

# Higher Valent Metal Pentadienyl Chemistry: Syntheses, Structures, and Reactions of $Zr(6,6\text{-dmch})_2X_2$ Complexes (dmch = dimethylcyclohexadienyl; X = Cl, Br, I) and Related Species

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The zirconium(II) complex  $Zr(6,6\text{-dmch})_2(PMe_3)_2$  undergoes facile reactions with 1,2-dihaloalkanes, yielding the formal oxidative addition products  $Zr(6,6\text{-dmch})_2X_2$  (X = Cl, Br, I). A similar reaction with 1-chloro-2-methoxyethane yields  $Zr(6,6\text{-dmch})_2(Cl)(OCH_3)$ . Each of the complexes has been characterized analytically, spectroscopically, and structurally. A direct oxidative addition reaction occurs with  $CH_3Br$ , yielding the thermally unstable  $Zr(6,6\text{-dmch})_2(CH_3)(Br)$ , which has been characterized spectroscopically and structurally. As had been observed for related  $Zr(C_5H_5)(6,6\text{-dmch})X_2$  complexes, the Zr–dmch coordination is severely skewed, with quite short Zr–C3 interactions and substantially lengthened interactions with the remaining carbon atoms of the dienyl fragment. This may be attributed to an inability of the contracted Zr(IV) orbitals to interact effectively with all the carbon atoms in the wide, electronically open dienyl ligands.

## Introduction

For some time it has been apparent that  $\eta^5$ -pentadienyl ligands have an overwhelming preference to bond to metals in low ( $\leq +2$ ) oxidation states, and even complexes with metals in the +3 oxidation state have been uncommon.<sup>1</sup> This trend appears to result from the high delta acidities of pentadienyl ligands and their large girths, which can result in poor overlap with the contracted orbitals of metals in higher oxidation states.<sup>2</sup> The relatively few higher oxidation state species have typically incorporated strong  $\pi$ -donor ligands,<sup>3</sup> which could enhance metal–ligand overlap and potentially also lead to some  $\delta$  back-bonding, by reducing the positive charge on the metal center. Recently, however, it has become clear that zirconium, arguably the largest transition metal, can yield stable tetravalent pentadienyl complexes.<sup>4</sup> Particularly interesting are the  $Zr(C_5H_5)(6,6\text{-dmch})X_2$  (X = Cl, Br, I) compounds, which have been thoroughly investigated via structural, photoelectron spectroscopy, and theoretical studies.<sup>5</sup> Especially notable was the observation that while lower valent half-open titanocenes and zirconocenes typically

display M–C bonds that are much shorter for the pentadienyl versus cyclopentadienyl ligands,<sup>1,2,4,6</sup> exactly the opposite was found for the tetravalent species,<sup>4,5</sup> revealing a dramatic reversal in bonding favorability. In addition, the M(IV) center was not able to interact effectively with all of the carbon atoms in the electronically open dienyl fragments, in accord with the earlier proposal that metal–pentadienyl overlap could suffer in higher oxidation state species.

Given the great importance of compounds of the type  $M(C_5H_5)_2X_2$ ,<sup>7</sup> and higher valent metal cyclopentadienyl compounds in general,<sup>8</sup> the missing field of higher valent metal pentadienyl chemistry has long represented an apparently major lost opportunity. The general class of  $Zr(C_5H_5)(6,6\text{-dmch})X_2$  species has recently opened the door to at least some opportunities in this area, and we now report an analogous set of  $Zr(6,6\text{-dmch})_2X_2$  complexes (X = Cl, Br, I), as well as  $Zr(6,6\text{-dmch})_2(CH_3)(Br)$  and  $Zr(6,6\text{-dmch})_2(Cl)(OCH_3)$ , which will allow for further extensions into the chemistry of higher valent metal pentadienyl chemistry.

## Experimental Section

**General Procedures.** All reactions were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus. Organic solvents and reagents were obtained commercially. Reagents were used as received, while solvents were dried and deoxygenated using activated alumina under a nitrogen atmosphere. Spectroscopic data were obtained as previously described.<sup>9</sup> Elemental analyses were obtained from Desert Analytics. The dihalide complexes decompose thermally prior to melting.

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**Dichlorobis(6,6-dimethylcyclohexadienyl)-zirconium, Zr(6,6-dmch)<sub>2</sub>Cl<sub>2</sub>.** To a dark black-red solution of Zr(6,6-dmch)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub><sup>4c</sup> (0.90 g, 2.0 mmol) in 30 mL of hexanes under N<sub>2</sub> at 0 °C was added 1,2-dichloroethane (0.31 mL, 3.9 mmol). A bright red precipitate immediately formed. The reaction mixture was allowed to stir for 1 h at room temperature. The solvent was removed in vacuo, leaving a bright red residue in a crude yield of 55–65%. The product was extracted with ca. 40 mL of toluene. The solution was filtered through a Celite pad on a coarse frit. The product was crystallized by concentration of the red filtrate in vacuo to ca. 5 mL and placement into a –30 °C freezer, affording 0.31 g (40% yield) of orange to red (depending on size) crystals.

<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, ambient): δ 0.59 (s, 6H, exo CH<sub>3</sub>), 1.32 (s, 6H, endo CH<sub>3</sub>), 4.51 (d, 4H, *J* = 7.8 Hz, H<sub>1,5,9,13</sub>), 5.27 (t, 2H, *J* = 5.7 Hz, H<sub>3,11</sub>), 5.89 (t, 4H, *J* = 6.3 Hz, H<sub>2,4,10,12</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, ambient): δ 28.0 (q, 2C, *J* = 125.1 Hz, exo CH<sub>3</sub>), 31.7 (s, 2C, C<sub>6,14</sub>), 34.5 (q, 2C, *J* = 126.6 Hz, endo CH<sub>3</sub>), 96.5 (dt, 2C, *J* = 173.2, 7.8 Hz, C<sub>3,11</sub>), 108.6 (d, 4C, *J* = 163.4 Hz, C<sub>1,5,9,13</sub>), 125.3 (dd, 4C, *J* = 160.8, 6.9 Hz, C<sub>2,4,10,12</sub>). MS (EI, 23 eV) *m/z* (relative intensity): 91.0 (30.2), 92.0 (29.6), 93.1 (27.4), 107.1 (30.2), 108.1 (14.4), 250.9 (100.0), 251.9 (32.8), 252.9 (97.4), 253.9 (24.1), 254.9 (66.1), 256.9 (28.8), 266.9 (92.0), 267.9 (29.3), 268.9 (89.3), 269.9 (20.2), 270.9 (60.1), 272.9 (26.9), 339.0 (36.4), 341.0 (25.9), 343.0 (16.2), 359.0 (53.8), 360.0 (19.6), 360.9 (56.2), 362.0 (15.5), 363.0 (36.1), 365.0 (15.9), 374.0 (18.2), 376.0 (19.1), 378.0 (12.6). Anal. Calc for C<sub>16</sub>H<sub>22</sub>Cl<sub>2</sub>Zr: C, 51.05; H, 5.89. Found: C, 51.31; H, 5.54.

**Diiodobis(6,6-dimethylcyclohexadienyl)zirconium, Zr(6,6-dmch)<sub>2</sub>I<sub>2</sub>.** To a dark red solution of Zr(6,6-dmch)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (1.0 g, 2.2 mmol) in 40 mL of hexanes under N<sub>2</sub> at room temperature was added 1,2-diiodoethane (0.19 mL, 2.2 mmol). A bright red-orange precipitate immediately formed. The reaction mixture was allowed to stir for 1 h. The solvent was removed in vacuo, leaving a bright red residue. The product was extracted with ca. 40 mL of toluene. The solution was filtered through a Celite pad on a coarse frit. The product was crystallized by concentration of the red filtrate in vacuo to ca. 10 mL and placement into a –60 °C freezer, affording 0.43 g (42% yield) of orange-red crystals.

<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, ambient): δ 0.58 (s, 6H, exo CH<sub>3</sub>), 1.23 (s, 6H, endo CH<sub>3</sub>), 4.59 (d, 4H, *J* = 7.8 Hz, H<sub>1,5,9,13</sub>), 5.49 (t, 2H, *J* = 6.0 Hz, H<sub>3,11</sub>), 5.97 (t, 4H, *J* = 6.8 Hz, H<sub>2,4,10,12</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, ambient): δ 28.5 (q, 2C, *J* = 126.3 Hz, exo CH<sub>3</sub>), 32.0 (s, 2C, C<sub>6,14</sub>), 34.8 (q, 2C, *J* = 123.5 Hz, endo CH<sub>3</sub>), 97.9 (dt, 2C, *J* = 173.7, 7.7 Hz, C<sub>3,11</sub>), 108.5 (d, 4C, *J* = 163.2, C<sub>1,5,9,13</sub>), 124.9 (dd, 4C, *J* = 163.4, 7.3 Hz, C<sub>2,4,10,12</sub>). Anal. Calc for C<sub>16</sub>H<sub>22</sub>Br<sub>2</sub>Zr: C, 41.30; H, 4.76. Found: C, 41.42; H, 4.62.

**Diiodobis(6,6-dimethylcyclohexadienyl)zirconium, Zr(6,6-dmch)<sub>2</sub>I<sub>2</sub>.** To a dark red solution of Zr(6,6-dmch)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.77 g, 1.7 mmol) in 20 mL of hexanes under N<sub>2</sub> at room temperature was added 1,2-diiodoethane (0.57 g, 2.0 mmol). A dark red crystalline solid precipitated out. After 15 min, the supernatant was removed via syringe. The dark red precipitate was dissolved in toluene. The concentrated solution was placed in a –60 °C freezer to yield Zr(6,6-dmch)<sub>2</sub>I<sub>2</sub> (33% yield). Allowing the supernatant to stand at room temperature resulted in the precipitation of a mixture of red and white products. The red solid consisted of two products, the major product being additional Zr(6,6-dmch)<sub>2</sub>I<sub>2</sub>, while the minor product is Zr(6,6-dmch)I<sub>3</sub>(PMe<sub>3</sub>), in addition to a white solid of an unknown composition. However, it was difficult to

separate the three products from each other. An X-ray diffraction study of the other red product revealed a highly disordered molecule of the expected composition, with a four-legged piano stool arrangement.<sup>10</sup>

<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, ambient): δ 0.58 (s, 6H, exo CH<sub>3</sub>), 1.08 (s, 6H, endo CH<sub>3</sub>), 4.78 (dd, 4H, *J* = 6.6, 1.5 Hz, H<sub>1,5,9,13</sub>), 5.87 (tt, 2H, *J* = 5.9, 1.6 Hz, H<sub>3,11</sub>), 6.06 (m, 4H, H<sub>2,4,10,12</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, ambient): δ 29.4 (q, 2C, *J* = 126.1 Hz, exo CH<sub>3</sub>), 32.3 (s, 2C, C<sub>6,14</sub>), 35.3 (q, 2C, *J* = 126.9 Hz, endo CH<sub>3</sub>), 99.3 (dt, 2C, *J* = 175.5, 7.7 Hz, C<sub>3,11</sub>), 107.6 (d, 4C, *J* = 164.4 Hz, C<sub>1,5,9,13</sub>), 123.4 (dd, 4C, *J* = 163.4, 7.3 Hz, C<sub>2,4,10,12</sub>). Anal. Calc for C<sub>16</sub>H<sub>22</sub>I<sub>2</sub>Zr: C, 34.38; H, 3.97. Found: C, 33.98; H, 3.68. Anal. Calc for C<sub>11</sub>H<sub>20</sub>PI<sub>3</sub>Zr: C, 20.17; H, 3.08. Found: C, 20.18; H, 3.29.

**(Bromo)(methyl)bis(6,6-dimethylcyclohexadienyl)zirconium, Zr(6,6-dmch)<sub>2</sub>(CH<sub>3</sub>)(Br).** A dark black-red solution of Zr(6,6-dmch)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.27 g, 5.9 mmol) in 30 mL of hexanes was exposed to CH<sub>3</sub>Br gas at room temperature. The color of the solution immediately changed to orange. The solvent was removed in vacuo, leaving an orange oil, which was extracted with ca. 40 mL of hexanes and filtered through a Celite pad on a coarse frit. The product was crystallized by concentration of the orange filtrate in vacuo to ca. 2 mL and placement into a –60 °C freezer. The compound decomposes on standing at room temperature, necessitating expeditious manipulations of its solutions.

<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, ambient): δ 0.53 (s, 3H, CH<sub>3</sub>), 0.68 (s, 6H, exo CH<sub>3</sub>), 1.11 (s, 6H, endo CH<sub>3</sub>), 4.08 (dt, 2H, *J* = 7.2, 2.3 Hz, H<sub>1,5</sub> or 9,13), 4.52 (dm, 2H, *J* = 7 Hz, H<sub>1,5</sub> or 9,13), 5.39 (m, 4H), 5.76 (m, 2H).

**(Chloro)(methoxy)bis(6,6-dimethylcyclohexadienyl)zirconium, Zr(6,6-dmch)<sub>2</sub>(OMe)(Cl).** To a dark red solution of Zr(6,6-dmch)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.53 g, 1.2 mmol) in 20 mL of hexane at –78 °C was added 1-chloro-2-methoxyethane (0.12 mL, 1.3 mmol). The reaction mixture was allowed to warm to room temperature, during which time the color of the solution turned orange. The reaction mixture was stirred for 3 h, after which time the solvent was removed in vacuo. The crude orange solid was extracted with diethyl ether, and the extracts were filtered through a Celite pad on a coarse frit. The orange solution was cooled to –60 °C, yielding orange crystals (0.20 g, 48% yield).

<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, ambient): δ 0.74 (s, 6H, exo CH<sub>3</sub>), 1.30 (s, 6H, endo CH<sub>3</sub>), 3.66 (s, 3H, OMe), 4.35 (d, 2H, *J* = 8.1 Hz, H<sub>1,9</sub> or 5,13), 4.42 (d, 2H, *J* = 8.4 Hz, H<sub>1,9</sub> or 5,13), 5.32 (t, 2H, *J* = 5.7 Hz, H<sub>3,11</sub>), 5.75 (t, 2H, *J* = 6.9 Hz, H<sub>2,10</sub> or 4,12), 5.84 (t, 2H, *J* = 6.9 Hz, H<sub>2,10</sub> or 4,12). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, ambient): δ 28.2 (q, 2C, *J* = 124.0 Hz, exo CH<sub>3</sub>), 31.6 (s, 2C, C<sub>6,14</sub>), 33.9 (q, 2C, *J* = 123.8 Hz, endo CH<sub>3</sub>), 62.7 (q, 2C, *J* = 141.0 Hz, OMe), 93.2 (dt, 2C, *J* = 171.2, 7.7 Hz, C<sub>3,11</sub>), 101.3 (d, 2C, *J* = 161.9 Hz, H<sub>5,13</sub> or 1,9), 107.3 (d, 2C, *J* = 160.9 Hz, H<sub>5,13</sub> or 1,9), 124.4 (dd, 2C, *J* = 159.3, 7.2 Hz, C<sub>4,12</sub> or 2,10), 125.7 (dd, 2C, *J* = 159.1, 5.8 Hz, C<sub>4,12</sub> or 2,10). Anal. Calc for C<sub>17</sub>H<sub>25</sub>OClZr: C, 54.88; H, 6.77. Found: C, 54.51; H, 6.41.

**X-ray Structural Studies.** Single crystals of the compounds were protected from oxidation by a thin coat of Paratone oil and transferred to a cold stream on a Nonius Kappa CCD autodiffractometer. All structure solutions were obtained by a combination of direct methods, difference Fourier maps, and least-squares refinements using the SIR97 and SHELX97 programs.<sup>11</sup> In the dichloride, diiodide, and methoxy complexes, two independent molecules were present in the asymmetric unit. In the first two cases, the two forms appeared nearly identical, while for the methoxy complex, the second dmch ligand had its edge bridge located near the methoxy

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**Table 1. Crystallographic Data for Zr(6,6-dmch)<sub>2</sub>Cl<sub>2</sub>, Zr(6,6-dmch)<sub>2</sub>Br<sub>2</sub>, Zr(6,6-dmch)<sub>2</sub>I<sub>2</sub>, Zr(6,6-dmch)<sub>2</sub>Cl(OCH<sub>3</sub>), and Zr(6,6-dmch)<sub>2</sub>Br(CH<sub>3</sub>)**

formula	C <sub>16</sub> H <sub>22</sub> Cl <sub>2</sub> Zr	C <sub>19.5</sub> H <sub>26</sub> Br <sub>2</sub> Zr	C <sub>16</sub> H <sub>22</sub> I <sub>2</sub> Zr	C <sub>17</sub> H <sub>25</sub> ClOZr	C <sub>17</sub> H <sub>25</sub> BrZr
fw	376.46	511.44	559.36	372.04	400.50
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	<i>Cc</i>	<i>P2<sub>1</sub>/n</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/n</i>
color	red	orange	red	red	orange
<i>a</i> (Å)	20.8990(12)	7.1237(1)	14.0924(2)	15.3259(3)	8.7645(2)
<i>b</i> (Å)	14.2703(8)	21.4219(4)	14.7885(2)	12.4301(1)	13.2038(4)
<i>c</i> (Å)	11.6892(8)	13.1976(2)	34.5267(6)	17.8510(3)	15.2106(5)
α (deg)	105.302(2)	98.8385(9)	90	97.6764(7)	105.208(1)
temp (K)	150(1)	150(1)	150(1)	150(1)	150(1)
<i>Z</i>	8	4	16	8	4
<i>R</i> (2θ)	0.0479	0.0283	0.0274	0.0290	0.0281
<i>R<sub>w</sub></i> <sup>2</sup> (2σ)	0.1033	0.0595	0.0421	0.0709	0.0606
GOF	1.047	1.056	1.048	1.034	1.065

**Table 2. Pertinent Bonding Parameters for Zr(6,6-dmch)<sub>2</sub>Cl<sub>2</sub>**

Bond Distances (Å)							
Zr–C1	2.699(5)	Zr–C11	2.4683(15)	Zr2–C1'	2.730(6)	Zr2–C11'	2.4589(16)
Zr–C2	2.498(6)	Zr–C12	2.4508(15)	Zr2–C2'	2.540(6)	Zr2–C12'	2.4515(15)
Zr–C3	2.468(6)	C1–C2	1.369(9)	Zr2–C3'	2.460(6)	C1'–C2'	1.379(9)
Zr–C4	2.509(6)	C2–C3	1.411(9)	Zr2–C4'	2.506(6)	C2'–C3'	1.401(9)
Zr–C5	2.686(6)	C3–C4	1.400(10)	Zr2–C5'	2.077(6)	C3'–C4'	1.395(10)
Zr–C9	2.782(5)	C4–C5	1.356(9)	Zr2–C9'	2.737(6)	C4'–C5'	1.356(10)
Zr–C10	2.576(5)	C9–C10	1.361(9)	Zr2–C10'	2.529(5)	C9'–C10'	1.367(10)
Zr–C11	2.484(6)	C10–C11	1.416(10)	Zr2–C11'	2.453(6)	C10'–C11'	1.410(10)
Zr–C12	2.523(6)	C11–C12	1.390(9)	Zr2–C12'	2.510(6)	C11'–C12'	1.408(9)
Zr–C13	2.635(6)	C12–C13	1.347(10)	Zr2–C13'	2.694(6)	C12'–C13'	1.383(9)
Bond Angles (deg)							
C11–Zr1–C12	93.46(6)	C10–C11–C12	116.2(6)	C5'–C6'–C1'		101.1(5)	
C11'–Zr2–C12'	93.76(6)	C11–C12–C13	121.4(6)	C6'–C1'–C2'		120.2(6)	
C1–C2–C3	120.4(6)	C12–C13–C14	119.5(6)	C9'–C10'–C11'		120.9(6)	
C2–C3–C4	116.8(6)	C13–C14–C9	102.7(5)	C10'–C11'–C12'		117.2(6)	
C3–C4–C5	120.0(6)	C14–C9–C10	120.2(6)	C11'–C12'–C13'		119.6(6)	
C4–C5–C6	120.7(6)	C1'–C2'–C3'	119.8(6)	C12'–C13'–C14'		120.3(6)	
C5–C6–C1	101.3(5)	C2'–C3'–C4'	117.4(7)	C13'–C14'–C9'		103.2(5)	
C6–C1–C2	120.3(6)	C3'–C4'–C5'	120.4(6)	C14'–C9'–C10'		118.7(6)	
C9–C10–C11	121.3(7)	C4'–C5'–C6'	120.0(6)				

**Table 3. Pertinent Bonding Parameters for Zr(6,6-dmch)<sub>2</sub>Br<sub>2</sub>**

Bond Distances (Å)							
Zr–C1	2.744(3)	Zr–C9	2.733(3)	Zr–Br1	2.6350(3)	Zr–Br2	2.6322(4)
Zr–C2	2.555(3)	Zr–C10	2.556(3)	C1–C2	1.360(4)	C9–C10	1.369(4)
Zr–C3	2.471(3)	Zr–C11	2.476(3)	C2–C3	1.428(4)	C10–C11	1.431(4)
Zr–C4	2.537(3)	Zr–C12	2.535(3)	C3–C4	1.409(4)	C11–C12	1.409(4)
Zr–C5	2.657(3)	Zr–C13	2.624(3)	C4–C5	1.385(4)	C12–C13	1.382(4)
Bond Angles (deg)							
Br1–Zr–Br2	93.591(12)	C5–C6–C1	103.4(2)	C11–C12–C13		120.3(3)	
C1–C2–C3	121.1(3)	C6–C1–C2	120.6(3)	C12–C13–C14		120.0(3)	
C2–C3–C4	116.9(3)	C9–C10–C11	120.8(3)	C13–C14–C9		103.5(2)	
C3–C4–C5	120.4(3)	C10–C11–C12	117.1(3)	C14–C9–C10		121.6(3)	
C4–C5–C6	119.1(2)						

ligand rather than near the chloride. All non-hydrogen atoms were successfully refined anisotropically, while most hydrogen atoms could be refined isotropically. The exceptions include the hydrogen atoms in the dichloride structure, those of a disordered toluene molecule in the dibromide structure, and one methyl group in the methyl complex. In the methoxy complex, one dmch ligand of the second independent molecule was subject to substantial librational motion and/or disorder, and as a result, one of its methyl groups had to be treated as two partial contributions, and its hydrogen atoms were also not refined isotropically. Hydrogen atoms not refined isotropically were assigned idealized parameters and allowed to ride on their respective carbon atoms. Pertinent structural data are presented in Tables 1–6, while perspective views of the molecules are presented in Figures 1–5.

## Results and Discussion

**Syntheses and Spectroscopy.** As in the case of the Zr(C<sub>5</sub>H<sub>5</sub>)(6,6-dmch)(PMe<sub>3</sub>)<sub>2</sub> complex,<sup>5</sup> Zr(6,6-dmch)<sub>2</sub>-

(PMe<sub>3</sub>)<sub>2</sub> was found to react readily with 1,2-dihaloalkanes, yielding Zr(6,6-dmch)<sub>2</sub>X<sub>2</sub> complexes (Scheme 1; X = Cl, Br, I). A side product in the iodide reaction was Zr(6,6-dmch)I<sub>3</sub>(PMe<sub>3</sub>), presumably formed via additional halogenation as a consequence of the weakness of C–I bonds. Each of the dihalide compounds has been characterized analytically, spectroscopically, and crystallographically (vide supra). While the <sup>13</sup>C NMR spectra of these species are all quite similar, the <sup>1</sup>H NMR data show more significant shifts. One can note consistent downfield shifts for the protons on any of the metal-bound carbon atoms as the halogen becomes heavier. In contrast, the endo methyl group, downfield from the other methyl group residing above the aromatic ligand, shows an opposite trend. As opposed to their essentially colorless C<sub>5</sub>H<sub>5</sub> analogues, the 6,6-dmch compounds are brightly colored, ranging from orange-red (X = Cl) to dark red (X = I). On the basis of the results obtained

**Table 4. Pertinent Bonding Parameters for Zr(6,6-dmch)<sub>2</sub>I<sub>2</sub>**

Bond Distances (Å)							
Zr–C1	2.727(3)	Zr–I1	2.8838(3)	Zr2–C1'	2.751(3)	Zr2–I1'	2.8848(3)
Zr–C2	2.550(3)	Zr–I2	2.8667(3)	Zr2–C2'	2.548(3)	Zr2–I2'	2.8667(3)
Zr–C3	2.471(3)	C1–C2	1.366(4)	Zr2–C3'	2.454(3)	C1'–C2'	1.367(4)
Zr–C4	2.538(3)	C2–C3	1.424(4)	Zr2–C4'	2.531(3)	C2'–C3'	1.420(4)
Zr–C5	2.648(3)	C3–C4	1.403(4)	Zr2–C5'	2.682(3)	C3'–C4'	1.406(4)
Zr–C9	2.733(3)	C4–C5	1.380(4)	Zr2–C9'	2.731(3)	C4'–C5'	1.380(4)
Zr–C10	2.567(3)	C9–C10	1.373(4)	Zr2–C10'	2.559(3)	C9'–C10'	1.360(4)
Zr–C11	2.482(3)	C10–C11	1.426(4)	Zr2–C11'	2.470(3)	C10'–C11'	1.434(4)
Zr–C12	2.525(3)	C11–C12	1.402(4)	Zr2–C12'	2.533(3)	C11'–C12'	1.400(4)
Zr–C13	2.598(3)	C12–C13	1.380(4)	Zr2–C13'	2.630(3)	C12'–C13'	1.385(4)
Bond Angles (deg)							
I1–Zr1–I2	94.343(10)	C10–C11–C12	117.8(3)	C5'–C6'–C1'		103.4(2)	
I1'–Zr2–I2'	92.957(10)	C11–C12–C13	119.7(3)	C6'–C1'–C2'		120.1(3)	
C1–C2–C3	121.0(3)	C12–C13–C14	120.0(3)	C9'–C10'–C11'		121.5(3)	
C2–C3–C4	117.4(3)	C13–C14–C9	103.7(2)	C10'–C11'–C12'		116.8(3)	
C3–C4–C5	120.0(3)	C14–C9–C10	121.2(3)	C11'–C12'–C13'		120.4(3)	
C4–C5–C6	119.0(3)	C1'–C2'–C3'	121.0(3)	C12'–C13'–C14'		120.9(3)	
C5–C6–C1	103.4(2)	C2'–C3'–C4'	116.9(3)	C13'–C14'–C9'		104.1(2)	
C6–C1–C2	119.6(3)	C3'–C4'–C5'	120.4(3)	C14'–C9'–C10'		121.7(3)	
C9–C10–C11	120.3(3)	C4'–C5'–C6'	119.1(3)				

**Table 5. Pertinent Bonding Parameters for Zr(6,6-dmch)<sub>2</sub>Cl(OCH<sub>3</sub>)**

Bond Distances (Å)							
Zr–C1	2.691(2)	Zr–Cl1	2.4852(5)	Zr2–C1'	2.772(2)	Zr2–Cl1'	2.4828(5)
Zr–C2	2.547(2)	Zr–O1	1.968(2)	Zr2–C2'	2.558(2)	Zr2–O1A	2.045(2)
Zr–C3	2.479(2)	C1–C2	1.370(3)	Zr2–C3'	2.455(3)	C1'–C2'	1.351(5)
Zr–C4	2.555(2)	C2–C3	1.414(3)	Zr2–C4'	2.563(3)	C2'–C3'	1.377(6)
Zr–C5	2.750(2)	C3–C4	1.427(3)	Zr2–C5'	2.774(2)	C3'–C4'	1.382(5)
Zr–C9	2.793(2)	C4–C5	1.368(3)	Zr2–C9'	2.685(2)	C4'–C5'	1.345(5)
Zr–C10	2.585(2)	C9–C10	1.356(4)	Zr2–C10'	2.536(2)	C9'–C10'	1.376(3)
Zr–C11	2.482(2)	C10–C11	1.425(4)	Zr2–C11'	2.516(2)	C10'–C11'	1.405(4)
Zr–C12	2.528(2)	C11–C12	1.414(4)	Zr2–C12'	2.542(2)	C11'–C12'	1.419(4)
Zr–C13	2.697(2)	C12–C13	1.368(3)	Zr2–C13'	2.697(2)	C12'–C13'	1.380(3)
Bond Angles (deg)							
Cl1–Zr1–O1	97.18(4)	C10–C11–C12	116.6(2)	C5'–C6'–C1'		102.7(2)	
Cl1'–Zr2–O1A	98.75(4)	C11–C12–C13	119.7(2)	C6'–C1'–C2'		120.2(3)	
C1–C2–C3	120.5(2)	C12–C13–C14	120.3(2)	C9'–C10'–C11'		120.7(2)	
C2–C3–C4	116.9(2)	C13–C14–C9	102.5(2)	C10'–C11'–C12'		116.9(2)	
C3–C4–C5	121.3(2)	C14–C9–C10	120.3(2)	C11'–C12'–C13'		120.8(2)	
C4–C5–C6	120.3(2)	C1'–C2'–C3'	121.3(3)	C12'–C13'–C14'		119.5(2)	
C5–C6–C1	103.8(2)	C2'–C3'–C4'	117.0(3)	C13'–C14'–C9'		103.0(2)	
C6–C1–C2	120.2(2)	C3'–C4'–C5'	121.2(3)	C14'–C9'–C10'		120.0(2)	
C9–C10–C11	120.9(2)	C4'–C5'–C6'	120.6(3)				

**Table 6. Pertinent Bonding Parameters for Zr(6,6-dmch)<sub>2</sub>Br(CH<sub>3</sub>)**

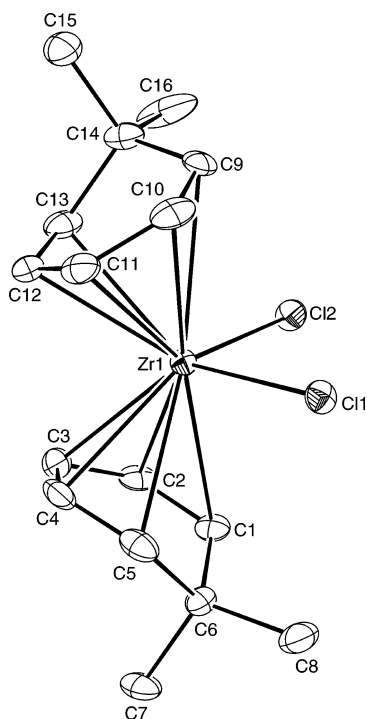
Bond Distances (Å)							
Zr–C1	2.661(2)	Zr–C9	2.568(2)	Zr–Br1	2.6602(4)	Zr–C17	2.481(2)
Zr–C2	2.511(2)	Zr–C10	2.507(2)	C1–C2	1.377(3)	C9–C10	1.392(4)
Zr–C3	2.486(2)	Zr–C11	2.504(3)	C2–C3	1.414(3)	C10–C11	1.396(4)
Zr–C4	2.562(2)	Zr–C12	2.578(2)	C3–C4	1.416(3)	C11–C12	1.428(4)
Zr–C5	2.734(2)	Zr–C13	2.734(2)	C4–C5	1.373(4)	C12–C13	1.360(4)
Bond Angles (deg)							
Br1–Zr–C17	89.08(4)	C5–C6–C1	103.0(2)	C11–C12–C13		121.0(3)	
C1–C2–C3	120.2(2)	C6–C1–C2	118.7(2)	C12–C13–C14		121.3(2)	
C2–C3–C4	117.3(2)	C9–C10–C11	119.9(2)	C13–C14–C9		103.7(2)	
C3–C4–C5	120.7(2)	C10–C11–C12	117.6(2)	C14–C9–C10		119.6(2)	
C4–C5–C6	119.0(2)						

for the Zr(C<sub>5</sub>H<sub>5</sub>)(6,6-dmch)X<sub>2</sub> species,<sup>5</sup> these colors can be ascribed to ligand-to-metal charge transfer transitions, which occur in the visible region due to the filled HOMO localized on the dmch ligand being destabilized by about 1 eV relative to that of corresponding HOMO derived from the C<sub>5</sub>H<sub>5</sub> ligand.

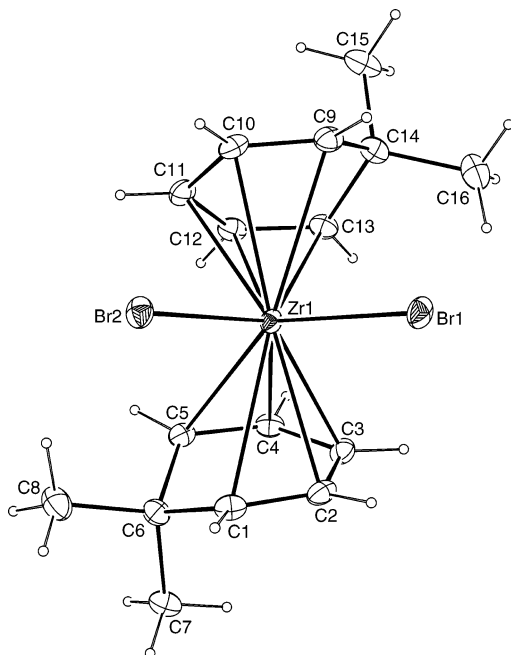
Reactions designed to prepare mixed halide complexes, utilizing reagents such as 1-bromo-2-chloroethane, however, were found to be ineffective, perhaps due to the significant differences in C–X bond energies. It nonetheless appeared possible that a variation of this approach might succeed if one of the two substituents was more likely to coordinate to the metal center during

(and perhaps prior to) the process of halogen atom abstraction. While coordination of a lone pair of a carbon-bound chlorine atom to zirconium can occur,<sup>12</sup> it is nonetheless far less common than coordination by an ether's oxygen atom. Therefore, a reaction of Zr(6,6-dmch)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> with 1-chloro-2-methoxyethane was attempted, and this indeed led to the desired Zr(6,6-dmch)<sub>2</sub>Cl(OCH<sub>3</sub>) (Scheme 1). Monitoring this reaction by NMR spectroscopy revealed that other potential metal-containing products were not formed in detectable

(12) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 3222; **2004**, *126*, 11170.

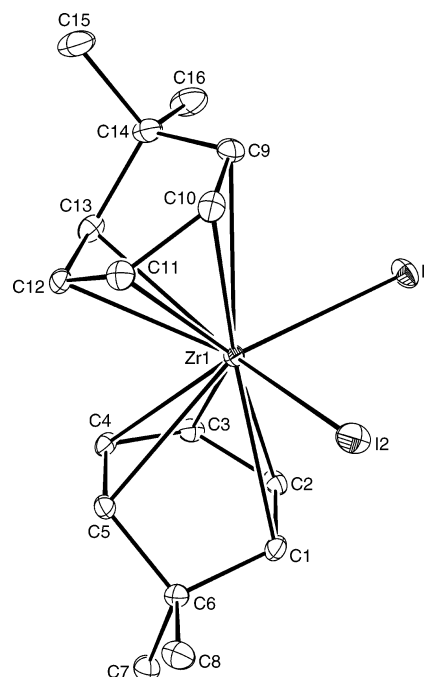


**Figure 1.** Perspective view of  $\text{Zr}(\text{6,6-dmch})_2\text{Cl}_2$ .

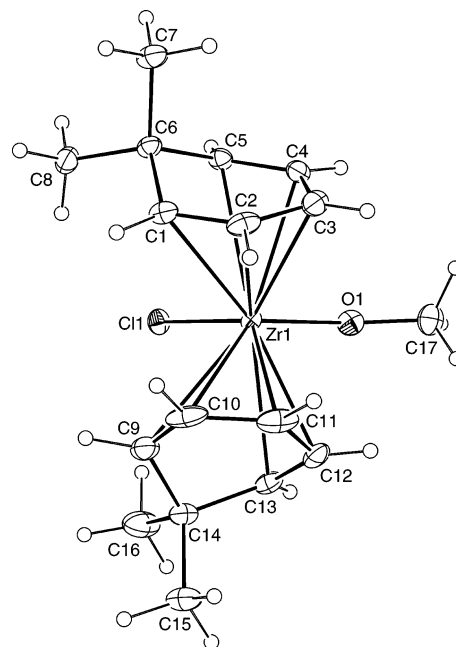


**Figure 2.** Perspective view of  $\text{Zr}(\text{6,6-dmch})_2\text{Br}_2$ .

quantities. One can therefore propose two possibilities. In one alternative, the ether coordination occurs first, and the oxygen atom “sticks” to the metal center long enough that the halogen abstraction can take place. Even though  $\text{O} \rightarrow \text{Zr}$  coordination does not generally give rise to cleavage of a  $\text{C}-\text{OCH}_3$  bond, the breakage of the  $\text{C}-\text{OCH}_3$  bond in this case would be accompanied by the conversion of a  $\text{C}-\text{C}$  single bond to a double bond. A slight variation of the above process entails the metal center first initiating the halogen atom abstraction, during which the ether oxygen atom finds its way to the metal center, leading to the same net result. In either case, it is the greater ability of the oxygen donor center to “stick” to the zirconium center that is the likely



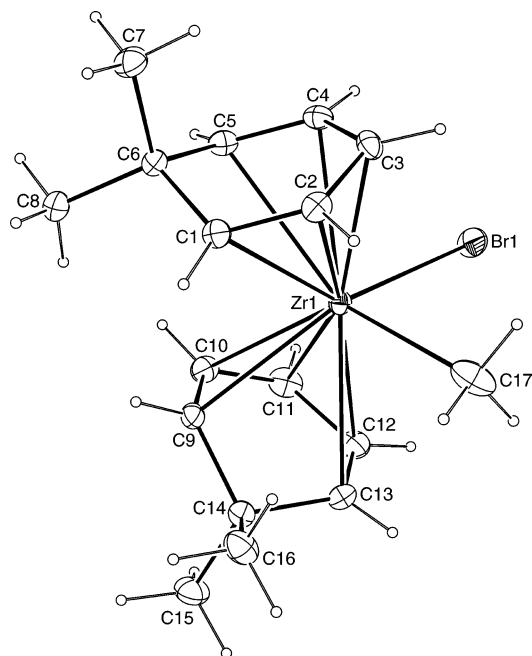
**Figure 3.** Perspective view of  $\text{Zr}(\text{6,6-dmch})_2\text{I}_2$ .



**Figure 4.** Perspective view of  $\text{Zr}(\text{6,6-dmch})_2(\text{OCH}_3)\text{Cl}$ .

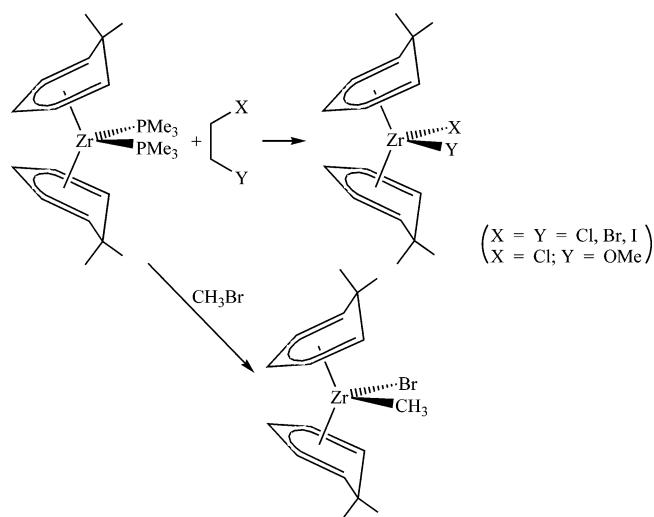
key. It can therefore be expected that this approach could also be used to deliver combinations of halogens and dialkylamino groups (as well as sulfur, phosphorus, and heavier analogues) to low valent metal complexes, whether pentadienyl, cyclopentadienyl, or other ligands happen to be present. Although other routes are available to such species already, notably nucleophilic displacement of halides, the approach applied here could be advantageous in some cases.

A well-known alternative approach to related species is through direct oxidative addition. The  $\text{Zr}(\text{6,6-dmch})_2$  fragment was also found to be susceptible to this approach, as exposure of  $\text{Zr}(\text{6,6-dmch})_2(\text{PMe}_3)_2$  to  $\text{CH}_3\text{-Br}$  vapor led to an immediate reaction, with the formation of the expected, orange  $\text{Zr}(\text{6,6-dmch})_2\text{Br}(\text{CH}_3)$  complex. Unfortunately, the compound lasts only briefly at



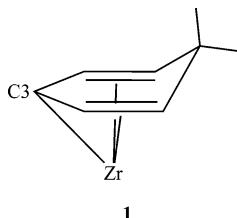
**Figure 5.** Perspective view of  $\text{Zr}(6,6\text{-dmch})_2(\text{CH}_3)\text{Br}$ .

### Scheme 1



room temperature, but it could be characterized through  $^1\text{H}$  NMR spectroscopy and a low-temperature X-ray diffraction study (*vide infra*). Interestingly, reactions of these halide complexes with methyllithium led to a bright yellow oil, presumed to be the dimethyl complex, but this could not be adequately characterized.<sup>10</sup>

**Structural Studies.** The structures of the dihalide complexes follow a trend exhibited by other high valent metal-pentadienyl compounds,<sup>4,5</sup> in which the central (C3) dienyl carbon atom is closest to the metal center, and the others become progressively further removed, consistent with resonance form **1**. The wide nature of



**1**

the electronically open pentadienyl ligands appears to lead to poor overlap with the contracted orbitals of metals in higher ( $= +4$ ) oxidation states, resulting in a significant contribution from a resonance structure with a substantially localized  $\text{M}-\text{C}3$  interaction (**1**). Indeed, an inspection of the  $\text{Zr}-\text{C}$  distances in the three dihalide complexes reveals that all the  $\text{Zr}-\text{C}3$  distances are essentially equivalent, averaging  $2.469(3)$  Å, while the values for the subsequent, further atoms become not only larger but also less well-defined. Thus, the average  $\text{Zr}-\text{C}[2,4]$  distance is  $2.536(5)$  Å, and that for  $\text{Zr}-\text{C}[1,5]$  is  $2.695(11)$  Å. For the related  $\text{Zr}(\text{C}_5\text{H}_5)(6,6\text{-dmch})\text{X}_2$  complexes, the corresponding averages are nearly the same as the above, at  $2.465$ ,  $2.54$ , and  $2.70$  Å.

The average  $\text{Zr}-\text{X}$  distances show marked increases from  $\text{X} = \text{Cl}$  to  $\text{X} = \text{I}$  ( $2.457(4)$ ,  $2.634(3)$ ,  $2.876(5)$  Å), although the increases exceed expectations based on the halogen covalent radii ( $0.99$ ,  $1.14$ ,  $1.33$  Å).<sup>13</sup> A similar observation has been made for  $\text{Zr}(\text{C}_5\text{H}_5)_2\text{X}_2$  complexes.<sup>14</sup> For the  $\text{Zr}(\text{C}_5\text{H}_5)(6,6\text{-dmch})\text{X}_2$  complexes, the respective average  $\text{Zr}-\text{X}$  distances were  $2.456(1)$ ,  $2.620(10)$ , and  $2.858(4)$  Å. The  $\text{X}-\text{Zr}-\text{X}$  angles in each complex average very close to  $93.6^\circ$ , whereas the values in the  $\text{Zr}(\text{C}_5\text{H}_5)_2\text{X}_2$  complexes are ca.  $96.2^\circ$ ,  $97^\circ$ , and  $96.2^\circ$ , respectively, for  $\text{X} = \text{F}$ ,  $\text{Cl}$ , and  $\text{I}$ .

Also of interest are some parameters related to the ligand orientations. In the open metallocenes themselves, the relative twists (conformation angles) between the ligands appear to reflect significant electronic differences in the bonding as a function of the metal center and/or its charge.<sup>1,2,15</sup> With the additional halide ligands in these complexes, there would seem to be less importance associated with the degree of twist between the dienyl ligands. Even though electronically there may be little importance to such differences, the dichloride complex adopts an arrangement somewhat different from that in the dibromide and diiodide complexes. In particular, in the latter complexes the  $\text{C}1-\text{C}2$  and  $\text{C}9-\text{C}10$  vectors are nearly aligned, but not so in the dichloride complex. Most likely the smaller size of chlorine allows for the adoption of a different conformation. This may also lead to some other differences between the dichloride and other dihalide structures. Thus, the angles between the dienyl ligand planes are  $124.7^\circ$ ,  $128.1^\circ$ , and  $127.7^\circ$ , respectively, for the  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$  compounds. For comparison, the values in the  $\text{Zr}(\text{C}_5\text{H}_5)(6,6\text{-dmch})\text{X}_2$  complexes are  $125.5^\circ$ ,  $125.5^\circ$ , and  $125.3^\circ$ , while the values for the  $\text{Zr}(\text{C}_5\text{H}_5)_2\text{X}_2$  complexes are  $127.8^\circ$ ,  $129^\circ$ , and  $126.3^\circ$ , respectively for  $\text{X} = \text{F}$ ,<sup>14</sup>  $\text{Cl}$ ,<sup>16</sup> and  $\text{I}$ .<sup>14</sup> Additionally, there is only a slight difference in fold angles (angle between the dienyl ligand plane and the  $\text{C}1$ ,  $\text{C}5$ ,  $\text{C}6$  plane), being  $39.9^\circ$ ,  $36.9^\circ$ , and  $36.9^\circ$ . The significant fold angles reflect a major difference between these and related boratabenzene complexes, for which the boron center does not experience

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a notable deviation from the “dienyl” plane, thereby establishing the presence of  $\eta^6$  coordination.<sup>17</sup>

The structure of  $\text{Zr}(6,6\text{-dmch})_2(\text{OCH}_3)\text{Cl}$  also follows the general pattern expected for higher valent metal pentadienyl complexes. Thus, for the two independent molecules, the average  $\text{Zr}-\text{C}[1,5]$ ,  $\text{Zr}-\text{C}[2,4]$ , and  $\text{Zr}-\text{C}[3]$  distances are 2.732, 2.552, and 2.483 Å, respectively. That these distances are consistently longer than those in the  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$  species can be attributed to the potential of the methoxy ligand to serve as a five-electron donor, as has been established already for related titanium complexes.<sup>18</sup> In particular, the average  $\text{Zr}-\text{O}-\text{C}$  angle of  $153.2(1)^\circ$  is significantly larger than the ideal value of  $133^\circ$  estimated for three-electron donation.<sup>19</sup> Of course, for this complex to reach the 18-electron configuration, the alkoxy ligand only needs to serve as a three-electron donor. However, the same could be said for either of the 6,6-dmch ligands, given the possibility of the alkoxide serving as a five-electron donor.<sup>20</sup> Hence, one expects that partial coordination of the alkoxide ligand's second lone pair is occurring in competition with the  $\text{dmch}\rightarrow\text{Zr}$  interactions. Had this been a “half-open”  $\text{Zr}(\text{C}_5\text{H}_5)(6,6\text{-dmch})(\text{OCH}_3)\text{Cl}$  complex instead, one would expect even more dramatic lengthening of the  $\text{Zr}-\text{dmch}$  coordination, as the competition with the alkoxy ligand should tend to involve the one dmch ligand more than the aromatic  $\text{C}_5\text{H}_5$  ligand. Interestingly, the average  $\text{Zr}-\text{Cl}$  distance of  $2.484(1)$  Å is longer than the value of  $2.457(4)$  Å in the dichloride complex. While chloride is not often considered a strong  $\pi$  donor,<sup>21</sup> it is nonetheless possible that the presence of the methoxy ligand does lead to loss of some  $\pi$  donation for the chloride ligand. It is notable that the  $\text{O}-\text{Zr}-\text{Cl}$  angles average  $98.0^\circ$ , significantly larger than the values of ca.  $93.6^\circ$  for the dihalide complexes. The average  $\text{C}[1]-\text{C}[2]$  and  $\text{C}[2]-\text{C}[3]$  distances, 1.364 and 1.408 Å, are similar to those in the dihalide compounds. The average angle between the dmch ligand planes is  $126.2^\circ$ , while the average fold angle is  $38.1^\circ$ .

The structure of  $\text{Zr}(6,6\text{-dmch})_2(\text{CH}_3)\text{Br}$  has, overall, the longest average  $\text{Zr}-\text{C}[3]$  distance, 2.495 Å, while the  $\text{Zr}-\text{C}[2,4]$  and  $\text{Zr}-\text{C}[1,5]$  distances are more in line with the other structures, at 2.540 and 2.674 Å. However, closer inspection reveals that the distances for one of the dmch ligands are consistently shorter than those of the other. The solid state conformation is unique among those reported here, in that the bridges of the two dmch ligands are both directed away from the

additional ligands ( $\text{CH}_3$ ,  $\text{Br}$ ). The angle between the two dienyl ligand planes is  $134.3^\circ$ , while the average fold angle is  $38.9^\circ$ . The average  $\text{C}[1]-\text{C}[2]$  and  $\text{C}[2]-\text{C}[3]$  distances, 1.376 and 1.414 Å, are again consistent with a resonance hybrid involving substantial  $\sigma$ -bond character between the metal center and the central carbon atom of the dienyl ligand (1).

The  $\text{Br}-\text{Zr}-\text{CH}_3$  angle of  $89.08(4)^\circ$  is the smallest in the observed structures. Given that the greatest angle was observed for the  $\text{Zr}(6,6\text{-dmch})_2(\text{OCH}_3)\text{Cl}$  complex, there seems to be a correlation between these angles and the  $\pi$ -donor abilities of the additional ligands. The  $\text{Zr}-\text{CH}_3$  and  $\text{Zr}-\text{Br}$  distances, at face value, are 2.481(2) and 2.6602(4) Å. The  $\text{Zr}-\text{C}$  distance appears long compared to values in related complexes,<sup>22</sup> and there is reason to believe it is subject to a systematic error arising from a ca. 91:9 disorder between the  $\text{CH}_3$  and  $\text{Br}$  positions. Taking this into account,<sup>23</sup> one could estimate corrected  $\text{Zr}-\text{CH}_3$  and  $\text{Zr}-\text{Br}$  distances of 2.374 and 2.665 Å. The “corrected”  $\text{Zr}-\text{CH}_3$  distance appears more in line with expectations.

## Conclusions

The halogen transfer reactions between 1,2-dihaloalkanes and  $\text{Zr}(6,6\text{-dmch})_2(\text{PMe}_3)_2$  provide effective routes to  $\text{Zr}(6,6\text{-dmch})_2\text{X}_2$  complexes and potentially to  $\text{Zr}(6,6\text{-dmch})\text{X}_3$  species as well. Although the reported yields could likely be optimized significantly, the approach does suffer from the loss of some of the 6,6-dmch anions in the original syntheses of the  $\text{Zr}(\text{II})$  starting materials. Now that it is clear that these  $\text{Zr}(\text{IV})$  6,6-dmch complexes are stable, it would seem possible to develop alternative routes involving the selective, direct incorporation of the 6,6-dmch ligand into  $\text{Zr}(\text{IV})$  complexes using  $\text{ZrX}_4$  starting materials.

The  $\text{Zr}(\text{IV})$  complexes reported in this study continue a significant structural trend observed previously, in that a single, short  $\text{Zr}-\text{C}$  interaction is present for each pentadienyl ligand, involving the central carbon atom. Apparently, the substantial contraction of the  $\text{Zr}(\text{IV})$  orbitals leads then to successively poorer interactions with the rest of the carbon atoms. The higher oxidation state also would greatly diminish the  $\delta$  back-bonding interaction, which can be important in the lower valent compounds.<sup>1,2</sup> The 6,6-dmch ligand, by virtue of its shorter  $\text{C}1-\text{C}5$  separation and enhanced donor abilities,<sup>24</sup> thus appears to be the ideal pentadienyl ligand for higher valent complexes. In the related half-open zirconocene analogues, much longer  $\text{M}-\text{C}$  distances were found for the pentadienyl ligand as compared to cyclopentadienyl, whereas for the  $\text{Zr}(\text{II})$  complexes, just the opposite was observed, reflecting a dramatic reversal in bonding preference. At any rate, the availability of

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higher valent metal pentadienyl compounds finally provides for an opportunity to explore this heretofore "missing" area of chemistry, particularly analogues of the ubiquitous  $M(C_5H_5)_2X_2$  complexes. Already it has become clear that the chemistry of the higher valent complexes, especially coupling reactions with unsaturated organic molecules,<sup>10,25</sup> differs dramatically from that exhibited by the much more common low valent compounds. The chemistry of these new complexes thus offers substantial potential for further study.

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**Supporting Information Available:** Positional coordinates, anisotropic thermal parameters, and additional bonding parameters for  $Zr(6,6\text{-dmch})_2Cl_2$ ,  $Zr(6,6\text{-dmch})_2Br_2$ ,  $Zr(6,6\text{-dmch})_2I_2$ ,  $Zr(6,6\text{-dmch})_2Cl(OCH_3)$ , and  $Zr(6,6\text{-dmch})_2Br(CH_3)$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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