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Bis(isodicyclopentadienyl) Complexes of the Group 4 Transition Metals. Stereoselective Synthesis and Crystal Structures of the Titanocene and Zirconocene Dichloride Derivatives[1]

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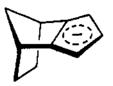
Reactions of the isodicyclopentadienide anion with $TiCl_3$ in tetrahydrofuran at 25 °C, with $ZrCl_4$ in dimethoxyethane at reflux for 70 h, and with $HfCl_4$ in dimethoxyethane (reflux, 100 h) have been performed in order to assess the π-facial stereoselectivity of complexation to group 4 transition metals. In all three instances, a single complex was isolated. X-ray crystallographic analysis of the titanocene and zirconocene dichlorides demonstrate both to be the result of dual coordination to the exo surfaces. By ^1H NMR comparison, the hafnocene is shown to be closely similar and therefore of the same stereochemistry. The three-dimensional features of the complexes are discussed.

Introduction

The considerable bias for above-plane complexation exhibited by the isodicyclopentadienide anion **1** during its conversion to ferrocene, ruthenocene, nickelocene, and related systems[4,5] is not followed to a comparable degree when **2** reacts with group 6 transition-metal hexacarbonyls.[6] However, a return to exclusive production of exo complexes has recently been noted upon direct condensation of fulvene **3** with $M(CO)_6$ reagents (M = Cr, Mo, W).[6] In an effort to broaden our appreciation of the stereochemical course of complexation to **1** as a function of the transition-metal center, we have investigated the condensation of **1** with those elements that comprise group 4. The purposeful selection of **1** was intended to provide basal stereochemical information relevant to the parent system that could be compared with the complexation face selectivity realized with optically active, homochiral homologues of this interesting ligand.[7,8]



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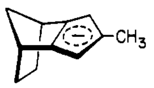

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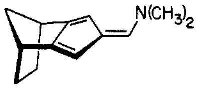

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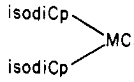
Results

For the three systems examined, stereochemically homogeneous, air-stable dichloride complexes **4**–**6** were isolated by reaction of **1**, prepared at −80 °C from isodicyclopentadiene and *n*-butyllithium in hexane, with the appropriate metal tri- or tetrachloride. The methodology utilized in each specific instance was a function of the halide salt.



$$(isodiCp)_2MCl_2$$

4, M=Ti; **5**, M=Zr; **6**, M=Hf

Most straightforward was the titanium example. By reaction of **1** with titanium trichloride in tetrahydrofuran according to Bercaw[9] for the synthesis of (pentamethylcyclopentadienyl)titanium, the sole complex **4** was conveniently isolated in 49% yield after treatment of the mixture with hydrogen chloride. On the other hand, no zirconium complex was obtained when the experimental procedure described for the synthesis of bis(*tert*-butylcyclopentadienyl)zirconocene[10] was implemented. Only upon heating in dimethoxyethane for long periods of time (70 h) as for the pentamethylcyclopentadienyl series[11] was complex **5** formed in modest yield (38%). Somewhat similar conditions (DME, reflux, 100 h) gave rise to the hafnium complex **6** (27%). All attempts to improve the yields just cited went unrewarded. Importantly, however, careful high-field ^1H NMR analysis of the various reaction mixtures failed to detect the presence of a second stereoisomer in any of these transformations.

Usually, one simple recrystallization sufficed to afford the product in a pure state. The hafnium complex appeared to be the least stable in solution, and well-formed crystals of **6** were not obtained.

The vigorous conditions required for successful coordination, and the relatively low yields realized can be attributed with reasonable certainty to the steric congestion offered above and below plane by the pendant norbornane moiety.

Spectral Analysis

The ^1H and ^{13}C NMR parameters determined for **4**–**6** are compiled in Tables I and II. Assignment of the individual proton signals has been accomplished by reference to similar molecules already published.[4] As regards the ^{13}C spectra, the values cited were obtained by the "off-

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[1] This paper represents our 35th contribution to the chemistry of isodicyclopentadienes. For part 34, consult: Paquette, L. A.; Gugelchuk, M.; Hsu, Y.-L. *J. Org. Chem.* **1986**, *51*, 3864.

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Table I. Comparative ^{1}H NMR spectral Data for 4–6 ($CDCl_3$ Solution, δ)

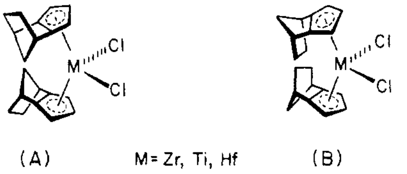
proton (area)	4 (M = Ti)	5 (M = Zr)	6 (M = Hf)
central cyclopentadienide (2)	6.27 (s)	6.27 (t, J = 2.9 Hz)	6.18 (t, J = 3.0 Hz)
peripheral cyclopentadienide (4)	6.08 (s)	5.82 (d, J = 2.9 Hz)	5.80 (d, J = 3.0 Hz)
bridgehead (4)	3.34 (s)	3.29 (s)	3.36 (s)
exo-ethano bridge (4)	1.86 (d, J = 7 Hz)	1.80 (d, J = 8 Hz)	1.84 (d, J = 8 Hz)
methano bridge (4)	1.31 (d)	1.46 (s)	1.50 (s)
endo-ethano bridge (4)	1.11 (d, J = 7 Hz)	0.99 (d, J = 8 Hz)	1.04 (d, J = 8 Hz)

Table II. Comparative ^{13}C NMR Spectral Data for 4–6 ($CDCl_3$ Solution, ppm)

carbon	4	5	6
central cyclopentadienide	106.80	102.62	101.16
peripheral cyclopentadienide	128.44	121.68	120.46
quaternary cyclopentadienide	144.78	142.15	140.31
ethano bridge	28.01	28.25	28.55
bridgehead	41.43	40.80	40.66
methano bridge	47.71	48.93	48.78

resonance" technique and specific chemical shifts were identified in relation to data for other known metallocene dichlorides.[12,13]

It is clear that the high apparent symmetry of the spectra requires all three molecules to possess exo,exo (A) or endo,endo (B) stereochemistry. Relevantly, while the carbon shifts are little influenced by the nature of the transition metal, the proton signals are more sensitive to these changes. Thus, the cyclopentadienyl protons experience a gradual upfield drift when passing from titanium to zirconium to hafnium.[14] In addition, the electronegativity of the metal exerts an influence of approximately 0.2 ppm on the chemical shifts of the protons of the methano bridge, whereas those of the ethano bridge are not modified. This specific effect is without doubt closely related to the three-dimensional structure of the complexes, one of the two faces of the π system being clearly more influenced by the metal. It is to be noted that the two magnetically nonequivalent protons of the methano bridge appear as a singlet for **5** and **6** in the solvent used ($CDCl_3$). In the titanium complex **4**, this pair of protons exhibits the expected anisochronous characteristics. Although the close correspondence between the ^{1}H NMR spectra of **4** and **5** suggested similar structural features, the chemical shifts were viewed as inadequately diagnostic of stereochemistry at this stage.



The mass spectra of 4–6 clearly exhibit the molecular isotopic pattern. The exact masses determined by high-resolution techniques and the excellent correspondence between observed and calculated values confirm the proposed structures. For complex **4**, the fragmentation pattern observed is characteristic of the loss of one chlorine atom or one isodicyclopentadienyl ligand followed by the subsequent fragmentation of this ligand.[14,15] The spectra of the zirconium and hafnium complexes are not so amenable to a first-order analysis because of the immediate and systematic fragmentation of the π ligands.

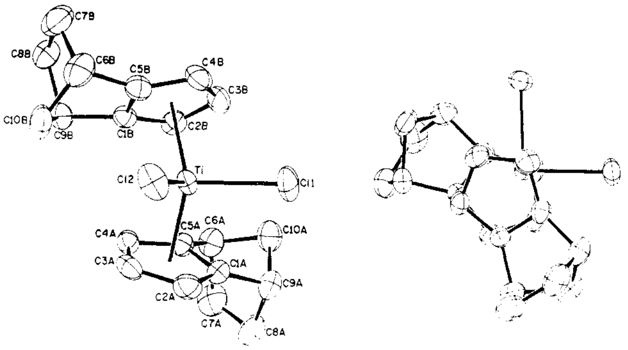


Figure 1. Two ORTEP representations of **4**. The view on the right is a projection of the isodicyclopentadiene ligands onto the $TiCl_2$ plane. Atoms are drawn with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table III. Experimental Crystallographic Data for 4 and 5

	4	5
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.296 (2)	11.409 (1)
b, Å	12.066 (1)	12.288 (1)
c, Å	7.077 (1)	7.195 (1)
α, deg	92.65 (1)	93.28 (1)
β, deg	108.13 (1)	108.10 (1)
γ, deg	71.73 (1)	71.06 (1)
V, Å^3	869	906
Z	2	2
mol wt	381.20	424.52
D_{calcd}, g cm^{-3}	1.46	1.56
bounding planes	{100}, {110}, ($\bar{1}$10), (011), (10$\bar{1}$)	{1$\bar{1}$0}, {001}, (100), ($\bar{1}\bar{1}$0), (1$\bar{1}\bar{1}$)
cryst size	0.14 mm × 0.28 mm × 0.30 mm	0.10 mm × 0.22 mm × 0.27 mm
linear abs coeff, cm^{-1}	7.93	8.91
transmissn factors	0.794–0.904	0.816–0.928
T, °C	19	19
2θ limits[a]	$4° \leq 2\theta \leq 55°$	$4° \leq 2\theta \leq 55°$
scan speed, deg min^{-1} in 2θ	2.0–24.0	2.0–24.0
bkgd time/scan time	0.5	0.5
scan range	($K\alpha_1$ – 1.0°) to ($K\alpha_2$ + 1.1°)	($K\alpha_1$ – 1.0°) to ($K\alpha_2$ + 1.0°)
data collected	$+h,\pm k,\pm l$	$+h,\pm k,\pm$l
unique data	4019	4173
reflctns obsd[b]	3137	3319
$R(F)$[c]	0.032	0.028
$R_w(F)$[d]	0.038	0.031
error in observn of unit wt, e	1.83	1.36

[a] Data were collected with a Syntex P$\bar{1}$ diffractometer using graphite-monochromated Mo Kα radiation. [b] Reflections were regarded as significant if $F_o^2 > 3\sigma(F_o)^2$. [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 $w = 1/\sigma^2(F_o)$.

X-ray Results

The molecular structure of $(isodiCp)_2TiCl_2$ (**4**) is shown in Figure 1. No drawing of the Zr complex is displayed since **4** and **5** are isostructural. The numbering schemes used for both molecules are the same. Final bond lengths and angles are listed in Tables IV and V. As expected, the geometry about the metal atom is pseudotetrahedral,

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Table IV. Final Bond Lengths (Å) for 4 and 5[a]

bond	4 (M = Ti)	5 (M = Zr)	bond	4 (M = Ti)	5 (M = Zr)
M–Cl1	2.366 (1)	2.446 (1)	M–Cl2	2.356 (1)	2.441 (1)
M–C1A	2.416 (2)	2.537 (3)	M–C1B	2.389 (2)	2.509 (3)
M–C2A	2.378 (2)	2.508 (3)	M–C2B	2.376 (2)	2.501 (3)
M–C3A	2.348 (2)	2.477 (3)	M–C3B	2.347 (2)	2.479 (4)
M–C4A	2.377 (2)	2.502 (3)	M–C4B	2.386 (2)	2.516 (4)
M–C5A	2.394 (2)	2.517 (3)	M–C5B	2.419 (2)	2.537 (3)
C1A–C2A	1.394 (2)	1.404 (4)	C1B–C2B	1.404 (3)	1.402 (3)
C2A–C3A	1.408 (3)	1.411 (4)	C2B–C3B	1.400 (3)	1.401 (4)
C3A–C4A	1.404 (3)	1.400 (4)	C3B–C4B	1.404 (4)	1.413 (4)
C4A–C5A	1.410 (3)	1.413 (3)	C4B–C5B	1.398 (3)	1.405 (4)
C5A–C1A	1.410 (3)	1.406 (3)	C5B–C1B	1.400 (3)	1.406 (3)
C5A–C6A	1.500 (3)	1.505 (4)	C5B–C6B	1.496 (3)	1.497 (4)
C6A–C7A	1.548 (3)	1.551 (4)	C6B–C7B	1.544 (4)	1.551 (4)
C7A–C8A	1.555 (4)	1.564 (5)	C7B–C8B	1.553 (4)	1.542 (5)
C8A–C9A	1.542 (4)	1.544 (4)	C8B–C9B	1.546 (3)	1.559 (4)
C9A–C1A	1.502 (3)	1.501 (4)	C9B–C1B	1.500 (3)	1.506 (3)
C9A–C10A	1.544 (3)	1.535 (4)	C9B–C10B	1.531 (3)	1.524 (4)
C6A–C10A	1.541 (3)	1.540 (4)	C6B–C10B	1.537 (3)	1.539 (4)
M···RC(A)[b]	2.061	2.204	M···RC(B)[b]	2.064	2.205

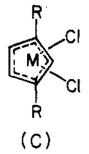
[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] RC is the ring centroid of the ring defined by atoms C1, C2, C3, C4, and C5.

Table V. Final Bond Angles (deg) for 4 and 5

	4		5	
angle	molecule A	molecule B	molecule A	molecule B
C2–C1–C5	108.7 (2)	108.3 (2)	108.4 (2)	108.9 (2)
C2–C1–C9	143.1 (2)	142.8 (2)	143.1 (3)	142.5 (2)
C5–C1–C9	106.8 (2)	106.9 (2)	107.0 (2)	106.7 (2)
C1–C2–C3	107.1 (2)	107.0 (2)	106.9 (2)	106.9 (2)
C2–C3–C4	109.3 (2)	109.2 (2)	109.5 (2)	109.2 (3)
C3–C4–C5	106.8 (2)	107.0 (2)	106.8 (2)	107.0 (2)
C4–C5–C1	108.0 (2)	108.5 (2)	108.4 (2)	108.0 (2)
C4–C5–C6	142.6 (2)	143.6 (2)	142.9 (2)	144.1 (3)
C1–C5–C6	107.0 (2)	106.7 (2)	106.6 (2)	106.6 (2)
C5–C6–C7	104.3 (2)	104.6 (2)	104.3 (2)	104.8 (3)
C5–C6–C10	100.1 (2)	100.7 (2)	100.2 (2)	100.5 (2)
C7–C6–C10	100.1 (2)	100.3 (2)	100.5 (2)	99.9 (3)
C6–C7–C8	103.9 (2)	103.3 (2)	103.2 (3)	103.8 (2)
C7–C8–C9	103.4 (2)	103.4 (2)	103.3 (3)	103.2 (2)
C8–C9–C10	100.5 (2)	100.4 (2)	100.5 (3)	100.2 (2)
C8–C9–C1	103.9 (2)	105.0 (2)	104.3 (2)	105.2 (2)
C1–C9–C10	100.5 (2)	100.1 (2)	100.6 (2)	100.0 (2)
C9–C10–C6	95.5 (2)	95.2 (2)	95.4 (2)	95.5 (2)

4		5	
Cl1–Ti–Cl2	92.94 (2)	Cl1–Zr–Cl2	95.00 (3)
Cl1–Ti–RC(A)	106.2	Cl1–Zr–RC(A)	106.4
Cl1–Ti–RC(B)	106.7	Cl1–Zr–RC(B)	106.8
Cl2–Ti–RC(A)	107.0	Cl2–Zr–RC(A)	107.4
Cl2–Ti–RC(B)	106.5	Cl2–Zr–RC(B)	107.0
RC(A)–Ti–RC(B)	131.0	RC(A)–Zr–RC(B)	129.0

with the tetrahedron defined by the two chlorine atoms and the centroids of the approximately planar five-membered rings of the isodicyclopentadiene ligands. Each isodiCp group is coordinated to the metal atom in an exo fashion, resulting in exo,exo stereochemistry for the complexes. A projection of the isodiCp ligands onto the MCl_2 plane shows that the five-membered rings are almost eclipsed and that the norbornane substituents on the rings (i.e., the remainder of the isodiCp ligand) are oriented away from each other and adopt a type I conformation (C).[16]



(C)

The metrical differences between these two structures can be attributed to the larger covalent radius of zirconium as compared to the radius for titanium. Table VI is a summary of some structural features for $(\eta^5\text{-RCp})_2MCl_2$ compounds with both M = Ti and M = Zr. As observed for other pairs of titanium and zirconium compounds,[16-24] the Zr–Cl distance is an average of 0.08 Å longer than the Ti–Cl bond, and the Zr–ring centroid distance is an average of 0.14 Å longer than the Ti–ring centroid distance. The only exception to this trend is for the $(\eta^5\text{-}C_5(CH_3)_4)_2(CH_2)_2MCl_2$ pair of structures where the Zr–Cl bond length and the Zr–ring centroid distance are both 0.12 Å longer than the analogous distance in the titanium compound.[17]

The angles about the metal atoms are also in the expected ranges with the ring centroid–Zr–ring centroid (129.0°) and Cl–Zr–Cl (95.0°) angles slightly smaller and larger than the respective angles in the titanium structure, 131.0° and 92.9°. The five-membered rings of the isodiCp groups are approximately planar, and the dihedral angles between the least-squares planes through these rings are 130.8° for **4** and 128.6° for **5**.

The metal–ring carbon distances indicate that the metal–ring interaction is asymmetric. These distances are in the ranges of 2.348–2.416 and 2.347–2.419 Å for the titanium compound and 2.477–2.537 and 2.479–2.537 Å for the zirconium compound. As noted for the other $(\eta^5\text{-RCp})_2MCl_2$ structures, the metal–ring carbon distance is greatest for the carbon atom bonded to the substituent group.[16] In this case the carbon atoms C1 and C5 of the five-membered ring are each bonded to a "substituent", but only one of these atoms attains the farthest distance from the metal atom. These are the atoms which, when viewed in projection in Figure 1, happen to be closest to the Cl atoms: C1A and C5B.

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Table VI. Metrical Parameters for Pairs of (η-RCp)$_2$MCl$_2$ Compounds (M = Ti and Zr)

compd	M–Cl, Å	M–RC,[d] Å	Cl–M–Cl, deg	RC–M–RC, deg	plane–M–plane,[c] deg	ref
(η^5-*t*-BuCp)$_2$ZrCl$_2$	2.457	2.217	94.2	128.6	125.8	16
(η^5-*t*-BuCp)$_2$TiCl$_2$	2.370	2.093	92.5	131.5	126.0	18
(η^5-C$_5$H$_4$CH$_3$)$_2$ZrCl$_2$	2.442	2.206	95.1	128.9	125.6	19
	2.443					
(η^5-C$_5$H$_4$CH$_3$)$_2$TiCl$_2$	2.359	2.067	93.2	130.2	126.7	20
	2.362					
(η^5-C$_5$H$_4$)$_2$(CH$_2$)$_3$ZrCl$_2$	2.451	2.192	96.9	129.5	129.8	21
	2.431	2.193				
(η^5-C$_5$H$_4$)$_2$(CH$_2$)$_3$TiCl$_2$	2.372	2.061	93.7	132.6	133.6	22
	2.364	2.060				
(η^5-C$_5$H$_5$)$_2$ZrCl$_2$[a]	2.446	2.196	97.1	129.0	126.6	23
	2.436	2.193				
(η^5-C$_5$H$_5$)$_2$TiCl$_2$[b]	2.367	2.060	94.4	130.9	128.3	
	2.361	2.056	94.6	131.0	128.7	24
	2.363	2.059				
	2.365	2.059				
(η^5-C$_5$(CH$_3$)$_4$)$_2$(CH$_2$)$_2$ZrCl$_2$	2.441	2.211	98.4	127.7	122.3	17
(η^5-C$_5$(CH$_3$)$_4$)$_2$(CH$_2$)$_2$TiCl$_2$	2.325	2.088	96.1	131.0	124.1	17
(isodiCp)$_2$ZrCl$_2$	2.446	2.204	95.0	129.0	128.6	this work
	2.441	2.205				
(isodiCp)$_2$TiCl$_2$	2.366	2.061	92.9	131.0	130.8	this work
	2.356	2.064				

[a] Only the ordered molecule is listed here. [b] This structure contains two molecules in the asymmetric unit. [c] Angle between the normals to the least-squares planes through the five-membered rings. [d] RC is ring centroid of the cyclopentadiene ring.

For each isodiCp ligand, the C6 and C9 atoms lie significantly out of the least-squares plane through the five-membered ring C1–C2–C3–C4–C5, and these atoms are directed away from the metal atom. In effect, the isodiCp ligand is bent about the C1–C5 bond, and a measure of the bending is described by the dihedral angle between the least-squares planes through atoms C1–C2–C3–C4–C5 and atoms C6–C5–C1–C9. For the titanium complex, these angles are 168.1° and 169.3°, while for the zirconium structure they are 168.6° and 169.4°.

Conclusion

Compounds **1**, **2**, and **3** round out the family of di(isodicyclopentadienyl) transition-metal complexes that have been prepared. Complexation of the isodicyclopentadienyl anion with group 4 transition metals shows a high π-facial stereoselectivity leading to the exo,exo stereoisomer. At the metal level, it could be of interest to compare the electronic effect of the isodicyclopentadienyl ligand to that of the pentamethylcyclopentadienyl ligand.[25]

Experimental Section

All manipulations were conducted under an argon atmosphere. The solvents were distilled from sodium benzophenone ketyl prior to use. Elemental analyses were performed by the "Service central de microanalyses du CNRS". ^{1}H and ^{13}C NMR spectra were recorded with a JEOL FX 100 spectrometer. Mass spectra were determined with a ZABZF instrument (V. G. Analytical, Manchester, England; electronic ionization = 8 kV; data system 20/50).

Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trien-6-yl)titanium Dichloride (4). A solution of isodicyclopentadiene (0.65 g, 5 mmol) in tetrahydrofuran (5 mL) was treated dropwise at −80 °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 (−80 °C) to titanium trichloride (0.38 g, 2.5 mmol), stirred for 14 h at room temperature, and poured into 20 mL of concentrated hydrochloric acid. The aqueous layer was extracted three times with chloroform. The combined organic layers were dried over magnesium sulfate and evaporated. The red solid was recrystallized from methylene chloride (saturated with hydrogen chloride) and hexane: yield 0.47 g (49%); mp 244 °C; MS, *m/z* (M$^+$) calcd 380.0578, obsd 380.0457; *m/z*, (relative intensity) 249 (25), 213 (13), 185 (15), 131 (45), 103 (100).

Anal. Calcd for C$_{20}$H$_{22}$TiCl$_2$: C, 63.02; H, 5.77; Ti, 12.58; Cl, 18.62. Found: C, 63.10; H, 5.94; Ti, 12.37; Cl, 18.91.

Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trien-6-yl)zirconium Dichloride (5). (Isodicyclopentadienyl)lithium was prepared as for titanium complex from 0.65 g (5 mmol) of isodicyclopentadiene in 15 mL of dimethoxyethane (DME) and 4 mL (5.4 mmol) of *n*-butyllithium in hexane. After 30 min of stirring at room temperature, the solution was cooled at −80 °C and treated gradually with zirconium tetrachloride (0.58 g, 2.5 mmol). The mixture was heated at the reflux temperature for 70 h. After the mixture was cooled, chloroform (25 mL) and 5 M hydrochloric acid (10 mL) were added. The aqueous layer was extracted with chloroform (3×). The combined organic layers were washed with water, dried, and evaporated. One recrystallization from dichloromethane–hexane afforded 400 mg (38%) of pale yellow crystals: mp 187 °C; MS, *m/z* (M$^+$) calcd 422.0142, obsd 422.0159; *m/z* (relative intensity) 386 (33), 358 (87), 291 (21), 255 (40), 227 (76), 131 (20), 103 (55), 83 (100).

Anal. Calcd for C$_{20}$H$_{22}$ZrCl$_2$: C, 56.58; H, 5.22; Zr, 21.49; Cl, 16.70. Found: C, 56.60; H, 5.26; Zr, 21.54; Cl, 17.07.

Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trien-6-yl)hafnium Dichloride (6). (Isodicyclopentadienyl)lithium prepared as mentioned above [0.65 g (5 mmol) of isodicyclopentadiene in 10 mL of DME and 4 mL (5.4 mmol) of *n*-butyllithium in hexane] was treated gradually at −80 °C with hafnium tetrachloride (0.8 g, 2.5 mmol). After a reflux period of 100 h, the cooled reaction mixture was treated with 25 mL of chloroform and 10 mL of 1 M hydrochloric acid. The aqueous layer was extracted three times with chloroform, and the combined organic layers were washed with water and dried. Evaporation of the solvent gave a yellow powder which was recrystallized from dichloromethane–hexane. Powder: 350 mg (27%); mp 182 °C; MS, *m/z* (M$^+$) calcd 512.0508 and 512.0566, obsd 512.0515 and 512.0558; *m/z* (relative intensity) 476 (24), 448 (43) 379 (26), 317 (54), 104 (100), 83 (97).

Anal. Calcd for C$_{20}$H$_{22}$HfCl$_2$: C, 46.93; H, 4.30; Hf, 34.90; Cl, 13.86. Found: C, 46.87; H, 4.51; Hf, 33.85; Cl, 14.10.

X-ray Crystallographic Analysis of 4. Preliminary examination of the diffraction pattern of the dark red platelike crystals of this compound revealed $\bar{1}$ Laue symmetry, restricting the space group possibilities to *P*1 or *P*$\bar{1}$. The unit-cell constants were determined by the least-squares fit of the diffractometer setting angles for 28 reflections in the 2θ range 21–30° with Mo Kα radiation (λ(K$\bar{\alpha}$) = 0.710 69 Å). The θ–2θ scan method was used for intensity measurement. The data were corrected for Lorentz and polarization effects and put onto an absolute scale by means of a Wilson plot.[26] The following reflections saturated the detector

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[25] Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

Table VII. Final Positional Parameters for 4

atom	x^a	y	z	B_{eq},^{b} Å^2
Ti	0.21655 (3)	0.23563 (3)	0.30307 (5)	2.19 (2)
Cl1	0.09556 (6)	0.29249 (5)	−0.03522 (7)	3.80 (3)
Cl2	0.40880 (6)	0.12984 (5)	0.22765 (8)	3.59 (3)
C1A	0.04751 (21)	0.14385 (18)	0.24524 (29)	2.86 (9)
C2A	0.16424 (23)	0.05831 (17)	0.24696 (32)	3.25 (10)
C3A	0.25288 (21)	0.04986 (16)	0.44034 (31)	2.99 (9)
C4A	0.19225 (20)	0.13088 (17)	0.55755 (29)	2.66 (9)
C5A	0.06441 (19)	0.19086 (17)	0.43437 (28)	2.55 (9)
C6A	−0.06911 (22)	0.26345 (20)	0.44009 (35)	3.58 (11)
C7A	−0.14035 (25)	0.17315 (25)	0.44288 (41)	4.81 (14)
C8A	−0.15902 (26)	0.12314 (26)	0.23297 (41)	5.00 (15)
C9A	−0.09641 (23)	0.18978 (21)	0.13215 (35)	4.05 (12)
C10A	−0.13355 (24)	0.31028 (21)	0.22100 (37)	4.34 (12)
C1B	0.29578 (19)	0.33161 (16)	0.59582 (27)	2.42 (9)
C2B	0.16258 (20)	0.39368 (16)	0.50643 (31)	2.90 (10)
C3B	0.15080 (23)	0.43964 (17)	0.32101 (33)	3.52 (10)
C4B	0.27544 (25)	0.40844 (18)	0.29605 (31)	3.49 (11)
C5B	0.36491 (20)	0.34289 (17)	0.46820 (30)	2.82 (10)
C6B	0.50764 (22)	0.29701 (22)	0.58415 (36)	4.02 (13)
C7B	0.53098 (27)	0.39039 (25)	0.73544 (39)	4.89 (15)
C8B	0.45382 (25)	0.38016 (22)	0.87760 (35)	4.04 (13)
C9B	0.39592 (22)	0.28136 (18)	0.79235 (29)	3.07 (10)
C10B	0.50711 (23)	0.20204 (21)	0.72113 (34)	3.96 (11)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the equivalent isotropic thermal parameter is $B_{eq} = {}^8/_3\pi^2\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

during data collection and are omitted from the data set: (020), $(1\bar{1}0)$, and (110). Six standard reflections were measured after every 100 reflections and gave no indication of crystal decomposition.

Successful solution and refinement of the structure was performed in space group $P\bar{1}$. The positions of the titanium atom and the two chlorine atoms were located by the Patterson method. These three atoms were then phased on in the DIRDIF procedure,[27] with the result that both isodicyclopentadiene rings were clearly visible on an electron density map. The SHELX-76 package[28] was used for all full-matrix least-squares refinements. Isotropic refinement of the non-hydrogen atoms converged to an R factor of 0.123. An absorption correction was applied at this point by the Gaussian grid method with an 8 × 8 × 8 grid. After a cycle of anisotropic refinement, all 22 hydrogen atoms were easily located on a difference electron density map. The hydrogen atoms were included in the model as fixed contributions in their calculated positions with C–H = 0.98 Å and $B_H = B_{C(iso)} + 1.0$ Å^2. The final refinement cycle yielded agreement indices of $R = 0.032$ and $R_w = 0.038$ (based on F) for the 3137 intensities with $F_o{}^2 > 3\sigma(F_o{}^2)$ and the 208 variables (anisotropic nonhydrogen atoms, hydrogen atoms fixed). The maximum and minimum peak heights in the final difference electron density map are 0.36 and −0.31 e/Å^3. Scattering factors for the titanium atom and for the other atoms are from the usual sources[29] and include real and imaginary components for the anomalous dispersion correction. Table III contains further crystallographic details for this structure and for structure 5. Final positional parameters with equivalent isotropic thermal parameters are listed in Table VII.

Table VIII. Final Positional Parameters for 5

atom	x^a	y	z	B_{eq},^{b} Å^2
Zr	0.21988 (2)	0.23312 (2)	0.29335 (3)	2.28 (1)
Cl1	0.09258 (8)	0.29409 (6)	−0.04769 (9)	4.21 (4)
Cl2	0.41962 (7)	0.12252 (6)	0.22086 (10)	4.03 (4)
C1A	0.04477 (26)	0.13976 (21)	0.24439 (36)	3.01 (12)
C2A	0.16000 (29)	0.05200 (22)	0.24415 (41)	3.62 (14)
C3A	0.24904 (26)	0.04321 (21)	0.43384 (40)	3.25 (12)
C4A	0.19096 (24)	0.12454 (21)	0.55045 (36)	2.79 (11)
C5A	0.06386 (24)	0.18539 (20)	0.43105 (34)	2.65 (11)
C6A	−0.06811 (26)	0.26087 (24)	0.43808 (43)	3.71 (14)
C7A	−0.14149 (31)	0.17517 (32)	0.44266 (52)	5.04 (19)
C8A	−0.16292 (32)	0.12637 (32)	0.23350 (50)	5.26 (19)
C9A	−0.09796 (28)	0.18836 (26)	0.13509 (42)	4.09 (15)
C10A	−0.13158 (29)	0.30694 (26)	0.22328 (45)	4.50 (16)
C1B	0.29732 (24)	0.33561 (19)	0.59490 (34)	2.62 (11)
C2B	0.16540 (25)	0.39778 (20)	0.50664 (38)	3.16 (12)
C3B	0.15545 (31)	0.44451 (21)	0.32714 (43)	4.00 (13)
C4B	0.28078 (31)	0.41319 (23)	0.30470 (41)	3.86 (16)
C5B	0.36875 (26)	0.34598 (22)	0.47281 (37)	3.04 (13)
C6B	0.50981 (28)	0.29837 (29)	0.58944 (45)	4.41 (17)
C7B	0.53270 (34)	0.38878 (32)	0.74398 (50)	5.38 (20)
C8B	0.45467 (32)	0.37959 (27)	0.87975 (43)	4.42 (17)
C9B	0.39512 (27)	0.28381 (22)	0.78862 (37)	3.28 (13)
C10B	0.50573 (28)	0.20510 (25)	0.71897 (43)	4.32 (15)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the equivalent isotropic thermal parameter is $B_{eq} = {}^8/_3\pi^2\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

X-ray Crystallographic Analysis of 5. The crystals of 5 are pale yellow rectangular plates. Preliminary examination of the diffraction pattern revealed $\bar{1}$ Laue symmetry and that the unit cell is isomorphous with that of 4. The cell constants were determined by the least-squares fit of the diffractometer setting angles for 28 reflections in the 2θ range 21–29° with Mo Kα radiation.

Data collection was done with the θ–2θ scan method. Six standard reflections were measured after every 100 reflections, and there was no indication of crystal decomposition. The data were corrected for Lorentz and polarization effects and put onto an absolute scale by means of a Wilson plot.[26]

Since the structure is isomorphous with the titanium compound, the coordinates of the titanium complex were used as a starting model. As before, the SHELX-76 package[28] was used for all full-matrix least-squares refinements. After isotropic refinement of the model converged, an absorption correction was applied to the data by the Gaussian grid method with an 8 × 8 × 8 grid. All 22 hydrogen atoms were easily located on a difference electron density map after a cycle of anisotropic refinement. Hydrogen atoms were then included in the model as fixed contributions in their calculated positions with C–H = 0.98 Å and $B_H = B_{C(iso)} +$ 1.0 Å^2. The final refinement cycle resulted in agreement indices of $R = 0.028$ and $R_w = 0.031$ (based on F) for the 3319 intensities with $F_o{}^2 > 3\sigma(F_o{}^2)$ and the 208 variables (anisotropic non-hydrogen atoms and hydrogen atoms fixed). Three reflections were omitted during the final refinement stages as the F_c values were significantly greater than F_o values; these reflections are $(1\bar{1}0)$, (020), and (011). The final difference electron density map is featureless with maximum and mimimum peak heights of 0.41 and −0.33 e/Å^3. Scattering factors are from the usual sources and include anomalous dispersion terms for all the non-hydrogen atoms.[29] Final positional parameters and equivalent isotropic thermal parameters are listed in Table VIII.

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Supplementary Material Available: Tables of calculated hydrogen atom parameters, anisotropic thermal parameters, and least-squares planes for structures 4 and 5 (Tables IX–XIV) (8 pages); listings of observed and calculated structure factors for 4 and 5 (Tables XV and XVI) (28 pages). Ordering information is given on any current masthead page.

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(26) The programs used for data reduction are from the CRYM crystallographic computing package: Duchamp, D. J.; Trus, B. L.; Westphal, B. J. California Institute of Technology, Pasadena, CA, 1964, and modified by G. G. Christoph at The Ohio State University, Columbus, OH.

(27) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van den Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Haltiwanger, R. C. DIRDIF, Direct Methods for Difference Structures; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1983.

(28) Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination; University Chemical Laboratory: Cambridge, England, 1976.

(29) Scattering factors for the C, H, and Cl atoms were those supplied by SHELX-76. The values for the Ti atom and the Zr atom were obtained from: *International Tables for X-ray Crystallography*; Birmingham, England, 1974; Vol. IV.