

Communications to the Editor

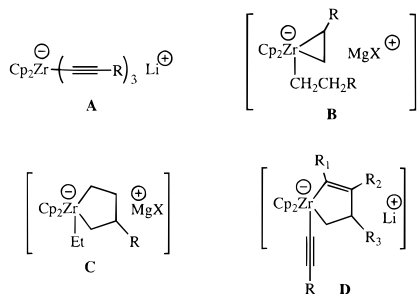
Zirconocene-ate Zwitterionic Complexes: Preparation and X-ray Structure

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Anionic transition metal complexes are important organometallic reagents in organic synthesis.¹ However, it is only very recently that the formation of anionic early transition metallocene complexes of the type $[\text{Cp}_2\text{Zr}(\text{R}_1)(\text{R}_2)(\text{R}_3)]^-$ with $\text{R}_1, \text{R}_2, \text{R}_3 =$ alkyl, alkenyl, alkynyl have been postulated as key intermediates in a number of reactions.² Thus, the ate complex **A**³ has been spectroscopically identified in a novel class of carbon–carbon bond-forming reactions. Mechanistic studies have implicated the anionic cyclic complexes **B**⁴ and **C**⁵ as intermediates in zirconocene-catalyzed carbomagnesiation and hydrogenation reactions while a form such as **D**⁶ is claimed to take part in tandem insertion of metal carbenoids and electrophiles into zirconacycles.



All of these ate complexes appear to be extremely unstable, and to the best of our knowledge none of them has been isolated in

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(1) See, for example: Hauske, J. R. In *Comprehensive Organic Chemistry*, 2nd ed.; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, p 86. Meikelburger, B. H.; Wilcox, C. S. *Ibid.*; Vol. 2, p 119–124. Tamao, K. *ibid.*; Vol. 3, p 463. Elschenbroich, Ch.; Salzer, A. In *Organometallics*, 2nd ed.; von der Saal, K. Ed.; VCH Publishers Inc.: NY, 1992.

(2) In marked contrast, there is a large number of pentavalent neutral 18-electron zirconocene complexes of the type $[\text{Cp}_2\text{M}(\text{R}_1)(\text{R}_2)\text{L}]$ where L is a 2-electron donor ligand, see: Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986; and references therein.

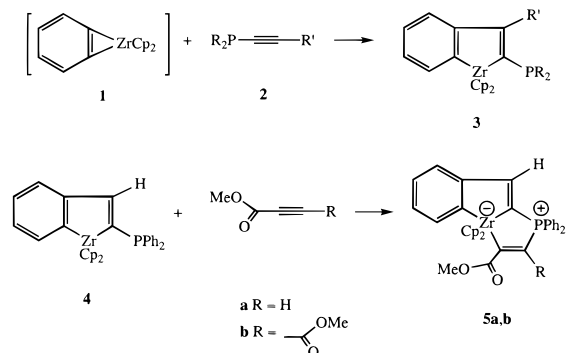
(3) Takagi, K.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 1440.

(4) Hoveyda, A. H.; Morken, J. P.; Hourri, A. F.; Xu, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6692 and references therein. Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E.-I. *Chem. Lett.* **1991**, 1579.

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(6) Fillery, S. F.; Gordon, G. J.; Luker, T.; Whitby, R. *J. Pure Appl. Chem.* **1997**, *69*, 633. Gordon, G. J.; Whitby, R. *J. Chem. Commun.* **1997**, 1321.

Scheme 1



pure form.⁷ Herein, we report an unprecedented formal [3 + 2] cycloaddition reaction⁸ between a 2-phosphino-1-zirconaindene (**4**) and alkyne derivatives leading to *stable* 18-electron zirconate complexes in which all atoms directly bonded to zirconium are carbon atoms.⁹ We also describe the first X-ray crystal structure of such a complex.

We recently developed the preparation of 2-phosphino-1-zirconaindenes (**3**)¹⁰ from treatment of zirconabenzynes (**1**) generated in situ at 80 °C from the corresponding zirconocene complex $[\text{Cp}_2\text{ZrPh}_2]$ and alkynylphosphines **2**. Addition of methylpropionate (1 equiv) to a solution of **4** in toluene at room temperature gave in 70% isolated yield the stable complex **5a** as one regioisomer (see Scheme 1).¹¹ From its elemental analysis and mass spectrum ($m/e = 592, \text{M}^+$) compound **5a** appears to have a correct composition for a formally 1/1 adduct of the two starting reagents [4·MeCO₂CCH]. The ³¹P NMR spectrum of **5a** displays a singlet at 33.4 ppm. The ¹H NMR spectrum exhibits (beside the signals corresponding to the protons of the aromatic rings) two doublets at δ 6.86 (²J_{HP} = 40.5 Hz) and 8.27 (³J_{HP} = 29.6

(7) Transient formation of benzyne-ylide metallocene complexes are already reported: de Boer, H. J. R.; Akkermann, O. S.; Bickelhaupt, F.; Erker, G.; Czisch, P.; Mynott, R.; Wallis, J. M.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 639–40.

(8) As defined by Huisgen, we indicate the number of ring atoms contributed by the individual components for the classification of cycloadditions. Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 321.

(9) Other types of (η^2 -Cp)-ate-complexes have been identified or postulated. The anionic trihydride $[\text{Cp}^*\text{ZrH}_3]^-$ has been recently isolated and structurally characterized (Etkin, N.; Hoskin, A. J.; Stephan, D. W. *J. Am. Chem. Soc.* **1997**, *119*, 11420). The ate complexes $[\text{Cp}_2\text{ZrH}(\text{CH}_2\text{PR}_3)\text{X}]^-$ are involved in the methylene transfer reactions with phosphorus ylides $\text{R}_3\text{P}=\text{CH}_2$ (Kerry, I. G.; Schwartz, J. *Inorg. Chem.* **1980**, *19*, 3207. Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310). X-ray structure analysis revealed a zwitterionic zirconocene triazido complex (Luker, T.; Whitby, R. J.; Webster, M. *J. Organomet. Chem.* **1995**, *492*, 53–57). A structure consistent with (η^5 -Cp)trialkylzirconium has been formulated (Kondakov, D.; Negishi, E.-I. *Chem. Commun.* **1996**, 963).

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(11) Most characteristic NMR data for **5a** and **5b** (C₆D₆, 273 K, Bruker AMX400). ¹³C NMR assignments were confirmed by inverse gradient $\delta^1\text{H}-\delta^{13}\text{C}\{^{13}\text{C}, ^{31}\text{P}\}$ HMQC and ³¹P-¹H INEPT NMR experiments. **5a**: ³¹P{¹H} δ 33.4; ¹H δ 3.72 (s, 3H, CH₃), 6.00 (s, 10H, CH_{CP}), 6.86 (d, ²J_{HP} = 40.5 Hz, 1H, PCH), 8.27 (d, ³J_{HP} = 29.6 Hz, 1H, PCCH); ¹³C{¹H} δ 51.2 (s, Me), 107.3 (s, Cp), 122.8 (d, ¹J_{CP} = 118.6 Hz, PCH), 156.9 (d, ¹J_{CP} = 7.3 Hz, ZrCP), 157.9 (d, ³J_{CP} = 31.5 Hz, ZrCC), 170.4 (s, ZrCCH), 179.3 (d, ³J_{CP} = 41.4 Hz, CO), 194.4 (d, ⁴J_{CP} = 5.6 Hz, ZrC), 222.3 (d, ²J_{CP} = 51.6 Hz, ZrCCO). **5b**: ³¹P{¹H} δ 42.3; ¹H δ 3.20 (s, 3H, CH₃), 3.84 (s, 3H, CH₃), 6.03 (s, 10H, CH_{CP}), 8.17 (d, ³J_{HP} = 29.1 Hz, 1H, PCCH); ¹³C{¹H} δ 51.3 (s, Me), 51.7 (s, Me), 107.6 (s, Cp), 123.4 (d, ²J_{CP} = 1.2 Hz, CH_{arom}), 125.6 (d, ¹J_{CP} = 123.5 Hz, PCCO), 157.0 (d, ¹J_{CP} = 13.6 Hz, ZrCP), 157.2 (d, ³J_{CP} = 31.5 Hz, ZrCC), 161.5 (d, ²J_{CP} = 28.3 Hz, PCCO), 170.5 (d, ²J_{CP} = 1.9 Hz, ZrCCH), 177.8 (d, ³J_{CP} = 36.3 Hz, ZrCCO), 193.8 (d, ⁴J_{CP} = 4.5 Hz, ZrC), 243.4 (d, ²J_{CP} = 56.9 Hz, ZrCCO).

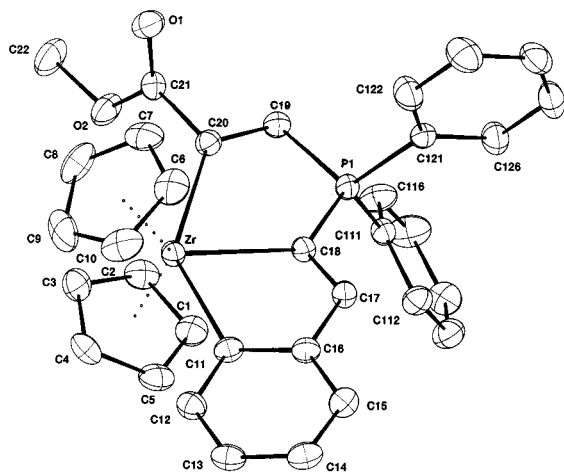


Figure 1. CAMERON view of the structure of **5a**. Selected bond lengths (Å) and angles (deg): Zr(1)–C(11), 2.407(2); Zr(1)–C(18), 2.371(2); Zr(1)–C(20), 2.446(2); C(19)–C(20), 1.346(4); P(1)–C(19), 1.760(2); P(1)–C(18), 1.748(2); C(11)–Zr(1)–C(20) 140.22(2); C(18)–Zr(1)–C(20) 71.71(8).

Hz) ppm integrating each for one proton; Cp groups and CO₂Me resonances appear as one singlet at δ 6.00 and 3.72 ppm, respectively. ¹³C NMR indicates that the carbon atoms coming from the alkynyl moiety of the starting methylpropiolate are coupled with the phosphorus atom of the complex: two doublets are detected at 122.8 ($^1J_{\text{CP}} = 118.6$ Hz) and 222.3 ($^2J_{\text{CP}} = 51.6$ Hz) ppm. The marked deshielded chemical shift observed for the latter carbon strongly suggests that this carbon is directly linked to the zirconium atom. All other observed signals are typical of the zirconaindene framework.^{10,12} However, since the spectral characterization did not yield unequivocal assignment of a structure for **5a**, X-ray diffraction analysis was performed (see Figure 1).¹³ The zirconium atom is coordinated to two η^5 -Cp (Cp = cyclopentadienyl) ligands and three different sp²-carbon atoms arranged around the central metal in a pseudo tetrahedral geometry. All atoms involved in the composition of the metal-

(12) Zablocka, M.; Cénac, N.; Igau, A.; Donnadiu, B.; Majoral, J. P.; Skowronska, A.; Meunier, P. *Organometallics* **1996**, *15*, 5436. Zablocka, M.; Igau, A.; Donnadiu, B.; Majoral, J. P.; Skowronska, A.; Meunier, P. *Chem. Commun.* **1997**, 1239. Dupuis, L.; Pirio, N.; Meunier, P.; Igau, A.; Donnadiu, B.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 987.

(13) Crystal data of C₃₄H₂₉O₂PZr belong to the space group P2₁/c with $a = 11.267(2)$ Å, $b = 15.885(2)$ Å, $c = 15.538(2)$ Å, $\beta = 101.50(1)^\circ$, $V = 2725.28$ Å³, $Z = 4$. Single-crystal X-ray diffraction intensity data were collected at low temperature ($T = 180$ K). The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. No important fluctuations of the intensity were observed over the course of the measurement. Data collected: 17 219 unique; 4283, reflections used; 3516 with the criterion [$I > 3\sigma(I)$]. All hydrogen atoms were located on a difference Fourier maps, but they were introduced in calculation in idealized positions ($d(\text{C}-\text{H}) = 0.96$ Å), their atomic coordinates were recalculated after each cycle of refinement, and they were given isotropic thermal parameters 20% higher than those of the carbon atoms to which they were connected. All non-hydrogen atoms were anisotropically refined. Model reached convergence with $R = 0.028$, and $R_w = 0.029$. Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data centre, 12 Union Road, GB-Cambridge CB21EZ UK, on quoting the full journal citation.

lapolycycle lie in the same plane that bisects the Cp₂Zr fragment. The bond lengths and angles around P(1) are consistent with a four-coordinate cyclic phosphonium salt.¹⁴ The truly outstanding structural features of **5a** are (a) the large C(11)–Zr(1)–C(20) angle value of 140.22(2)° and (b) the unusual long Zr–C(sp²) bond lengths [Zr(1)–C(11) 2.407(2) Å, Zr(1)–C(18) 2.371(2) Å, Zr(1)–C(20) 2.446(2) Å]. This unprecedented large angle is due to the necessity of achieving good orbital overlap with the single acceptor 1a₁ orbital available in **4** for bonding of a fifth ligand, as well as the resolving of the steric requirements of the ligands. The Zr–C(sp²) bond lengths in **5a** are halfway from typical neutral Cp₂Zr(IV)–C σ bonds and Zr–C distances in Cp₂Zr(IV)–olefin π -type interaction.¹⁵ The long Zr–C(sp²) bond lengths in the complex **5a** are consistent with the calculations¹⁶ which predict that filling of the metal-based LUMO (through the sp²-carbon atom coming from the acetylenic substrate in this case) will result in lengthening of the remaining metal–ligand bonds compared to those in 16-electron Cp₂ML₂ complexes. This illustrates the effect of the zirconium atom achieving an 18-electron configuration which suggests that the metal–ligand bonding situation in **5a** is best described as consisting of three different σ -bonds. The Zr–C(17) and Zr–C(19) distances are about 0.8 Å (or 32%) longer than the averaged Zr–C(η^5 -Cp) distance [Zr–C(η^5 -Cp) 2.526(3) Å], this suggests that no π -interaction is involved between the different atoms of the metallapolycycle and the metal. Both the carbonyl and methoxy oxygen atoms of the carboxylic function are turned away from the zirconium center. Therefore, X-ray data clearly confirm the zwitterionic character of **5a**.

Under the same experimental conditions, **5b** was formed after treatment of dimethylacetylene dicarboxylate with **4**. Zirconate complex **5b** displays the same spectroscopic features with those observed for **5a**.¹¹

In marked contrast with transient species already postulated in previous reactions (vide supra), these 18-electron zirconate complexes are very stable and can be stored under inert atmosphere over months as powders or weeks in solution.

Extension of this methodology for the preparation of other stable zirconate species, mechanistic studies on the novel [3 + 2] cycloaddition reaction leading to zwitterionic complexes **5a,b**, and studies of the chemical properties and reactivity of these complexes are currently under active investigation.

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Supporting Information Available: Experimental details for **5a** and **5b** and tables of positional parameters and anisotropic thermal parameters for **5a** (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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