

## Synthesis and Electronic Structure of Tetrakis( $\eta^3$ -phenylpropargyl)zirconium<sup>†</sup>

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Tetrakis( $\eta^3$ -phenylpropargyl)zirconium (**3**) was synthesized from ZrCl<sub>4</sub> and (phenylpropargyl)magnesium bromide. The crystallographically determined structure of **3** exhibits  $D_{2d}$  symmetry, consistent with the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The electronic structure of **3** was analyzed using DFT calculations, and a HOMO– LUMO gap of 5.3 eV was calculated. The  $\eta^3$  coordination of the propargyl ligands and steric hindrance around the Zr center prevent the coordination of additional ligands, resulting in a homoleptic complex.

Alkylzirconium compounds have been used as singlesource precursors for chemical vapor deposition (CVD) of zirconium carbide (ZrC) thin films<sup>1-5</sup> as an alternative to growth from ZrCl<sub>4</sub> and methane under a reducing H<sub>2</sub> atmosphere at high temperatures (> 1500 °C).<sup>6-8</sup> The best established single-source precursor for the CVD of ZrC is tetraneopentylzirconium (Np<sub>4</sub>Zr).<sup>1,3,4,9</sup> Successful CVD from Np<sub>4</sub>Zr is possible because the lack of  $\beta$ -hydrogen atoms on the alkyl ligands renders it stable enough for volatilization and transport in a CVD reactor.

The range of compounds that have been used as singlesource precursors for early-metal carbides is very small. Ligands that contain heteroatoms are undesirable, as incorporation of the additional element into the resulting thin films can be an issue. Early-transition-metal alkyls with  $\beta$ -H's are known to undergo  $\beta$ -H elimination under mild conditions,<sup>10</sup> making them unsuitable for CVD. The result is that few ligands meet the necessary criteria for use in singlesource ZrC precursors. Propargyl ligands are potential

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candidates, as they contain no heteroatoms and no  $\beta$ -H atoms.<sup>11–14</sup> We thus undertook a study of zirconium propargyl complexes as possible precursors for the CVD of ZrC.

To our knowledge, no homoleptic propargyl complex has been reported. However, propargyl derivatives of zirconocene have been previously reported in the literature.<sup>11,13,15–18</sup> The 18-electron bis(phenylpropargyl)zirconocene complex **1** contains one  $\eta^1$ -propargyl ligand, with the second propargyl coordinated in the  $\eta^3$ -bonding mode.<sup>13</sup> The signals of the methylene protons of the propargyl ligand in the <sup>1</sup>H NMR spectrum are characteristic of the bonding mode and were assigned at  $\delta$  1.9 for the  $\eta^1$  ligand, while the corresponding protons in the  $\eta^3$  ligand were observed at 3.3 ppm. The 16-electron phenylpropargyl methylzirconocene complex **2** was subsequently described, and a crystal structure confirmed  $\eta^3$  coordination of the phenylpropargyl ligand.<sup>16</sup> The <sup>1</sup>H NMR spectrum of this compound also showed the methylene protons of the  $\eta^3$  ligand at the expected value of 3.37 ppm.



**Results and Discussion** 

In an effort to prepare homoleptic propargylzirconium compounds for use in the CVD of ZrC, we first reacted  $ZrCl_4$  with  $CH_3C \equiv CCH_2MgBr$ . Since we were unable to isolate tetrakis( $\eta^3$ methylpropargyl)zirconium from the oligomeric material that

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Scheme 1. Synthesis of Complex 3





| empiricai formula                              | C361128Z1   |
|--|---|
| formula wt                                     | 551.80  |
| temp   | 173(2) K  |
| wavelength                                     | 0.710 73 Å  |
| cryst syst                                     | monoclinic  |
| space group                                    | C2/c  |
| unit cell dimens                               |   |
| a  | 20.7551(14) Å   |
| b  | 8.6203(6) Å   |
| С  | 17.4685(11) Å   |
| α  | 90°   |
| β  | 116.0410(10)°   |
| γ  | 90°   |
| V  | 2808.1(3) Å <sup>3</sup>                                  |
| Ζ  | 4   |
| calcd density                                  | $1.305 \text{ Mg/m}^3$                                    |
| abs coeff                                      | $0.413 \text{ mm}^{-1}$                                   |
| F(000)   | 1136  |
| cryst size                                     | $0.19 \times 0.11 \times 0.04 \text{ mm}^3$               |
| $\theta$ range for data collection             | 2.18-27.50°   |
| index ranges                                   | $-20 \le h \le 26, -11 \le k \le 11, \\ -22 \le l \le 15$ |
| no. of rflns collected                         | 9334  |
| no. of indep rflns                             | 3226 (R(int) = 0.0272)                                    |
| completeness to $\theta = 27.50^{\circ}$       | 99.8%   |
| abs cor  | integration   |
| max and min transmissn                         | 0.9861 and 0.9103   |
| refinement method                              | full-matrix least squares on $F^2$                        |
| no. of data/restraints/params                  | 3226/0/168  |
| goodness of fit on $F^2$                       | 1.065   |
| final <i>R</i> indices $(I > 2\sigma(I))^a$    | R1 = 0.0244, wR2 = 0.0676 (2730)                          |
| R indices (all data) <sup><math>a</math></sup> | R1 = 0.0312, wR2 = 0.0700                                 |
| largest diff peak and hole                     | 0.300 and $-0.346 \text{ e.\AA}^{-3}$                     |

<sup>*a*</sup> R1 =  $\sum(||F_o| - |F_c||) \sum |F_o|$ . wR2 =  $[\sum[w(F_o^2 - F_c^2)^2] \sum [w(F_o^2)^2]]^{1/2}$ .  $S = [\sum[w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$ .  $w = 1/[\sigma^2(F_o^2) + (mp)^2 + np]$ ;  $p = [\max(F_o^2, 0) + 2F_c^2]/3$ , and *m* and *n* are constants.

meta, and para carbons at 127.5, 128.8, and 126.7 ppm, respectively. The quaternary carbon on the phenyl moiety (C<sub>ipso</sub>), at 129.1 ppm, coupled with the meta protons. The ortho protons coupled with a quaternary carbon at 113.5 ppm, which was assigned as  $\alpha$  to the phenyl. The methylene protons, on the carbon at 38.7 ppm, coupled with this latter carbon, with another quaternary carbon at 129.4 ppm, assigned as  $\beta$  to the phenyl, and, surprisingly, to the ortho carbons on the phenyl ring. These <sup>13</sup>C shifts are consistent with those previously reported for the ( $\eta^3$ -phenylpropargyl)zirconium compounds 1 and 2. The quaternary carbons of 1 were shown to be located at 120.5 and 114.1 ppm with the methylene shift at 55.5 ppm. Dynamic exchange between  $\eta^3$  and  $\eta^1$  coordination of the phenylpropargyl ligand of 2 in solution gave shifts of 112.9, 98.8, and 30.7 ppm.<sup>15</sup> The methylene protons displayed an NOE with the ortho protons in the NOESY spectrum. Examination of the X-ray crystal structure (vide infra) leads to the conclusion that the NOE is from the methylene group on one propargyl ligand to the phenyl group of an adjacent ligand.



Figure 1. <sup>1</sup>H and <sup>13</sup>C chemical shifts for one of the four equivalent phenylpropargyl ligands of 3. NMR spectra were obtained at -60 °C in THF-d8.

resulted, we synthesized tetrakis( $\eta^3$ -phenylpropargyl)zirconium (3) as a model compound for the preparation of more volatile homoleptic propargylzirconium species. The phenylpropargyl Grignard reagent was synthesized as described in the literature (Scheme 1).<sup>19,20</sup> The commercially available phenylpropargyl alcohol was reacted with PBr<sub>3</sub>, and the resulting bromide was then converted to the corresponding Grignard reagent. Reaction with ZrCl<sub>4</sub> afforded 3 in 74% crude yield. Single crystals of the pure material can be obtained by recrystallization, but continued handling of the complex resulted in decomposition, rendering it unsuitable for CVD studies.

After recrystallization, the <sup>1</sup>H NMR of **3** at room temperature in toluene- $d_8$  showed only a single aliphatic resonance at  $\delta$  3.21 ppm, consistent with  $\eta^3$ -phenylpropargyl ligands. All of the ligands were symmetry-equivalent by NMR, and although the complex was prepared in ethereal solvents, no other signals corresponding to additional ligands such as coordinated solvent were observed in the <sup>1</sup>H NMR spectrum.

The <sup>1</sup>H spectrum in THF- $d_8$  at -60 °C displays distinct signals for the aromatic protons of the four equivalent phenyl rings at 7.35 (t, 7.7 Hz, 8H), 7.23 (t, 7.7 Hz, 4H), and 6.96 (d, 7.7 Hz, 8H), which were assigned as meta, para, and ortho, correspondingly, on the basis of their multiplicity and intensity (Figure 1).

The intensity was referenced to the signal for the four CH<sub>2</sub> groups at 3.10 ppm. The <sup>13</sup>C chemical shifts were measured in the gHMBC spectrum, which was acquired with two different spectral windows in f1 to detect possible folding. One-bond couplings with the protons identified the ortho,

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**Figure 2.** Thermal ellipsoids drawing of the molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogens on the phenyl rings are omitted for clarity.

|           | -         |           |           |
|-----------|-----------|-----------|-----------|
| Zr-C1     | 2.4955(2) | C1-C2     | 1.3760(2) |
| Zr-C2     | 2.4043(1) | C2-C3     | 1.2490(0) |
| Zr-C3     | 2.4474(2) | C3-C4     | 1.4500(2) |
| C2-Zr-C12 | 98.49(5)  | C4-C3-Zr  | 137.87(1) |
| C2-Zr-C2A | 96.11(7)  | C1-Zr-C1A | 128.88(8) |
| C2-C1-Zr  | 70.08(9)  | C11-Zr-C1 | 131.95(5) |
| C3-C2-C1  | 154.38(2) | C2-Zr-C11 | 108.31(6) |
| C3-C2-Zr  | 77.01(1)  | C3-Zr-C11 | 82.21(5)  |
|           |           |           |           |

 Table 3. Selected Bond Distances (Å) for 2<sup>16</sup>

| $C1-C2^a$ | 1.344(5) |
|-----------|----------|
| C2-C3     | 1.259(4) |
| Zr-C1     | 2.658(4) |
| Zr-C2     | 2.438(3) |
| Zr-C3     | 2.361(3) |
|           |          |

<sup>*a*</sup> The numbering system of the propargyl ligand is as shown for compound **3** in Figure 2.

A crystallographic structure determination (Table 1) confirmed the identification of **3** as tetrakis( $\eta^3$ -phenylpropargyl)zirconium. The crystal structure of **3** verified the presence of only the four propargyl ligands, all displaying  $\eta^3$  coordination (Figure 2). Complex **3** has an overall  $D_{2d}$  symmetry, a point group previously but rarely observed in other Zr compounds.<sup>21,22</sup> An EAN of 16 electrons for **3** results from each phenylpropargyl ligand donating four electrons. Selected bond angles and distances of **3** are shown in Table 2.

Although structural data have been reported for several  $\eta^3$ -propargyl complexes,<sup>16</sup> the (phenylpropargyl)methylzirconocene complex **2** (Table 3) is perhaps the best model for the geometry of the propargyl ligands of **3**. The phenylpropargyl ligands of complexes **2** and **3** exhibit nearly identical C-C-C bond angles of 154.4(3) and 154.38(2)°, respectively, indicating similar bonding of the propargyl moiety to the Zr center. The Zr-C2 bond lengths are approximately the same in the two structures. However, the three Zr-C bond distances in **3** are roughly the same length, differing only by a net 0.09 Å overall, whereas those in **2** differ by a much larger value, 0.29 Å, with the C1–C2–C3 plane of **2** canted so that the methylene carbon C1 is farther from the metal center. For both complexes, an assignment of the phenylpropargyl bonding as intermediate between the  $\eta^3$ -propargyl and allenyl limiting resonance structures (**A** and **B**) is supported by the bond lengths and angles. A similar assignment of the bonding in Cp\*(TBM)Zr( $\eta^3$ -CH<sub>2</sub>C≡ CCH<sub>3</sub>) was made on the basis of the crystal structure.<sup>17</sup>



The bonding of the propargyl ligands to the metal center in 3 was further analyzed by density functional theory calculations. Geometry optimizations and single-point calculations were performed using the DFT B3LYP<sup>23,24</sup> functional and the lanl2d $z^{25,26}$  basis set utilized in the Gaussian 03 program package.<sup>27</sup> Compositions of molecular orbitals were calculated using the AOMix program.<sup>28,29</sup> Molecular orbital pictures were generated from Gabedit.<sup>30</sup> Initial calculations were performed on 3 itself; however, the presence of the phenyl rings complicated the interpretation by delocalizing the molecular orbitals to such an extent that visualization was difficult. In order to simplify the analysis, calculations were carried out on the parent tetrapropargylzirconium complex 4, in which the phenyl rings were replaced with hydrogen to provide a computational model structure. The crystallographically determined structure of 3 was used for the positions of the non-H atoms of 4. Hydrogen atoms were placed by geometry optimization, and the  $D_{2d}$  symmetry of **3** was enforced in 4.



A molecular orbital diagram (see the Supporting Information) was generated from the computational results

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Figure 3. Degenerate HOMO (top) and HOMO-2 (bottom) of the propargyl complex 4.

for 4 and showed a calculated HOMO-LUMO gap of 5.2 eV. This substantial splitting of the frontier orbitals is consistent with the lack of reactivity of 3 with other species in the reaction mixtures during synthesis. While other  $D_{2d}$ group 4 metal complexes have been reported in the litera-ture,<sup>31–33</sup> examples of computational results are rare. An electronically similar  $D_{2d}$ -symmetric bis(pentalene)titanium complex had a calculated HOMO-LUMO gap of 1.93 eV, far smaller than that of 3.<sup>31</sup> Tetrakis( $\eta^3$ -allyl)zirconium is also a known compound, described as a bright red solid which decomposes at -20 °C.<sup>34,35</sup> The red color and lability of tetrakis( $\eta^3$ -allyl)zirconium suggest that its HOMO-LUMO gap must also be smaller than that of 3, which is a colorless solid that is stable for moderate periods of time at room temperature.

The high-lying occupied orbitals of 4 are depicted in Figure 3. The HOMO is largely comprised of two degenerate orbitals containing the p orbitals of C1 and C3 of the propargyl ligands. The symmetry dictates that one HOMO orbital includes the  $d_{vz}$  orbital of Zr (20.7%) and the p orbitals in the yz plane of the propargyl ligands, while the other HOMO orbital utilizes the  $d_{xz}$  orbital of Zr (20.7%) and the xz plane of the p orbitals on the propargyl ligand. The HOMO-2 is comprised mainly of  $d_{z^2}$  on Zr (21.3%) and the xy plane of the p orbitals on the ligand. Metal-propargyl bonding dominated by interactions of metal d orbitals with propargyl MO's localized on C1 and C3 is consistent with the calculated MO diagrams for bonding in  $[(\eta^3-CH_2C\equiv CPh) Pt(PPh_3)_2].^{36}$ 

The LUMO of 4 (Figure 4) has the strongest p orbital contributions from C2 in the propargyl groups. This is consistent with its derivation from the antibonding C1-C2-



Figure 4. LUMO (top left), LUMO+1 (top right), and degenerate LUMO+2 (bottom) of propargyl complex 4.

C3  $\pi$  orbital, which has its largest coefficient on C2. The largest contributions to the LUMO from Zr are s (14.2%), and  $d_{z^2}$  (11.9%). The LUMO+1 is mainly comprised of the nonbonding  $d_{xv}$  orbital of Zr (86.7%). The LUMO+2 consists of two degenerate orbitals, one composed primarily of Zr  $d_{xz}$  (25.3%) and the other  $d_{yz}$  (25.3%).

The AO composition of the LUMO provides insight into why this 16-electron early-transition-metal complex does not have an open coordination site for addition of another ligand. The section of the LUMO derived from metal AO's is sterically blocked by the CH<sub>2</sub> groups of the four propargyl ligands. Although complex 3 was recrystallized from THF with vapor diffusion of pentanes, coordinated THF is not detected in either the NMR or the crystal structure.

## Conclusion

The synthesis of 3 yields, to the best of our knowledge, the first example of a homoleptic propargyl complex and has been shown by <sup>1</sup>H NMR spectroscopy and X-ray crystallography to have all four phenylpropargyl ligands coordinated to the Zr center in an  $\eta^3$  mode, resulting in a complex of  $D_{2d}$  symmetry. The  $\pi$  bonding in **3** was analyzed by DFT calculations on the model compound 4. The  $\pi$  bonding from the four symmetry-equivalent  $\eta^3$ -propargyl ligands and HOMO-LUMO gap of 5.3 eV is consistent with the stability of the molecule and the lack of reactivity toward coordinating solvents.

## **Experimental Section**

General Procedures. All chemicals were purchased in reagent grade purity and used with no further purification unless otherwise noted. All manipulations were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of argon or nitrogen. All solvents, unless otherwise noted, were purchased from Fisher and passed through an M. Braun MB-SP solvent purification system or were distilled from sodium/benzophenone prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on Varian Gemini 300, VXR 300, Mercury 300, and Inova 500 spectrometers. Infrared spectra were measured on a Perkin-Elmer 1600 FT-IR.

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**Phenylpropargyl Bromide.** A 50 mL Schlenk flask containing 5.0 mL of ether, 4.8 g (3.7 mmol) of phenylpropargyl alcohol, and 1.0 g of pyridine was cooled to 0 °C, and 5.0 g (18 mmol) of phosphorus tribromide was added dropwise over a 45 min period with strong stirring under nitrogen in accordance with the literature procedure.<sup>19</sup> The resulting mixture was added to 25 mL of ice to quench the excess PBr<sub>3</sub> and extracted with ether (3 × 25 mL). The organics were then washed with NaHCO<sub>3</sub>, dried over MgSO<sub>4</sub>, and filtered, and the ether was then removed by reduced pressure. Yield: 6.0 g, 83%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.1 (s, 2H), 7.4 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  15.3, 84.2, 86.6, 121.9, 128.1, 128.7, 131.7.

(Phenylpropargyl)magnesium Bromide. An addition funnel was charged with 12.0 g (61.6 mmol) of phenylpropargyl bromide and 30 mL of ether, and the mixture was added dropwise to a three-neck flask cooled to 0 °C containing 1.80 g (75.0 mmol) of activated Mg turnings with a few crystals of HgCl<sub>2</sub> in ether over a 4 h period, in accordance with the literature preparation.<sup>20</sup> After the addition, the reaction mixture was refluxed for 1 h. The resulting mixture was filtered through a 1 cm pad of Celite (previously dried and evacuated) to yield a dark yellow solution. Yield: 30 mL of a 1.85 M solution of the Grignard reagent, 90.1%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.11 (s, 2H), 6.8 (m, 5H).

Tetrakis( $\eta^3$ -phenylpropargyl)zirconium (3). An addition funnel was charged with 20.0 mL of 1.85 M phenylpropargylmagnesium bromide (37.0 mmol) and added dropwise into a threeneck flask containing 2.16 g (9.25 mmol) of ZrCl<sub>4</sub> slurried in 100 mL of ether over a 1 h period and stirred overnight at room temperature. Volatiles were then removed via reduced pressure to afford a brown solid. The solid was extracted with 150 mL of toluene and filtered through a fine glass frit. The filtrate was concentrated to afford a solution of **3**, from which the compound was then precipitated by the addition of hexanes. The resulting suspension was filtered through a fine glass frit to collect the solid precipitate of **3**. Yield: 3.44 g, 74%. The product was tan in color. Single crystals could be obtained by repeated vapor diffusion recrystallization using THF and pentanes until a colorless to white solid remained. <sup>1</sup>H NMR (THF- $d_8$ , -60 °C):  $\delta$ 

3.10 (s, 8H), 6.96 (d, 7.7 Hz, 8H), 7.23 (t, 7.7 Hz, 4H), 7.35 (t, 7.7 Hz, 8H).  $^{13}$ C NMR (THF- $d_8$ , -60 °C):  $\delta$  38.7, 113.5, 126.7, 127.5, 128.8, 129.1, 129.4.

**Crystallographic Structure Determination of 3.** X-ray experimental data for **3** were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the  $\omega$ -scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on *I* was <1%). Absorption corrections by integration were applied on the basis of measured indexed crystal faces.

The structure was solved by direct methods in SHELXTL6<sup>37</sup> and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The complexes are located on 2-fold rotation axes; thus, a half-complex occupies the asymmetric unit. A total of 168 parameters were refined in the final cycle of refinement using 2730 reflections with  $I > 2\sigma(I)$  to yield R1 and wR2 values of 2.44% and 6.76%, respectively. Refinement was done using  $F^2$ .

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**Supporting Information Available:** Tables and a CIF file giving crystallographic data for **3** (including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters) and figures, text, and tables giving a calculated molecular orbital diagram for **4** and <sup>1</sup>H and gHMBC NMR spectra of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

<sup>(37)</sup> SHELXTL6; Bruker-AXS, Madison, WI, 2000.