

## Identification of Zr(III) Allyl Species in the Negishi System [Cp<sub>2</sub>ZrCl<sub>2</sub>, 2LiBu]. An ESR Study

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The development of new, efficient methods for the synthesis of functionalized compounds represents a central theme of research in the area of organic synthesis. The chemistry of the group 4 elements is widely used and developed in this field.<sup>1</sup> In this context, one of the valuable processes for the reductive coupling of unsaturated organic molecules<sup>2</sup> relies on the use of the [Cp<sub>2</sub>ZrCl<sub>2</sub>, 2LiBu] system as a precursor for zirconocene "Cp<sub>2</sub>Zr" species at low temperature (−78 °C) and is based on the method described by Negishi.<sup>3c</sup> Cp<sub>2</sub>Zr(Bu)<sub>2</sub> and the corresponding alkene zirconocene, trapped as the phosphine adduct Cp<sub>2</sub>Zr(CH=CH<sub>2</sub>Et)(PR<sub>3</sub>),<sup>3</sup> were among the Zr complexes identified in these reactions.

Recently, the [Cp<sub>2</sub>ZrCl<sub>2</sub>, 2LiBu] system was also reported as being an efficient catalyst for alkene hydrosilylation using primary and secondary silane reagents at 90 °C.<sup>4</sup> The mechanism of these reactions remains unclear despite numerous attempts to elucidate it.<sup>4b,5</sup> Corey et al.<sup>6</sup> suggest that paramagnetic species could be responsible for the hydrosilylation catalytic process, although no evidence was established by them to support their assumption. Active Ti<sup>III</sup> species from Cp<sub>2</sub>TiMe<sub>2</sub> are detected in the case of silane polymerization. However, there is no evidence that the Zr<sup>III</sup> species from Cp<sub>2</sub>ZrMe<sub>2</sub> are important in the polymerization mechanism.<sup>7</sup>

This article sheds a new light on the [Cp<sub>2</sub>ZrCl<sub>2</sub>, 2LiBu] system. We find that the thermal decomposition of Cp<sub>2</sub>ZrCl<sub>2</sub> with 2 equiv of LiBu at room temperature leads to the Zr<sup>III</sup> species Cp<sub>2</sub>Zr(Me-allyl) as demonstrated by ESR spectroscopy

and chemical derivatization. Simple allyl Cp<sub>2</sub>Zr(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>) is also obtained from Cp<sub>2</sub>ZrCl<sub>2</sub> and <sup>1</sup>PrMgCl and characterized by ESR.

The addition, at room temperature, of 2 equiv of LiBu in hexane to a stirred solution of Cp<sub>2</sub>ZrCl<sub>2</sub> in toluene, followed by stirring the mixture for at least 15 min, produced an orange solution which was analyzed by ESR spectroscopy.<sup>8</sup> At room temperature, the ESR spectrum (Figure 1a) shows at least 25 lines and consists of a badly resolved central signal with well-resolved Zr satellites on both sides ( $g = 1.994$ ;  $a(^1\text{H}) = 0.59$  G,  $a(^{91}\text{Zr}) = 33.4$  G). It also appears to have similar features to spectra obtained from Ti<sup>III</sup> allyl complexes at low temperature.<sup>9</sup> Although we were unable to obtain unambiguous assignments of all the peaks of this spectrum, we concluded that the ESR signal is due to the complex Cp<sub>2</sub>Zr(η<sup>3</sup>-Me-allyl) based upon the comparison with ESR spectra measured for analogous titanium(allyl) complexes. Even though Ti<sup>III</sup> allyl complexes are well-known and fully characterized,<sup>10</sup> no Zr<sup>III</sup> allyl complexes have so far been reported in the literature. Further evidence for the formation of a (η<sup>3</sup>-Me-allyl) Zr<sup>III</sup> complex comes from the low temperature ESR spectrum obtained at 203 K from a solution prepared at room temperature (Figure 1b). A well-resolved spectrum is observed consisting of 30 lines separated by 0.56 G and with a line intensity near zero at the center of the ESR pattern. Computer simulation allows us to attribute it unambiguously to the interaction of the unpaired electron on Zr with 10 proton nuclei of the 2 equivalent cyclopentadienyl ligands ( $a(^1\text{H}) = 0.56$  G), 3 equivalent proton nuclei of the allyl group (or at least with a similar hyperfine coupling constant) (CH<sub>3</sub>)CHCH-CH<sub>2</sub> ( $a(^1\text{H}) = 2.85$  G), and 1 proton nucleus of hydrogen perturbed by the proximal presence of the methyl group ( $a(^1\text{H}) = 3.705$  G) (Figure 1c). Further evidence for the formation of an allyl Zr<sup>III</sup> comes from the formation of unsaturated ketone PhCOCH(CH<sub>3</sub>)CH=CH<sub>2</sub> or its isomer (characterized by GC/MS and quantified to determine the amount of the Zr<sup>III</sup> allyl species formed, i.e., 40–45% depending upon the experiments) by the reaction with PhCOCl.<sup>11</sup> When the reaction of Cp<sub>2</sub>ZrCl<sub>2</sub> with 2LiBu is monitored by ESR from −78 °C to room temperature, the ESR signal of the allyl Zr<sup>III</sup> species is observed at −40 °C. When the same reaction is performed with deuterated solvents (toluene-*d*<sub>8</sub> or benzene-*d*<sub>6</sub>), a similar ESR spectrum is observed which precludes the intervention of deuterium from the solvent in the reaction mixture. Evolution of Cp<sub>2</sub>Zr(η<sup>3</sup>-Me-allyl) to "Cp<sub>2</sub>ZrH" as a characteristic ESR doublet ( $g = 1.987$ ;  $a(^1\text{H}) = 6.9$  G) occurs when the solution is heated to 90 °C.<sup>12ab</sup> Identification of Zr<sup>III</sup> species from the [Cp<sub>2</sub>ZrCl<sub>2</sub>, 2LiBu] system provides an experimental support which suggests the presence of paramagnetic species responsible for the hydrosilylation catalytic process.<sup>6,7</sup>

Encouraged by these results, we were prompted to enlarge our studies to investigate other allyl Zr<sup>III</sup> species such as Cp<sub>2</sub>Zr(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>). Assignment of ESR spectra would be much simpler in this case since all five protons of the allyl group are expected to be equivalent (or at least with a similar hyperfine coupling constant). Upon addition of 2 equiv of <sup>1</sup>PrMgCl to Cp<sub>2</sub>ZrCl<sub>2</sub>, the ESR spectrum of the purple solution exhibited a

(8) In a glovebox, LiBu in hexane (22 mmol, of a 1.6 M solution) was added to a stirred dry, oxygen-free toluene (2 mL) containing Cp<sub>2</sub>ZrCl<sub>2</sub> (30 mg, 10.3 mmol). The resulting orange solution developed after 15 min was monitored by ESR technique.

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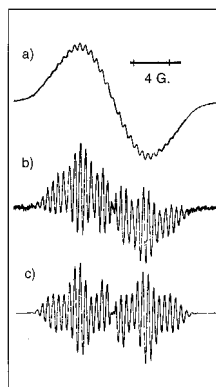
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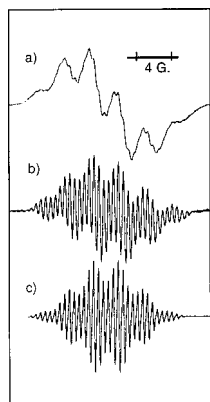
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**Figure 1.** X-band ESR spectra of toluene solution [ $\text{Cp}_2\text{ZrCl}_2$ , 2LiBu]: (a) at room temperature; (b) at low temperature 203 K; (c) computer simulation: see text for details.



**Figure 2.** X-band ESR spectra of toluene solution [ $\text{Cp}_2\text{ZrCl}_2$ , 2 $^i\text{PrMgCl}$ ]: (a) at room temperature; (b) at low temperature 203 K; (c) computer simulation: see text for details.

signal at room temperature (Figure 2a) in which a sextet with a hyperfine coupling could be observed ( $g = 1.994$ ;  $a(^1\text{H}) = 2.6$  and  $0.56$  G). The superhyperfine structure is also resolved on the Zr satellites on both sides of the central signal ( $a(^{91}\text{Zr}) = 31.5$  G). At low temperature (203 K), the splitting of the lines is better resolved and appears as a clear sextet splitting, with a 1:5:10:10:5:1 intensity distribution (Figure 2b). It is rational to identify  $\text{Cp}_2\text{Zr}(\eta^3\text{-allyl})$  as a  $\text{Zr}^{\text{III}}$  species present in the solution where the unpaired electron on the Zr center interacts with the five nearly magnetically equivalent proton nuclei of the allyl ( $a(^1\text{H}) = 2.52$  G) and the ten equivalent proton nuclei of the two cyclopentadienyl ligands ( $a(^1\text{H}) = 0.52$  G). Computer simulations also allowed us to analyze the characteristic values of the ESR spectrum (Figure 2c;  $a(^1\text{H}) = 2.5$  and  $0.5$  G).

It is worthy to note that further support for our assignment comes from the chemical reduction of  $\text{Cp}_2\text{Zr}(\text{Me-allyl})_2$ <sup>12</sup> and  $\text{Cp}_2\text{Zr}(\text{C}_3\text{H}_5)_2$ <sup>10</sup> with Na/naphthalene; identical ESR spectra to those from  $[\text{Cp}_2\text{ZrCl}_2, 2\text{LiBu}]$  or from  $[\text{Cp}_2\text{ZrCl}_2, ^i\text{PrMgCl}]$  systems were obtained both at room and at low temperature.<sup>13</sup>

These allyl complexes are formed in roughly 40/50% from the starting  $\text{Cp}_2\text{ZrCl}_2$ , established with a study of paramagnetism monitored by  $^1\text{H}$  NMR (Evans' method)<sup>14</sup> or by chemical derivatization with  $\text{PhCOCl}$  as mentioned above. The paramagnetism of the toluene solution decreases to approximately 10% after a 24 h period depending on different runs. We also identified the formation of free cyclopentadienyl  $\text{C}_5\text{H}_6$  in the

(12) (a) Complex  $\text{Cp}_2\text{Zr}(\text{Me-allyl})_2$  is prepared by treatment of  $\text{Cp}_2\text{ZrCl}_2$  with allyl Grignard  $\text{CH}_2=\text{CH-CH}(\text{CH}_3)\text{MgCl}$  according to ref 10b. Satisfactory C,H analyses are obtained. NMR spectroscopic data, in agreement with our formulation, will be fully described in a full account. A toluene solution of  $\text{Cp}_2\text{Zr}(\text{Me-allyl})_2$ , in a sealed tube, heated to 90 and 100 °C for 1 h, does not show an ESR signal. (b) On the other hand, the evolution of the ESR spectrum from  $\text{Cp}_2\text{Zr}(\eta^3\text{-allyl})$  species to " $\text{Cp}_2\text{ZrH}$ " was not observed when the solution was heated to 90 °C for 3 h.

solution by GC/MS in different experiments, but the hydrolysis of the solution could account for its formation. No dihydrogen was produced in the reaction by analyzing the head gases of the reaction by MS.

When a solution of  $\text{Cp}_2\text{Zr}(\eta^3\text{-Me-C}_3\text{H}_4)$  is mixed with  $\text{PPhMe}_2$  phosphine, a doublet of triplets ESR signal is obtained with the characteristic coupling values of a hyperfine interaction to one phosphorus and two protons of a methylene group ( $g = 1.989$ ,  $a(^{31}\text{P}) = 23.7$  G,  $a(^1\text{H}) = 3.7$  G,  $a(^{91}\text{Zr}) = 21.2$  G).<sup>15</sup> We assign this spectrum to the formation of the paramagnetic  $\sigma$ -allyl complex  $\text{Cp}_2\text{Zr}(\sigma\text{-Me-allyl})(\text{PR}_3)$ .<sup>16</sup> In the presence of styrene, butene is evolved (as already observed by Waymouth in an attempt to understand the mechanism of the hydrosilylation using the same system), and a new broad, badly resolved, paramagnetic signal at room and at low temperature (220 K) appears at  $g = 1.993$ , whereas the  $\text{Zr}^{\text{III}}$  allyl signal disappears.

The mechanism for the formation of  $\text{Zr}^{\text{III}}$  allyl complexes requires the elimination of a hydrogen atom from the suggested  $\text{Cp}_2\text{Zr}(\text{butene})$  complex (or  $\text{Cp}_2\text{Zr}(\text{propene})$ ) produced from  $\text{Cp}_2\text{Zr}(\text{Bu})_2$  and identified at  $-78$  °C. The formation of an intermediate  $\eta^3$ -allyl hydride complex from the  $\eta^2$ -olefin metal complex is a recognized mechanism.<sup>17</sup>  $\text{Cp}_2\text{ZrH}(\text{Me-allyl})$  complex has recently been identified from  $\text{Cp}_2\text{ZrCl}_2, 2\text{LiBu}$ , at a low temperature ( $-20$  °C).<sup>18</sup> A plausible pathway would then be the hydride transfer from the Zr ( $\eta^3$ -allyl) hydride to  $\text{Cp}_2\text{Zr}(\text{butene})$ —still present in solution—through a homobimetallic complex  $\text{Zr}^{\text{IV}}\text{-Zr}^{\text{II}}$ ,<sup>19a</sup>—followed by the formation of  $\text{Zr}^{\text{III}}$  species, namely  $\text{Cp}_2\text{Zr}(\eta^3\text{-Me-allyl})$  and unstable  $\text{Cp}_2\text{Zr}(\text{butyl})$  which decomposes<sup>19b</sup> into an unidentified species.

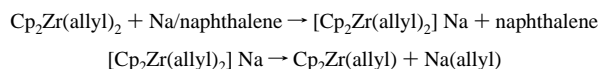
Following the work of Waymouth<sup>4b</sup> and Corey,<sup>6</sup> we add a new piece in the mechanistic puzzle of the thermal decomposition process of the  $[\text{Cp}_2\text{ZrCl}_2, 2\text{LiBu}]$  system. Definitely, we are able to point out that we have observed the formation of allyl  $\text{Zr}^{\text{III}}$  species in the  $[\text{Cp}_2\text{ZrCl}_2, 2\text{LiBu}]$  system; however, it is difficult to surmise the process or processes by which the  $\text{Zr}^{\text{III}}$  allyl is formed and thereby to propose a mechanism which explains, in its entirety, all the experimental results.<sup>20</sup>

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**Supporting Information Available:** ESR, mass, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (14 pages). See any current masthead page for ordering and Internet access instructions.

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(13) We suggest the following pathway for the chemical reduction of



Only 20–25% of  $\text{Cp}_2\text{Zr}^{\text{III}}(\text{allyl})$  species (allyl:  $\text{C}_3\text{H}_5$ ,  $\text{Me-C}_3\text{H}_4$ ) were assumed with paramagnetic moment measurements by Evans' method.<sup>14</sup>

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