approach control.

The reactivity of 5,5-dialkyl-substituted cyclopentadienes toward various metal carbonyl reagents has been the subject of intense investigation,[3-9] particularly in recent times at the hands of Eilbracht and co-workers.[10] Notably prevalent in the resulting reactions is migration of an alkyl group from the five-membered ring to the metal so as to permit the establishment of (η^5-cyclopentadienyl)metal coordination. Spiro[4.4]nona-1,3-diene (**1**) and spiro[2.4]hepta-4,6-diene (**4**) have served as interesting substrates for study. Heating **1** with iron enneacarbonyl in benzene rapidly provides **2** and more slowly results in conversion predominantly to **3**.[10a,c,f,h,g,l] With $Fe_2(CO)_9$ in ether at 20 °C, **4** has been successfully transformed into the σ-acyl π-cyclopentadienyl complex **5**. At higher temperatures, the dinuclear complexes **6** and **7** are generated in turn.



Such C–C bond cleavage reactions also operate in monocyclic systems typified by **8**. In these examples, the availability of stereoisomeric complexes represented by **9** has permitted crossover experiments to be undertaken. The stereochemical results, e.g., **9** → **10**, have provided

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[1] Part 48 in the series dealing with isodicyclopentadienes and related molecules. (a) For part 47, see: Paquette, L. A.; Shen, C.-C.; Krause, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2351. (b) For part 46, see: Moriarty, K. J.; Rogers, R. D.; Paquette, L. A. *Organometallics* **1989**, *8*, 1512.

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