J. Am. Chem. Soc. **1993,** *115,* 8859–8860

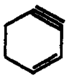
Synthesis of Zirconocene Complexes of a 1,2,3-Cyclohexatriene and a Cyclohexen-3-yne

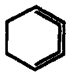
Jianguo Yin, Khalil A. Abboud, and W. M. Jones*

Department of Chemistry
University of Florida
Gainesville, Florida 32611

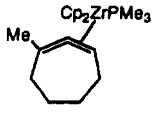
Received May 10, 1993

Shakespeare and Johnson[1] recently reported an elegant synthesis of two new isomers of benzene, **1** and **2**, the smallest and most highly strained cyclic alken-3-yne[2] and cyclic 1,2,3-butatriene (estimated 60.5 kcal/mol strain)[3] recorded to date.[3,4]

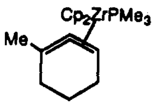

1


2

Both hydrocarbons were detected by trapping with diphenylisobenzofuran. For some time we have been interested in metal complexes of strained cyclic cumulenes,[7] and we recently succeeded in preparing zirconocene complexes of 1-methyl-1,2-cycloheptadiene (**3**) and 1-methyl-1,2-cyclohexadiene (**4**)[8] using the method that has been successfully applied to the preparation of zirconocene complexes of alkenes[9] (including strained cycloalkenes),[10,11a] acyclic alkynes,[11a,12] benzynes, and other highly strained cyclic alkynes[11] (down to and including a substituted cyclopentyne).[13] Success with the strained allenes prompted us to attempt the same method for preparation of a zirconocene complex of a cyclohexa-1,2,3-triene. At this time, we report success in this attempt, but only if formation of the complex of cyclohexen-3-yne (Johnson's second isomer of benzene) is prevented by an appropriately placed blocking group.



3



4

The zirconocene σ complexes **6** were prepared as shown in Scheme I. When a benzene solution of **6** (R = H) was allowed to react with Me_3P at 7 °C for 4 days, elimination of 1,3-cyclohexadiene occurred with concomitant formation of an inseparable mixture of two new zirconocene complexes **7** and **8** (47%) in a ratio of 2:1.[14] That elimination had occurred exclusively (within experimental error) to give complexes of cyclohexen-3-yne rather than cyclohexa-1,2,3-triene was shown in two ways. First, the NMR spectrum of the crude product showed only four hydrogens in the vinyl region which, by irradiation, were shown to consist of adjacent pairs; irradiation of any vinyl resonance decoupled another vinyl resonance. This property is consistent with **7** and **8** but not with a 1,2,3-cyclohexatriene complex. Second, additional evidence against the triene complex was obtained by treating the crude reaction mixture with I_2; only 1,2-diiodocyclohexa-1,3-diene (**9**) was formed. No trace of 2,3-diiodocyclohexa-1,3-diene could be detected. Preferential elimination of 1,3-cyclohexadiene from **6** (R = H) to give **7** and **8** was not unexpected, because the adjacent vinyl hydrogen that would lead to the alkyne is kinetically more accessible than H^1 (shorter bond and more favorable dihedral angle), a characteristic that appears to be important for this kind of reaction.[13,15] In addition, molecular mechanics calculations predict cyclohexen-3-yne to be somewhat less strained than 1,2,3-cyclohexatriene.[16]

Zirconocene complexes of 1,2-cyclohexadiene and 1,2-cycloheptadiene could be prepared only if cyclohexyne formation were prevented by blocking C1 with a substituent, in this case, a methyl.[8] Unfortunately, all attempts to prepare 1-methyl-2-bromocyclohexa-1,3-diene failed.[18] 1-Phenyl-2-bromocyclohexa-1,3-diene was therefore prepared and converted to the zirconocene complex **6** (R = Ph), as shown in Scheme I. Allowing a benzene solution of **6** (R = Ph) to remain at room temperature (rt) for 3 days or to be warming at 35 °C for 12 h in the presence of excess Me_3P led to elimination of 1-phenyl-1,3-cyclohexadiene and clean formation of the zirconocene complex of 1-phenyl-1,2,3-cyclohexatriene **10** as a yellow, air-sensitive solid. These reaction conditions were noticeably milder than those required for formation of the complex of 1-methyl-1,2-cyclohexadiene (53 °C for 8 h), a cyclic cumulene that is undoubtedly significantly

---

(1) Shakespeare, W. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 8578.

(2) For review of cycloalkenynes: Meier, H.; Hanold, N.; Molz, T.; Bissinger, J. J.; Kolshorn, H.; Zountsas, J. *Tetrahedron* **1986**, *42*, 1711.

(3) For review of cyclic cumulenes: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(4) 1,2,3-Cyclononatriene is the smallest cyclic 1,2,3-triene isolated to date.[5] The $(Ph_3P)_2RhCl$ complex of this triene has also been prepared.[6]

(5) Angus, R. O., Jr.; Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 2880.

(6) Angus, R. O., Jr.; Janakiraman, M. N.; Jacobson, R. A.; Johnson, R. P. *Organometallics* **1987**, *6*, 1909.

(7) (a) Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069–1072. (b) Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, *4*, 2228–2230. (C) Oon, S. M.; Koziol, A., Palenik, G. J.; Jones, W. M. *J. Chem. Soc., Chem. Commun.* **1987**, 491–492. (d) Oon, S. M.; Jones, W. M. *Organometallics* **1988**, *7*, 2172–2177. (e) Abboud, K. A.; Lu, Z.; Jones, W. M. *Acta Crystallogr.* **1992**, *C48*, 909. (f) Lu, Z.; Jones, W. M.; Winchester, W. R. *Organometallics* **1993**, *12*, 1344. (g) Lu, Z.; Abboud, K. A.; Jones, W. M. *Organometallics* **1993**, *12*, 1471.

(8) Yin, J.; Abboud, K. A.; Jones, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 3810.

(9) (a) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761. (b) Binger, P.; Muller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035. (c) Takahashi, T.; Nitto, Y.; Seki, T.; Saburi, M.; Negishi, E. *Chem. Lett.* **1990**, 2259.

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

(11) For reviews: (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (b) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. For more recent references: (a) Cuny, G. D.; Gutierrez, A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 537. (b) Cuny, G. D.; Buchwald, S. L. *Organometallics* **1991**, *10*, 363. (c) Buchwald, S. L.; King, S. M. *Organometallics* **1991**, *113*, 258.

(12) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1987**, *109*, 2544.

(13) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113.

(14) Stereoisomer assignment for **7** and **8** are based on NOE: 15% enhancement of H^1 upon irradiation of Me_3P; no enhancement in **8**. For **7**: ^1H NMR (C_6D_6) δ 6.47 (dt, 1H, $^3J_{H1,2}$ = 8.6 Hz, $^4J_{H1,3}$ = 2.0 Hz), 5.93 (dt, 1H, H^2, $^3J_{H2,1}$ = 8.5 Hz, $^3J_{H2,3}$ = 4.3 Hz), 5.36 (d, 10 H, C_5H_5, $^3J_{PC}$ = 1.7 Hz), 2.98 (t, 2H, H^4, $^3J_{H4,3}$ = 9.0 Hz), 2.32 (tdd, 2H, H^3, $^3J_{H3,4}$ = 9.0 Hz, $^3J_{H3,2}$ = 4.3 Hz, $^4J_{H3,1}$ = 2.0 Hz), 0.99 (d, 9H, PMe_3, $^2J_{PH}$ = 6.0 Hz). **8**: ^1H NMR (C_6D_6) δ 7.10 (dt, 1H, H^1, $^3J_{H1,2}$ = 8.4 Hz, $^4J_{H1,4}$ = 1.8 Hz), 6.02 (dt, 1H, H^2, $^3J_{H2,1}$ = 8.4 Hz, $^3J_{H2,3}$ = 3.7 Hz), 5.37 (d, 10H, C_5H_5, $^3J_{PH}$ = 1.7 Hz), 2.38 (td, 2H, H^4, $^3J_{H4,3}$ = 8.4 Hz, $^4J_{H4,2}$ = 2.1 Hz), 2.21 (m, 2H, H^3), 0.93 (d, 9H, $^2J_{PH}$ = 5.9 Hz). ^{13}C NMR for the mixture of **7** and **8** (C_6D_6): δ 192.30 (d, J_{PC} = 10.5 Hz), 179.25 (d, J_{PC} = 8.2 Hz), 161.25 (d, J_{PC} = 29.7 Hz), 148.90 (d, J_{PC} = 30.8 Hz), 131.25 (d, J_{PC} = 2.9 Hz), 130.1 (d, J_{PC} = 1.9 Hz), 123.69, 123.49, 103.44, 103.39, 33.17 (d, J_{PC} = 2.7 Hz), 31.65 (d, J_{PC} = 2.9 Hz), 26.68, 26.56, 17.60 (d, $^1J_{PC}$ = 17.5 Hz), 17.35 (d, $^1J_{PC}$ = 16.8 Hz). **10**: ^1H NMR (C_6D_6) δ 8.10 (dd, 2H, C_6H_5), 7.52 (t, 2H, C_6H_5), 7.26 (t, 1H, C_6H_5), 6.21 (t, 1H, H^1, $^3J_{H1,2}$ = 3.8 Hz), 5.33 (d, 10H, C_5H_5, $^3J_{PH}$ = 1.8 Hz), 2.82 (t, 2H, H^3, $^3J_{H3,2}$ = 9.1 Hz), 2.66 (m, 2H, H^2); ^{13}C NMR (C_6D_6) δ 162.65 (d, J_{PC} = 9.7 Hz), 150.56 (d, J_{PC} = 28 Hz), 145.15 (d, J_{PC} = 2.3 Hz), 130.74 (d, J_{PC} = 3.2 Hz), 128.95, 128.27, 124.61, 124.55, 102.59, 30.43 (d, J_{PC} = 1.7 Hz), 28.42; IR (KBr) ν 2933.3, 2910.1, 2792.9, 1630.8, 1588.5, 1525.4, 1484.8, 1384.5, 1010.1, 9548.8, 813.5, 795.9, 699.8.

(15) (a) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171. (b) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (c) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

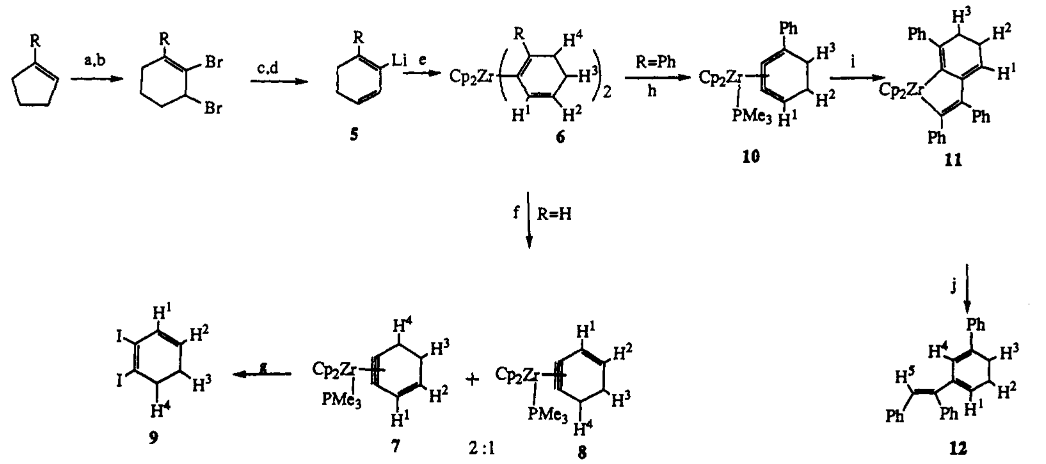
(16) Estimated strain energies for cyclohexen-3-yne and cyclohexyne are 54 and 28 kcal/mol, respectively,[17] while 1,2,3-cyclohexatriene and 1,2-cyclohexadiene have been estimated by (MNDO)[3] to have strain energies of 60.5 and 31 kcal/mol (83 and 36 kcal/mol by MMX), respectively.

(17) From molecular mechanics calculations using an MMX program generously provided by Professor Joe Gajewski, University of Indiana.

(18) Attempts to induce 1,2-elimination from 1-methyl-2,3-dibromocyclohexene led exclusively to 1-methylene-2-bromocyclohex-2-ene.

0002-7863/93/1515-8859$04.00/0

Scheme I[a]



[a] (a) $CHBr_3$, KO^{t}Bu, −10 °C. (b) 85 °C. (c) KO^{t}Bu, ^{t}BuOH, rt, 95%. (d) 1.1 equiv of BuLi, −100 °C. (e) $^1/_2$ Cp_2ZrCl_2, −60 to −10 °C, R = Ph, 71%; R = H, 55%. (f) Excess PMe_3, 7 °C, 4 days, 47%. (g) I_2, rt, 62%. (h) Excess PMe_3, rt 3 days, or 35 °C, 12 h, 72%. (i) Ph_2C_2, rt 5 days, or 35 °C 24 h, 95%. (j) 2.5 equiv of HCl.

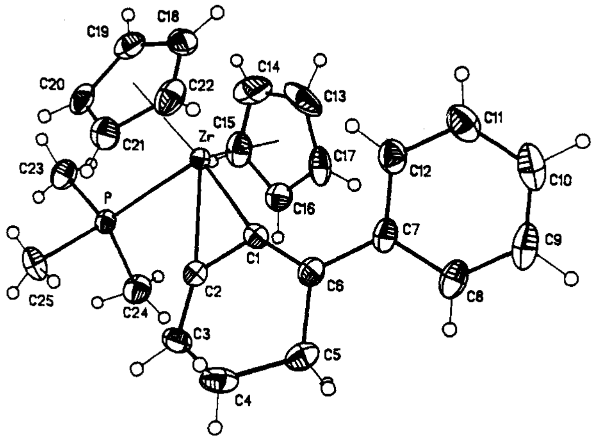


Figure 1. Structure and labeling scheme for **10** with 50% probability of thermal ellipsoids. Important bond distances (Å) and angles (deg): Zr–C(1), 2.237(4); Zr–C(2), 2.297(5); Zr–P, 2.6948(12); C(1)–C(2), 1.425(7); C(2)–C(3), 1.329(7); C(3)–C(4), 1.494(8); C(4)–C(5), 1.521(8); C(5)–C(6), 1.512(7); C(6)–C(1), 1.356(6); P–Zr–C(1), 111.53(12); P–Zr–C(2), 75.29(12); C(1)–C(2)–C(3), 120.8(4); C(2)–C(3)–C(4), 119.2(5); C(3)–C(4)–C(5), 111.4(4); C(4)–C(5)–C(6), 112.5(4); C(6)–C(1)–C(2), 122.4(4).

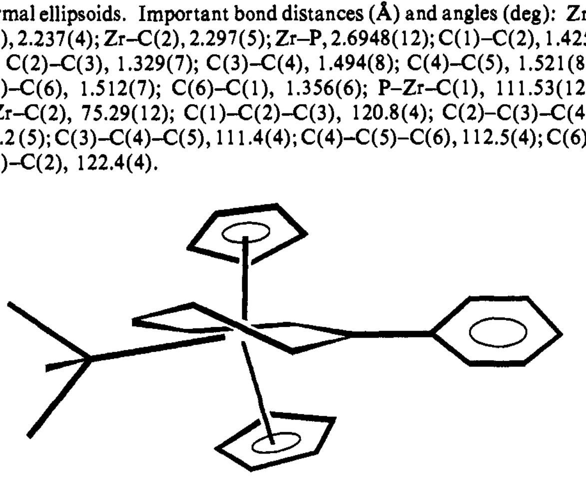
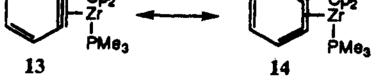


Figure 2. Projection showing nonplanarity of the 1,2,3-cyclohexatriene ring.

less strained than 1,2,3-cyclohexatriene.[16] As in the formation of the cyclohexen-3-yne complex, this rather surprising result is probably due to kinetic accessibility of the β-vinyl hydrogen;[13,15] in **6** (R = Ph), the bond length between the carbon bearing the metal and the β-hydrogen is presumably shorter (sp^2–sp^2 vs sp^3–sp^2)[19] than in the precursor to **4**. The metal and vinyl hydrogens are also probably much more nearly coplanar. Structural assignment to **10** is based on NMR,[14] elemental analyses, and reductive coupling with diphenylacetylene to give **11**,[20] which, upon reaction with HCl, gave the substituted stilbene **12**.

Finally, the structure of **10** (R = Ph) was confirmed by single crystal X-ray crystallography. The molecular structure, the atom numbering scheme, and important bond distances and angles are shown in Figure 1, and the lack of planarity of the 1,2,3-cyclohexatriene ring is highlighted in the projection drawing in Figure 2. The Zr atom in **10** is asymmetrically bonded to the C1–C2 double bond [Zr–C1 and Zr–C2 are 2.237(4) and 2.297(5) Å, respectively]. Asymmetry is also observed in the dihedral angles between the plane of Zr, C1, and C2 and those of the Cp rings. The former has angles of 30.5(3)° and 19.4(2)° with the planes of the C13–C17 ring and the C18–C22 ring, respectively. The internal bond angles of the butatriene moiety, C1–C2–C3 and C2–C1–C6 are 122.4(4)° and 120.8(4)°, respectively. Both angles are smaller than the internal angle of **4** which, in turn, is smaller than the central angle of any simple allene metal complex previously reported.[7] Indeed, these two bonds angles are virtually identical to those reported for the corresponding zirconocene complex of benzyne[11a] [122.1(5)°, 120.2(5)°], which may be represented as a resonance hybrid that includes the cyclic butatriene canonical form **14**. Interestingly, the alkyne bond



13 **14**

length in the corresponding benzyne complex (1.365 Å)[11a] is almost exactly midway between the C1–C2 bond of **10** (1.425(7) Å) and that of the corresponding cyclohexyne complex (1.295 Å),[11a] suggesting significant contribution from both **13** and **14** in the benzyne complex (which is also consistent with the absence of detectable bond alternation in the benzyne complex).[11a]

Acknowledgment. This research was supported by the National Science Foundation, the University of Florida Division of Sponsored Research, and the Chevron Research and Technology Company, to whom the authors are most grateful.

Supplementary Material Available: X-ray data for **10** and details of experimental preparations of 1-phenyl-2,3-dibromocyclohexene, 1-phenyl-2-bromo-1,3-cyclohexadiene, **6** (R = H, Ph), **7**, **8**, **9**, **10**, **11**, and **12** (16 pages); observed and calculated structure factors for **10** (10 pages). Ordering information is given on any current masthead page.

---

(19) *Advanced Organic Chemistry*, 4th Ed.; March, J., Ed. John Wiley & Sons: New York, 1992; pp 21–31.

(20) The coupling product is formed with the sterically dictated regiospecificity previously observed for zirconocene complexes of substituted cyclopentyne[13] ortho-substituted benzynes[11a] **3** and **4**.