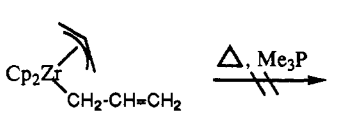
Synthesis and Structure of (Trimethylphosphine)zirconocene-3-methyl-1,2-cyclohexadiene: First Metal Complex of a Six-Membered Allene

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

Department of Chemistry
University of Florida
Gainesville, Florida 32611

Received July 20, 1992

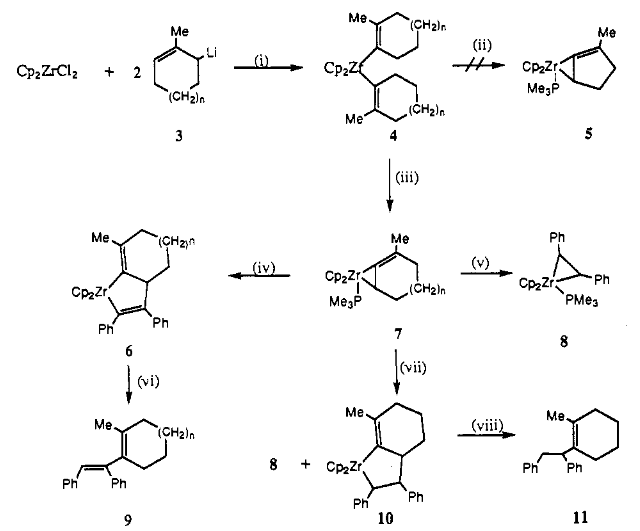
Despite recent progress in the isolation and characterization of alkene complexes of zirconocene, to date reactions that may have led to complexes of allenes have failed; reaction of Cp_2Zr (Cp = cyclopentadiene) with allenes gave only zirconacyclopentanes,[1] and thermolysis of **1**[2] in the presence of Me_3P[3] gave no sign of propene or the allene complex **2**. Similarly, all previous attempts to prepare stable transition-metal complexes of 1,2-cyclohexadiene, the most highly strained allene that has been successfully generated to date,[4] have failed.[5,8]



1 **2**

At this time we report the successful preparation and characterization (including crystal structures) of (trimethylphosphine)zirconocene complexes of 3-methyl-1,2-cycloheptadiene and 3-methyl-1,2-cyclohexadiene (**7**, *n* = 1, 2)[9] (perhaps better represented as metallamethylenecyclopropanes). These two compounds are the first examples of allene complexes of zirconium (or, to our knowledge, any of the early transition metals) and have a unique feature in that the two carbons bonded to zirconium have different hybridization, a feature which may influence their chemistry. The cyclohexadiene complex is also unique in that it is probably the most highly strained allene complex reported to date, showing an internal bond angle that is over 35° more acute than the most highly bent acyclic allene complex[10] and 13° more acute than the Fe(II) complex of 1,2-cycloheptadiene.[7]

Scheme I[a]



[a] Reagents and conditions: (i) *n* = 0, 1, 2; –60 to –10 °C; (ii) *n* = 0, 120 °C, 12 h; Me_3P; (iii) *n* = 1; 53 °C, 8 h, Me_3P; *n* = 2; 30 °C, 12 h, Me_3P; (iv) *n* = 1, 2, PhCCPh, rt; (v) *n* = 2, stilbene, 73 °C, 20 h; (vi) *n* = 1, 2; HCl; (vii) *n* = 1, stilbene, 48 °C, 10 h; (viii) *n* = 1, HCl.

Syntheses of **7** (*n* = 1, 2) are outlined in Scheme I.[11] Methyl-substituted cycloalkenes were used to prevent the previously reported[9] cyclohexyne and (likely) cycloheptyne formation. Conversion of **4** (*n* = 2) to the cycloheptadiene complex (60% isolated yield) and 1-methylcycloheptene was complete upon warming for 12 h at 30 °C. Conversion of **4** (*n* = 1) to the cyclohexadiene complex (71% isolated yield) and 1-methylcyclohexene required somewhat more robust conditions, warming at 53 °C for 8 h, and the complex of methyl-1,2-cyclopentadiene (**5**) could not be prepared by this method; even when heated to 120 °C for 12 h, neither **5** nor 1-methylcyclopentene was observed although significant decomposition occurred.

Both allene complexes **7** (*n* = 1, 2) are air-sensitive (both in the solid state and in solution) yellow solids that are soluble in polar organic solvents but rapidly decompose in halogenated solvents. Crystal structures are shown in Figures 1 and 2. As expected, the Zr–C2 bonds are shorter in each case than the Zr–C1 bonds [e.g., for **7** (*n* = 1): 2.240(3) and 2.375(3) Å, respectively]. These differences are presumably due to the bulk of the Me_3P group[9] and the different hybridization of the two carbons. It is interesting that the Zr–C2 distances are equivalent to the Zr–C bond in a closely related Zr–benzyne[12] complex [two bonds between Zr and the triple-bond atoms are 2.228(5) and

---

[1] (a) Duggan, D. M. *Inorg. Chem.* **1981**, *20*, 1164. (b) Schmidt, J. R.; Duggan, D. M. *Inorg. Chem.* **1981**, *20*, 318.

[2] Martin, H. A.; LeMaire, P. J.; Jellinek, F. *J. Organomet. Chem.* **1968**, *14*, 149.

[3] Yin, J., unpublished results, University of Florida.

[4] Uncomplexed 1,2-cyclohexadiene has been successfully generated and characterized by trapping at ambient temperature and has been observed directly in a low-temperature matrix.[5] The strain energy of this allene is unknown. However, MMX calculations (program generously provided by Professor J. Gajewski of the University of Indiana) predict a strain energy of 36.3 kcal/mol, 14.2 kcal/mol higher than that of 1,2-cycloheptadiene and 8.6 kcal/mol higher than that of cyclohexyne).

[5] For an excellent review of strained cyclic allenes, see: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

[6] Fe(II) and Pt(0) complexes of 1,2-cycloheptadiene and Pt(0) of two 1,2,4,5-cycloheptatetraenes are known.[7]

[7] (a) Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069. (b) Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, *4*, 2228. (c) Oon, S. M.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Chem. Commun.* **1987**, 491. (d) Oon, S. M.; Jones, W. M. *Organometallics* **1988**, *7*, 2172. (e) Abboud, K. A.; Lu, Z.; Jones, W. M. *Acta. Crystallogr.* **1992**, *C48*, 909. (f) Visser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 178.

[8] Indirect evidence for the carbonyl(η^5-cyclopentadienyl)tributylphosphineiron complex of 1,2-cyclohexadiene has been obtained, but the compound was too unstable to be characterized: Oon, S. M., unpublished results, University of Florida.

[9] For reviews of Cp_2ZrPMe_3 complexes of strained alkenes and alkynes, see: (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 examples (including cyclopentyne and cyclobutene), see: (c) Buchwald, S. L.; Lum, T. R.; Fischer, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113. (d) Fisher, R. A.; Buchwald, S. L. *Organometallics* **1990**, *9*, 871. (e) Cuny, G. D.; Gutierrez, A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 537. (f) Binger, P.; Biedenbach, B.; Mynott, R.; Regitz, M. *Chem. Ber.* **1988**, *121*, 1455.

[10] (a) Cf. Jacobs, T. L. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: New York, NY, 1982; Vol. II, Chapter 4. (b) Gallop, M. R.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

[11] **7** (*n* = 1): ^{1}H NMR (in C_6D_6, 300 MHz) δ 5.25 (d, 5H, $^3J_{P-H} = 1.7$ Hz), 5.16 (d, 5H, $^3J_{P-H} = 1.9$ Hz), 2.6 (m, 1H), 2.7–2.4 (m, 2H), 2.23 (d, 3H, $^4J_{H-H} = 3.3$ Hz), 1.9 (m, 2H), 0.84 (d, 9H, $^2J_{P-H} = 5.8$ Hz), 0.5 (m, 1H), 0.2 (1H, m); ^{13}C NMR (C_6D_6, 75 MHz) δ 168.0 (d, $J_{PC} = 6.1$ Hz), 129.7, 101.8, 101.2, 39.4, 34.3, 30.3 (d, $J_{PC} = 2.2$ Hz), 17.8 (d, $J_{PC} = 20.1$ Hz), 17.3 (d, $J_{PC} = 16.0$ Hz); ^{31}P NMR (C_6D_6, 85% H_3PO_4 as external reference) δ –1.36; HRMS calcd for $C_{20}H_{30}PZr$ 391.1128, found 391.1098; IR (KBr cm^{-1}) 2911, 2845, 1632, 1437, 1142, 1017. Anal. Calcd for $C_{20}H_{30}PZr$: C, 61.33; H, 7.46. Found: C, 61.09; H, 7.47. **7** (*n* = 2): ^{1}H NMR (in C_6D_6, 300 MHz) δ 5.15 (d, 5H, $^3J_{P-H} = 1.7$ Hz), 5.14 (d, 5H, $^3J_{P-H} = 1.8$ Hz), 2.82 (m, 1H), 2.58 (m, 1H), 2.1–2.4 (m, 3H), 2.21 (s, 3H), 1.68 (m, 2H), 1.55 (m, 1H), 0.83 (d, 9H, $^2J_{PH} = 5.7$ Hz), 0.75 (m, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ 170.73 (d, $J_{PC} = 6.3$ Hz), 131.49 (d, $J_{PC} = 3.6$ Hz), 101.9, 100.98, 39.9, 37.7, 36.8 (d, $J_{PC} = 3.1$ Hz), 29.5, 26.9, 16.3 (d, $J_{PC} = 16.5$ Hz), 17.6 (d, $J_{PC} = 15.2$ Hz); ^{31}P NMR (C_6D_6, 85% H_3PO_4 as external reference) δ 0.0014. Anal. Calcd for $C_{21}H_{32}PZr$: C, 62.17; H, 7.70. Found: C, 62.17; H, 7.58.

[12] Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

0002-7863/93/1515-3810$04.00/0

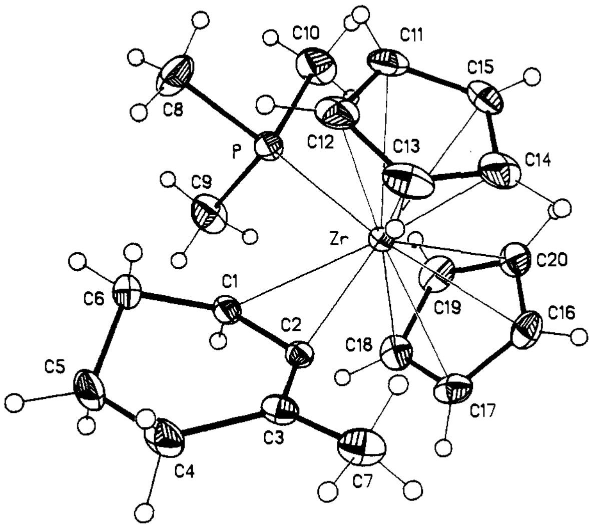


Figure 1. Structure and labeling scheme of 7 ($n = 1$) with 50% probability of thermal ellipsoids. Important bond distances (Å) and angles (deg): Zr–C1 = 2.375(3), Zr–C2 = 2.240(3), Zr–P = 2.6931(12), C1–C2 = 1.443(5), C2–C3 = 1.333(5), C3–C4 = 1.530(6), C4–C5 = 1.512(8), C5–C6 = 1.529(8), C6–C1 = 1.512(6), P–Zr–C1 = 75.50(9), P–Zr–C2 = 111.74(9), C1–C2–C3 = 125.1(3), C2–C1–C6 = 112.4(3), C2–C3–C4 = 119.6(4), C1–C6–C5 = 108.4(4).

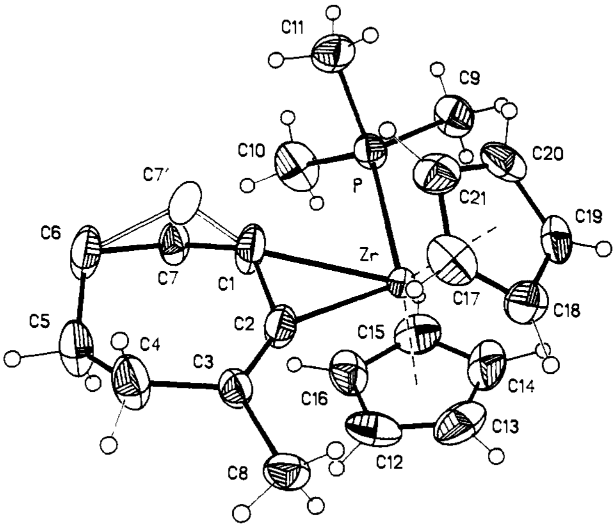


Figure 2. Structure and labeling scheme of 7 ($n = 2$) with 50% probability of thermal ellipsoids. Hydrogens on C1, C6, and C7 are omitted for clarity. Important bond distances (Å) and angles (deg): Zr–C1 = 2.389(6), Zr–C2 = 2.238(6), Zr–P = 2.696(2), C1–C2 = 1.442(9), C2–C3 = 1.326(9), C3–C4 = 1.503(9), C4–C5 = 1.450(9), C5–C6 = 1.490(11), C6–C7 = 1.594(13), C7–C1 = 1.362(10), P–Zr–C1 = 76.9(2), P–Zr–C2 = 113.05(15), C1–C2–C3 = 131.8(5), C2–C1–C7 = 125.3(7), C2–C3–C4 = 123.2(5), C1–C7–C6 = 113.5(9).

2.267(5) Å]; Zr–C1 in both allene complexes, as expected, is longer than either of these Zr–C bonds. Additionally, for both the six- and seven-membered rings, the coordinated double bonds, C1–C2, are significantly longer than the uncoordinated double bonds, indicating significant metallacyclopropane character. The most notable difference between the two zirconium complexes and transition-metal complexes of acyclic allenes is their deviation from linearity. The seven-membered ring is bent by 48°, and its six-membered counterpart is bent by 54.9°; metal complexes of acyclic allenes are typically bent by no more than 35°.[10] It is interesting that the internal allene angle for 7 ($n = 2$) is somewhat more acute than that in other seven-membered allenes [131.8(5)° vs 138° for Fp^+-1,2-cycloheptadiene and 135° for the bis(triphenylphosphine)platinum complex of 1,2,4,6-cycloheptatetraene],[5] consistent with more metallacyclopropane character in the zirconium complex. In both of the allene complexes, the angles that the planes containing atoms Zr, C1, and C2 form with the planes connecting atom C1, C2, and C3 deviate significantly from 180° [e.g., 157.0(4)° for 7 ($n = 1$)]. These deviations probably are contributing factors in the significant differences in the chemical shifts of the two Cps in both the ^{1}H and ^{13}C NMR spectra of these two complexes.

The effect of strain on the chemistry of the cyclohexadiene adduct is most directly reflected in its reaction with trans-stilbene in that it gives a mixture of the reductive coupling product **10**[13] and the stilbene adduct of zirconocene **8** (presumably from displacement of the allene), while the seven-membered analogue gives only the latter. Both of the allene complexes react cleanly with diphenylacetylene at room temperature to give the coupling products **6** ($n = 1, 2$) in essentially quantitative yields. The same adducts can also be prepared directly by warming **4** in the presence of diphenylacetylene. All of the reductive coupling reactions are, within detection limits, completely regiospecific. Duggan[1] has proposed a radical mechanism for allene dimerizations induced by Cp_2ZrN_2 with the suggestion that the regiochemistry is dictated by the relative stabilities of intermediate radicals. However, for the complexes at hand, it is more likely that the coupling reactions involve initial coordination of the alkyne to 16-electron zirconocene–allene intermediates and that the regiochemistry is dominated by steric effects; the alkyne attacks away from the methyl substituent which is the sterically less encumbered side of the two rings. Similar regiochemistry has been observed for reductive coupling to very similar zirconium complexes of substituted benzynes.[9] Hybridization differences in the coupling products (e.g., Zr–sp^{2}C and sp^{2}C–sp^{3}C for **7** vs Zr–sp^{3}C and sp^{2}C–sp^{2}C for the opposite regioisomers) could also influence regiochemistry, although this cannot be evaluated in the cases at hand.

Finally, as expected,[13] **6** and **10** react instantaneously with HCl to give the corresponding hydrocarbons and Cp_2ZrCl_2. Characterization of the hydrocarbons confirmed the structures assigned to the metallacycles.

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

Supplementary Material Available: Details of the experimental procedures for preparation of **4** ($n = 1, 2$), **6** ($n = 1, 2$), **7** ($n = 1, 2$), **9**, **10**, and **11**; X-ray data for **7** ($n = 1, 2$); tables of fractional coordinates and isotropic thermal parameters, crystallographic data, bond lengths and angles, and anisotropic thermal parameters for **7** ($n = 1, 2$) (23 pages); listing of observed and calculated structure factors for **7** ($n = 1, 2$) (26 pages). Ordering information is given on any masthead page.

---

(13) Reductive coupling of Cp_2Zr complexes of alkenes and alkynes with a variety of π-systems has been extensively studied. For reactions with strained alkenes, see ref 9. For coupling with unstrained π-complexes, see: (a) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (b) Takahashi, T. P.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623. (c) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C83. (d) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (e) Binger, P.; Muller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035. (f) Takahashi, T.; Nitto, Y.; Seki, T.; Saburi, M.; Negishi, E. *Chem. Lett.* **1990**, 2259.