

## Communications to the Editor

### Planar Tetracoordinate Carbon in $\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1,\eta^2\text{-Me}_3\text{SiCCPh})(\mu\text{-Cl})\text{AlMe}_2$

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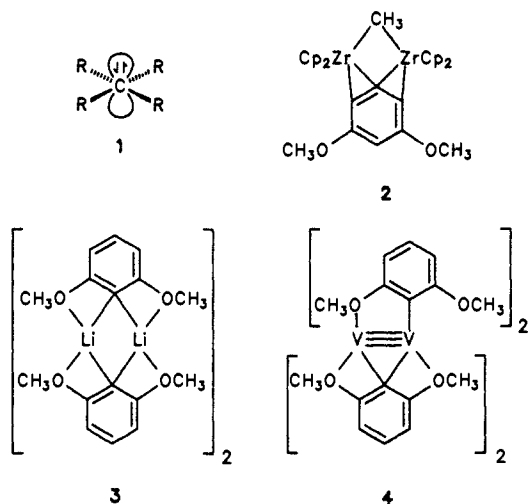
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Planar tetracoordinate carbon exhibits an electron-deficient  $\sigma$ -system (a total of six electrons making four  $\sigma$ -bonds) and a filled (two electrons) p orbital perpendicular to the  $\sigma$ -plane (1).<sup>1</sup>



Accordingly,  $\sigma$ -donating/ $\pi$ -accepting metal substituents have been calculated to electronically stabilize this uncommon coordination geometry of carbon to some extent.<sup>2</sup> To our knowledge, the very few examples of an experimental realization of this concept had to make use of an extensive delocalization of the surplus p-electron density into an extended conjugated organic  $\pi$ -system (such as typically observed in 2-4).<sup>3</sup> We have now found a first example (7) where the planar coordination geometry of tetravalent carbon in a simple olefinic bonding situation is sufficiently stabilized by the combined electron-donating abilities of a main-group and a transition metal to become the global minimum of the system.

The hydrozirconation of phenyl(trimethylsilyl)acetylene yielded the  $\beta$ -CH agostic alkenylzirconocene chloride complex 5, as previously described.<sup>4</sup> Complex 5 was reacted with 1 molar equiv

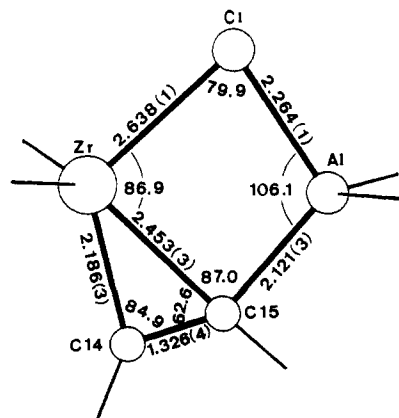


Figure 1. Distances and angles within the central part of 7 (maximum deviation from the mean plane,  $\pm 0.04$  Å). Bond angles C(14),C(15),C(16) 120.8 (2)°, C(16),C(15),Al 89.8 (2)°, Zr,C(14),Si 144.4 (1)°, Si,C(14),C(15) 130.4 (2)°. Bond lengths C(15)-C(16) 1.513 (4) Å, C(14)-Si 1.876 (3) Å.

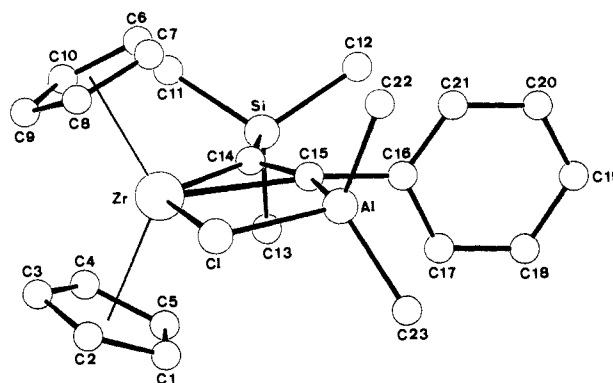
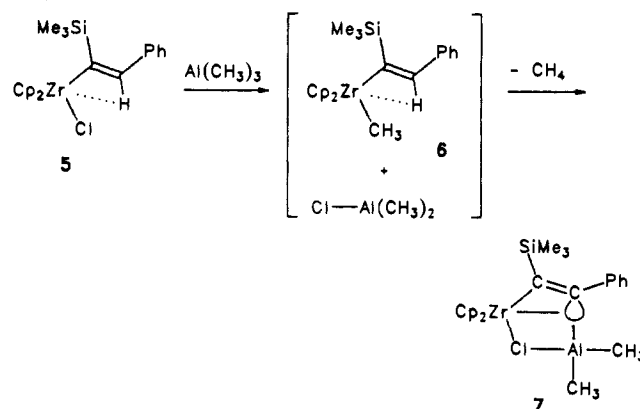


Figure 2. A view of the molecular structure of complex 7, featuring the planar and tetracoordinate geometry of the olefinic carbon atom C(15).

of trimethylaluminum in toluene solution at ambient temperature. We assume that this leads to chloride vs methyl exchange at zirconium to give the intermediate 6. Acid/base reaction between the acidic agostic  $\beta$ -alkenyl hydrogen bond and the zirconium-bound methyl group gives methane plus a reactive ( $\eta^2$ -alkyne)-metallocene complex, which is trapped by the in situ formed dimethylaluminum chloride to give  $\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1,\eta^2\text{-Me}_3\text{SiCCPh})(\mu\text{-Cl})\text{AlMe}_2$  (7) (90% isolated).<sup>5</sup>



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Complex **7** was characterized by X-ray diffraction. It contains a planar central five-membered metallabicyclic ring system (Zr-C(14)-C(15)-Al-Cl) with very unusual bonding parameters. The plane of this ring system bisects the Cp-Zr-Cp angle, and the substituents at the carbon atoms C(14) and C(15) are oriented in the plane of the metallacycle. These features are evident from Figure 1, which gives geometric parameters of the central part of the molecule.

Carbon atom C(15) is planar and tetracoordinate. Its bonding situation is best described by forming four  $\sigma$ -bonds to its neighboring atoms. These bonds are oriented normal to the plane of the  $\pi$ -bond between atoms C(14) and C(15). The angle Cl-Zr-C(14) ( $119.5(1)^\circ$ ) is about  $20\text{--}30^\circ$  larger than typically found in tetracoordinated bis( $\eta$ -cyclopentadienyl)ZrX<sub>2</sub> complexes.<sup>6</sup> The bonding angles at C(14) deviate strongly from the expected values for a sp<sup>2</sup>-hybridized carbon atom. The angle Zr-C(14)-C(15) ( $84.9(2)^\circ$ ) is very small. As a consequence, the angles Zr-C(14)-Si and Si-C(14)-C(15) are larger than  $120^\circ$ . These structural features support a bonding interaction between atoms Zr and C(15).

The plane of the aromatic substituent at atom C(15) is oriented perpendicular to the mean plane of the metallabicyclic. This completely eliminates any conjugation between the aromatic and olefinic  $\pi$ -systems present. It may be that this orientation is favored because it allows for a small stabilizing electronic interaction between the electron-rich aromatic  $\pi$ -system and the electron-deficient  $\sigma$ -system around the planar and tetracoordinate carbon atom C(15) or a weak bonding interaction between Al and C(16) (the distance is  $2.602(3) \text{ \AA}$ ).<sup>7</sup>

The Zr-Cl bond ( $2.638(1) \text{ \AA}$ ) is quite long. This and an elongated Al-C(15) bond ( $2.121(3) \text{ \AA}$ )—the Al-methyl distances (Al-C average,  $1.96(1) \text{ \AA}$ ) are normal—support an alternative description of the bonding situation as a Cp<sub>2</sub>Zr-alkyne ("metallacyclopentene") fragment stabilized by addition of R<sub>2</sub>AlCl.

Controlled stoichiometric hydrolysis of **7** leads to the formation of the agostic alkylmetallocene complex **5**. With excess aqueous acid, *cis*-1-phenyl-2-(trimethylsilyl)ethene is formed. Exposure of **7** to molecular oxygen leads to the formation of phenyl(tri-

methylsilyl)acetylene. A regioisomeric complex (**8**), where the positions of the phenyl and trimethylsilyl substituents at the Zr,Al-bridging alkyne moiety are exchanged, is formed upon thermolysis of **7** (benzene solution, room temperature). Equilibrium ( $[\mathbf{7}]:[\mathbf{8}] = 0.7$ ) is reached after 2 weeks at  $25^\circ\text{C}$ . The isomerization reaction presumably proceeds via a ring-opened ( $\eta^2$ -alkyne)zirconocene-ClAlMe<sub>2</sub> adduct.<sup>8</sup> We are currently investigating whether the presence of a planar-tetracoordinate carbon in **7** gives rise to uncommon chemical behavior of such a metal complex.

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**Registry No.** **5**, 119747-83-0; **7**, 129265-56-1; **7a**, 129265-58-3; **8**, 129265-57-2; **8a**, 129265-59-4; AlMe<sub>3</sub>, 75-24-1; AlEt<sub>3</sub>, 97-93-8; *cis*-1-phenyl-2-(trimethylsilyl)ethene, 19319-11-0; phenyl(trimethylsilyl)acetylene, 2170-06-1.

**Supplementary Material Available:** Tables of crystal structure and details of data collection, bond distances and angles, and atomic positional and thermal parameters of **7** (8 pages); listings of observed and calculated structure factors of **7** (17 pages). Ordering information is given on any current masthead page.

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## A Negative Catalytic Term Requires a Common Intermediate in the Imidazole Buffer Catalyzed Cleavage and Rearrangement of Ribodinucleotides

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(5) **7**: 90% isolated; mp  $140\text{--}142^\circ\text{C}$  dec; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $-0.42$  (s, 6 H, AlMe<sub>2</sub>),  $-0.12$  (s, 9 H, SiMe<sub>3</sub>),  $5.63$  (s, 10 H, Cp),  $6.60\text{--}7.12$  (m, 5 H, Ph); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $-5.9$  (AlMe<sub>2</sub>),  $1.2$  (SiMe<sub>3</sub>),  $110.4$  (Cp),  $126.4$ ,  $127.4$ ,  $130.5$ ,  $143.2$  (Ph),  $221.4$  (Zr=C=), signal of =C-Al not observed. Anal. Calcd for C<sub>23</sub>H<sub>30</sub>AlClSiZr: C, 56.58; H, 6.19. Found: C, 56.61; H, 6.45. X-ray crystal structure analysis: space group C2/c;  $a = 18.146(6)$ ,  $b = 9.731(1)$ ,  $c = 27.218(3) \text{ \AA}$ ;  $\beta = 102.97(2)^\circ$ ;  $V = 4683.5 \text{ \AA}^3$ ;  $d_{\text{calc}} = 1.39 \text{ g cm}^{-3}$ ;  $\mu = 6.69 \text{ cm}^{-1}$ ;  $Z = 8$ ;  $\lambda = 0.71069 \text{ \AA}$ ; measured reflections  $5790 (\pm h, \pm k, \pm l)$ ;  $\sin \theta/\lambda_{\text{max}} = 0.65$ ; independent reflections 5350, observed reflections 4703; refined parameters 244,  $R = 0.037$ ,  $R_w = 0.049$ ; residual electron density  $0.56 \text{ e \AA}^{-3}$ ; structure was solved by heavy atom method; hydrogen atom positions were calculated and kept fixed in the final refinement stages. **8**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $-0.12$  (s, 6 H, AlMe<sub>2</sub>),  $0.12$  (s, 9 H, SiMe<sub>3</sub>),  $5.47$  (s, 10 H, Cp),  $6.60\text{--}7.15$  (m, 5 H, Ph); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $-3.3$  (AlMe<sub>2</sub>),  $4.6$  (SiMe<sub>3</sub>),  $110.6$  (Cp),  $123.3$ ,  $124.7$ ,  $128.1$ ,  $150.5$  (Ph),  $231.4$  (Zr=C=), =C-Al signal not observed. The reaction of **5** with triethylaluminum gave the analogous Cp<sub>2</sub>Zr( $\mu$ - $\eta^2$ -Me<sub>2</sub>SiCCPh)( $\mu$ -Cl)AlEt<sub>2</sub> compounds (**7a**, **8a**). **7a**: 45% isolated; mp  $104\text{--}106^\circ\text{C}$  dec; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $-0.11$  (s, 9 H, SiMe<sub>3</sub>),  $0.15$  (q, 4 H) and  $1.23$  (t, 6 H, AlEt<sub>2</sub>),  $5.65$  (s, 10 H, Cp),  $6.70\text{--}7.12$  (m, 5 H, Ph); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $1.3$  (SiMe<sub>3</sub>),  $3.2$  and  $10.4$  (AlEt<sub>2</sub>),  $110.3$  (Cp),  $126.5$ ,  $127.8$ ,  $129.6$ ,  $143.7$  (Ph),  $221.0$  (Zr=C=), =C-Al signal not observed. Anal. Calcd for C<sub>27</sub>H<sub>34</sub>AlClSiZr: C, 58.14; H, 6.64. Found: C, 57.86; H, 6.82. **8a**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $0.11$  (s, 9 H, SiMe<sub>3</sub>),  $0.30$  (q, 4 H) and  $1.45$  (t, 6 H, AlEt<sub>2</sub>),  $5.49$  (s, 10 H, Cp),  $6.70\text{--}7.12$  (m, 5 H, Ph); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $4.5$  (SiMe<sub>3</sub>),  $5.6$  and  $10.6$  (AlEt<sub>2</sub>),  $110.6$  (Cp),  $123.4$ ,  $124.7$ ,  $128.1$ ,  $141.7$  (Ph),  $232.8$  (Zr=C=), =C-Al signal not observed. The [**7a**]:[**8a**] equilibrium ratio is 1.7 at room temperature.

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We have described a detailed kinetic study of the reactions of 3',5''-uridyridine (UpU) catalyzed by imidazole buffer.<sup>1</sup> The cyclization/cleavage to form uridine 2',3'-cyclic phosphate with cleavage of uridine was catalyzed by a sequential bifunctional mechanism in which a phosphorane monoanion is formed in one early step and then is cleaved to product in a later step. Imidazole (Im) catalyzes one of these steps, imidazolium ion (ImH<sup>+</sup>) the other, but the sequence of their operation is kinetically ambiguous. By contrast, the rearrangement of 3',5''-UpU to its 2',5''-UpU isomer is catalyzed by ImH<sup>+</sup> alone. If this also proceeds through the same phosphorane monoanion, then the ambiguity is removed, and in the cleavage the first catalyst is ImH<sup>+</sup> (or its kinetic equivalent, H<sup>+</sup> followed by Im, as in Scheme I).

The mechanism that this implies was described<sup>1</sup> (Scheme I), and we showed<sup>2</sup> that it probably can be extended to the mechanism of the enzyme ribonuclease A (with suitable modification, in which some sequential steps in the model become simultaneous in the enzyme). Calculations by the Karplus group are consistent with our proposals.<sup>3</sup> The mechanism also guided us in the redesign of a ribonuclease enzyme mimic.<sup>4,5</sup> However, the issue is sufficiently important that it needed to be checked further. We now report that our findings are not special to uridine nucleotides, but are also seen with adenosine derivatives. Most importantly, we

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