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Zirconacyclopropanes and Zirconacyclopropenes. Their Synthesis, Characterization, and Reactions(1)

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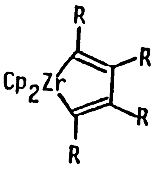
Zirconacyclopropenes represented by $Cp_2Zr(PhCCPh)(PR_3)$ (4), where PR_3 is PMe_3 or $PMePh_2$, have been prepared by the reaction of $Cp_2Zr(PR_3)_2$ with PhC≡CPh, isolated as yellowish crystals, and spectroscopically characterized. Zirconacyclopropenes readily react with proton donors, carbonyl compounds, e.g., acetone, and alkynes to induce dimerization of alkynes and are likely intermediates in the $ZrCp_2$-induced bicyclization of enynes.

Zirconacyclopropanes and zirconacyclopropenes have been suggested as intermediates in the formation of five-membered zirconacycles from alkenes and alkynes.(2) Until recently, however, none had been isolated and characterized.(3) In the reaction of "$ZrCp_2$", where Cp = η^5-C_5H_5, with alkynes to form zirconacyclopentadienes, for example, it is conceivable that the formation of a zirconacyclopentadiene 1 is either a concerted single-stage reaction or a process involving single-stage formation of a π-complex 2 which then is converted into 1. Neither process may be readily conducive to selective "cross" dimerization of alkynes, whereas discrete formation of a zirconacyclopropene 3 would be (Eq.1). It is therefore of both structural and synthetic interest to attempt to prepare and characterize zirconacyclopropanes and zirconacyclopropenes.



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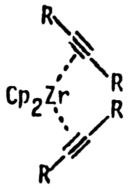

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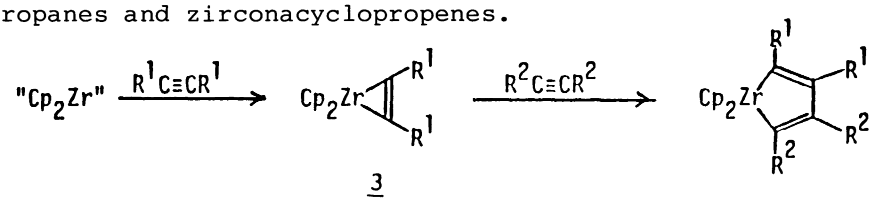

(1)

Herein we report (i)the preparation of zirconacyclopropenes complexed with PMe_3 or $PMePh_2$, i.e., 4, in which R^1 = Ph, as discrete and isolable species, (ii)their characterization including X-ray analysis of 4a, and (iii) some reactions of 4 and those of a zirconacyclopropane 5.(2b) The reaction of 4 with alkynes not only supports the intermediacy of zirconacyclopropenes in the Zr-promoted cyclization of diynes but also permits selective, albeit stoichiometric, "cross" dimerization of two different alkynes.(4)

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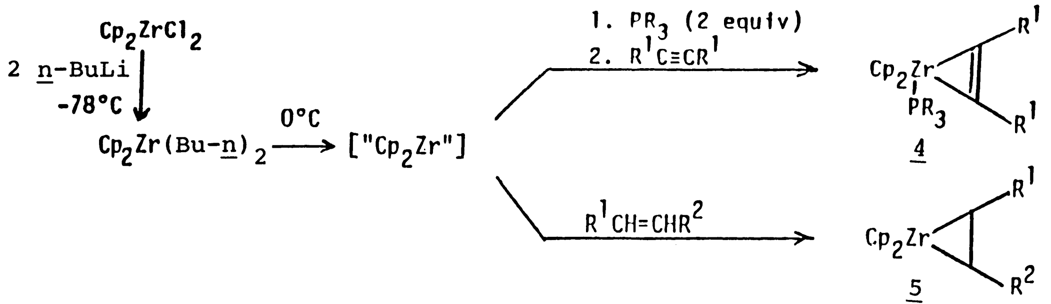
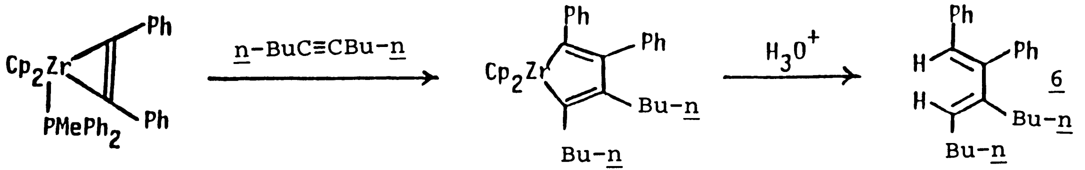


(2)

4a: R = Me, R^1 = Ph. 4b: PR_3 = $PMePh_2$, R^1 = Ph.
5a: R^1 = R^2 = Ph. 5b: R^1 = Ph, R^2 = H.

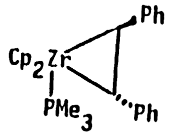
We recently reported a convenient method for generating "Cp_2Zr" by treating Cp_2ZrCl_2 with 2 equiv. of n-BuLi.[2b)] The reaction of "Cp_2Zr" generated in this manner with 1 equiv. of PhCH=CHPh gave one major product tentatively identified as 5a in high yield.[2b)] On the other hand, the reaction of "Cp_2Zr" with PhC-CPh in a 1:1 molar ratio did not give 3a (R^1 = Ph) in a significant yield, the major products obtained after protonolysis being bibenzyl and 1,2,3,4-tetraphenyl-1,3-butadiene.[2b)] We were therefore pleased to find that treatment of $Cp_2Zr(Bu\text{-}n)_2$[2b)] with 2 equiv. of PMe_3 in THF to produce $Cp_2Zr(PMe_3)_2$, ^1H NMR (THF, Me_4Si) δ 5.02 (t, J = 2 Hz, 10 H), followed by addition of 1 equiv. of PhC≡CPh provided 4a in 91% yield. The reaction was first order in both $Cp_2Zr(PMe_3)_2$ and PhC≡CPh, and the second-order rate constant was (2.1 + 0.2) x 10^{-1} $dm^3 \cdot mol^{-1} \cdot min^{-1}$ at 20 °C. A yellow crystalline sample of 4a, mp(dec.) 201-203 °C, obtained by recrystallization from THF-ether (1:2), yielded satisfactory IR, ^1H and ^{13}C NMR, and elemental analytical data.[5)] The X-ray crystallographic data[6)] for 4a shown in Fig. 1 are in agreement with the zirconacyclopropene formulation of 4. In a similar manner, 4b was prepared in 90% yield. These compounds represent the first examples of zirconacyclopropenes derived from stable and readily isolable alkynes.

Protonolysis of 4a and 4b with 3 $mol \cdot dm^{-3}$ HCl produced (Z)-stilbene in 80% yield, which was essentially 100% Z. Addition of 1 equiv. of PhC≡CPh to 4b gave a 92% yield of 1a (R = Ph) identified by matching its spectral data with those of an authentic sample prepared in the absence of a phosphine.[2b)] As hoped, treatment of 4b with 1 equiv. of 5-decyne followed by protonolysis with 3 $mol \cdot dm^{-3}$ HCl produced an 86% yield of the desired "mixed" diene 6,[7)] which shows a clean ^1H NMR triplet at 5.50 (J = 7 Hz) and a singlet at 6.82 for the two alkenyl protons (Eq. 3). The amounts of the two possible homo-dimers were < 2-3% each.



(3)

Quite unexpectedly, the E and Z isomers of PhCH=CHPh reacted with $Cp_2Zr(Bu\text{-}n)_2$ to give within 1 h at room temperature ca. 80% yields of isomerically homogeneous products that are identical with each other: ^1H NMR (THF, Me_4Si)[8)] δ 5.25 (s, 10 H), 6.8-7.6 (m, 10 H); ^{13}C NMR (THF, Me_4Si) δ 50.94, 107.43, 116.98, 123.06, 126.37. The results indicate that the two Cp groups are equivalent and that 5a must be the E isomer. The reaction of $Cp_2Zr(Bu\text{-}n)_2$ with 7 equiv. of (Z)-PhCH=CHPh at room temperature led to isomerization of the residual PhCH=CHPh (6 equiv.). The E/Z ratio was only ca. 0.5 after 1 h, but the essentially pure E isomer was obtained within 24 h. Since no isomerization took place in the absence of the Zr reagent under otherwise the same conditions, this isomerization is catalyzed by the Zr reagent. These results indicate that the reaction of "Cp_2Zr" with PhCH=CHPh is reversible and stepwise. Treatment of 5a with 1 equiv. of PMe_3 at room temperature for 1 h provided an 83% yield of 7[9] as orange crystals, mp(dec.) 201-202 °C. This compound can also be prepared by the reaction of $Cp_2Zr(PMe_3)_2$ with (E)-PhCH=CHPh. The second-order rate constant for the reaction is $(1.4 + 0.3) \times 10^{-3}$ $dm^3 \cdot mol^{-1} \cdot min^{-1}$ at 20 °C, indicating that PhC≡CPh is at least 100 times as reactive as (E)-PhCH=CHPh.



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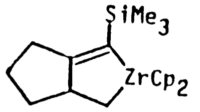

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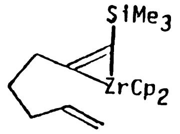

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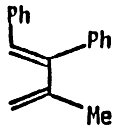

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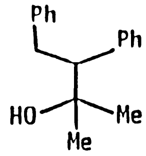

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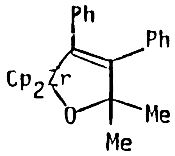

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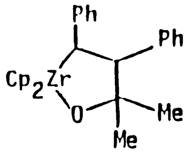

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The reaction of $Cp_2Zr(PMe_3)_2$ with 7-trimethylsilyl-1,6-heptenyne gave a 91% yield of 8, which was identified by comparing its spectral data with those of an authentic sample prepared previously.[2b] The results indicate that a Zr(II) compound, such as Cp_2Zr, is most probably the actual reactive species in the Zr-promoted bicyclization of enynes. The relative reactivities of PhC-CPh and PhCH=CHPh toward "Cp_2Zr" as well as the facile formation of a zirconacyclopropene, i.e., 4b, from PhC≡CPh strongly support the previously proposed stepwise mechanism involving the intermediacy of 9.[2b]

Treatment of 4a and 5 with acetone (4 equiv.) at room temperature for 1 h followed by protonolysis with 3 $mol \cdot dm^{-3}$ HCl produced 10[7] and 11,[7] respectively, which most probably were formed via 12 and 13, respectively.[10] The reactivity toward carbonyl compounds further supports the zirconacyclopropene and zirconacyclopropane structures for 4a and 5, respectively. Zirconacyclopropenes and zirconacyclopropanes appear to be reactive toward various other types of compounds as well, and such reactions are under current investigation.

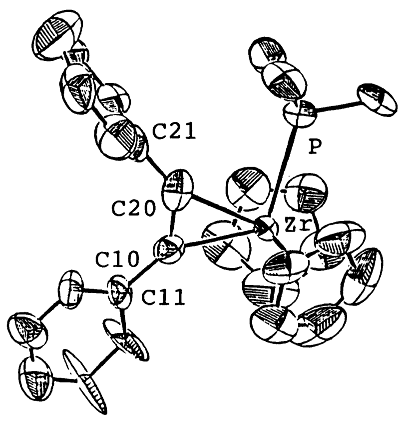

Fig. 1. Molecular structure and labeling scheme for $Cp_2Zr(PhC{=}CPh)(PMe_3)$, 50% thermal ellipsoids Zr-C(10), 2.20(4) (Å); Zr-C(20) 2.25(4); Zr-P 2.70(1); C(10)-C(20), 1.36(6); C(10)-Zr-C(20) 36(1)°; Zr-C(10)-C(20), 74(2) ; Zr-C(20)-C(10), 70(2) ; C(11)-C(10)-C(20), 134(4) ; C(10)-C(20)-C(21), 133(4) .

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X-ray crystallographic analysis was performed by Dr. P. E. Fanwick of our Department. We thank Professor S. L. Buchwald of MIT for informing us of related, unpublished results.

References

1) Metal-Promoted Cyclization. 14. Part 13. E. Negishi and J. M. Tour, Tetrahedron Lett., 27, 4869 (1986).

2) a)For a review containing pertinent references, see E. Negishi and T. Takahashi, Aldrichim. Acta, 18, 31 (1985); b) E. Negishi, F. E. Cederbaum, and T. Takahashi, Tetrahedron Lett., 27, 2829 (1986); c) (Benzyne)zirconocene was originally proposed as a π-complex. G. Erker, and K. Knopp, J. Am. Chem. Soc., 101, 3659 (1979).

3) After completion of this study (September, 1986), two papers reporting the preparation and characterization of Cp_2Zr-alkyne complexes containing highly unstable cyclic alkynes,i.e., benzyne and cyclohexyne, have been reported. a)S. L. Buchwald, B. T. Watson, and J. C. Huffman, J. Am. Chem. Soc., 108,7411 (1986); b) S. L. Buchwald, R. T. Lum, and J. C. Dewan, ibid., 108, 7441 (1986).

4) For a related Ti-catalyzed reaction, see M. Akita, H. Yasuda, and A. Nakamura, Bull. Chem. Soc. Jpn., 57,480 (1984).

5) 4a: mp(dec.) 201-203 °C; IR (Nujol) 1660 (s), 1582 (s), 1280 (m), 1010 (m), 950 (s), 790 (s), 780 (s), 770 (s), 720 (m), 700 (m), 690 (m) cm^{-1}; ^{1}H NMR (benzene-d_6, Me_4Si) δ 0.83 (d, *J* = 7 Hz, 9 H), 5.47 (s, 5 H), 5.49 (s, 5 H), 6.8-7.9 (m, 10 H); ^{13}C NMR (THF, Me_4Si) δ 16.02, 16.35, 102.63, 120.63, 120.75, 122.78, 124.57, 127.31, 128.97, 141.61, 156.42. Anal Calcd for $C_{27}H_{29}PZr$: C, 68.17; H, 6.14. Found: C, 68.02; H, 6.30.

6) This complex crystallized in the monoclinic space group $P2_1$ with cell dimensions *a* = 8.677(4), *b* = 8.327(3), *c* = 16.635(5) Å and β = 97.811(9)°. Collected 1150 reflections ($|Fo| \geq 3\sigma|Fo|$) were used in the structure solution and refinement. The final residuals were *R* = 0.08, and *R*w = 0.12. It was not feasible to obtain more refined crystallographic data using the sample obtained in this study. In view of two recent papers (Ref. 3) reporting related results, however, the currently available data are presented as part of the identification of 4a.

7) Satisfactory spectral and analytical data have been obtained for the compound.

8) The two benzylic proton signals have not been detected.

9) 7: mp(dec.) 201-202 °C; IR (Nujol) 1580 (m), 1300 (m), 1280 (m), 1210 (m), 1010 (m), 945 (m), 800 (m), 740 (m), 720 (m) 695 (m) cm^{-1}; ^{1}H NMR (THF, Me_4Si)8) δ 1.05 (d, *J* = 1 Hz, 5 H), 6.9-7.7 (m, 10 H); ^{13}C NMR (THF, Me_4Si) δ 15.43 (d, *J* = 17 Hz), 40.87 (d, *J* = 10 Hz), 46.42 (d, *J* = 5 Hz), 102.95, 103.41, 118.28, 119.16, 123.18, 126.19, 127.01, 127.16, 128.26, 128.32.

10) Some related five-membered species containing a Zr-O bond have recently been reported. a)G. Erker and F. Rosenfeldt, J. Organometal. Chem. 224, 29 (1982); b) H. Takaya, M. Yamakawa, and K. Mashima, J. Chem. Soc., Chem. Commun., 1983, 1283.

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