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Synthesis and molecular structures of titanocene, zirconocene, and uranocene dichlorides containing 1,2-di-*tert*-butylcyclopentadienyl ligands

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Abstract

The 1,2-di-*tert*-butylcyclopentadienyl anion (**1**) has been used to prepare 1,1',2,2'-tetra-*tert*-butyltitanocene dichloride (**5**), 1,1',2,2'-tetra-*tert*-butylzirconocene dichloride (**6**), and 1,1',2,2'-tetra-*tert*-butyluranocene dichloride (**7**). The bent metallocene structures of **5–7** have been confirmed by X-ray crystallography, and illustrate that the 1,2-di-*tert*-butylcyclopentadienyl ligands are arranged with all four *tert*-butyl groups in the open part of the wedge between the two canted cyclopentadienyl rings, but that steric interactions between the substituents afford a conformationally dictated C₂ symmetry for the molecules. In solution compounds **5** and **6** exhibit NMR spectra consistent with a facile dynamic process involving exchange between *tert*-butyl sites that are inequivalent in the solid state. The nature of this site exchange is discussed, and comparisons are made with related metallocene dichlorides of Group 4 metals.

Keywords: Titanium; Zirconium; Uranium; Cyclopentadienyls; Fluxional molecules

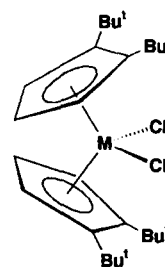
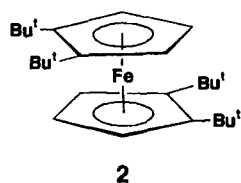
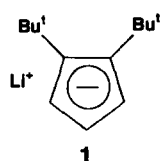
1. Introduction

Transition metal complexes containing cyclopentadienyl ligands with bulky substituents have been a subject of considerable recent interest. A large range of metallocenes containing such ligands with sterically demanding substituents such as 1,3-bis(trimethylsilyl)-, 1,2,4-tris(trimethylsilyl)-, tetra(isopropyl)-, 1,2,3-tri-*tert*-butyl-, 1,2,4-tri-*tert*-butyl-, and 1,3-diphenyl-cyclopentadienyl ligands have been prepared and studied [1–12]. Incorporation of such ligands can result in significant barriers to rotation about the metal–cyclopentadienyl bond, and the bulky substituents often impart enhanced kinetic stability to complexes of these ligands. There is also a specific interest in metallocenes of the Group 4 metals, particularly chiral *ansa*-metallocenes of C₂ symmetry, owing to their use as catalyst

precursors for the homogeneous polymerization of ethylene, and the stereoregular polymerization of propylene [13–16].

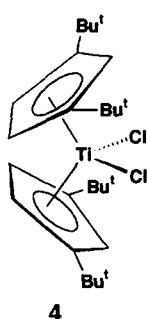
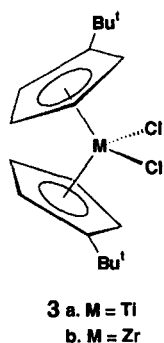
We have become interested recently in the synthesis and properties of transition metal complexes containing the 1,2-di-*tert*-butylcyclopentadienyl ligand (**1**), and have reported the synthesis of this anion [17] and a number of its main group [18] and transition metal [17–19] complexes. In the structurally characterized ferrocene derivative (**2**) the cyclopentadienyl rings are, of course, parallel, and the rings adopt the expected conformation in which the *tert*-butyl groups are as far removed from each other as possible [17]. This results in a ground state of overall C_{2h} symmetry controlled by the conformational preference of the two parallel 1,2-di-*tert*-butylcyclopentadienyl ligands. However, for bent metallocenes in which the two cyclopentadienyl rings are mutually canted to give a wedge-like structure, *tert*-butyl groups (and other bulky substituents) exhibit a strong preference to occupy sites in the open part of the wedge, but repulsions between *tert*-butyl substituents

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6 M = Zr

7 M = U



Here we report a continuation of this series to the preparation and molecular structures of the bent metallocene dichlorides of titanium and zirconium containing the 1,2-di-*tert*-butylcyclopentadienyl ligand, and further extension to the isostructural analogue of uranium.

2. Results and discussion

Reaction of lithium 1,2-di-*tert*-butylcyclopentadienide (**1**) [17] with $\text{TiCl}_3 \cdot 3\text{THF}$ in tetrahydrofuran (THF) at reflux for 4 h followed by oxidation of Ti(III) to Ti(IV) with HCl, affords 1,1',2,2'-tetra-*tert*-butyltitanocene dichloride (**5**) in 30% yield. One reported preparation of the corresponding 1,1',3,3'-tetra-*tert*-butyltitanocene dichloride (**4**) uses TiCl_4 as the titanium source [23], but using this approach with **1** resulted only in intractable products. However, the corresponding 1,1',2,2'-tetra-*tert*-butylzirconocene dichloride (**6**) was afforded directly from $\text{ZrCl}_4 \cdot 2\text{THF}$ and two equivalents of **1**, in a yield of 24%. While Jordan and coworkers

on different rings cause the rings to adopt a mutually staggered conformation. This conformational control has already been observed in solid state structures of titanocene and zirconocene dichlorides (**3**) [20,21] containing mono-*tert*-butylcyclopentadienyl ligands, affording molecules in which an overall C_2 symmetric structure is achieved by a conformationally controlled self-assembly of two achiral cyclopentadienyl ligands. In the corresponding titanocene complex containing 1,3-di-*tert*-butylcyclopentadienyl ligands (**4**) [22], the conformational preference of the substituents leads to an unexpected conformer in the solid state in which the *tert*-butyl groups are almost eclipsed.

Table 1
Crystallographic determinations for **5**, **6**, and **7**

	5	6	7
Chemical formula	$\text{C}_{26}\text{H}_{42}\text{Cl}_2\text{Ti}$	$\text{C}_{26}\text{H}_{42}\text{Cl}_2\text{Zr}$	$\text{C}_{26}\text{H}_{42}\text{Cl}_2\text{U}$
Formula weight	473.4	516.7	663.5
Lattice type	orthorhombic	orthorhombic	orthorhombic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>
a (Å)	16.379(4)	16.394(1)	16.431(1)
b (Å)	13.185(3)	13.309(9)	13.607(7)
c (Å)	24.017(6)	24.241(3)	24.493(6)
V (Å ³)	5182(5)	5289.8(8)	5476(3)
Z	8	8	8
ρ_{calc} (g cm ⁻³)	1.213	1.298	1.610
T (K)	297	296	298
($\text{MO K } \alpha$) (cm ⁻¹)	5.46	6.28	61.33
Radiation		Mo K α ($\lambda = 0.71073$ Å)	
$R(F)$, %	5.94 ^a	4.77 ^a	4.31 ^b
$R(wF)$, %	6.93 ^a	5.48 ^a	8.71 ^b

^a Quantity minimized is $\sum w\Delta^2$; $R = \sum \Delta / \sum (F_o)$; $R(w) = \sum \Delta w^{1/2} / \sum (F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$.

^b Quantity minimized is $R(wF^2) = \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^2]^2$; $R = \sum \Delta / \sum (F_o)$, $\delta = |(F_o - F_c)|$.

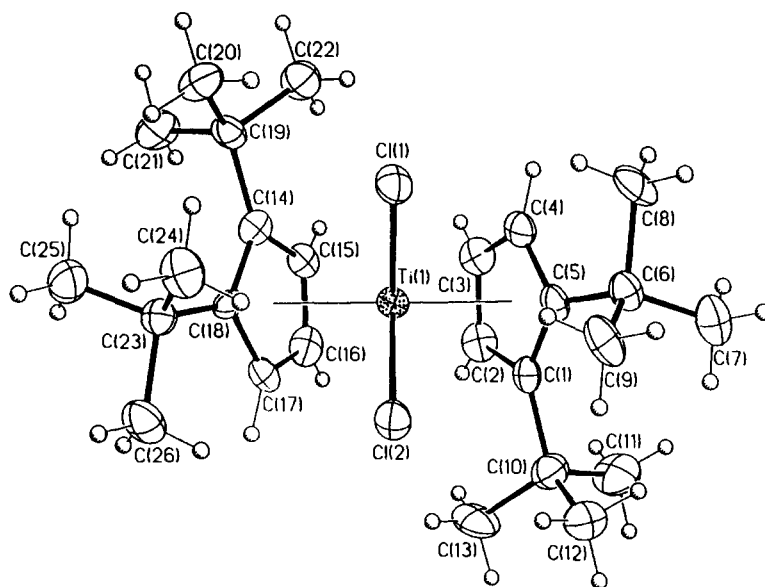


Fig. 1. Molecular structure of $[\text{Ti}(1,2\text{-C}_5\text{H}_3\text{Bu}_2)_2\text{Cl}_2]$ (**5**) drawn with 35% thermal ellipsoids. Selected bond distances and angles: $\text{Ti}(1)\text{-CNT}(1)$, 2.128(10) Å; $\text{Ti}(1)\text{-CNT}(2)$, 2.121(10) Å; $\text{Ti}(1)\text{-Cl}(1)$, 2.337(3) Å; $\text{Ti}(1)\text{-Cl}(2)$, 2.359(3) Å; $\text{CNT}(1)\text{-Ti}(1)\text{-CNT}(2)$, 132.1(3)°; $\text{Cl}(1)\text{-Ti}(1)\text{-Cl}(2)$, 93.3(1)°.

ers have been successful in increasing the yields of zirconocene dihalides by the reaction of the cyclopentadiene itself with $\text{Zr}(\text{NMe}_2)_4$ followed by reaction of the intermediate $\text{ZrCp}_2(\text{NMe}_2)_2$ with HCl [24], attempts to increase the yield of **6** by this method have been unsuccessful in our laboratory. A similar reaction of **1** with UCl_4 afforded the very air- and moisture-sensitive uranocene dichloride **7** in 32% yield. Notably, this latter

reaction was carried out in the presence of an excess of **1**, but no tris(cyclopentadienyl)uranium chloride was obtained, presumably due to the steric effects of the ring substituents precluding incorporation of the third ring.

Single crystal X-ray diffraction analyses of compounds **5–7** have been carried out. Details summarizing the structure determinations and refinement are presented in Table 1, and ORTEP representations of the three

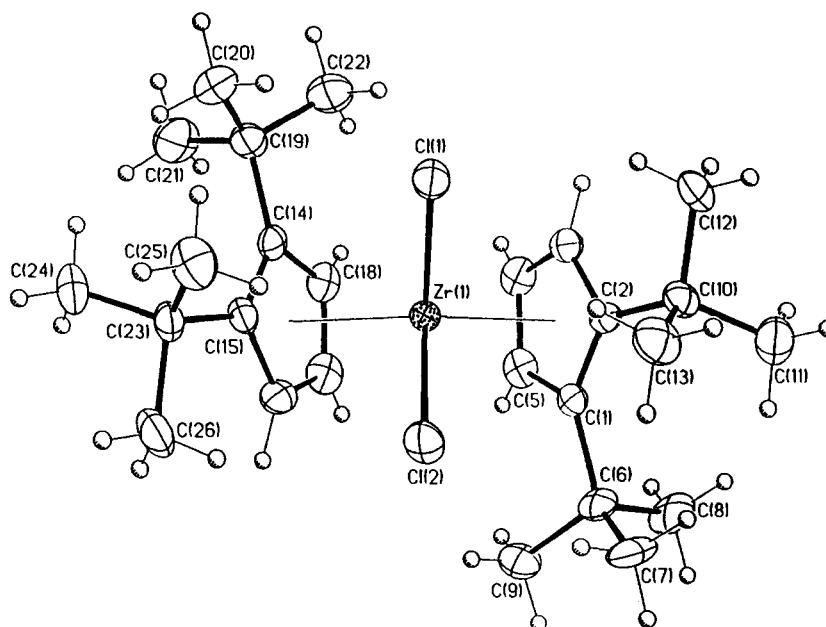


Fig. 2. Molecular structure of $[\text{Zr}(1,2\text{-C}_5\text{H}_3\text{Bu}_2)_2\text{Cl}_2]$ (**6**) drawn with 35% thermal ellipsoids. Selected bond distances and angles: $\text{Zr}(1)\text{-CNT}(1)$, 2.236(10) Å; $\text{Zr}(1)\text{-CNT}(2)$, 2.247(10) Å; $\text{Zr}(1)\text{-Cl}(1)$, 2.449(2) Å; $\text{Zr}(1)\text{-Cl}(2)$, 2.430(2) Å; $\text{CNT}(1)\text{-Zr}(1)\text{-CNT}(2)$, 128.7(4)°; $\text{Cl}(1)\text{-Zr}(1)\text{-Cl}(2)$, 95.1(1)°.

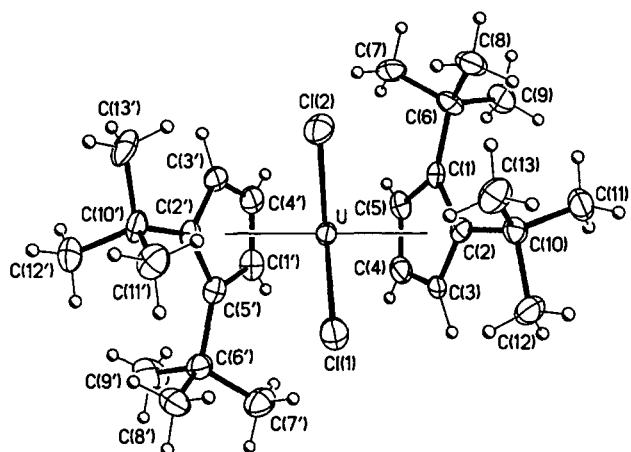


Fig. 3. Molecular structure of $[U(1,2-C_5H_3Bu_2)_2Cl_2]$ (7) drawn with 35% thermal ellipsoids. Selected bond distances and angles: U–CNT(1), 2.427(4) Å; U–CNT(2), 2.435(4) Å; U–Cl(1), 2.591(4) Å; U–Cl(2), 2.576(4) Å; CNT(1)–U–CNT(2), 123.3(8)°; Cl(1)–U–Cl(2), 97.6(1)°.

molecules are shown in Figs. 1–3. Fractional atomic coordinates for the three molecules appear in Tables 2–4, and bond lengths and angles for each compound are shown in Tables 5–7.

Table 2

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for 5

	x	y	z	U_{eq}^a
Ti(1)	1203(1)	1111(1)	6817(1)	33(1)
Cl(1)	199(2)	2309(2)	7031(1)	47(1)
Cl(2)	2164(1)	2356(2)	6554(1)	48(1)
C(1)	1407(6)	578(7)	5816(4)	37(4)
C(2)	1292(7)	–252(7)	6178(4)	48(4)
C(3)	499(7)	–224(8)	6391(4)	49(4)
C(4)	127(6)	645(8)	6183(4)	44(4)
C(5)	661(5)	1166(8)	5817(4)	39(4)
C(6)	339(6)	2035(7)	5445(4)	44(4)
C(7)	301(7)	1663(8)	4844(4)	69(5)
C(8)	–554(5)	2284(9)	5617(5)	67(5)
C(9)	824(6)	3020(7)	5507(5)	63(5)
C(10)	2198(6)	595(9)	5456(5)	55(4)
C(11)	2034(7)	–203(9)	4985(5)	83(6)
C(12)	2438(7)	1586(9)	5177(5)	73(5)
C(13)	2927(6)	229(9)	5803(5)	73(5)
C(14)	1014(6)	748(7)	7847(4)	39(4)
C(15)	1155(6)	–122(7)	7517(4)	39(4)
C(16)	1943(7)	–88(8)	7297(4)	53(4)
C(17)	2296(6)	803(8)	7465(4)	44(4)
C(18)	1756(5)	1330(7)	7811(4)	34(4)
C(19)	248(5)	752(7)	8215(4)	45(4)
C(20)	–69(6)	1782(7)	8406(4)	59(4)
C(21)	455(7)	101(9)	8723(4)	70(5)
C(22)	–477(6)	236(8)	7913(5)	63(5)
C(23)	2041(6)	2286(8)	8133(4)	45(4)
C(24)	1561(6)	3243(7)	8015(4)	60(5)
C(25)	2048(7)	2045(9)	8766(4)	67(5)
C(26)	2952(6)	2508(8)	7989(5)	63(4)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for 6

	x	y	z	U_{eq}^a
Zr(1)	3799.1(4)	1181.1(4)	3168.6(3)	28.8(2)
Cl(1)	2764(1)	2420(1)	3429(1)	47(1)
Cl(2)	4848(1)	2414(1)	2961(1)	47(1)
C(1)	3995(4)	743(5)	2122(3)	31(2)
C(2)	3252(4)	1345(5)	2139(3)	30(2)
C(3)	2706(4)	792(5)	2479(3)	38(3)
C(4)	3049(5)	–106(6)	2660(3)	47(3)
C(5)	3848(4)	–124(5)	2446(3)	41(2)
C(6)	4767(4)	771(5)	1765(3)	43(3)
C(7)	5064(4)	1803(6)	1573(3)	59(3)
C(8)	4591(5)	127(7)	1254(3)	68(3)
C(9)	5488(4)	295(6)	2077(3)	59(3)
C(10)	2956(4)	2266(5)	1824(3)	41(2)
C(11)	2975(5)	2027(7)	1200(3)	65(3)
C(12)	2062(4)	2494(6)	1968(3)	56(3)
C(13)	3444(4)	3225(6)	1953(3)	60(3)
C(14)	3616(4)	561(5)	4189(3)	37(2)
C(15)	4360(4)	1140(5)	4190(3)	36(2)
C(16)	4903(4)	645(6)	3829(3)	44(3)
C(17)	4541(5)	–212(6)	3613(3)	48(3)
C(18)	3744(5)	–258(5)	3822(3)	43(3)
C(19)	2817(4)	566(6)	4543(3)	47(3)
C(20)	2564(5)	1551(6)	4806(6)	63(3)
C(21)	2971(5)	–220(7)	5002(3)	80(4)
C(22)	2098(5)	193(7)	4191(3)	70(4)
C(23)	4657(4)	2010(5)	4557(3)	41(3)
C(24)	4677(5)	1647(6)	5155(3)	62(3)
C(25)	4165(5)	2994(5)	4500(3)	60(3)
C(26)	5552(4)	2286(6)	4401(3)	61(3)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The three molecules are isomorphous, and each has overall C_2 symmetry in the solid state. Figs. 1–3 show perspectives viewed directly down the C_2 axis that bisects the Cl–M–Cl angle; views of one enantiomer are presented for 5 and 6, and a view of the other enantiomer has been chosen for 7. As predicted, the conformational preferences of the *tert*-butyl groups control the ground state conformations of the cyclopentadienyl rings. The structures contain no particularly unexpected features. As expected, the metal–chlorine and metal–ring centroid distances increase (Figs. 1–3) as the metal gets larger on going from $M = Ti < Zr < U$. The Cl–M–Cl angle also increase in the same sense, but the angle subtended by the ring centroids at the metal center actually decreases as $M = Ti > Zr > U$. Presumably, when the metal is smaller, there are greater interactions between the ring substituents and the chlorine ligands such that the rings splay open to a wider angle. As the metal centers get larger, this interaction is diminished, and the inter-ring angle relaxes to a more acute value. Distances and angle within the 1,2-di-*tert*-butylcyclopentadienyl ligands are similar to those found in other crystallographically characterized complexes of

Table 4

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **7**

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
U	−3775(3)	3695.2(4)	1858(2)	35(1)
C1(1)	−2623(2)	2479(3)	1603(1)	59(1)
C1(2)	−4892(2)	2414(3)	2054(1)	60(1)
C(1)	−3976(7)	4254(11)	2942(5)	34(4)
C(2)	−3204(7)	3673(11)	2927(5)	37(4)
C(3)	−2654(8)	4218(13)	2608(5)	50(5)
C(4)	−3021(9)	5082(13)	2414(5)	59(5)
C(5)	−3808(8)	5084(11)	2618(4)	43(4)
C(6)	−4762(8)	4219(12)	3273(5)	51(4)
C(7)	−5465(7)	4645(12)	2932(6)	67(5)
C(8)	−5039(8)	3183(12)	3462(6)	67(5)
C(9)	−4621(8)	4871(13)	3773(5)	88(6)
C(10)	−2951(8)	2745(12)	3258(5)	46(4)
C(11)	−2951(8)	2983(12)	3865(5)	68(5)
C(12)	−2026(7)	2500(12)	3120(5)	64(5)
C(13)	−3398(9)	1822(13)	3121(6)	67(5)
C(1')	−3651(7)	4473(10)	823(6)	39(4)
C(2')	−4382(7)	3891(10)	801(5)	39(4)
C(3')	−4950(8)	4325(11)	1165(5)	43(4)
C(4')	−4593(8)	5170(12)	1397(5)	56(5)
C(5')	−3802(8)	5240(11)	1193(5)	50(4)
C(6')	−2835(8)	4514(12)	479(5)	53(5)
C(7')	−2127(8)	4852(13)	845(6)	71(5)
C(8')	−2551(8)	3547(12)	220(6)	72(6)
C(9')	−2980(9)	5287(13)	37(6)	96(7)
C(10')	−4647(8)	3036(12)	436(5)	51(4)
C(11')	−4131(8)	2090(11)	491(6)	65(5)
C(12')	−4656(9)	3401(12)	−169(5)	78(6)
C(13')	−5536(8)	2719(11)	572(6)	66(5)

^a Equivalent isotropic *U* is defined as one third of the trace of the orthogonalized U_{ij} tensor.

this ligand [17,19]. Finally, the two cyclopentadienyl rings in each complex **5–7** are almost completely eclipsed with the *tert*-butyl group on each ring located in the widest part of the wedge eclipsing its counterpart on the second ring.

It is clear that, in solution, the overall C_2 symmetry found in the solid state for compounds **5** and **6** is not maintained on the NMR timescale; were this the case, two different *tert*-butyl environments would be expected, as shown in Fig. 4. However, the ¹H NMR spectrum of titanocene **5** exhibits one sharp singlet (1.50 ppm) for all of the *tert*-butyl protons. Similarly, a doublet (6.30 ppm, ³ $J_{\text{HH}} = 3.2$ Hz, 4H) and a triplet (5.69 ppm, ³ $J_{\text{HH}} = 3.2$ Hz, 2H) are observed for the cyclopentadienyl ring protons. The ¹H NMR spectrum of zirconocene **6** is nearly identical to that of **5** with one sharp singlet (1.49 ppm) for the *tert*-butyl protons, and a doublet (6.21 ppm, ³ $J_{\text{HH}} = 3.2$ Hz, 4H) and a triplet (5.64 ppm, ³ $J_{\text{HH}} = 3.2$ Hz, 2H) for the cyclopentadienyl ring protons. These ¹H NMR spectra are invariant down to -80 °C. The ¹³C{¹H} NMR spectra for **5** and **6** each contain five singlets, two for the methyl and quaternary carbons of the equivalent *tert*-butyl groups and three for

Table 5

Bond lengths (Å) and angles (deg) for **5**

Ti(1)–Cl(1)	2.337(3)	Ti(1)–Cl(2)	2.359(3)
Ti(1)–C(1)	2.528(9)	Ti(1)–C(2)	2.368(10)
Ti(1)–C(3)	2.341(10)	Ti(1)–C(4)	2.410(10)
Ti(1)–C(5)	2.563(9)	Ti(1)–C(14)	2.537(9)
Ti(1)–C(15)	2.339(9)	Ti(1)–C(16)	2.302(11)
Ti(1)–C(17)	2.407(10)	Ti(1)–C(18)	2.570(9)
C(1)–C(2)	1.411(13)	C(10)–C(5)	1.447(13)
C(1)–C(10)	1.558(14)	C(2)–C(3)	1.395(15)
C(3)–C(4)	1.391(14)	C(4)–C(5)	1.419(14)
C(5)–C(6)	1.545(14)	C(6)–C(7)	1.525(15)
C(6)–C(8)	1.555(13)	C(6)–C(9)	1.530(14)
C(10)–C(11)	1.569(16)	C(10)–C(12)	1.519(16)
C(10)–C(13)	1.534(15)	C(14)–C(15)	1.414(13)
C(14)–C(18)	1.440(13)	C(14)–C(19)	1.535(13)
C(15)–C(16)	1.394(15)	C(16)–C(17)	1.370(15)
C(17)–C(18)	1.399(13)	C(18)–C(23)	1.550(13)
C(19)–C(20)	1.525(14)	C(19)–C(21)	1.529(15)
C(19)–C(22)	1.548(14)	C(23)–C(24)	1.513(14)
C(23)–C(25)	1.554(14)	C(23)–C(26)	1.559(13)
Cl(1)–Ti(1)–Cl(2)	93.3(1)	Cl(1)–Ti(1)–C(1)	119.3(2)
Cl(2)–Ti(1)–Cl(1)	81.4(2)	Cl(1)–Ti(1)–C(2)	134.3(3)
Cl(2)–Ti(1)–C(1)	108.3(3)	C(1)–Ti(1)–C(2)	33.3(3)
Cl(1)–Ti(1)–C(3)	104.9(3)	Cl(2)–Ti(1)–C(3)	137.3(3)
C(1)–Ti(1)–C(3)	55.9(3)	C(2)–Ti(1)–C(3)	34.5(4)
Cl(1)–Ti(1)–C(4)	78.3(2)	Cl(2)–Ti(1)–C(4)	119.8(2)
C(1)–Ti(1)–C(4)	54.8(3)	C(2)–Ti(1)–C(4)	56.0(4)
C(3)–Ti(1)–C(4)	34.0(3)	Cl(1)–Ti(1)–C(5)	86.7(2)
Cl(2)–Ti(1)–C(5)	87.7(2)	C(1)–Ti(1)–C(5)	33.0(3)
C(3)–Ti(1)–C(5)	55.6(3)	C(3)–Ti(1)–C(5)	56.0(3)
C(4)–Ti(1)–C(5)	33.0(3)	Cl(1)–Ti(1)–C(14)	80.1(2)
Cl(2)–Ti(1)–C(14)	118.3(2)	C(1)–Ti(1)–C(14)	153.0(3)
C(3)–Ti(1)–C(14)	119.7(3)	C(3)–Ti(1)–C(14)	102.9(3)
C(4)–Ti(1)–C(14)	118.6(3)	C(5)–Ti(1)–C(14)	151.2(3)
Cl(1)–Ti(1)–C(15)	106.8(3)	Cl(2)–Ti(1)–C(15)	134.3(3)
C(1)–Ti(1)–C(15)	119.6(3)	C(3)–Ti(1)–C(15)	86.5(3)
C(3)–Ti(1)–C(15)	77.0(3)	C(4)–Ti(1)–C(15)	104.6(3)
C(5)–Ti(1)–C(15)	132.9(3)	C(14)–Ti(1)–C(15)	33.4(3)
Cl(1)–Ti(1)–C(16)	136.4(3)	Cl(2)–Ti(1)–C(16)	105.1(3)
C(1)–Ti(1)–C(16)	102.5(3)	C(3)–Ti(1)–C(16)	76.8(4)
C(3)–Ti(1)–C(16)	87.8(4)	C(4)–Ti(1)–C(16)	121.8(4)
C(5)–Ti(1)–C(16)	132.2(4)	C(14)–Ti(1)–C(16)	56.4(3)
Cl(1)–Ti(1)–C(17)	155.5(3)	Cl(2)–Ti(1)–C(17)	119.7(3)
C(1)–Ti(1)–C(17)	55.2(3)	C(3)–Ti(1)–C(17)	118.0(3)
C(3)–Ti(1)–C(17)	33.7(4)	C(4)–Ti(1)–C(17)	121.5(4)
Cl(2)–Ti(1)–C(17)	104.2(4)	C(5)–Ti(1)–C(17)	150.3(3)
C(4)–Ti(1)–C(17)	155.5(3)	Cl(1)–Ti(1)–C(18)	88.2(2)
Cl(1)–Ti(1)–C(18)	86.3(2)	C(1)–Ti(1)–C(18)	150.3(3)
C(3)–Ti(1)–C(18)	131.7(3)	C(3)–Ti(1)–C(18)	131.6(3)
C(4)–Ti(1)–C(18)	150.9(3)	C(5)–Ti(1)–C(18)	171.9(3)
Cl(2)–Ti(1)–C(18)	32.8(3)	Cl(1)–Ti(1)–C(18)	54.7(3)
C(3)–Ti(1)–C(18)	55.0(3)	C(3)–Ti(1)–C(18)	32.4(3)
Ti(1)–C(1)–C(2)	67.1(5)	Ti(1)–C(1)–C(5)	74.8(5)
C(2)–C(1)–C(5)	107.5(8)	Ti(1)–C(1)–C(10)	129.3(6)
C(2)–C(1)–C(10)	117.7(9)	C(5)–C(1)–C(10)	134.1(9)
Ti(1)–C(2)–C(1)	79.6(6)	Ti(1)–C(2)–C(3)	71.7(6)
C(1)–C(2)–C(3)	109.3(9)	Ti(1)–C(3)–C(2)	73.8(6)
Ti(1)–C(3)–C(4)	75.7(6)	C(2)–C(3)–C(4)	107.4(9)
Ti(1)–C(4)–C(3)	70.3(6)	Ti(1)–C(4)–C(5)	79.4(6)
C(3)–C(4)–C(5)	110.5(9)	Ti(1)–C(5)–C(1)	72.2(5)
Ti(1)–C(5)–C(4)	67.6(5)	C(1)–C(5)–C(4)	105.2(8)
Ti(1)–C(5)–C(6)	132.9(6)	C(1)–C(5)–C(6)	133.2(8)

Table 5 (continued)

C(4)–C(5)–C(6)	120.4(8)	C(5)–C(6)–C(7)	108.8(8)
C(5)–C(6)–C(8)	108.9(8)	C(7)–C(6)–C(8)	106.4(8)
C(5)–C(6)–C(9)	113.3(8)	C(7)–C(6)–C(9)	112.7(9)
C(8)–C(6)–C(9)	106.4(8)	C(1)–C(10)–C(11)	104.4(8)
C(1)–C(10)–C(12)	118.1(9)	C(11)–C(10)–C(12)	107.7(9)
C(1)–C(10)–C(13)	109.9(9)	C(11)–C(10)–C(13)	108.3(9)
C(12)–C(10)–C(13)	108.0(9)	Ti(1)–C(14)–C(15)	65.6(5)
Ti(1)–C(14)–C(18)	74.9(5)	C(15)–C(14)–C(18)	105.1(8)
Ti(1)–C(14)–C(19)	131.4(6)	C(15)–C(14)–C(19)	117.4(8)
C(18)–C(14)–C(19)	136.2(8)	Ti(1)–C(15)–C(14)	81.0(6)
Ti(1)–C(15)–C(16)	71.1(6)	C(14)–C(15)–C(16)	109.7(9)
Ti(1)–C(16)–C(15)	74.0(6)	Ti(1)–C(16)–C(17)	77.3(6)
Ti(1)–C(16)–C(17)	107.9(9)	Ti(1)–C(17)–C(16)	68.9(6)
Ti(1)–C(17)–C(18)	80.2(6)	C(16)–C(17)–C(18)	109.5(9)
Ti(1)–C(18)–C(14)	72.4(5)	Ti(1)–C(18)–C(17)	67.4(5)
C(14)–C(18)–C(17)	107.7(8)	Ti(1)–C(18)–C(23)	131.3(6)
C(14)–C(18)–C(23)	131.2(8)	C(17)–C(18)–C(23)	120.6(8)
C(14)–C(19)–C(20)	117.0(8)	C(14)–C(19)–C(21)	106.0(8)
C(20)–C(19)–C(21)	109.7(8)	C(14)–C(19)–C(22)	110.8(8)
C(20)–C(19)–C(22)	105.7(8)	C(21)–C(19)–C(22)	107.3(8)
C(18)–C(23)–C(24)	115.4(8)	C(18)–C(23)–C(25)	108.8(8)
C(24)–C(23)–C(25)	110.9(8)	C(18)–C(23)–C(26)	109.3(8)
C(24)–C(23)–C(26)	107.4(8)	C(25)–C(23)–C(26)	104.4(8)

the ring carbon atoms. The NMR data for uranocene dichloride **7** are also consistent with those for **5** and **6**, although the resonances are paramagnetically shifted, as observed for other uranocene dichlorides [25].

These observations indicate clearly that the 1,2-di-*tert*-butylcyclopentadienyl rings in **5** and **6** are undergoing a rapid dynamic process on the NMR timescale that causes, *inter alia*, the *tert*-butyl groups to appear to be symmetry equivalent. The observation that this process is fast on the NMR timescale at $-80\text{ }^{\circ}\text{C}$ indicates that the activation barrier must be equal to or less than $8\text{--}9\text{ kcal mol}^{-1}$. In order to interconvert the *tert*-butyl environments the dynamic process requires an intermediate (or transition state) in which the *tert*-butyl groups are related by an element of symmetry. The simplest version of such a process is depicted in Fig. 4. Starting with the ground state enantiomer A, in which the two *tert*-butyl environments are shown as Bu_A and Bu_B , rotation of the two rings in opposite directions as shown passes through intermediate B, in which the *tert*-butyl groups are related by a plane of symmetry, before continuing to enantiomer C with interconversion of *tert*-butyl environments. This oscillation, or windshield-wiper motion, of the two cyclopentadienyl ligands, with epimerization at the metal center and exchange of the relative positions of the *tert*-butyl groups on each ring, is indistinguishable from a process involving complete rotation of the cyclopentadienyl rings. The latter process would require that the bulky *tert*-butyl groups pass through the narrow part of the wedge as shown in Fig. 3, and would presumably be a higher energy pathway. In either case, in order to interconvert *tert*-butyl environments the relative mo-

Table 6

Bond lengths (\AA) and angles (deg) for **6**

Zr(1)–C(1)	2.449(2)	Zr(1)–C(2)	2.430(2)
Zr(1)–C(1)	2.623(7)	Zr(1)–C(2)	2.660(6)
Zr(1)–C(3)	2.505(7)	Zr(1)–C(4)	2.443(7)
Zr(1)–C(5)	2.468(7)	Zr(1)–C(14)	2.626(7)
Zr(1)–C(15)	2.641(7)	Zr(1)–C(16)	2.520(7)
Zr(1)–C(17)	2.466(8)	Zr(1)–C(18)	2.487(7)
C(1)–C(2)	1.459(9)	C(1)–C(5)	1.417(9)
C(1)–C(6)	1.533(9)	C(2)–C(3)	1.420(9)
C(2)–C(10)	1.524(9)	C(3)–C(4)	1.391(10)
C(4)–C(5)	1.408(10)	C(6)–C(7)	1.530(10)
C(6)–C(8)	1.535(11)	C(6)–C(9)	1.539(10)
C(10)–C(11)	1.544(10)	C(10)–C(12)	1.537(9)
C(10)–C(13)	1.538(10)	C(14)–C(15)	1.444(9)
C(14)–C(18)	1.423(10)	C(14)–C(19)	1.565(10)
C(15)–C(16)	1.411(10)	C(15)–C(23)	1.539(10)
C(16)–C(17)	1.387(11)	C(17)–C(18)	1.403(11)
C(19)–C(20)	1.516(11)	C(19)–C(21)	1.547(12)
C(19)–C(22)	1.538(11)	C(23)–C(24)	1.530(10)
C(23)–C(25)	1.543(10)	C(23)–C(26)	1.560(10)
C(1)–Zr(1)–C(1)	95.1(1)	C(1)–Zr(1)–C(1)	118.9(1)
C(1)–Zr(1)–C(1)	82.1(1)	C(1)–Zr(1)–C(2)	87.3(1)
C(1)–Zr(1)–C(2)	89.4(1)	C(1)–Zr(1)–C(2)	32.0(2)
C(1)–Zr(1)–C(3)	79.4(2)	C(1)–Zr(1)–C(3)	120.5(2)
C(1)–Zr(1)–C(3)	52.8(2)	C(2)–Zr(1)–C(3)	31.7(2)
C(1)–Zr(1)–C(4)	104.7(2)	C(1)–Zr(1)–C(4)	136.5(2)
C(1)–Zr(1)–C(4)	54.4(2)	C(2)–Zr(1)–C(4)	54.1(2)
C(3)–Zr(1)–C(4)	32.6(2)	C(1)–Zr(1)–C(5)	132.8(2)
C(1)–Zr(1)–C(5)	107.8(2)	C(1)–Zr(1)–C(5)	32.1(2)
C(2)–Zr(1)–C(5)	53.3(2)	C(3)–Zr(1)–C(5)	53.4(2)
C(4)–Zr(1)–C(5)	33.3(2)	C(1)–Zr(1)–C(14)	83.6(2)
C(1)–Zr(1)–C(14)	119.3(2)	C(1)–Zr(1)–C(14)	148.8(2)
C(2)–Zr(1)–C(14)	150.6(2)	C(3)–Zr(1)–C(14)	118.8(2)
C(4)–Zr(1)–C(14)	101.4(2)	C(5)–Zr(1)–C(14)	116.8(2)
C(1)–Zr(1)–C(15)	90.8(2)	C(1)–Zr(1)–C(15)	87.8(2)
C(1)–Zr(1)–C(15)	149.2(2)	C(2)–Zr(1)–C(15)	176.4(2)
C(3)–Zr(1)–C(15)	150.5(2)	C(4)–Zr(1)–C(15)	129.4(2)
C(5)–Zr(1)–C(15)	129.8(2)	C(14)–Zr(1)–C(15)	31.8(2)
C(1)–Zr(1)–C(16)	121.6(2)	C(1)–Zr(1)–C(16)	79.3(2)
C(1)–Zr(1)–C(16)	117.6(2)	C(2)–Zr(1)–C(16)	149.5(2)
C(3)–Zr(1)–C(16)	151.6(2)	C(4)–Zr(1)–C(16)	118.9(2)
C(5)–Zr(1)–C(16)	103.2(2)	C(14)–Zr(1)–C(16)	52.7(2)
C(15)–Zr(1)–C(16)	31.6(2)	C(1)–Zr(1)–C(17)	137.3(2)
C(1)–Zr(1)–C(17)	104.4(2)	C(1)–Zr(1)–C(17)	101.3(2)
C(2)–Zr(1)–C(17)	129.6(2)	C(3)–Zr(1)–C(17)	119.3(2)
C(4)–Zr(1)–C(17)	86.7(2)	C(5)–Zr(1)–C(17)	76.4(2)
C(14)–Zr(1)–C(17)	53.7(2)	C(15)–Zr(1)–C(17)	53.3(2)
C(16)–Zr(1)–C(17)	32.3(2)	C(1)–Zr(1)–C(18)	109.2(2)
C(1)–Zr(1)–C(18)	132.7(2)	C(1)–Zr(1)–C(18)	116.7(2)
C(2)–Zr(1)–C(18)	130.4(2)	C(3)–Zr(1)–C(18)	103.9(2)
C(4)–Zr(1)–C(18)	76.3(2)	C(5)–Zr(1)–C(18)	84.9(2)
C(14)–Zr(1)–C(18)	32.2(2)	C(15)–Zr(1)–C(18)	53.1(2)
C(16)–Zr(1)–C(18)	53.4(2)	C(17)–Zr(1)–C(18)	32.9(3)
Zr(1)–C(1)–C(2)	75.4(4)	Zr(1)–C(1)–C(5)	67.9(4)
C(2)–C(1)–C(5)	106.7(5)	Zr(1)–C(1)–C(6)	129.9(4)
C(2)–C(1)–C(6)	133.9(6)	C(5)–C(1)–C(6)	118.2(6)
Zr(1)–C(2)–C(1)	72.6(4)	Zr(1)–C(2)–C(3)	68.1(4)
C(1)–C(2)–C(3)	105.0(5)	Zr(1)–C(2)–C(10)	130.1(4)
C(1)–C(2)–C(10)	133.8(6)	C(3)–C(2)–C(10)	120.5(5)
Zr(1)–C(3)–C(2)	80.2(4)	Zr(1)–C(3)–C(4)	71.2(4)
C(2)–C(3)–C(4)	111.9(6)	Zr(1)–C(4)–C(3)	76.1(4)
Zr(1)–C(4)–C(5)	74.3(4)	C(3)–C(4)–C(5)	105.9(6)
Zr(1)–C(5)–C(1)	80.0(4)	Zr(1)–C(5)–C(4)	72.4(4)
C(1)–C(5)–C(4)	110.4(6)	C(1)–C(6)–C(7)	117.1(6)

Table 6 (continued)

C(1)–C(6)–C(8)	106.6(6)	C(7)–C(6)–C(8)	108.4(6)
C(1)–C(6)–C(9)	110.3(6)	C(7)–C(6)–C(9)	106.0(6)
C(8)–C(6)–C(9)	108.1(6)	C(2)–C(10)–C(11)	108.6(6)
C(2)–C(10)–C(12)	110.4(6)	C(11)–C(10)–C(12)	106.4(6)
C(2)–C(10)–C(13)	113.6(6)	C(11)–C(10)–C(13)	111.0(6)
C(12)–C(10)–C(13)	106.6(6)	Zr(1)–C(14)–C(15)	74.7(4)
Zr(1)–C(14)–C(18)	68.5(4)	C(15)–C(14)–C(18)	106.5(6)
Zr(1)–C(14)–C(19)	127.7(5)	C(15)–C(14)–C(19)	134.8(6)
C(18)–C(14)–C(19)	118.1(6)	Zr(1)–C(15)–C(14)	73.5(4)
Zr(1)–C(15)–C(16)	69.4(4)	C(14)–C(15)–C(16)	106.4(6)
Zr(1)–C(15)–C(23)	129.5(5)	C(14)–C(15)–C(23)	132.0(6)
C(16)–C(15)–C(23)	120.7(6)	Zr(1)–C(16)–C(15)	78.9(4)
Zr(1)–C(16)–C(17)	71.7(4)	C(15)–C(16)–C(17)	110.4(6)
Zr(1)–C(17)–C(16)	76.0(4)	Zr(1)–C(17)–C(18)	74.4(4)
C(16)–C(17)–C(18)	107.3(6)	Zr(1)–C(18)–C(14)	79.3(4)
Zr(1)–C(18)–C(17)	72.7(4)	C(14)–C(18)–C(17)	109.3(6)
C(14)–C(19)–C(20)	117.6(6)	C(14)–C(19)–C(21)	104.8(6)
C(20)–C(19)–C(21)	109.1(6)	C(14)–C(19)–C(22)	109.6(6)
C(20)–C(19)–C(22)	107.6(6)	C(21)–C(19)–C(22)	107.7(7)
C(15)–C(23)–C(24)	108.5(6)	C(15)–C(23)–C(25)	114.9(6)
C(24)–C(23)–C(25)	111.3(6)	C(15)–C(23)–C(26)	109.5(6)
C(24)–C(23)–C(26)	106.5(6)	C(25)–C(23)–C(26)	105.7(6)

tions of the rings must sample a conformation in which *tert*-butyl groups are eclipsed; it would seem that this eclipsing is most favorably accomplished in the wide part of the wedge, as shown.

In the case of 1,1',2,2',4,4'-hexakis(trimethylsilyl)zirconocene dichloride (**8**) and its hafnium analogue (**9**), their ¹H NMR spectra show variable temperature behavior [1]. At low temperatures three resonances are observed for the Me₃Si groups, consistent with a ground state conformation of C₂ symmetry; on warming, two of these resonances coalesce. The activation barrier for the process causing this site exchange has been determined to be ca. 11 kcal mol⁻¹ for each complex [1]. It has been suggested that the site exchange process must involve full rotation of the cyclopentadienyl rings. A windshield-wiper motion analogous to that depicted in Fig. 5 has been discounted, since it requires eclipsing of Me₃Si groups somewhere along the rotational pathway [1]. Unfortunately, this premise must be in error, for if both rings rotate such that there is no eclipsing of Me₃Si groups, no site exchange can occur because no conformation is sampled in which the substituents Si_A and Si_B are related by symmetry. Consequently, we favor a windshield-wiper mechanism for this site-exchange, as shown in Fig. 5, with the higher activation energy in this system arising from the fact that eclipsing of at least two Me₃Si groups (Si_C in Fig. 5) must occur in the narrow part of the wedge.

The hexa-*tert*-butyl analogues of **8** and **9** are unknown; apparently the 1,2,4-tri-*tert*-butylcyclopentadienyl anion is too bulky for two such ligands to be accommodated in a bent metallocene system [8]. However, zirconocenes **10** and **11**, containing two different cyclopentadienyl ligands, including one 1,2,4-tri-*tert*-

butylcyclopentadienyl ring, have been prepared, and their variable temperature NMR spectra have been interpreted in terms of a windshield-wiper oscillation of the 1,2,4-tri-*tert*-butylcyclopentadienyl that interconverts the environments ¹Bu_A and ¹Bu_B [8]. Notably, the barrier for this process in **10** is equal to or less than 8 kcal mol⁻¹; as with **5** and **6**, there is no group in the narrow end of the wedge to impede the passage of ¹Bu_C. However, in zirconocene **11**, in which the pentamethylcyclopentadienyl ring must have substituents occupying the narrow end of the wedge, the oscillation of ¹Bu_C is more severely impeded, and the barrier for interconversion of ¹Bu_A and ¹Bu_B rises 13.2 kcal mol⁻¹ [1]. Consideration of all these data provides a compelling and consistent set of results favoring ring oscillation as the mechanism for site exchange in all these bent metallocene compounds.

3. Experimental

Unless otherwise noted, all reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried using Aquasorb[®]. Diethyl ether (Et₂O) and THF were distilled under nitrogen from sodium–potassium alloy benzophenone ketyl, and hexanes from CaH₂. ¹H NMR (300 MHz), ¹³C and ¹³C{¹H} (75 MHz) NMR spectra were recorded on a Varian UNITY plus 300 System in the solvent indicated. Chemical shifts are reported as ppm downfield of internal TMS and are referenced to the solvent peak. IR spectra were recorded on a Perkin Elmer Model 1600 FT-IR spectrophotometer. Melting points of samples in capillaries open to the air were obtained using a Thomas Hoover device, and are uncorrected. Microanalysis was performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY).

TiCl₃ was purchased from Aldrich, ZrCl₄ from Johnson-Matthey Aesar/Alfa, and UCl₄ from Strem, and all were used without further purification. Li[1,2-C₅H₃Bu₂] (**1**) [17], TiCl₃ · 3THF [26], and ZrCl₄ · 2THF [26] were prepared according to the literature procedures.

3.1. Preparation of [Ti(1,2-C₅H₃Bu₂)₂Cl₂] (**5**)

Li[1,2-C₅H₃Bu₂] (**1**) (480 g, 2.61 mmol) was suspended in THF (15 ml) and cooled to –78 °C. TiCl₃ · 3THF (0.483 g, 1.31 mmol) was dissolved in THF (15 ml), in a separate flask, and also cooled to –78 °C. The TiCl₃ · 3THF solution was then transferred via cannula to the suspended Li[1,2-C₅H₃Bu₂] to give a dark blue solution that was then warmed to room temperature with stirring. The solution was then refluxed for 4 h, cooled to –40 °C, and conc. HCl (100 μl) was added via syringe. The brown solution was then warmed to

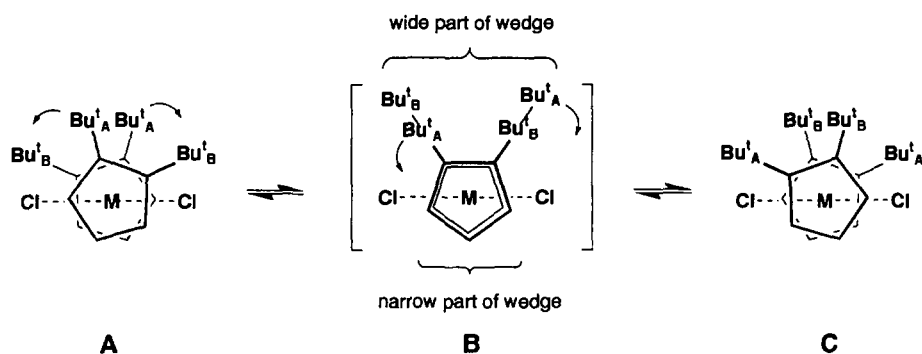


Fig. 4. Oscillating windshield-wiper motion of the cyclopentadienyl rings in **5** and **6** giving rise to site exchange between Bu_A^t and Bu_B^t and pimerization at the metal center.

room temperature with stirring, opened to the atmosphere, and stirred for an additional 1 h. Following solvent removal in vacuo, the resultant brown solid was chromatographed on silica gel (2 × 30 cm) using Et_2O as the eluent. Once again the solvent was removed and the solid crystallized by slow evaporation from an Et_2O –hexane solution to give $[\text{Ti}(1,2\text{-C}_5\text{H}_3\text{Bu}_2)_2\text{Cl}_2]$ (**5**) (0.188 g, 30%) as a brownish-red, microcrystalline solid. X-ray quality crystals of **5** were grown from chloroform–nitromethane (80:20): m.p. 208–210 °C; $^1\text{H NMR}$ (300 MHz, C_6D_6): δ_{H} (ppm) 6.30 (d, $^3J_{\text{HH}} = 3.2$ Hz, 4H, CH–CH–CH), 5.69 (t, $^3J_{\text{HH}} = 3.2$ Hz, 2H, CH–CH–CH), 1.50 (s, 36H, CH_3); $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (75 MHz, C_6D_6): δ_{C} (ppm) 146.9 (s, Cp(C1,2)), 122.2 (s, CH–CH–CH), 107.1 (s, CH–CH–CH), 36.1 (s, $\text{C}(\text{CH}_3)_3$), 32.6 (s, $\text{C}(\text{CH}_3)_3$); IR (Nujol): 3116 (w), 2956 (vs), 2921 (vs), 2857 (vs), 1490 (s), 1458 (vs), 1422 (w), 1390 (w), 1364 (s), 1307 (w), 1264 (w), 1222 (w), 1200 (w), 1165 (s), 1093 (w), 978 (w), 924 (w), 882 (w), 850 (s), 826 (s), 704 (w). Anal. Found: C, 66.17; H, 9.25. $\text{C}_{26}\text{H}_{42}\text{Cl}_2\text{Ti}$. Calc.: C, 65.96; H, 8.94%.

3.2. Preparation of $[\text{Zr}(1,2\text{-C}_5\text{H}_3\text{Bu}_2)_2\text{Cl}_2]$ (**6**)

$\text{Li}[1,2\text{-C}_5\text{H}_3\text{Bu}_2]$ (**1**) (0.500 g, 2.71 mmol) was suspended in THF (15 ml) and in a separate flask ZrCl_4

(0.490 g, 1.36 mmol) was dissolved in THF (15 ml). The solution of **1** was then transferred via cannula to the ZrCl_4 solution, at room temperature. The resultant solution turned yellow immediately. The solution was stirred for 48 h and the solvent was then removed under reduced pressure. The resultant orange solid was extracted with Et_2O and filtered through a Celite pad on a Schlenk frit. The solvent was again removed and the complex purified by column chromatography on silica gel and eluted as a yellow band with Et_2O –hexane (40:60). Solvent removal in vacuo followed by crystallization from layered dichloromethane and hexane gave $[\text{Zr}(1,2\text{-C}_5\text{H}_3\text{Bu}_2)_2\text{Cl}_2]$ (**6**) (0.134 g) as X-ray quality, analytically pure, colorless crystals. A second crop of crystals, grown by the same method, yielded an additional 0.037 g of $[\text{Zr}(1,2\text{-C}_5\text{H}_3\text{Bu}_2)_2\text{Cl}_2]$ for a total yield of 24%: m.p. 193–196 °C; $^1\text{H NMR}$ (300 MHz, C_6D_6): δ_{H} 6.21 (d, $^3J_{\text{HH}} = 3.2$ Hz, 4H, CH–CH–CH), 5.64 (t, $^3J_{\text{HH}} = 3.2$ Hz, 2H, CH–CH–CH), 1.49 (s, 36H, CH_3); $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (75 MHz, C_6D_6): δ_{C} 142.0 (s, C^tBu), 118.2 (s, CH–CH–CH), 105.0 (s, CH–CH–CH), 35.7 (s, $\text{C}(\text{CH}_3)_3$), 33.5 (s, $\text{C}(\text{CH}_3)_3$); $^{13}\text{CNMR}$ (75 MHz, C_6D_6): δ_{C} 142.0 (m, C^tBu), 118.2 (dm, $^1J_{\text{CH}} = 171.2$ Hz, CH–CH–CH), 105.0 (dm, $^1J_{\text{CH}} = 172.9$ Hz, CH–CH–CH), 35.7 (s, $\text{C}(\text{CH}_3)_3$), 33.5 (quart, $^1J_{\text{CH}} = 126.1$ Hz, $\text{C}(\text{CH}_3)_3$); IR (Nujol): 3105 (w),

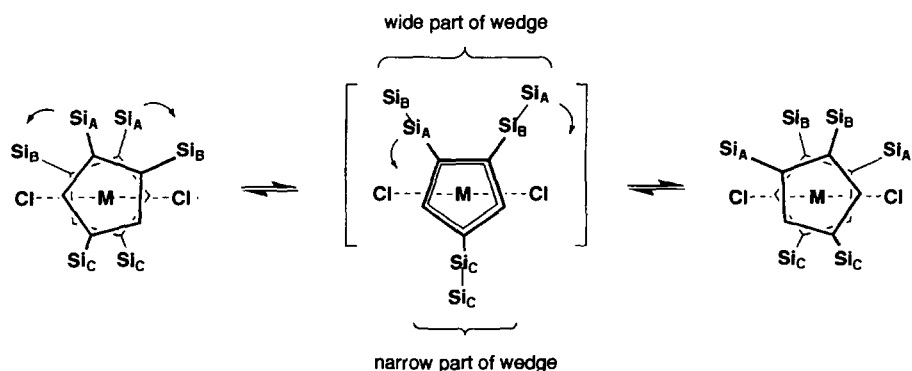


Fig. 5. Oscillating windshield-wiper motion of the cyclopentadienyl rings in **8** and **9** giving rise to site exchange between Si_A and Si_B , and illustrating the requirement for eclipsing Si_C in the narrow end of the wedge between the two canted cyclopentadienyl rings.

Table 7
Bond lengths (Å) and angles (degrees) for 7

U–C1(2)	2.576(4)	U–C1(1)	2.591(4)
U–C(4)	2.64(2)	U–C(4')	2.666(14)
U–C(5)	2.653(12)	U–C(5')	2.660(14)
U–C(3)	2.697(12)	U–C(3')	2.709(12)
U–C(1')	2.755(12)	U–C(1)	2.781(11)
U–C(2)	2.781(11)	U–(2')	2.788(11)
C(1)–C(5)	1.41(2)	C(1)–C(2)	1.49(2)
C(1)–C(6)	1.53(2)	C(2)–C(3)	1.41(2)
C(2)–C(10)	1.56(2)	C(3)–C(4)	1.40(2)
C(4)–C(5)	1.39(2)	C(6)–C(9)	1.53(2)
C(6)–C(7)	1.54(2)	C(6)–C(8)	1.55(2)
C(10)–C(13)	1.49(2)	C(10)–C(11)	1.52(2)
C(10)–C(12)	1.59(2)	C(1')–C(5')	1.40(2)
C(1')–C(2')	1.44(2)	C(1')–C(6')	1.58(2)
C(2')–C(3')	1.42(2)	C(2')–C(10')	1.53(2)
C(3')–C(4')	1.41(2)	C(4')–C(5')	1.39(2)
C(6')–C(9')	1.53(2)	C(6')–C(8')	1.53(2)
C(6')–C(7')	1.54(2)	C(10')–C(11')	1.55(2)
C(10')–C(12')	1.56(2)	C(10')–C(13')	1.56(2)
C1(2)–U–C1(1)	97.66(14)	C1(2)–U–C(4)	136.3(3)
C1(1)–U–C(4)	103.8(4)	C1(2)–U–C(4')	103.2(3)
C1(1)–U–C(4')	138.3(3)	C(4)–U–C(4')	85.3(5)
C1(2)–U–C(5)	109.7(3)	C1(1)–U–C(5)	129.7(3)
C(4)–U–C(5)	30.4(4)	C(4')–U–C(5)	75.6(4)
C1(2)–U–C(5')	129.5(3)	C1(1)–U–C(5')	111.7(3)
C(4)–U–C(5')	76.0(5)	C(4')–U–C(5')	30.4(4)
C(5)–U–C(5')	82.3(4)	C1(2)–U–C(3)	122.6(3)
C1(1)–U–C(3)	80.4(4)	C(4)–U–C(3)	30.5(4)
C(4')–U–C(3)	115.7(5)	C(5)–U–C(3)	49.3(4)
C(5')–U–C(3)	102.7(5)	C1(2)–U–C(3')	79.8(3)
C1(1)–U–C(3')	124.9(3)	C(4)–U–C(3')	115.6(5)
C(4')–U–C(3')	30.4(4)	C(5)–U–C(3')	101.5(4)
C(5')–U–C(3')	49.8(4)	C(3)–U–C(3')	146.1(5)
C1(2)–U–C(1')	118.9(3)	C1(1)–U–C(1')	88.2(3)
C(4)–U–C(1')	99.5(4)	C(4')–U–C(1')	50.1(4)
C(5)–U–C(1')	111.9(4)	C(5')–U–C(1')	30.0(4)
C(3)–U–C(1')	118.3(4)	C(3')–U–C(1')	49.8(4)
C1(2)–U–C(1)	85.6(3)	C1(1)–U–C(1)	119.4(3)
C(4)–U–C(1)	50.7(4)	C(4')–U–C(1)	98.0(4)
C(5)–U–C(1)	29.9(4)	C(5')–U–C(1)	111.5(4)
C(3)–U–C(1)	50.1(3)	C(3')–U–C(1)	115.3(4)
C(1')–U–C(1)	141.5(4)	C1(2)–U–C(2)	93.3(3)
C1(1)–U–C(2)	88.5(3)	C(4)–U–C(2)	50.4(4)
C(4')–U–C(2)	125.2(4)	C(5)–U–C(2)	49.8(4)
C(5')–U–C(2)	126.2(4)	C(3)–U–C(2)	29.7(4)
C(3')–U–C(2)	146.5(4)	C(1')–U–C(2)	147.7(4)
C(1)–U–C(2)	31.2(3)	C1(2)–U–C(2')	89.0(3)
C1(1)–U–C(2')	95.7(3)	C(4)–U–C(2')	125.4(5)
C(4')–U–C(2')	49.8(4)	C(5)–U–C(2')	125.2(4)
C(5')–U–C(2')	49.4(4)	C(3)–U–C(2')	148.4(4)
C(3')–U–C(2')	29.9(3)	C(1')–U–C(2')	30.1(3)
C(1)–U–C(2')	144.9(4)	C(2)–U–C(2')	174.9(4)
C(5)–C(1)–C(2)	104.1(11)	C(5)–C(1)–C(6)	119.3(13)
C(2)–C(1)–C(6)	135.7(12)	C(5)–C(1)–U	70.0(7)
C(2)–C(1)–U	74.4(6)	C(6)–C(1)–U	126.9(8)
C(3)–C(2)–C(1)	106.3(12)	C(3)–C(2)–C(10)	123.0(12)
C(1)–C(2)–C(10)	130.0(11)	C(3)–C(2)–U	71.8(7)
C(1)–C(2)–U	74.4(6)	C(10)–C(2)–U	126.1(8)
C(4)–C(3)–C(2)	110.7(13)	C(4)–C(3)–U	72.4(8)
C(2)–C(3)–U	78.5(7)	C(5)–C(4)–C(3)	106.3(13)
C(5)–C(4)–U	75.5(8)	C(3)–C(4)–U	77.1(9)
C(4)–C(5)–C(1)	112.6(13)	C(4)–C(5)–U	74.1(8)
C(1)–C(5)–U	80.1(8)	C(9)–C(6)–C(1)	106.3(11)
C(9)–C(6)–C(7)	109.3(12)	C(1)–C(6)–C(7)	109.6(10)

Table 7 (continued)

C(9)–C(6)–C(8)	109.5(11)	C(1)–C(6)–C(8)	115.7(12)
C(7)–C(6)–C(8)	106.5(12)	C(13)–C(10)–C(11)	113.5(13)
C(13)–C(10)–C(2)	115.7(11)	C(11)–C(10)–C(2)	109.6(12)
C(13)–C(10)–C(12)	104.3(12)	C(11)–C(10)–C(12)	104.6(10)
C(2)–C(10)–C(12)	108.4(11)	C(5')–C(1')–C(2')	106.6(11)
C(5')–C(1')–C(6')	117.8(13)	C(2')–C(1')–C(6')	134.8(12)
C(5')–C(1')–U	71.3(7)	C(2')–C(1')–U	76.2(7)
C(6')–C(1')–U	124.4(7)	C(3')–C(2')–C(1')	107.2(12)
C(3')–C(2')–C(10')	119.8(12)	C(1')–C(2')–C(10')	132.6(11)
C(3')–C(2')–U	72.0(6)	C(1')–C(2')–U	73.7(6)
C(10')–C(2')–U	124.8(9)	C(4')–C(3')–C(2')	108.6(12)
C(4')–C(3')–U	73.1(7)	C(2')–C(3')–U	78.1(7)
C(3')–C(4')–C(5')	107.4(13)	C(3')–C(4')–U	76.5(8)
C(5')–C(4')–U	74.6(8)	C(4')–C(5')–C(1')	110.2(13)
C(4')–C(5')–U	75.1(8)	C(1')–C(5')–U	78.8(8)
C(9')–C(6')–C(8')	110.1(12)	C(9')–C(6')–C(7')	108.9(13)
C(8')–C(6')–C(7')	105.6(12)	C(9')–C(6')–C(1')	105.5(11)
C(8')–C(6')–C(1')	116.6(12)	C(7')–C(6')–C(1')	109.9(11)
C(2')–C(10')–C(11')	115.3(10)	C(2')–C(10')–C(12')	108.3(13)
C(11')–C(10')–C(12')	110.6(12)	C(2')–C(10')–C(13')	110.6(11)
C(11')–C(10')–C(13')	105.3(12)	C(12')–C(10')–C(13')	106.3(10)

2956 (vs), 2923 (vs), 2854 (vs), 1489 (s), 1466 (s), 1392 (w), 1365 (s), 1308 (w), 1246 (w), 1222 (w), 1201 (w), 1163 (s), 1092 (w), 977 (w), 923 (w), 861 (w), 834 (s), 814 (s). Anal. Found: C, 60.58; H, 8.42. $C_{26}H_{42}Cl_2Zr$. Calc.: C, 60.43; H, 8.19%.

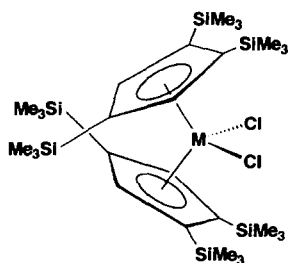
3.3. Preparation of $[U(1,2-C_5H_3Bu_2)_2Cl_2]$ (7)

UCl_4 (0.338 g, 0.890 mmol) and $Li[1,2-C_5H_3Bu_2]$ (1) (0.500 g, 2.71 mmol) were placed in a flask under argon and cooled to $-40^\circ C$. A second flask containing THF (30 ml) was also cooled to $-40^\circ C$. The THF was cannula transferred to the solid mixture and the resultant solution warmed to room temperature with stirring. The flask was transferred to a glove box and the stirring was continued for 65 h. The solvent was then removed under reduced pressure and the solid extracted with hexanes (2×15 ml). After filtering through a Celite pad on a Schlenk frit, the volume was reduced to about 20 ml and then the solution was cooled in the glove box freezer at $-20^\circ C$ overnight. Orange crystals of $[U(1,2-$

$C_5H_3Bu_2)_2Cl_2]$ formed and were collected after decantation and drying in vacuo. Further volume reduction of the decanted solution and subsequent cooling produced a second crop of 7 (total yield: 0.189 g, 32%); m.p. $143^\circ C$ (dec); 1H NMR (300 MHz, C_6D_6): δ_H –5.08 (br s, 4H, $CH-CH-CH$), 1.39 (br s, 2H, $CH-CH-CH$), 5.17 (br s, 36H, CH_3). Anal. Found: C, 46.81; H, 6.70. $C_{26}H_{42}Cl_2U$. Calc.: C, 46.77; H 6.94%.

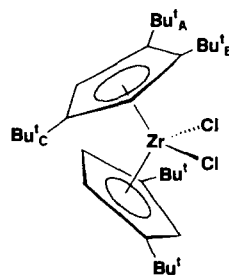
3.4. Crystal structure determinations

Crystal, data collection, and refinement parameters are collected in Table 1. Suitable crystals of 5, 6, and 7 were selected and mounted in thin-walled, nitrogen-flushed, glass capillaries. The unit-cell parameters were obtained by the least squares refinement of the angular settings of 24 reflections ($20 \leq 2\theta \leq 24^\circ$). The systematic absences in the diffraction data for 5, 6, and 7 are uniquely consistent for the reported space group. The isomorphous structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least squares proce-

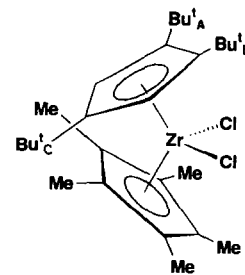


8 M = Zr

9 M = Hf



10



11

dures. Semi-empirical absorption corrections were applied for **7** but ignored for **5** and **6**. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized isotropic contributions. All software and the sources of the scattering factors are contained in either SHELXTL (5.3) or the SHELXTLPLUS (4.2) program libraries [27].

4. Supplementary material available

Anisotropic displacement coefficients, H-atom coordinates and isotropic displacement coefficients, and listings of experimental and calculated structure factors for **5**, **6**, and **7**.

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