Selective Intermolecular Coupling of Alkynes with Nitriles and Ketones via β,β′ Carbon−Carbon Bond Cleavage of Zirconacyclopentenes

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Selective intermolecular coupling of alkynes with nitriles and ketones was performed by the reaction of a mixture of alkynes and Cp_2ZrEt_2 with nitriles and ketones, respectively. Hydrolysis of the mixture gave α,β-unsaturated ketones and allylic alcohols in good to excellent yields, respectively. These reactions proceeded via zirconacyclopentenes which were prepared by the reaction of alkynes with Cp_2ZrEt_2. The structure of zirconacyclopentene, which was prepared from diphenylacetylene and Cp_2ZrEt_2, was determined by X-ray analysis. It clearly indicated that there is a single bond between the β- and β′-carbons of the zirconacyclopentene. The reaction of zirconacyclopentenes with nitriles or ketones proceeded via the β,β′ carbon−carbon bond cleavage of the zirconacyclopentenes. In a similar way, addition of PMe_3 to the zirconacyclopentene afforded a zirconocene−alkyne complex in 87% yield.

Introduction

Dialkylzirconocenes such as Cp_2ZrBu_2 and Cp_2ZrEt_2 are very useful reagents for organic synthesis.[2] They are in situ converted into zirconocene−olefin complexes by β-hydrogen abstraction. For example, Cp_2ZrBu_2 is converted into zirconocene−butene complex $Cp_2Zr(EtCH{=}CH_2)$, which has been used as a zirconocene "Cp_2Zr" equivalent,[3] since the butene ligand is very labile. On the other hand, Cp_2ZrEt_2 gives zirconocene−ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ in a similar way;[4] however, the behavior of the ethylene ligand is very different from the butene moiety of the zirconocene−butene complex in most cases.[2,5,6] The ethylene ligand reacts with various unsaturated compounds and is incorporated in the reaction products. We have preliminarily reported that Cp_2ZrEt_2 reacted with alkynes to give zirconacyclopentenes **1** by the coupling of an alkyne with ethylene derived from Cp_2ZrEt_2.[5] The zirconacyclopentenes thus formed reacted with various unsaturated compounds to give coupling products of alkynes with the unsaturated compounds.[5] Coupling reaction of alkynes with nitriles or ketones using phosphine-stabilized zirconocene−alkyne complexes has been reported.[7−12] From the point of view

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(6) (a) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880−1889. (b) Lipshutz, B. H.; Segi, M. *Tetrahedron* **1995**, *51*, 4407−4420.

(7) In the case of enyne cyclization using Cp_2ZrBu_2, an intermolecular coupling of a nitrile with the triple bond in an enyne in a competitive manner has been reported. See ref 3d.

(8) An intramolecular coupling of 1-cyano-5-heptyne providing an azazirconacyclopentadiene has been reported: Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310−2312.

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Table 1. Intermolecular Coupling Reaction of Alkynes with Nitriles on Zirconocene

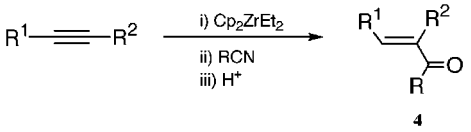
run	alkyne $R^1{\equiv}R^2$	nitrile RCN	zirconacycle	product	yield, %[a]
1	Ph≡Ph	PrCN	**2a**	**4a**	70 (94)
2	Bu≡Bu	PrCN	**2b**	**4b**	68 (91)
3	Pr≡Pr	PrCN	**2c**	**4c**	50 (80)
4	Bu≡Bu	MeCN	**2d**	**4d**	74 (95)
5	Ph≡Me	MeCN	**2e**	**4e**	54 (78)[b]
6	Ph≡Me	PrCN	**2f**	**4f**	80 (95)[c]
7	$Me_3Si{\equiv}Me$	PhCN	**2g**	**4g**	71 (88)

[a] Isolated yields. GC yields are given in parentheses. [b] Two isomers in a ratio of 1:1 were obtained. [c] Two isomers in a ratio of 1.5:1 were obtained.

of organic synthesis, the phosphine-free procedure is more practical, convenient, and useful. In our reactions, zirconacyclopentenes behaved as zirconocene−alkyne complexes without phosphine. In this paper we would like to report selective intermolecular coupling of alkynes with nitriles or ketones, and we also report the structure of a zirconacyclopentene having a single carbon−carbon bond between the β- and β'-carbons in it. This clearly shows that the coupling reaction of zirconacyclopentenes with nitriles or ketones proceeds via the β,β' carbon−carbon bond cleavage of the zirconacyclopentenes.[13−17]

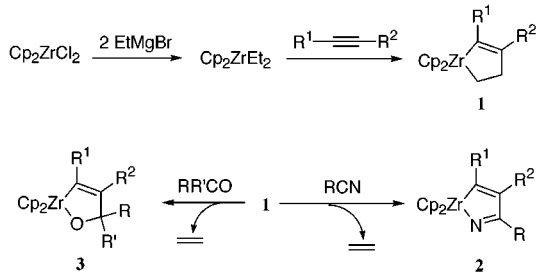
Results and Discussion

Intermolecular Coupling of Alkynes with Nitriles Using Cp_2ZrEt_2. When alkynes were treated with Cp_2ZrEt_2 and nitriles in this order, hydrolysis of the reaction mixture with 3 N HCl afforded α,β-unsaturated ketones **4** in good to excellent yields (eq 1, Table 1). As

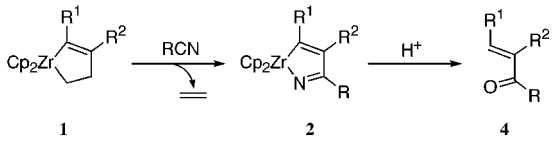


shown in Table 1, alkyl-, aryl-, and silyl-substituted α,β-unsaturated ketones are all formed in satisfactory yields. In the cases of unsymmetrical alkynes such as 1-phenylpropyne (runs 5 and 6), regioisomers were formed. The ratio of two regioisomers was 1:1 or 1.5:1. The regioselectivity of the 1-phenylpropyne moiety in this reaction is not the same as that observed in the formation of the zirconacyclopentene, where the selectivity was 20:1 (vide infra). In the case of silylated alkynes (run 7), although the formation of several species was observed by the reaction with Cp_2ZrEt_2, addition of benzonitrile gave a good yield of **4g** after hydrolysis. When terminal alkynes were used, the corresponding products were not obtained in good yields.

Scheme 1

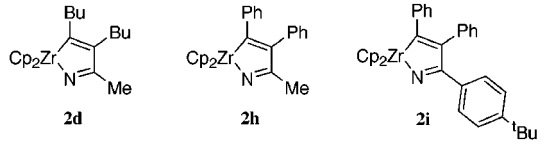


Scheme 2



Coupling of alkynes with nitriles or ketones using phosphine-stabilized zirconocene−alkyne complexes has been reported.[7−12] In our reaction described here, a zirconacyclopentene **1** was initially formed via a pair-selective coupling between an alkyne and ethylene of $Cp_2Zr(CH_2{=}CH_2)$ generated in situ from Cp_2ZrEt_2. Treatment of the zirconacyclopentene **1** with a nitrile at 50 °C for 1 h afforded an azazirconacyclopentadiene **2** along with elimination of the ethylene moiety of **1**.[5] This reaction provides direct intermolecular coupling products of an alkyne with a nitrile via a facile cleavage of the β,β' carbon−carbon bond of **1**.

Formation of azazirconacyclopentadienes **2** was characterized by NMR spectroscopy. Azazirconacyclopentadienes **2d**, **2h**, and **2i** were formed in 89%, 95%, and 91% NMR yield, respectively. Their ^{1}H NMR spectra showed a singlet peak assigned to Cp at 5.76 ppm for **2d**, 5.92 ppm for **2h**, and 5.88 ppm for **2i**. Their ^{13}C NMR spectra revealed characteristic signals for Cp, Zr−*C*, and *C*−N at 108.25, 188.99, and 217.50 ppm for **2d**, 109.53, 187.86, and 214.46 ppm for **2h**, and 110.52, 190.16, and 216.89 ppm for **2i**.



Two paths, a dissociative path and an associative path, should be considered from **1** to **2** as shown in Scheme 3.

Intermolecular Coupling of Alkynes with Ketones Using Cp_2ZrEt_2. Similar reactions proceeded when alkynes were treated with Cp_2ZrEt_2 and ketones (eq 2).[18] Hydrolysis of the reaction mixture pro-

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Scheme 3

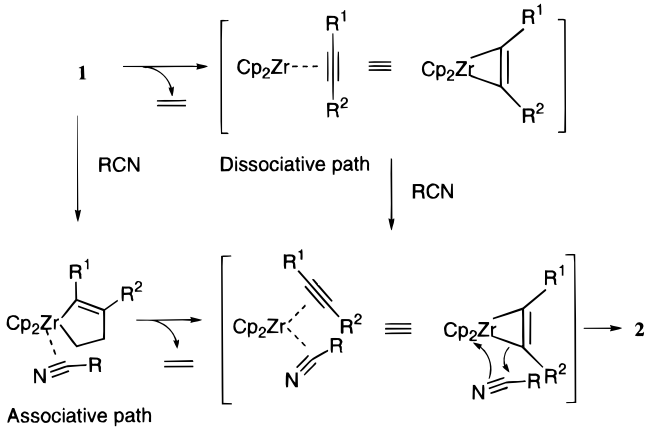
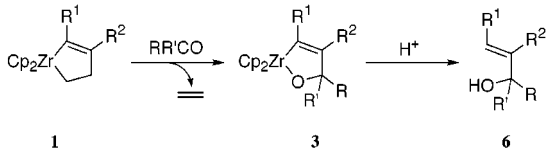


Table 2. Intermolecular Coupling Reaction of Alkynes with Ketones on Zirconocene

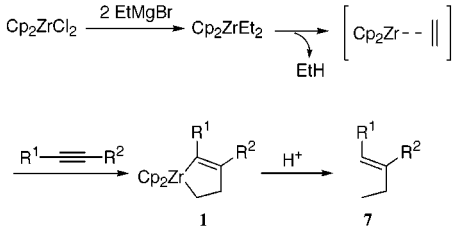
run	alkyne $R^1{\equiv}R^2$	ketone	zirconacycle	product	yield, %[a]
1	Bu≡Bu	Et_2CO	**3a**	**6a**	75 (93)
2	Pr≡Pr	Et_2CO	**3b**	**6b**	53 (83)
3	Bu≡Bu	PhCOMe	**3c**	**6c**	77
4	Ph≡Ph	Et_2CO	**3d**	**6d**	61 (85)

[a] Isolated yields. GC yields are given in parentheses.

Scheme 4



Scheme 5



videdallylic alcohols **6** in high yields (Table 2).[19] The reaction path is essentially the same as that described above for the intermolecular coupling of alkynes with nitriles.

Formation and Characterization of Zirconacyclopentenes. We have reported the formation of zirconocene−ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ in situ when zirconocene dichloride was treated with 2 equiv of EtMgBr.[4] When the zirconocene−ethylene complex thus formed was treated with alkynes, zirconacyclopentenes **1** were formed in >90% yields (Scheme 5, Table 3).[5]

Homo-coupled products of alkynes were formed in a small amount (1−3%) in most cases, as shown in Table 3. These results are in striking contrast with the case of Cp_2ZrBu_2, which quantitatively gave zirconacyclopentadienes by dimerization of alkynes.[3b] The zirconacyclopentenes gradually decomposed at room temperature. It

Table 3. Formation of Zirconacyclopentenes from Cp_2ZrCl_2, 2 equiv of EtMgBr, and Alkyne

run	alkyne $R^1{\equiv}R^2$	zirconacycle	product	yield, %[a]	dimer of alkyne, %[b]
1	Ph≡Ph	**1a**	**7a**[c]	(95)	<1
2	Pr≡Pr	**1b**	**7b**	86(94)	0
3	Bu≡Bu	**1c**	**7c**[c]	(91)	3
4	Ph≡Me	**1d**	**7d**[c]	(92)[d]	3
5	$Me_3Si{\equiv}Me$	**1e**	**7e**[c]	(60)	12

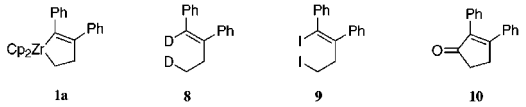
[a] Isolated yields. GC yields are in parentheses. [b] Maximum yield of alkyne dimer is 50%. [c] Reference 14a. [d] A mixture of two isomers in a ratio of 20:1.

is interesting that the stability of **1** in THF could be controlled by the presence of ethylene gas.

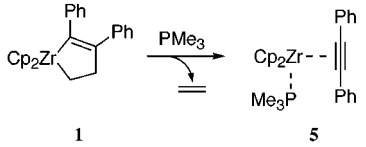
Recently, we have reported a highly selective preparative method of zirconacyclopentenes using Cp_2ZrBu_2, ethylene gas, and alkynes.[14a] In most cases the amount of the dimer of alkynes is negligible when zirconacyclopentenes are formed by the reaction of Cp_2ZrEt_2 with alkynes. For the coupling of alkynes with nitriles or ketones described here, the use of ethylene gas is practically not necessary. The small amount of the dimer of alkynes can be separated.

There have been several reports on cross-coupling of an alkyne with an alkene using zirconium complexes. In those procedures, either phosphine-stabilized zirconocene−alkene or −alkyne complexes[20] or intramolecular coupling[3] is involved. Cp_2ZrEt_2 provided a convenient preparative method of **1** without phosphines.

The characterization of 2,3-diphenyl-1-zirconacyclopentene **1a** ($R^1 = R^2 =$ Ph) was initially done by (a) deuteriolysis with DCl in D_2O to form **8** in 92% yield with >98% D incorporation, (b) iodinolysis with I_2 to give **9**[21] in 90% yield, and (c) carbonylation−iodinolysis to afford **10**[22] in 64% yield. All these results indicated that the five-membered zirconacyclopentene was formed. The structure of **1a** was determined by X-ray analysis and is shown in Figure 1. Erker and co-workers have reported its hafnium analogue by the reaction of hafnacyclopentane with diphenylacetylene.[15b] The distance of the β,β' carbon−carbon bond is 1.507 Å, which is in the range for a normal C−C single bond. This bond is cleaved in further reactions with unsaturated substrates, such as nitriles and ketones as described above.



Treatment of **1a** with 1 equiv of PMe_3 afforded zirconocene−alkyne complex **5**[12] in 87% NMR yield when zirconacyclopentene **1a** was heated in the presence of 1.5 equiv of PMe_3 at 50 °C for 3 h, as shown in eq 3. This



(3)

result also clearly indicates that zirconacyclopentenes

(19) For formation of allylic alcohols by intermolecular coupling of alkynes with aldehydes or ketones using tantalum, see: (a) Takai, K.; Kataoka, Y.; Uchimoto, K. *J. Org. Chem.* **1990**, *55*, 1707. For titanium, see: (b) Harada, K.; Urabe, H.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 3203−3206.

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(21) Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099−4102.

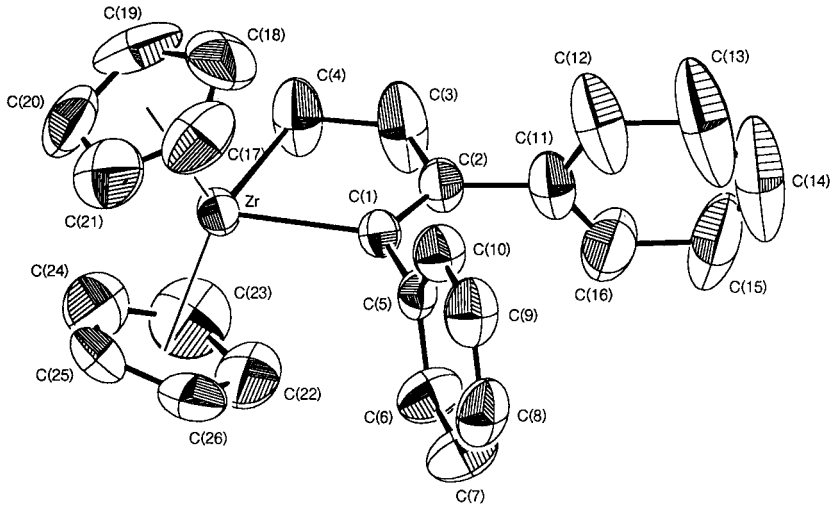

Figure 1. Structure of 2,3-diphenyl-1-zirconacyclopentene (1a). Selected bond distances [Å] and bond angles [deg]: Zr−C1 2.276(4), Zr−C4 2.271(5), C1−C2 1.336(5), C1−C5 1.490(5), C2−C3 1.507(7), C2−C11 1.502(6), C3−C4 1.443(7); C1−Zr−C4 79.1(2), Zr−C1−C2 111.6(3), C1−C2−C3 121.0(4), C2−C3−C4 118.9(4), Zr−C4−C3 109.1(3).

provide a straightforward and convenient source of zirconocene−alkyne complexes via a facile cleavage of the β,β' carbon−carbon bond. Such properties of the β,β' carbon−carbon bond of zirconacyclopentenes **1** may be attributable to the existence of the formal equilibrium between a zirconacyclopentene and a zirconocene−alkyne−ethylene complex.

Experimental Section[25]

Representative Procedure for the Preparation of Zirconacyclopentenes: Synthesis of (*Z*)-4-Ethyl-4-octene (7b). A 50 mL Schlenk tube under dried nitrogen was charged with Cp_2ZrCl_2 (1.46 g, 5 mmol) and THF (25 mL). To this solution was added ethylmagnesium bromide (1.0 M THF solution, 10 mmol, 10 mL) at −78 °C. After stirring for 1 h, 4-octyne (0.59 mL, 4 mmol) was added and the reaction mixture was stirred at 0 °C for 3 h. The above reaction mixture was then quenched with 3 N HCl and extracted with ether. The extract was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a light yellow liquid. Distillation provided the title compound **7b** as a colorless liquid, 0.48 g (isolated yield 86%, purity > 98%, GC yield 94%). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.82−0.86 (m, 6H), 0.93 (t, J = 7.3 Hz, 3H), 1.25−1.37 (m, 4H), 1.89−1.96 (m, 6H), 5.06 (t, J = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.00, 13.88, 14.21, 21.68, 23.33, 29.60, 29.86, 32.33, 123.58, 141.04. Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.90; H, 14.02.

Compounds **7a**, **7c**, **7d**, and **7e** are the same as those reported[14a] previously according to NMR data.

Characterization of 8. Deuteriolysis of **1a** prepared in situ as described above followed by usual workup afforded **8** in 92% yield with >99% deuterium incorporation. ^{1}H NMR (C_6D_6, Me_4Si): δ 1.01(tt, J = 8.0 Hz, 1.9 Hz, 2H), 2.55 (t, J = 8.0 Hz, 2H), 6.96−6.99 (m, 2H), 7.07−7.13 (m, 3H), 7.19−7.22 (m, 2H), 7.26−7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.70 (t, J = 19.6 Hz), 33.52, 125.06 (t, J = 23.8 Hz), 126.13, 126.90, 127.89, 128.56, 128.63, 129.07, 137.60, 141.63, 144.93. HRMS calcd for $C_{16}D_2H_{14}$ 210.1375, found 210.1388.

Representative Procedure for the Preparation of Azazirconacyclopentadienes 2 via Zirconacyclopentenes: Synthesis of (*Z*)-1,2-Diphenyl-1-hexen-3-one (4a). 2,3-Diphenylzirconacyclopentene (**1a**) was generated as described above and could be obtained as yellow single crystals suitable for X-ray crystal analysis. ^{1}H NMR (C_6D_6, Me_4Si): δ 1.47 (t, J = 6.7 Hz, 2H), 3.05 (t, J = 6.7 Hz, 2H), 5.91 (s, 10 H), 6.62−7.11 (m, 10H). ^{13}C NMR (C_6D_6, Me_4Si): δ 34.50, 42.88, 111.91, 122.82, 125.72, 126.78, 127.63, 128.06, 129.01, 145.13, 145.82, 149.77, 186.59. To the reaction mixture of zirconacyclopentene **1a** was added *n*-butyronitrile (0.35 mL, 4 mmol), and the mixture was stirred at 50 °C for 3 h. The above reaction mixture was quenched with 3 N HCl, stirred at room temperature for 9 h, and then extracted with ether. The extract was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a light brown liquid. Chromatography using a mixture of hexane and ether (5%) as the eluent provided the product **4a** as a colorless liquid, 0.70 g (isolated yield 70%, GC yield 94%). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, J = 7.4 Hz, 3H), 1.60−1.69 (m, 2H), 2.48 (t, J = 7.2 Hz, 2H), 7.00−7.25 (m, 5H), 7.28−7.40 (m, 5H), 7.62 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.65, 17.68, 41.71, 127.69, 128.07, 128.87, 129.48, 130.67, 134.66, 136.98, 137.54, 140.77, 201.92. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.51; H, 7.45.

(*E*)-5-Butyl-5-decen-4-one (4b): Yield 91%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.80−0.87 (m, 9H), 1.18−1.57 (m, 10H), 2.14−2.22 (m, 4H), 2.52 (t, J = 7.4 Hz, 2H), 6.48 (t, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.74, 13.78, 13.88, 18.35, 22.41, 22.75, 25.34, 28.44, 31.08, 31.46, 39.21, 142.02, 142.04, 201.78. Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 80.04; H, 12.42.

(*E*)-5-Propyl-5-nonen-4-one (4c): Yield 80%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.79−0.90 (m, 9H), 1.20−1.30 (m, 2H), 1.38−1.59 (m, 4H), 2.12−2.21 (m, 4H), 2.53 (t, J = 7.3 Hz, 2H), 6.48 (t, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.65, 13.69, 13.90, 18.30, 22.01, 22.32, 27.51, 30.70, 39.14, 141.90, 141.95, 201.62. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.57; H, 12.09.

(*E*)-3-Butyl-3-octen-2-one (4d): Yield 95%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.85−0.96 (m, 6H), 1.25−1.51 (m, 8H), 2.22−2.30 (m, 7H), 6.59 (t, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.93, 13.98, 22.57, 22.91, 25.28, 25.68, 28.70, 31.16, 31.57, 142.44, 143.88, 199.66. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.06. Found: C, 78.91; H, 12.14.

(*E*)-1-Phenyl-2-methyl-1-buten-3-one/(*E*)-3-Phenyl-3-penten-2-one (4e). Two regioisomers, (*E*)-1-phenyl-2-methyl-

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1-buten-3-one and (*E*)-3-phenyl-3-pentene-2-one, were obtained in a ratio of 1:1. Yield (combined): 78%. (*E*)-1-Phenyl-2-methyl-1-butene-3-one: ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.85 (d, J = 0.9 Hz, 3H), 2.06 (s, 3H), 6.90−6.91 (m, 1H), 7.06−7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 15.81, 27.44, 127.23, 128.07, 128.37, 136.15, 137.97, 139.78, 198.61. (*E*)-3-Phenyl-3-penten-2-one:^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.52−1.54 (d, J = 7.1 Hz, 3H), 2.25 (s, 3H), 6.80 (q, J = 7.0 Hz, 1H), 7.06−7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.11, 25.99, 128.28, 129.42, 129.52, 136.03, 139.18, 144.43, 200.35. HRMS calcd for $C_{11}H_{12}O$ 160.0888, found 160.0889.

(*E*)-3-Phenyl-2-heptene-4-one/(*E*)-1-Phenyl-2-methyl-1-hexen-3-one (4f). Two regioisomers, (*E*)-3-phenyl-2-hepten-4-one and (*E*)-1-phenyl-2-methyl-1-hexen-3-one, were obtained in a ratio of 1.5:1. Yield (combined): 95%. ^{1}H NMR ($CDCl_3$, Me_4Si) for the two regioisomers: δ 0.89 (t, J = 7.3 Hz), 0.98 (t, J = 7.6 Hz), 1.55−1.76 (m), 2.06 (d, J = 1.2 Hz), 2.51 (t, J = 7.3 Hz), 2.78 (t, J = 7.3 Hz), 6.93−7.00 (q, J = 7.3 Hz), 7.08−7.52 (m). ^{13}C NMR ($CDCl_3$, Me_4Si) for (*E*)-3-phenyl-2-hepten-4-one: δ 13.78, 15.49, 17.86, 41.37, 127.35, 128.26, 129.63, 136.06, 137.63, 143.93, 200.90. ^{13}C NMR ($CDCl_3$, Me_4Si) for (*E*)-1-phenyl-2-methyl-1-hexaten-3-one: δ 13.15, 13.96, 18.36, 39.57, 127.35, 128.42, 129.68, 137.46, 138.34, 143.93, 202.49. HRMS calcd for $C_{13}H_{16}O$ 188.1201, found 188.1209.

(*E*)-1-(Trimethylsilyl)-2-methyl-3-phenyl-1-propen-3-one (4g): Yield 88%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.01 (s, 9H), 1.92 (s, 3H), 6.04 (s, 1H), 7.21−7.52 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ −0.59, 17.69, 128.03, 129.52, 131.83, 137.43, 142.12, 150.67, 199.00. HRMS calcd for $C_{13}H_{18}OSi$ 218.1127, found 218.1123.

Observation of Formation of Azazirconacyclopentadienes (2) by NMR.

Azazirconacyclopentadiene 2d: NMR yield 89%. Characteristic NMR peaks: ^{1}H NMR (C_6D_6−THF, Me_4Si): δ 5.76 (s, 10H, 2 Cp); ^{13}C NMR (C_6D_6−THF, Me_4Si): δ 108.25, 143.89, 188.99, 217.50.

Azazirconacyclopentadiene 2h: NMR yield 95%. Isolated yield: 89%. ^{1}H NMR (C_6D_6, Me_4Si): δ 2.13 (s, 3H), 5.92 (s, 10H, 2 Cp), 6.97−7.13 (m, 10H). ^{13}C NMR (C_6D_6, Me_4Si): δ 30.77, 109.53, 122.80, 124.99, 125.56, 127.11, 127.29, 130.45, 143.91, 146.68, 153.02, 187.86, 214.46. Anal. Calcd for $C_{26}H_{23}NZr$: C, 70.86; H, 5.26; N, 3.18. Found: C, 70.60; H, 5.39; N, 3.17.

Azazirconacyclopentadiene 2i: NMR yield 91%. ^{1}H NMR (C_6D_6, Me_4Si): δ 1.23 (s, 9H), 5.88 (s, 10H, 2 Cp), 6.68−7.26 (m, 14H). ^{13}C NMR (C_6D_6, Me_4Si): δ 31.18 (3 CH_3), 34.51, 110.52, 123.31, 123.65, 123.74, 126.33, 127.16, 127.39, 128.65, 131.97, 143.36, 144.33, 148.84, 149.47, 153.55, 190.16, 216.89.

Representative Procedure for the Preparation of Allylic Alcohols 6 from the Reaction of Zirconacyclopentenes 1 with Ketones. The procedure for synthesis of allylic alcohols **6** was the same as that for **4**. Hydrolysis was fast (at room temperature for 30 min with 3 N HCl) in this case.

(*E*)-3-Ethyl-4-butyl-4-nonen-3-ol (6a): Yield 93%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.78 (t, J = 7.3 Hz, 6H), 0.83−1.0 (m, 6H), 1.25−1.65 (m, 12H), 1.89−2.12 (m, 5H), 5.35 (t, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.89, 13.93, 14.07, 22.52, 23.63, 27.76, 27.98, 32.02, 32.18, 32.33, 78.60, 125.82, 141.56. HRMS calcd for $C_{15}H_{30}O$ 226.2295, found 226.2297.

(*E*)-3-Ethyl-4-propyl-4-octen-3-ol (6b): Yield 83%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.69−0.86 (m, 12H), 1.27−1.55 (m, 8H), 1.80−1.99 (m, 5H), 5.30 (t, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.67, 13.74, 14.72, 23.07, 23.10, 30.05, 30.41, 31.94, 78.33, 125.64, 141.66. Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.61; H, 13.10.

(*E*)-2-Phenyl-3-butyl-3-octen-2-ol (6c): Isolated yield 77%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.79 (t, J = 6.9 Hz, 3H), 0.92 (t, J = 6.9 Hz, 3H), 1.10−1.4 1 (m, 8H), 1.64 (s, 3H), 1.78−2.15 (m, 5H), 5.62 (t, J = 7.3 Hz, 1H), 7.15−7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.80, 14.07, 22.61, 23.40, 27.74, 28.36, 29.43, 32.11, 32.70, 77.95, 125.59, 125.69, 126.56, 127.89, 144.38, 147.04. HRMS calcd for $C_{18}H_{28}O$ 260.2140, found 260.2145.

(*Z*)-1,2-Diphenyl-3-ethyl-1-penten-3-ol (6d): Yield 85%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.01 (t, J = 7.3 Hz, 6H), 1.57−1.73 (m, 5H), 6.78−7.30 (m, 11H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.83, 31.63, 78.35, 126.29, 127.02, 127.16, 127.69, 128.43, 129.11, 129.42, 136.86, 139.20, 145.55. HRMS calcd for $C_{19}H_{22}O$ 266.1678, found 266.1681.

X-ray Crystallographic Analysis of 2,3-Diphenylzirconacyclopentene (1a). A crystal of dimensions 0.2 × 0.4 × 0.5 mm^3 was sealed in a capillary tube and mounted on an Enraf-Nonius CAD4 diffractometer. The cell dimensions and crystal orientation matrixes were obtained from least-squares refinement of 25 well-centered strong reflections. Crystallographic data: fw = 427.70, monoclinic, space group *C*2/*c*, Z = 8, a = 9.1942(6) Å, b = 17.692(1) Å, c = 25.383(2) Å, β = 92.670(7)°, V = 4126.2(8) Å^3, D_x = 1.38 g cm^{-3}, and μ(Mo Kα) = 5.30 cm^{-1}. Diffraction data were collected at room temperature by using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) and a ω scan technique. Intensities were corrected for the gain (14%) observed in the intensities of the three standard reflections, monitored periodically during data collection. A total of 6365 reflections ($2\theta_{max}$ = 60°) were measured, of which 3061 reflections were unique with $|F_o| > 3\sigma(|F_o|)$. The structure was solved by direct methods (SHELXS-86)[23] and subsequently completed by Fourier recycling. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques using Xtal3.2 software.[24] All the hydrogen atoms were located at the calculated positions with isotropic displacement parameters of their parent carbon atoms. Refinement of positional and thermal parameters converged at R = 0.048, R_w = 0.045, and GOF = 1.42.

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Supporting Information Available: Crystallographic data, positional and thermal parameters, and lists of bond lengths and angles for **1a** and ^{1}H and ^{13}C NMR spectra of **4a**−**g**, **6a**−**d**, and **7b** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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