Organometallics **1993,** *12,* 2013–2014

Transition-Metal Complexes of Bicyclo[3.1.0]hex-5-ene and Bicyclo[4.1.0]hept-6-ene

Jianguo Yin and W. M. Jones*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received February 17, 1993

Summary: Zirconocene complexes of two strained cyclopropenes, bicyclo[3.1.0]hex-5-ene and bicyclo[4.1.0]hept-6-ene, have been prepared by elimination of bicyclo[3.1.0]hexane and bicyclo[4.1.0]heptane from bis(bicyclo[3.1.0]hexyl)- and bis(bicyclo[4.1.0]heptyl)zirconocene in the presence of Me_3P. The bicycloalkene complexes undergo reaction with diphenylacetylene to give reductive coupling products which react with HCl to give bicycloalkyl-substituted cis-stilbenes.

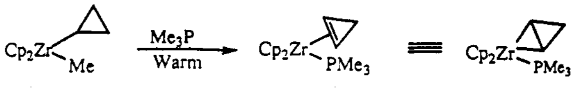
β-Hydrogen elimination to give π complexes is among the most ubiquitous reactions of alkyl groups σ-bonded to electron-deficient transition metals.[1] However, for reasons that are obscure, σ-bonded cyclopropanes normally do not undergo this reaction.[2,3] As a result, prior to a recent report by Buchwald,[4] cyclopropane complexes of transition metals have only been available from ligand exchange reactions[5] and complexes of unstable cyclopropenes such as bicyclo[4.1.0]hept-6-ene (**1**),[6] bicyclo[3.1.0]hex-5-ene (**2**),[8] and tricyclo[4.1.0.$0^{2,7}$]hept-1(7)-ene (**3**)[10] have not been accessible.


1


2

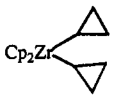

3

Buchwald recently reported the preparation of a zirconocene complex of cyclopropene (**4**; perhaps better represented as a metallabicyclobutane) by warming the σ complex in the presence of Me_3P.[4,11] This suggested that zirconocene complexes of cyclopropenes such as **1**–**3** might be synthesized similarly. At this time, we report the successful use of Buchwald's method for the preparation of zirconocene complexes of **1** (completely characterized) and its more highly strained homologue **2** (spectral and chemical evidence).[12] Attempts to apply this method to the preparation of a complex of **3** failed.

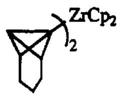


4

Bis(cyclopropyl)zirconocenes **5** (for comparison), **8**, **9**, and **10** were prepared by reaction of 2 equiv of the appropriate cyclopropyllithiums[13] with dichlorozirconocene (Scheme I for **9** and **10**). Both **9** and **10** were formed as mixtures of inseparable stereoisomers (1:3:0.5 and 1:1:0.05 *exo–exo*, *exo–endo*, and *endo–endo*, respectively; stereochemistry assignments based on $J_{H_1-H_2}$) even when prepared from stereochemically pure *exo*-bicycloalkyl bromides. All of the σ complexes are unstable to air and decompose fairly rapidly at room temperature under nitrogen in both solution and the solid state. Cyclopropene complexes (accompanied in each case by the corresponding saturated hydrocarbons; identified by NMR) were formed by warming C_6D_6 solutions of the σ complexes in the presence of an excess of Me_3P (Scheme II).[16] As expected, only those complexes with at least one *cis* β-hydrogen (*exo–exo* and *exo–endo*) gave cyclopropene products; both *endo–endo* isomers (e.g. **9c**) were inert, showing no tendency to eliminate an α-hydrogen to give either a cyclopropylidene



5



8

---

[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[2] (a) Omrcen, T.; Conti, N. J.; Jones, W. M. *Organometallics* **1991**, *10*, 913. (b) Conti, N. J.; Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1990**, *9*, 175–184. (c) Trace, R. L.; Jones, W. M. *J. Organomet. Chem.* **1989**, *376*, 103–113. (d) Conti, N. J.; Jones, W. M. *Organometallics* **1988**, *7*, 1666–1669. (e) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7436. (f) Lehmkuhl, H.; Grundke, J.; Myhnott, R. *Chem. Ber.* **1983**, *116*, 176. (g) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149. (h) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732. (i) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3252. (j) Phillips, R. L.; Puddephatt, R. J. *J. Organomet. Chem.* **1977**, *136*, C52. (k) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161. (l) Mushak, P.; Battiste, M. A. *J. Organomet. Chem.* **1969**, *17*, 46.

[3] Possible reasons for this reluctance to undergo β-hydrogen elimination have been discussed.[2f,h]

[4] Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

[5] Cf.: (a) Binger, P.; Muller, P.; Renn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 640. (b) Binger, P.; Buch, H. M. *Top. Curr. Chem.* **1987**, *135*, 79. (c) Fredericks, J.; Thomas, L. *J. Am. Chem. Soc.* **1978**, *100*, 350. (d) Viser, J. P.; Schipperijn, A. J.; Lukas, J.; Bright, D.; DeBoer, J. J. *J. Chem. Soc. D.* **1971**, 1266.

[6] Bicyclo[4.1.0]hept-6-ene has been prepared and is unstable above −90 °C.[7]

[7] Cf.: Billups, W. E.; Haley, M. M.; Lee, G. *Chem. Rev.* **1989**, *89*, 1147.

[8] To our knowledge, bicyclo[3.1.0]hex-5-ene has not been prepared, although a derivative was recently observed in a low-temperature matrix.[9]

[9] Sander, W.; Bucher, G.; Reichel, F.; Cremar, D. *J. Am. Chem. Soc.* **1991**, *113*, 5311.

[10] (a) Zoch, H. G.; Szeimies, G.; Romer, R.; Schmitt, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 877. (b) Zoch, H. G.; Szeimies, G.; Romer, R.; Germain, G.; Declerq, J. P. *Chem. Ber.* **1983**, *116*, 2285.

[11] For other examples of Cp_2Zr alkene complexes produced by β-hydrogen elimination and stabilized with Me_3P, see: (a) Fisher, R. A.; Buchwald, S. L. *Organometallics* **1990**, *9*, 871. (b) Takahashi, T.; Nitto, Y.; Seki, T.; Aaiur, M.; Negishi, E. *Chem. Lett.* **1990**, 2259. (c) Takahashi, T.; Murakami, M.; Kunishing, M.; Sauur, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761. (d) Fisher, A.; Buchwald, S. *Organometallics* **1990**, *9*, 871. (e) Binger, P.; Muller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035. (f) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623.

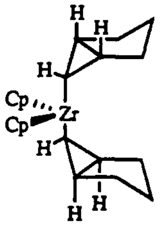
[12] Due to an extreme sensitivity to the atmosphere, neither C,H analytical data nor high-resolution mass spectra of some of the zirconium complexes could be obtained. However, a combination of their spectra and complete characterization of their protonolysis products leave no question as to the assigned structures. Most reactions were quite clean, their crude NMR spectra showing only traces of impurities.

[13] Bicycloalkyllithiums were prepared by refluxing the corresponding bicycloalkyl bromides[14] with lithium in ether.[15]

[14] Seyferth, D.; Cohen, H. M. *J. Organomet. Chem.* **1963**, *6*, 1521.

[15] Seyferth, D.; Yamazaki, J.; Alleston, D. L. *J. Org. Chem.* **1963**, *28*, 703.

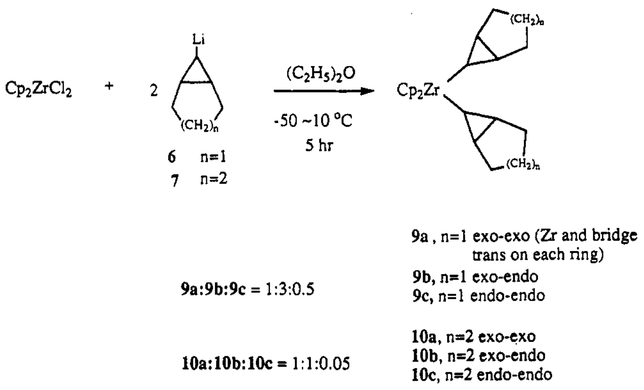
0276-7333/93/2312-2013$04.00/0 © 1993 American Chemical Society



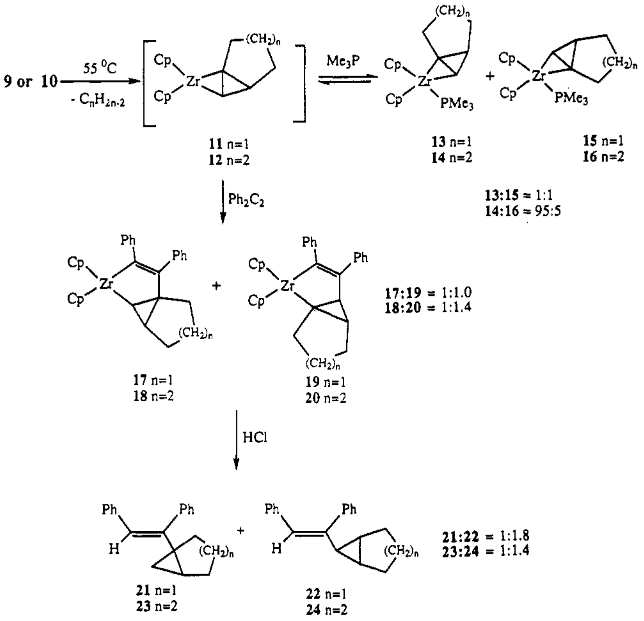
9c

or an allene complex.[17] Formation of **13–16** required somewhat more severe conditions for reaction than did the parent bis(cyclopropyl)zirconocene **5**,[18] and **8** showed significant decomposition with at most traces of the desired product when heated in the presence of Me_3P at 80 °C overnight in C_6D_6. Whether the latter is due to poor kinetic accessibility of the β-hydrogen,[19] strain in the potential cyclopropene complex (or metallopropellane), or both is unknown. Both **9** and **10** gave mixtures of cyclopropene isomes (**13–16**), although their ratios are notably different (**13**:**15** = 1:1, **14**:**16** = 95:5). Reasons for this rather striking difference are presumably steric in origin but are not clear from models. The larger preponderance of **14** in the product mixture permitted complete NMR assignments, analysis, etc. (stereochemical assignment based on NOE), although we were unsuccessful in attempts to grow a single crystal suitable for X-ray study. The nearly equal mixture of **13** and **15** was isolated as a white precipitate but could not be induced to crystallize, and their extreme instability (for instance, purification attempts even as mild as simply washing with appropriate solvents led to significant decomposition) precluded unique NMR assignments. As a result, structure assignments rest heavily on the ultimate conversion of **13** and **15** to **21** and **22** (*vide infra*).

Scheme I



Scheme II



In reactions analogous to those for other zirconocene alkene complexes[4,11] (including the cyclopropene complex from **5**),[4] warming either **9** or the cyclopropene complexes (**13**, **15** or **14**, **16**) with diphenylacetylene in C_6D_6 gave the respective metallocyclopentene adducts **17–20** (oils)[12,16,20] as inseparable pairs of isomers. Significantly, **9** and **13**, **15** gave identical ratios of **17**:**19** (1:1.8, respectively), consistent with the 16-electron intermediate **11**. Connectivities in the diphenylacetylene complexes **17–20** were confirmed by treating each mixture with HCl, which quantitatively (NMR) converted them into their corresponding hydrocarbons **21–24**[21] (stereochemistry confirmed by NOE) in the same ratio as their six- and seven-membered-ring precursors (1:1.8 and 1:1.4, respectively).

Acknowledgment. This work was supported by the National Science Foundation and the University of Florida Division of Sponsored Research.

Supplementary Material Available: Text giving experimental procedures and spectral data for **6–24** (4 pages). Ordering information is given on any current masthead page.

OM9300890

---

[16] Spectral properties of selected complexes are as follows. **4**: ^1H NMR (300 MHz, C_6D_6) δ 5.28 (5H, d, $^3J_{P-H}$ = 1.8 Hz), 5.25 (5H, d, $^3J_{P-H}$ = 1.9 Hz), 2.55 (1H, m), 1.75 (1H, m), 0.96 (9H, d, $^2J_{P-H}$ = 6.0 Hz), 0.91 (1H, m), 0.60 (1H, m); ^{13}C NMR (75 MHz, C_6D_6) δ 102.82, 101.86, 36.21, 35.77, 35.70, 30.66 (d, $^1J_{P-C}$ = 25.1 Hz). **13** and **15**: ^1H NMR (300 MHz, C_6D_6) δ 5.32 (10H, t), 5.28 (5H, d, $^3J_{P-H}$ = 1.83 Hz), 5.27 (5H, d, $^3J_{P-H}$ = 1.74 Hz), 2.68 (1H, m), 1.0–2.20 (15 H, m), 0.92 (9H, d, $^2J_{P-H}$ = 3.45 Hz), 0.90 (9H, d, $^2J_{P-H}$ = 3.51 Hz), –0.28 (m, 1H). All ^{13}C signals could not be assigned due to the presence of an impurity. However, the four Cp signals (in C_6D_6) of the two isomers appeared at δ 102.83, 102.39, 102.29, 102.05. ^1H NMR assignments for **14** are based on NOE and decoupling experiments. The vinyl proton in **14** appeared at high field (0.32 ppm) analogous to the zirconocene ethylene complex.[11c] **14**: ^1H NMR (C_6D_6) δ 5.26 (d, 5H, $^3J_{P-H}$ = 1.8 Hz, C_5H_5), 5.23 (d, 5H, $^3J_{P-H}$ = 1.7 Hz, C_5H_5), 3.12 (m, 1H), 1.52–2.16 (m, 7H), 1.10 (br, 1H, sp^3 H of cyclopropyl), 0.89 (d, $^2J_{P-H}$ = 5.8 Hz, 9H, PMe_3), 0.32 (m, 1H); ^{13}C NMR δ 102.27, 101.77, 44.66, 44.32, 42.68, 37.43, 32.59, 27.26, 21.53, 17.11 (d, $^1J_{P-C}$ = 18 Hz); ^{31}P NMR (C_6D_6, 85% H_3PO_4 as external reference) δ –1.01. **16**: ^1H NMR δ 5.28 (d, 5H, $^3J_{P-H}$ = 1.8 Hz), 5.24 (d, 5H, $^3J_{P-H}$ = 1.7 Hz), 0.89 (d, 9H, $^2J_{P-H}$ = 5.8 Hz). Other peaks cannot be observed due to the low concentration. For the same reason, only the two Cp signals in the ^{13}C NMR of **16** could be identified: δ 102.33, 102.81. Distinction between **14** and **16** was made by an NOE experiment in which the methyl protons on PMe_3 were irradiated and the resonance assigned to the vinyl hydrogen showed 8.2% enhancement. **17**: ^1H NMR (300 MHz, C_6D_6) δ 6.76–7.16 (8H, m), 6.65 (2H, m), 6.02 (5H, s), 5.58 (5H, s), 2.17 (1H, m), 0.8–1.8 (7H, m). **19**: ^1H NMR (300 MHz, C_6D_6) δ 7.22 (2H, m), 6.62 (2H, m), 5.97 (5H, s), 5.52 (5H, s), 2.1 (1H, m), 0.8–1.8 (7H, m).

[17] It is interesting that, in both the six- and seven-membered rings, when compared with the *exo–endo* isomer, reactions of the *exo–exo* complexes were significantly faster than expected solely on the basis of probability. This is presumably due to steric congestion (clearly seen for all conformations from molecular models) in the transition state as the hydrogen is delivered to the developing saturated hydrocarbon.

[18] Strain apparently significantly retards β-hydrogen elimination in zirconocene complexes. Kinetics are not available, but conditions required for "complete" reaction for Cp_2ZrR_2 as R was changed from *n*-butyl to bicyclo[3.1.0]hexyl increased from below 20 °C (unspecified time; dibutyl)[11e,f] to 35 °C for 10 h (R = cyclobutyl)[11a] to 45 °C for 20 h (R = cyclopropyl) to 55 °C for 20 h (R = bicyclo[3.1.0]hexyl).

[19] Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113.

[20] ^1H NMR assignments of the major and minor isomers are based on the structures of their respective protonolysis products.

[21] Pure samples of **22** and **24** were obtained by careful fractional crystallization from pentane at –10 °C.