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Communications

$Cp_2Zr(\eta^2$-benzocyclobutadiene$)(PMe_3)$, a Rare η^2-Cyclobutadiene Complex

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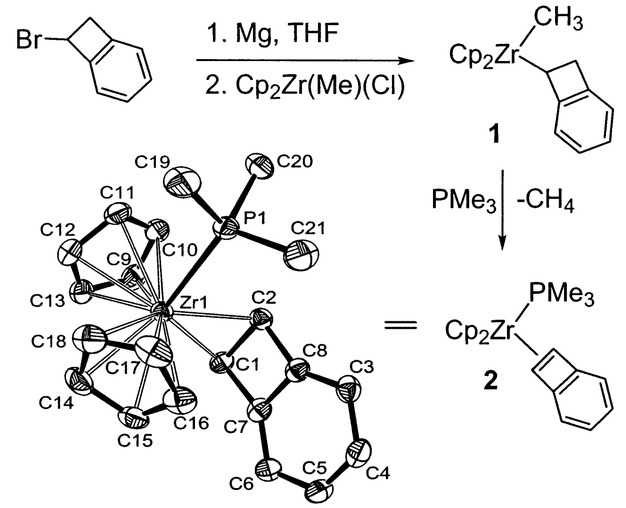
Summary: Thermal decomposition of Cp_2ZrMe(1-bromobenzocyclobutenyl) yields the η^2-cyclobutadiene complex $Cp_2Zr(\eta^2$-benzocyclobutadiene$)(PMe_3)$, which cycloadds alkenes, nitriles, and t-BuNC, in the last case giving a novel diamino—Dewar-naphthalene complex.

Zirconocene has been shown to stabilize reactive organic fragments with retention of substantial reactivity and the generation of new reactivity patterns.[1−3] In this report we describe the stabilization of a cyclobutadiene by a rare η^2 coordination mode. As a result, new reactivity patterns become available and coupling reactions of the complex with alkynes, nitriles, and isocyanides yield zirconocene cyclobutene derivatives, including a unique Dewar-naphthalene structure.

Utilizing the well-known ability of the Cp_2ZrMe fragment to activate C−H bonds,[1] $Cp_2ZrMeCl$ was treated with the Grignard reagent prepared from commercially available 1-bromobenzocyclobutene.[4] A smooth reaction occurs, yielding yellow Cp_2ZrMe(1-benzocyclobutenyl) (**1**; Scheme 1).

Scheme 1



Complex **1** is stable at ambient temperatures but slowly eliminates methane at 70 °C, producing, in the presence of PMe_3, the yellow η^2-benzocyclobutadiene complex **2** in 82% isolated yield (Scheme 1).[5] An X-ray structure determination[6] confirms the identity of **2** and establishes the rare η^2 coordination of the cyclobutadiene.[7,8] The structure is similar to that observed for the cyclobutene complex $Cp_2Zr(\eta^2$-cyclobutene$)(PMe_3)$,[9] which was prepared in an analogous manner, and shows a long

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[1] (a) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696−1701. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058.

[2] Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

[3] (a) Choukroun, R.; Cassoux, P. *Acc. Chem. Res.* **1999**, *32*, 494−502. (b) Fillery, S. F.; Gordon, G. J.; Luker, T.; Whitby, R. J. *Pure Appl. Chem.* **1997**, *69*, 633−638. (c) Majoral, J. P.; Meunier, P.; Igau, A.; Pirio, N.; Zablocka, M.; Skowronska, A.; Bredeau, S. *Coord. Chem. Rev.* **1998**, *180* (part 1), 145−167. (d) Ohff, A.; Pulst, S.; Lefeber, C.; Peulecke, N.; Arndt, P.; Burkalov, V. V.; Rosenthal, U. *Synlett* **1996**, 111−118.

[4] Aldrich Chemical Co. Catalog.

[5] Reviews on cyclobutadiene complexes: (a) Baker, P. K.; Silgram, H. *Trends Organomet. Chem.* **1999**, *3*, 21−33. (b) Efraty, A. *Chem. Rev.* **1977**, *77*, 691−744.

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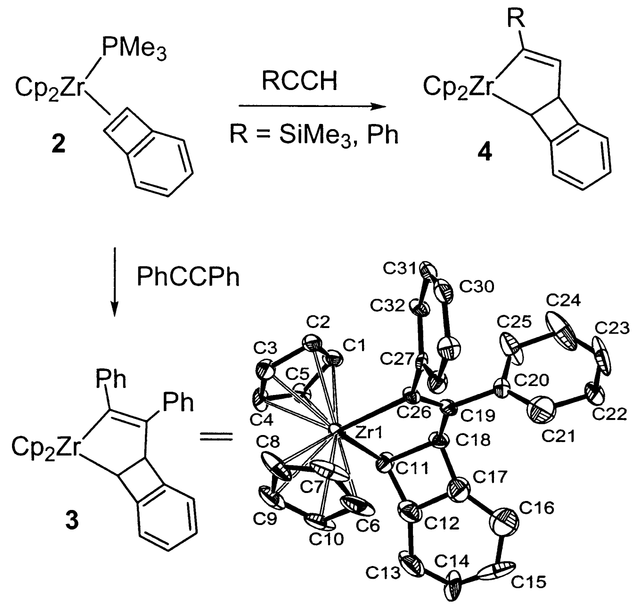
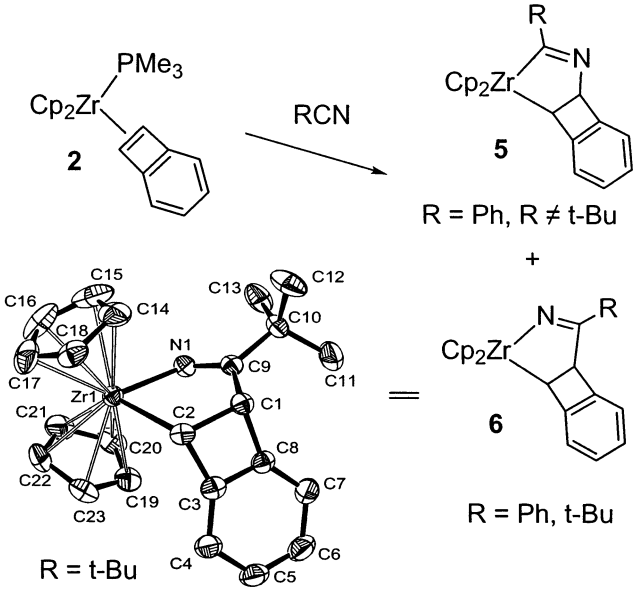
Scheme 2

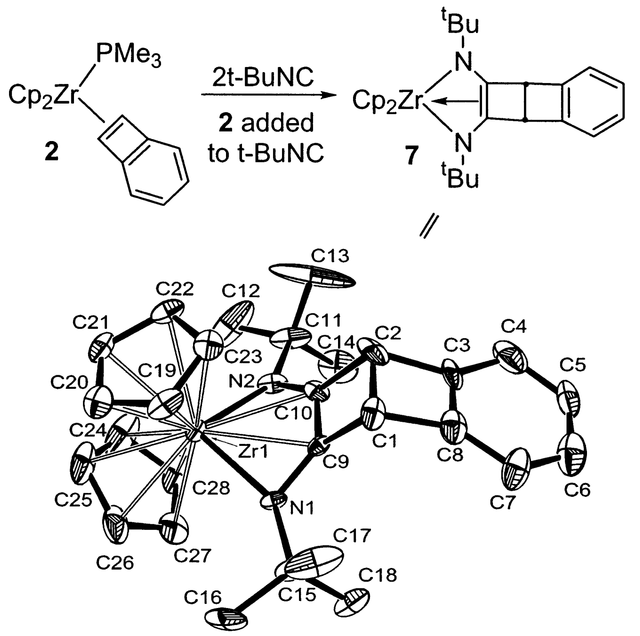


Scheme 3



C−C bond for the Zr-bonded ene (d(C1−C2) = 1.526(4) Å). This indicates a major contribution from a zirconacyclopropane[10] resonance form, the likely source of the stabilization of the cyclobutadiene.

Scheme 4



An unfortunate feature of the previously reported cyclobutene complex[9] and other zirconocene alkene complexes[1b,10] is facile displacement of the coordinated alkene by alkynes. This limits their synthetic usefulness in insertion reactions. The cyclobutadiene complex **2** does not suffer from this, most probably because displacement would result in the liberation of the unstable antiaromatic cyclobutadiene.[11] Thus, yellow solutions of **2** react with acetylenes at 40 °C (4 h) to yield the yellow insertion products **3** and **4** (88% yield) and free PMe_3[12] (Scheme 2). For the terminal alkyne product **4**, the alkyne R group is in the α-position. This is established by a triplet signal in the ^1H NMR spectrum for the cyclobutane hydrogen atom at the β'-position, indicating coupling to both the benzocyclobutene hydrogen atom at the α′-position and the former alkyne hydrogen atom. An X-ray crystal structure determination[13] of **3** confirms the cycloaddition of the alkyne.

Complex **2** also reacts with nitriles (Scheme 3). Benzonitrile gives a mixture of the two possible regioisomers **5** and **6** (35:65) with what is believed to be the nitrogen-bonded isomer **6** (R = Ph) predominating. The

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(6) X-ray data for **2** (173 K): $C_{21}H_{25}PZr$, a = 8.5796(7) Å, b = 14.8697(12) Å, c = 14.2085(12) Å, β = 91.411(2)°, monoclinic, $P2_1/n$, Z = 4. Data were collected using a Siemens SMART CCD diffractometer. The data were refined on F^2 (SHELXL) to R1 = 0.0413. Selected distances (Å) and angles (deg): Zr1−P1 = 2.7022(9), Zr1−C1 = 2.346(3), Zr1−C2 = 2.339(3), C1−C2 = 1.526(4), C1−C7 = 1.502(4), C2−C8 = 1.510(4), C3−C8 = 1.376(4), C6−C7 = 1.377(4), C7−C8 = 1.412(4); C2−Zr1−C1 = 38.01(11), C2−C1−Zr1 = 70.75(16), C2−C1−C7 = 87.9(2), C7−C1−Zr1 = 113.27(19), C1−C2−C8 = 87.8(2), C1−C2−Zr1 = 71.24(16), C8−C2−Zr1 = 113.14(19), C4−C3−C8 = 116.4(3), C3−C4−C5 = 121.8(3), C4−C5−C6 = 121.7(3), C5−C6−C7 = 116.4(3), C1−C7−C6 = 145.8(3), C1−C7−C8 = 92.4(2), C6−C7−C8 = 121.8(3), C2−C8−C3 = 146.2(3), C2−C8−C7 = 91.9(2), C3−C8−C7 = 121.9(3).

(7) Only one structurally characterized η^2-cyclobutadiene complex has been reported: Winter, W.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 128−129.

(8) Proposed η^2-cyclobutadiene complexes: (a) Sanders, A.; Giering, W. P. *J. Organomet. Chem.* **1976**, *104*, 49−65. (b) Sanders, A.; Magatti, C. V.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1610−1611.

(9) Fisher, R. A.; Buchwald, S. L. *Organometallics* **1990**, *9*, 871−873.

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(11) (a) Chapman, O. L.; Chang, C. C.; Rosenquist, N. R. *J. Am. Chem. Soc.* **1976**, *98*, 261−262. (b) Winter, W.; Straub, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 127−128 and references therein.

(12) Periodic removal of the free PMe_3 by exposing the reaction mixture to vacuum maximizes the yield and purity of **3**.

(13) X-ray data for **3** (173 K): $C_{32}H_{26}Zr\cdot 0.5C_7H_8$, a = 8.5915(16) Å, b = 19.945(4) Å, c = 15.720(3) Å, β = 98.407(4)°, monoclinic, $P2_1/n$, Z = 4. Data were collected using a Siemens SMART CCD diffractometer. The data were refined on F^2 (SHELXL) to R1 = 0.1101. Selected distances (Å) and angles (deg): Zr1−C11 = 2.250(12), Zr1−C26 = 2.298(10), C11−C12 = 1.527(17), C11−C18 = 1.631(15), C12−C13 = 1.47(2), C12−C17 = 1.475(19), C13−C14 = 1.26(2), C14−C15 = 1.33(2), C15−C16 = 1.35(2), C16−C17 = 1.51(2), C17−C18 = 1.482(17), C18−C19 = 1.535(15), C19−C26 = 1.347(14), C11−Zr1 = C26 87.9(4); C12−C11−C18 = 86.1(8), C12−C11−Zr1 = 119.0(9), C18−C11−Zr1 = 100.0(6), C13−C12−C17 = 114.1(14), C13−C12−C11 = 153.0(14), C17−C12−C11 = 92.2(10), C14−C13−C12 = 119.4(16), C13−C14−C15 = 127.8(17), C14−C15−C16 = 119.1(18), C15−C16−C17 = 116.8(18), C12−C17−C18 = 93.7(11), C12−C17−C16 = 119.0(14), C18−C17−C16 = 147.1(15), C17−C18−C19 = 114.6(10), C17−C18−C11 = 87.9(9), C19−C18−C11 = 121.7(9), C26−C19−C20 = 124.2(9), C26−C19−C18 = 123.9(9), C20−C19−C18 = 111.8(9), C19−C26−C27 = 122.6(9), C19−C26−Zr1 = 106.3(7), C27−C26−Zr1 = 131.0(7).

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formation of the carbon-bonded isomer **5** is exceptional for reactions of zirconocene complexes with nitriles.[1,14] With the bulkier t-BuCN a single regioisomer is produced in 91% yield, which an X-ray crystal structure[15] study shows is the usual nitrogen-bonded isomer **6** (R = t-Bu).

Two different products are obtained from the reaction of **2** with t-BuNC. Which product is obtained depends on the conditions of the reaction. Insertion product **7** (Scheme 4) is formed as the sole product when **2** is added to a solution of 2 equiv of t-BuNC. The structure of **7** was established by a single-crystal X-ray diffraction study[16] and reveals an unprecedented Dewar-naphthalene structure[17] with a new four-membered ring formed by isocyanide insertion and coupling.[18,19] Alternatively, the ligand may be viewed as a diaza diene complex.[20] The second product, **8**, is obtained by slow addition of 2 equiv of t-BuNC to a solution of **2**. The structure of **8** has not yet been established, but equivalent Cp groups and inequivalent t-Bu groups are indicated by NMR spectroscopy.

In conclusion, zirconocene is effective at stabilizing benzocyclobutadiene by a rare η^2-cyclobutadiene coordination mode. The complex shows excellent reactivity, allowing coupling of alkynes and nitriles with the cyclobutadiene moiety. Double insertion and coupling of *tert*-butyl isocyanide yields a novel diamino−Dewar-naphthalene complex. Many more cyclobutadiene moiety coupling products may be anticipated with this system.

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Supporting Information Available: Text and tables giving characterization data for **1**−**8**, including X-ray crystallographic data for **2**, **3**, **6** (R = t-Bu), and **7**; X-ray data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310−2312. (b) Takahashi, T.; Xi, C.; Xi, Z.; Kageyama, M.; Fischer, R.; Nakajima, K.; Negishi, E. *J. Org. Chem.* **1998**, *63*, 6802−6806.

(15) X-ray data for **6** (173 K): $C_{21}H_{25}PZr$, $a = 13.396(2)$ Å, $b = 16.028(3)$ Å, $c = 9.6200(16)$ Å, $\beta = 108.487(3)°$, monoclinic, $P2_1/c$, $Z = 4$. Data were collected using a Siemens SMART CCD diffractometer. The data were refined on F^2 (SHELXL) to R1 = 0.0310. Selected distances (Å) and angles (deg): Zr1−N1 = 2.0509(17), Zr1−C2 = 2.349(2), N1−C9 = 1.273(3), C1−C9 = 1.523(3), C1−C8 = 1.535(3), C1−C2 = 1.611(3), C2−C3 = 1.499(3), C3−C4 = 1.388(3), C3−C8 = 1.394(3), C4−C5 = 1.391(3), C5−C6 = 1.393(4), C6−C7 = 1.402(4), C7−C8 = 1.377(3); N1−Zr1−C2 = 78.29(8), C9−N1−Zr1 = 122.83(15), C9−C1−C8 = 117.70(17), C9−C1−C2 = 113.00(17), C8−C1−C2 = 85.56(16), C3−C2−C1 = 86.15(15), C3−C2−Zr1 = 123.21(14), C1−C2−Zr1 = 104.94(13), C4−C3−C8 = 121.1(2), C4−C3−C2 = 143.7(2), C8−C3−C2 = 95.18(18), C3−C4−C5 = 116.9(2), C4−C5−C6 = 121.7(2), C5−C6−C7 = 121.4(2), C8−C7−C6 = 116.3(2), C7−C8−C3 = 122.6(2), C7−C8−C1 = 144.5(2), C3−C8−C1 = 92.89(18), N1−C9−C1 = 118.22(19).

(16) X-ray data for **7** (173 K): $C_{28}H_{34}N_3Zr$, $a = 8.8770(13)$ Å, $b = 27.103(4)$ Å, $c = 30.421(4)$ Å, orthorhombic, $P2_12_12_1$, $Z = 12$. Data were collected using a Siemens SMART CCD diffractometer. The data were refined on F^2 (SHELXL) to R1 = 0.0413. Selected distances (Å) and angles (deg): Zr1−N1 = 2.130(6), Zr1−N2 = 2.152(7), Zr1−C9 = 2.470(7), Zr1−C10 = 2.479(8), N1−C9 = 1.375(10), N1−C15 = 1.497(9), N2−C10 = 1.338(10), N2−C11 = 1.498(10), C1−C9 = 1.529(10), C1−C8 = 1.534(12), C1−C2 = 1.555(15), C2−C3 = 1.568(13), C2−C10 = 1.592(11), C3−C8 = 1.327(14), C3−C4 = 1.409(12), C4−C5 = 1.394(14), C5−C6 = 1.396(17), C6−C7 = 1.326(14), C7−C8 = 1.395(12), C9−C10 = 1.402(11); N1−Zr1−N2 = 89.1(3), N1−Zr1−C9 = 33.8(2), N2−Zr1−C9 = 63.4(2), N1−Zr1−C10 = 64.4(3), N2−Zr1−C10 = 32.6(3), C9−Zr1−C10 = 32.9(3), C9−N1−C15 = 120.8(6), C9−N1−Zr1 = 86.8(4), C15−N1−Zr1 = 148.7(5), C10−N2−C11 = 117.9(8), C10−N2−Zr1 = 87.2(5), C11−N2−Zr1 = 150.7(7), C9−C1−C8 = 115.0(7), C9−C1−C2 = 86.4(6), C8−C1−C2 = 89.2(8), C1−C2−C3 = 82.4(8), C1−C2−C10 = 87.9(6), C3−C2−C10 = 115.7(7), C8−C3−C4 = 122.9(10), C8−C3−C2 = 96.7(8), C4−C3−C2 = 140.3(11), C5−C4−C3 = 112.8(12), C4−C5−C6 = 123.4(11), C7−C6−C5 = 121.3(12), C6−C7−C8 = 116.6(12), C3−C8−C7 = 122.9(10), C3−C8−C1 = 91.6(8), C7−C8−C1 = 145.5(12), N1−C9−C10 = 126.0(6), N1−C9−C1 = 136.2(7), C10−C9−C1 = 96.2(7), N1−C9−Zr1 = 59.4(4), C10−C9−Zr1 = 73.9(4), C1−C9−Zr1 = 137.3(5), N2−C10−C9 = 126.4(7), N2−C10−C2 = 142.6(8), C9−C10−C2 = 89.5(7), N2−C10−Zr1 = 60.2(4), C9−C10−Zr1 = 73.2(4), C2−C10−Zr1 = 136.0(5).

(17) Fisher and Buchwald obtained a double t-BuNC insertion product from the cyclobutene complex that may have a similar structure, but in the absence of an X-ray crystal structure determination the complex was formulated as a simple diiminoacyl insertion product.[9]

(18) Titanacyclobutane complexes add isocyanides in a similar fashion to produce five-membered rings: Greidanus-Strom, G.; Carter, C. A. G.; Stryker, J. M. *Organometallics* **2002**, *21*, 1011−1013.

(19) Isocyanide coupling reviews and recent references: (a) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90−97. (b) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059−1079. (c) Ong, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1−3. (d) Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 4442−4447. (e) Tomaszewski, R.; Lam, K.-C.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1999**, *18*, 4174−4182.

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