

## Synthesis and Structural Characterization of $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$ : An *ansa*-Zirconocene Ethylene–Hydride Complex

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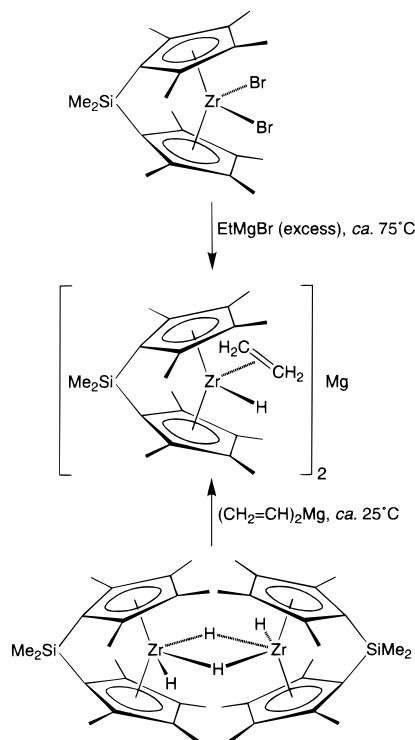
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Zirconocene olefin complexes have long been invoked as critical intermediates in a variety of synthetically important transformations. For example, zirconocene-catalyzed carbomagnesiation,<sup>1</sup> which involves the alkylation of an olefin by organomagnesium reagents, is commonly considered to occur via an olefin complex  $[\text{Cp}^R]_2\text{Zr}(\text{CH}_2=\text{CHR})$  that is generated by reaction of  $[\text{Cp}^R]_2\text{ZrCl}_2$  with  $\text{RCH}_2\text{CH}_2\text{MgX}$ . Likewise, zirconocene olefin–hydride and –alkyl species are important intermediates in catalytic olefin hydrogenation<sup>2</sup> and polymerization.<sup>3</sup> Furthermore, olefin–hydride complexes are viewed to be the likely intermediates responsible for alkyl group isomerization during hydrozirconation<sup>4</sup> and polymerization.<sup>5–7</sup> Despite their significance, however, zirconocene olefin–hydride complexes have not been isolated and structurally characterized. In this paper, we describe the first structurally characterized zirconocene ethylene–hydride complex, namely  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$ .

The reactions of zirconocene halide derivatives  $[\text{Cp}^R]_2\text{ZrX}_2$  with alkylating agents (e.g.,  $\text{RMgX}$ ,  $\text{RLi}$ ,  $\text{R}_3\text{Al}$ , and methylalumoxane) have been widely studied. Interestingly, even though these reactions may be surprisingly complex,<sup>8</sup> they nevertheless provide important reagents for organic synthesis<sup>9</sup> and catalysts for olefin polymerization.<sup>3</sup> Since *ansa* derivatives are also prevalent in the aforementioned applications, we have elected to investigate the reactions of the *ansa* complex  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrBr}_2$ <sup>10</sup> with Grignard reagents (Scheme 1). Significantly, whereas the reaction

Scheme 1



of  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrBr}_2$  with  $\text{MeMgBr}$  yields the dimethyl derivative  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrMe}_2$ ,<sup>11</sup> the corresponding reaction with  $\text{EtMgBr}$  yields the olefin–hydride complex  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$ . The latter complex may also be obtained by insertion of the vinyl group of  $(\text{CH}_2=\text{CH})_2\text{Mg}$  into the  $\text{Zr}-\text{H}$  bond of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\text{H})(\mu\text{-H})\}_2$  (Scheme 1).<sup>11</sup>

The molecular structure of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$  has been determined in the solid state by X-ray diffraction (Figure 1),<sup>12</sup> with the  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}^-$  fragment exhibiting the expected geometry for a bent metallocene derivative.<sup>13</sup> Furthermore, the diffraction study demonstrates that two of these  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}^-$  units are linked via a  $\text{Mg}^{2+}$  center, which interacts principally with the zirconium hydride ligands and the central methylene groups of the ethylene ligands; as such, the magnesium adopts a *pseudo*-tetrahedral coordination.<sup>14,15</sup> Presumably as a result of this interaction, the zirconium–olefin bonding is asymmetric, with  $d(\text{Zr}-\text{C}_{\text{cent}}) = 2.43 \text{ \AA}$  and  $d(\text{Zr}-\text{C}_{\text{lat}}) = 2.26 \text{ \AA}$ .<sup>16–18</sup> It is also evident that, with a C–C bond length of  $1.48 \text{ \AA}$ , the  $[\text{Zr}(\eta^2\text{-C}_2\text{H}_4)]$  moiety of  $\{[\text{Me}_2\text{-}$

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(12)  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg} \cdot (\text{C}_6\text{H}_6)$  is triclinic,  $P\bar{1}$  (No. 2),  $a = 10.379(1) \text{ \AA}$ ,  $b = 10.426(1) \text{ \AA}$ ,  $c = 22.868(1) \text{ \AA}$ ,  $\alpha = 97.901(1)^\circ$ ,  $\beta = 93.010(1)^\circ$ ,  $\gamma = 101.420(1)^\circ$ ,  $V = 2394.7(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $T = 293 \text{ K}$ .

(13) In benzene solution, the  $[\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}]$  moiety is characterized by two multiplets at  $\delta -0.64$  and  $-0.02$  in the  $^1\text{H}$  NMR spectrum for the central and lateral  $\text{CH}_2$  groups, respectively, and a singlet at  $-2.44$  for the zirconium hydride ligand.

(14) Individual bond lengths ( $\text{Å}$ ) are as follows:  $\text{Mg}-\text{C51}$  2.252(6),  $\text{Mg}-\text{C01}$  2.262(6),  $\text{Mg}-\text{H1}$  1.82,  $\text{Mg}-\text{H2}$  1.81.

(15) For an example of a metallocene olefin complex that exhibits an interaction with an aluminum center, namely,  $\text{Cp}^*_2\text{Ta}(\text{H})(\eta^2\text{-C}_2\text{H}_4)(\text{AlEt}_3)$ , see: McDade, C.; Gibson, V. C.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1–7.

(16) These values are the average of the two independent  $[\text{Zr}(\eta^2\text{-C}_2\text{H}_4)]$  interactions. Individual bond lengths ( $\text{Å}$ ) and angles (deg) are as follows:  $\text{Zr1}-\text{C51}$  2.425(6),  $\text{Zr1}-\text{C52}$  2.257(6),  $\text{C51}-\text{C52}$  1.485(7),  $\text{Zr1}-\text{H1}$  1.91(3),  $\text{Zr2}-\text{C01}$  2.436(6),  $\text{Zr2}-\text{C02}$  2.262(6),  $\text{C01}-\text{C02}$  1.482(7),  $\text{Zr2}-\text{H2}$  2.02(3);  $\text{C51}-\text{Zr1}-\text{C52}$  36.8(2),  $\text{C01}-\text{Zr2}-\text{C02}$  36.5(2).

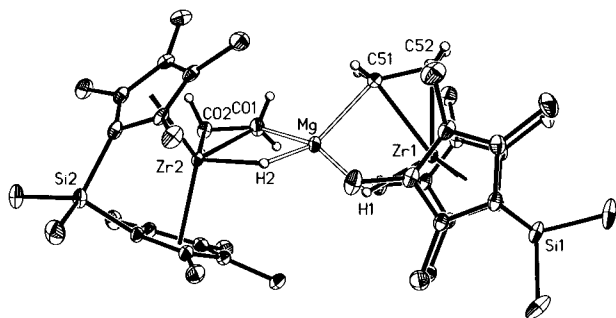


Figure 1. Molecular structure of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$ .

$\text{Si}(\text{C}_5\text{Me}_4)_2\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$  may be appropriately described as a metallacyclopropane.<sup>19</sup>

The synthesis of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$  is particularly noteworthy since zirconocene olefin-hydride complexes have not previously been isolated, even though olefin complexes have been obtained as phosphine adducts  $[\text{Cp}^R]_2\text{Zr}(\text{CH}_2=\text{CHR})(\text{PR}_3)$  from the reactions of  $[\text{Cp}^R]_2\text{ZrX}_2$  with  $\text{RCH}_2\text{CH}_2\text{MgX}$  in the presence of  $\text{PR}_3$ .<sup>20</sup> The formation of  $[\text{Cp}^R]_2\text{Zr}(\text{CH}_2=\text{CHR})(\text{PR}_3)$  is commonly considered to occur via elimination of alkane ( $\text{RCH}_2\text{CH}_3$ ) from the dialkyl  $[\text{Cp}^R]_2\text{Zr}(\text{CH}_2\text{CH}_2\text{R})_2$ . In certain instances, the reactions of zirconocene derivatives with  $\text{EtMgX}$  have also been reported to give dinuclear ethylene-bridged zirconocene complexes, e.g.,  $[\text{Cp}_2\text{ZrMe}]_2(\mu\text{-}\eta^2,\eta^2\text{-CH}_2=\text{CH}_2)$ <sup>21</sup> and  $\{[(\text{Me}_2\text{Si})_2(\text{C}_5\text{H}_3)]\text{ZrEt}\}_2(\mu\text{-}\eta^2,\eta^2\text{-CH}_2=\text{CH}_2)$ .<sup>7,22</sup>

Although the mechanism for the formation of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$  is undoubtedly complex, two species which have been identified prior to its generation are sequentially the ethyl-bromide complex,  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\text{Et})\text{Br}$ ,<sup>23</sup> and the metallacyclopentane derivative,  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_4\text{H}_8)$ ;<sup>24,25</sup>

(17) For comparison, the average bond lengths and angles for the two reported structures of  $\text{Cp}_2\text{Zr}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2$  are as follows:  $\text{Zr}-\text{C}_{\text{cent}} = 2.36$  Å,  $\text{Zr}-\text{C}_{\text{lat}} = 2.35$  Å,  $\text{C}-\text{C} = 1.47$  Å;  $\text{C}-\text{Zr}-\text{C} = 36.4^\circ$ . See: (a) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, 356, C83-C85. (b) Binger, P.; Müller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, 122, 1035-1042.

(18) In contrast, theoretical calculations indicate that the cationic olefin adduct  $[\text{Cp}_2\text{Zr}(\text{C}_2\text{H}_4)\text{H}]^+$  would be characterized by a considerably weaker interaction, i.e.  $\text{Zr}-\text{C}_{\text{cent}} = 2.75$  Å and  $\text{Zr}-\text{C}_{\text{lat}} = 2.46$  Å. See ref 5.

(19) For example, the C-C bond lengths in  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  are 1.53 and 1.33 Å, respectively.<sup>19a</sup> Furthermore, the C-C bond lengths in mononuclear transition metal olefin complexes span the range 1.3-1.49 Å.<sup>19b</sup> (a) Pauling L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; pp 222 and 230. (b) Cambridge Structural Database Version 5.14. *3D Search and Research Using the Cambridge Structural Database*; Allen, F. H.; Kennard, O. *Chem. Design Automation News* **1993**, 8 (1), p 1, 31-37.

(20) For examples of  $\text{Cp}^R_2\text{Zr}(\text{CH}_2=\text{CHR})(\text{PR}_3)$  complexes, see ref 9a and: Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, 88, 1047-1058.

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(22) For bridging zirconium olefin complexes that are not supported by cyclopentadienyl ligands, e.g.  $\text{Zr}_2\text{X}_6(\text{PEt}_3)_4(\text{C}_2\text{H}_4)$  (X = Cl, Br), see: Cotton, F. A.; Kibala, P. A. *Inorg. Chem.* **1990**, 29, 3192-3196.

the latter complex is presumably obtained via an ethylene intermediate,  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)$ . Assuming that the interconversion between  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_4\text{H}_8)$  and  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)$  is reversible,<sup>26</sup> a possible pathway for the formation of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}^-$  involves alkylation of the latter giving  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{Et}\}^-$ ,<sup>27</sup> followed by  $\beta$ -hydrogen elimination.

The reactivity of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}^-$  also provides supporting evidence for its characterization as an olefin adduct. For example, addition of  $\text{I}_2$  results in elimination of  $\text{C}_2\text{H}_4$  and formation of  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrI}_2$ . Likewise,  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}^-$  reacts with  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrBr}_2$  to generate, inter alia,  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\text{Et})\text{Br}$ .

In summary,  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$ , the first structurally characterized example of an olefin-hydride complex of zirconium, has been synthesized by (i) the reaction of  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrBr}_2$  with excess  $\text{EtMgBr}$  and (ii) insertion of  $(\text{CH}_2=\text{CH})_2\text{Mg}$  into the  $\text{Zr}-\text{H}$  bonds of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\text{H})(\mu\text{-H})\}_2$ .

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**Supporting Information Available:** Experimental details for all compounds and crystallographic data for  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{H}\}_2\text{Mg}$  (24 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(23)  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\text{Et})\text{Br}$  may be isolated by the reaction of  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrBr}_2$  with  $\text{EtMgBr}$  (ca. 1.5 equiv) in THF at room temperature.

(24)  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_4\text{H}_8)$  may be synthesized by the reaction of  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrBr}_2$  with  $\text{EtMgBr}$  (ca. 4 equiv) in THF at room temperature; however,  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_4\text{H}_8)$  is more conveniently obtained from the corresponding reaction of  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{ZrCl}_2$  with  $\text{EtMgCl}$  since the reaction is faster.  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_4\text{H}_8)$  may also be generated by reaction of the hydride complex  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\text{H})(\mu\text{-H})\}_2$  with  $\text{C}_2\text{H}_4$  at room temperature.

(25) The permethylcyclopentadienyl analogue  $\text{Cp}^*\text{Zr}(\eta^2\text{-C}_4\text{H}_8)$  is also known. See: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, 100, 2716-2724.

(26) In support of this suggestion,  $\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_4\text{H}_8)$  is unstable with respect to dissociation of ethylene and  $\text{Cp}^*_2\text{Ti}(\text{C}_2\text{H}_4)$ .<sup>26a</sup> Furthermore,  $\text{Cp}_2\text{Zr}(\text{C}_4\text{H}_8)$  reacts with  $\text{PMe}_3$  to give the olefin complex  $\text{Cp}_2\text{Zr}(\text{C}_2\text{H}_4)\text{PMe}_3$ .<sup>26b</sup> (a) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, 105, 1136-1143. (b) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1989**, 852-853.

(27) Supporting the notion that the reaction may proceed via  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Zr}(\eta^2\text{-C}_2\text{H}_4)\text{Et}\}^-$ , the reaction of  $\text{Cp}_2\text{ZrCl}_2$  with  $\text{EtMgBr}$  (3 equiv) in the presence of  $\text{PMe}_3$  has been reported to generate a species tentatively identified as  $[\text{Cp}_2\text{ZrEt}(\text{C}_2\text{H}_4)]\text{MgBr}$ ; the latter complex reacts with  $\text{H}_2$  to give an uncharacterized hydride derivative.<sup>27a</sup> Furthermore,  $[\text{Cp}_2\text{Zr}(\eta^2\text{-CH}_2=\text{CHR})\text{CH}_2\text{CH}_2\text{R}]^-$  species have also been suggested to be intermediates in carbomagnesiation reactions.<sup>27b-d</sup> (a) Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E. *Chem. Lett.* **1991**, 1579-1582. (b) Lewis, D. P.; Whitby, R. J.; Jones, R. V. H. *Tetrahedron* **1995**, 51, 4541-4550. (c) Hourai, A. F.; Didiuk, M. T.; Xu, Z.; Horan, N. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, 115, 6614-6624. (d) Hoveyda, A. H.; Morken, J. P.; Hourai, A. F.; Xu, Z. *J. Am. Chem. Soc.* **1992**, 114, 6692-6697.