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Reaction of Zirconacycles with 3-Iodopropenoates and 3-Iodocycloenones in the Presence of CuCl: A New Pathway for the Formation of Cyclopentadienes and Spirocyclic Compounds

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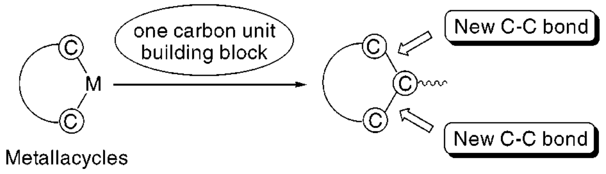
Formation of cyclic compounds from zirconacycles has been performed by a combination of Michael addition and coupling with an alkenyl iodide moiety in the presence of a stoichiometric amount of CuCl. The reaction of 3-iodopropenoates with various zirconacyclopentadienes in the presence of a stoichiometric amount of CuCl afforded penta- and hexasubstituted cyclopentadienes. The reaction of 3-iodocycloenones with zirconacyclopentadienes, zirconacyclopentenes, or zirconacyclopentanes gave spirocyclic compounds in good yields.

Introduction

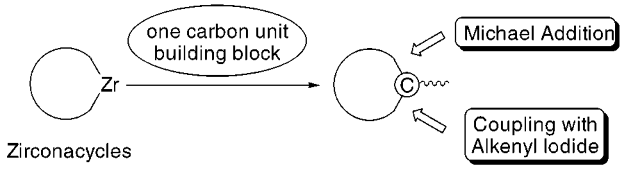
Metallacycles, which have two reactive metal−carbon bonds, are attractive intermediates for the formation of carbocyclic compounds. In particular, when the metallacycles are readily available such as zirconacycles, development of new C−C bond formations is synthetically useful, especially with regard to the synthesis of carbocyclic compounds (Scheme 1).

Zirconacycles, in comparison with other metallacycles, have several advantages: (i) they are easily prepared by reductive coupling of alkenes and alkynes on reduced zirconocene, and (ii) under normal conditions they can be easily handled.[1] Recently, we and other groups have reported several reactions of zirconacycles with a one-carbon unit building block affording five-membered ring compounds. These reactions were classified into several groups such as (i) insertion of carbon monoxide or isonitriles,[2] (ii) reactions with acid chlorides,[3] and (iii) double Michael addition.[4] In this paper we report the details of a novel combination of Michael addition/coupling with an alkenyl iodide moiety for two new C−C bond formations (Scheme 2).

Scheme 1



Scheme 2



Our attention was initially turned to (*Z*)-3-iodopropenoate **1**,[5] which contains a reactive C−I bond suitable to participate in cross-coupling reactions and also an activated double bond suitable for Michael addition. We envisioned that zirconacycles, after transmetalation with CuCl, would react in tandem reaction with (*Z*)-3-iodopropenoates **1**[5,6] by cross coupling−Michael addition to give five-membered ring compounds. Additionally, we as-

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10.1021/jo9905975 CCC: $19.00

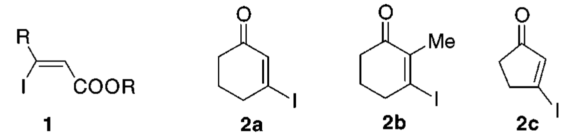
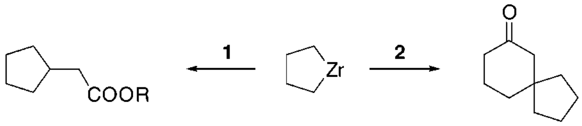
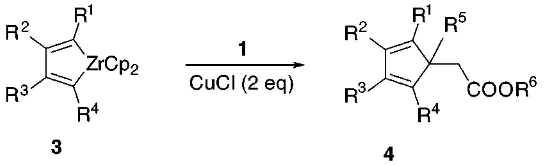


Figure 1.

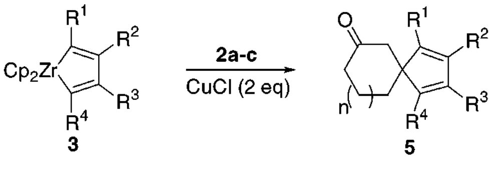
Scheme 3



Scheme 4



Scheme 5



sumed that the reaction of zirconacycles with 3-iodocycloenones **2**[7] could gain access to spirocyclic compounds (Scheme 3, Figure 1).

Results and Discussion

Formation of Cyclopentadienes. Our initial interest was to investigate the reaction of zirconacyclopentadienes **3** with ethyl (*Z*)-3-iodopropenoate **1** in the presence of a stoichiometric amount of CuCl. Indeed, the reaction proceeded as expected, and we were able to get a series of pentasubstituted cyclopentadienes.[8] Further investigation also showed that (*Z*)-3-iodo-3-substituted propenoates could be used as well and their reaction under identical conditions afforded hexasubstituted cyclopentadienes (Scheme 4, see Supporting Information).[8] The mechanism of this reaction is based on cross-coupling/Michael addition.

The structure of cyclopentadienes was unequivocally confirmed by single-crystal analysis of **4** (R^{1-5} = Ph, R^6 = Me). These results clearly showed that our concept for the construction of cyclic compounds based on the reaction with (*Z*)-3-iodopropenoate was on the right track, and we were encouraged to follow and expand this methodology.

Spiroannulation. Our special attention was focused on the development of a new procedure for the formation of spirocyclic compounds. A number of synthetic methods have been developed for the construction of the spirocyclic framework,[9−11] because it is the basic structural unit of many natural compounds.[12] One new procedure for spiroannulation, developed by Wender et al., is based on the reaction of bis(nucleophiles), organobis(heterocuprates), with haloenones.[13] Despite the significant importance of this methodology, the drawback is that organobis(heterocuprates) are prepared from dilithiocompounds, whose preparation can be often difficult and cumbersome. On the other hand, we assumed that zirconacycles could react with 3-iodocycloenones to afford spirocyclic compounds (Scheme 3). We found the advantage of this approach in the facile access to a variety of zirconacycles, which are easily prepared by reductive dimerization of alkynes and alkenes on reduced zirconocene.[1]

The initial investigation concerned the reaction of zirconacyclopentadienes with 3-iodocycloenones, because we anticipated the reaction to proceed in the same manner as with 3-iodopropenoates.[8] Indeed, the reaction of zirconacyclopentadienes **3** with 3-iodocycloenones **2** at

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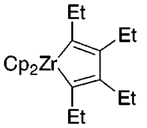
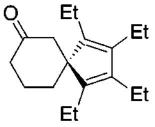
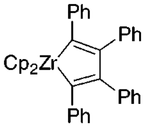
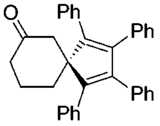
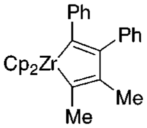
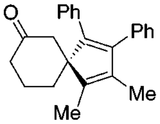
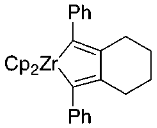
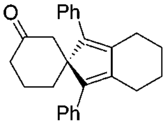
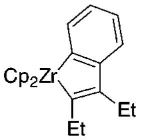
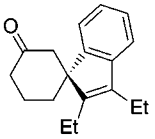
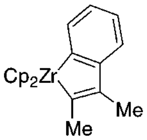
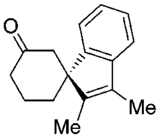
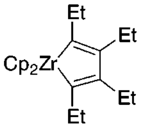
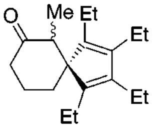
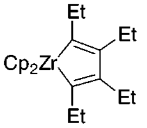
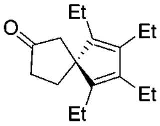
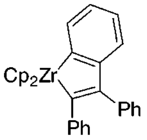
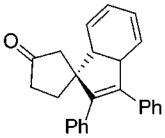
Table 1. Reaction of Zirconacyclopentadiene with 3-Iodocycloenones 2

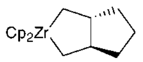
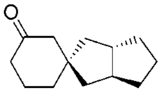
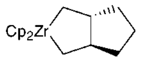
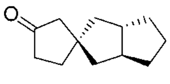
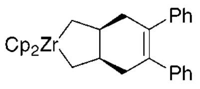
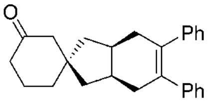
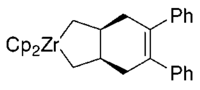
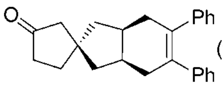
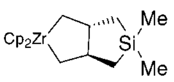
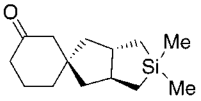
Entry	Zirconacycle	Enone	Reaction time (h)	Products	Yield (%)[a]
1		**2a**	1	 (**5a**)	96 (66)
2		**2a**	1	 (**5b**)	- (78)
3		**2a**	3	 (**5c**)	65 (48)
4		**2a**	1	 (**5d**)	- (48)
5		**2a**	3	 (**5e**)	84 (56)
6		**2a**	3	 (**5f**)	43 (32)
7		**2b**	12	 (**5g**)	53 (42)
8		**2c**	1	 (**5h**)	96 (78)
9		**2c**	6	 (**5i**)	- (61)

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

room temperature in the presence of a stoichiometric amount of CuCl proceeded as expected and afforded spirocyclic cyclopentadienes **5** in moderate to good yields (Scheme 5). The results are summarized in Table 1. The reaction of monocyclic zirconacyclopentadienes, symmetrically or unsymmetrically substituted, with iodocyclohexenone **2a** gave the corresponding spirocyclic compounds in good yields. Also the reaction of bicyclic zirconacyclopentadienes (entry 4) and zirconaindenes (entries 5 and 6) afforded tricyclic spirocompounds in good yields. The reaction of zirconacyclopentadiene with substituted iodocycloenone **2b** gave the expected product; however, the yield was moderate, and completion of the reaction required longer reaction time (entry 7). The use of iodocyclopentenone **2c** instead of **2a** gave similar results (entries 8 and 9). As far as the nature of the halide anion in copper(I) salt was concerned, the use of CuCl, CuBr, and CuI gave **5a** in comparable yields (GC) of 96%, 99%, and 98%, respectively. The structure of spirocyclic compounds was also confirmed by single-crystal X-ray analysis of compound **5i**.

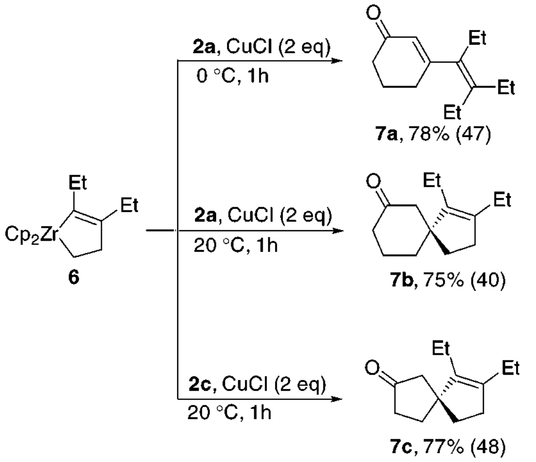
Further investigation was turned to the reactions of zirconacyclopentenes that are presented in Scheme 6. It was found that the reaction of zirconacyclopentene **6** with iodoenones **2** depended on the reaction conditions (temperature) and that the course of the reaction can be easily controlled by conducting it at 0 or 20 °C. Thus at 0 °C only cross-coupling took place, and dienone **7a** was obtained as the sole product. It is important to note that under these conditions we did not detect any formation

Table 2. Reaction of Zirconacyclopentanes with 3-Iodocycloenones 2

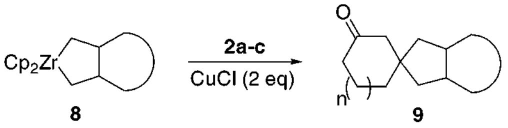
Entry	Zirconacycle	Enone	Reaction time (h)	Products	Yield (%)[a]
1		**2a**	1	 (**9a**)	98 (80)
2		**2c**	1	 (**9b**)	95 (69)
3		**2a**	3	 (**9c**)	- (56)
4		**2c**	3	 (**9d**)	- (50)
5		**2a**	3	 (**9e**)	53 (41)

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

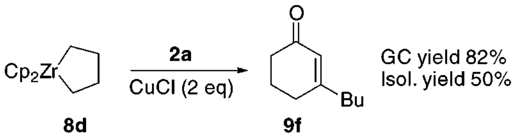
Scheme 6



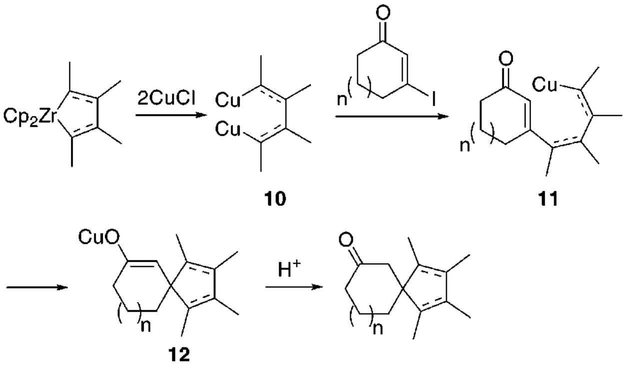
Scheme 7



Scheme 8



Scheme 9



of the spirocyclic compound **7b**. On the other hand, if the reaction was conducted at 20 °C only spirocyclic compound **7b** was obtained in good yield. These results again showed that it is possible to control the chemoselectivity of both the Zr-sp^2-carbon and Zr-sp^3-carbon bonds of zirconacyclopentenes.[14] As expected the reaction with **2c** proceeded at 20 °C and gave a good yield of **7c**.

Finally, zirconacyclopentanes **8** were the last class of zirconacycles tested in the reaction with 3-iodoenones (Scheme 7). As in the previous cases, all reactions proceeded as expected, and the results are summarized in Table 2. Both zirconabicyclooctanes and zirconabicyclononenes reacted under the standard conditions with **2a** (entries 1 and 3) or **2c** (entries 2 and 4) to give the corresponding tricyclic spirocompounds in good yields. Bimetallic zirconasilabicyclooctane (entry 5) also afforded a spirocyclic compound albeit in moderate yield.

Surprisingly, zirconacyclopentane **8d** in the reaction with **2a** afforded only the product of the cross-coupling reaction **9f** (Scheme 8). Despite further efforts to achieve

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[14] (a) Kasai, K.; Kotora, M.; Suzuki, N.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 109–110. (b) See ref 4a. (c) Lipshutz, B. H.; Segi, M. *Tetrahedron* **1995**, *51*, 4407–4420.

formation of a spirocyclic compound by the use of additives (HMPA and Me_3SiCl),[15] the cyclization did not occur.

With regard to the above presented results, we propose the following reaction mechanism that is common for all zirconacycles (zirconacyclopentadiene, -pentene, and -pentane) (Scheme 9). In the first step the transmetalation of the Zr−C bond in zirconacycle to the Cu−C bond affords bis(cuprate) **10** that further reacts via cross-coupling with the C−I bond of iodocycloenone to give the open-chain intermediate **11**. However, the question remains whether this step is a single-step cross-coupling reaction or a two-step Michael addition followed by elimination of CuI. Nevertheless, we assume it to be the cross-coupling reaction on the basis of the comparison of the reactions with 3-iodo- and 3-bromopropenoate.[8] In the next step **11** undergoes intramolecular Michael reaction to give spiroenolate **12** that, after hydrolysis, affords a spirocyclic compound.

Experimental Section[16]

Formation of Cyclopentadienes. Methyl 2-(1′,2′,3′,4′,5′-Pentaphenyl-1′-cyclopentadienyl)ethanoate (4). To a solution of tetraphenylzirconacyclopentadiene, prepared in situ from zirconocene dichloride (292 mg, 1 mmol), *n*-BuLi (2 mol), and diphenylacetylene (356 mg, 2 mmol) in THF (5 mL), were added methyl (*Z*)-3-iodo-3-phenylpropenoate (432 mg, 1.5 mmol) and CuCl (198 mg, 2 mmol) at room temperature. The reaction mixture was stirred at room temperature for 15 min, quenched with 3 N HCl, extracted with hexane, washed with a saturated solution of NaCl, dried ($MgSO_4$), and concentrated in vacuo. Column chromatography on silica gel (9/1 hexane/Et_2O) afforded the title compound as a colorless solid (405 mg, 78%): mp 172.5−173.0 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.29 (s, 2 H), 3.56 (s, 3 H), 6.28−7.23 (m, 25H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 36.56, 51.12, 64.38, 126.11, 126.49 (2C), 126.55 (2C), 126.81 (2C), 127.43 (4C), 127.53 (4C), 128.73 (2C), 129.80 (4C), 129.97 (4C), 135.52 (2C), 135.70 (2C), 138.54, 144.43 (2C), 149.63 (2C), 170.44; IR(neat) 1738 cm^{-1}. Anal. Calcd for $C_{38}H_{30}O_2$: C, 88.00; H, 5.83. Found: C, 87.93; H, 5.98.

Formation of Spirocyclic Compounds. 1,2-Dimethyl-3,4-diphenylspiro[4,5]deca-1,3-dien-7-one (5c). 3-Iodo-2-cyclohexen-1-one **2a** (244 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) were added to a solution of 2,3-diphenyl-4,5-dimethylzirconacyclopentadiene, prepared in situ from zirconocene dichloride (292 mg, 1 mmol) and *n*-BuLi (2 mol), followed by addition of diphenylacetylene (178 mg, 1 mmol) and 2-butyne (54 mg, 1 mmol) in THF (5 mL) at room temperature. After stirring at the same temperature for 1 h, the reaction mixture was quenched with 3 N HCl, extracted with hexane, washed with a saturated solution of NaCl, dried ($MgSO_4$), and concentrated in vacuo. The title compound was obtained as a colorless oil (158 mg, 48%) by column chromatography on silica gel (4/1 hexane/Et_2O): ^1H NMR ($CDCl_3$, Me_4Si) δ 1.63−2.00 (m, 10H), 2.13−2.18 (m, 1H), 2.26−2.35 (m, 2H), 2.59 (d, J = 14.8 Hz, 1H), 6.98−7.25 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.11 (2C), 22.07, 29.99, 40.10, 45.06, 60.41, 126.35, 126.70, 127.59 (2C), 127.95 (2C), 129.43 (2C), 130.72 (2C), 133.44, 136.11, 137.34, 142.93, 143.04, 148.81, 212.29; IR (neat) 1716 cm^{-1}; HRMS calcd for $C_{24}H_{24}O$, 328.1826; found, 328.1820.

2*H*-4,5,6,7-Tetrahydro-1,3-diphenylindene-2-spiro-3′-cyclohexanone (5d). 1,8-Diphenylocta-1,7-diyne (258 mg, 1 mmol) was added to dibutylzirconocene prepared in situ by the reaction of zirconocene dichloride (292 mg, 1 mmol) and *n*-BuLi (2 mol) in THF (5 mL). To the reaction mixture containing the bicyclic zirconacyclopentadiene were added 3-iodo-2-cyclohexen-1-one **2a** (244 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) at room temperature. The reaction mixture was quenched with 3 N HCl, extracted with hexane, washed with a saturated solution of NaCl, dried ($MgSO_4$), and concentrated in vacuo, after stirring for 1 h. A colorless solid (170 mg, 48%) was isolated by column chromatography on silica gel (4/1 hexane/Et_2O): mp 118−119 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.47−1.61 (m, 6H), 1.85−1.93 (m, 4H), 2.15−2.33 (m, 4H), 2.53 (s, 2H), 7.13−7.37 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.46, 23.36 (2C), 24.33 (2C), 30.06, 39.63, 45.10, 60.96, 126.89 (2C), 128.30 (4C), 129.95 (4C), 137.35 (2C), 137.62 (2C), 146.20 (2C), 211.87; IR(neat) 1710 cm^{-1}; HRMS calcd for $C_{26}H_{26}O$, 354.1982; found, 354.1990.

1,2,3,4,6-Pentaethylspiro[4,5]deca-1,3-dien-7-one (5g). To a solution of tetraethylzirconacyclopentadiene, prepared in situ from zirconocene dichloride (292 mg, 1 mmol), *n*-BuLi (2 mol), and 3-hexyne (164 mg, 2 mmol) in THF (5 mL), were added 3-iodo-2-methyl-2-cyclohexen-1-one **2b** (260 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) at room temperature. Quenching of the reaction mixture after 1 h of additional stirring with 3 N HCl, extration with hexane, washing with a saturated solution of NaCl, drying ($MgSO_4$), and concentration in vacuo, followed by column chromatography on silica gel (4/1 hexane/Et_2O), afforded the title compound as a colorless liquid (115 mg, 42%): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.5 (d, J = 7.5 Hz, 3H), 0.97−1.08 (m, 12H), 1.37 (m, 1H), 1.75 (m, 1H), 2.09−2.23 (m, 10H), 2.48 (t, J = 5.7 Hz, 2H), 2.54 (q, J = 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 7.53, 14.58, 14.67, 14.74, 14.91, 17.91, 18.60, 18.78, 19.85, 23.89, 30.86, 41.33, 46.65, 64.81, 141.23, 142.83, 144.36, 144.43, 214.47; HRMS calcd for $C_{19}H_{30}O$, 274.2295; found, 274.2297.

2,3-Diphenylindene-1-spiro-3′-cyclopentanone (5i). 3-Iodo-2-cyclopenten-1-one **2c** (229 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) were added to a solution of 2,3-diphenylzirconaindene, prepared in situ from zirconocene dichloride (292 mg, 1 mmol), PhLi (2 mol), and diphenylacetylene (178 mg, 1 mmol) in THF (5 mL), at 20 °C. The reaction mixture was stirred at the same temperature for 1 h, quenched with 3 N HCl, extracted with hexane, washed with a saturated solution of NaCl, dried ($MgSO_4$), and concentrated in vacuo. The title compound was obtained as a colorless solid (208 mg, 61%) after column chromatography on silica gel (4/1 hexane/Et_2O): mp 185−186 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.31−2.40 (m, 3H), 2.53−2.64 (m, 2H), 2.83 (d, J = 18.3 Hz, 1H), 7.07−7.38 (m, 14H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 31.46, 37.31, 46.26, 58.36, 121.00, 121.25, 125.93, 127.17, 127.19, 127.52, 128.07 (2C), 128.43 (2C), 129.27 (2C), 129.98 (2C), 134.28, 135.72, 139.48, 142.91, 149.28, 150.80, 218.09; IR (neat) 1715 cm^{-1}. Anal. Calcd for $C_{25}H_{20}O$: C, 89.25%; H, 5.99%. Found: C, 89.25%; H, 6.21%.

1,2-Diethyl-1-butenyl-cyclohexane-3-one (7a). 2,3-Diethylzirconacyclopentene was prepared from zirconocene dichloride (292 mg, 1 mmol), EtMgBr (2 mol), and 3-hexyne (82 mg, 1 mmol) in THF (5 mL) in situ. To this were added 3-iodo-2-cyclohexen-1-one **2a** (244 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) at 0 °C. After 1 h, the reaction mixture was quenched with 3 N HCl, extracted with hexane, washed with a saturated solution of NaCl, dried ($MgSO_4$), and concentrated in vacuo. A colorless liquid (97 mg, 47%) of **7a** was obtained after column chromatography on silica gel (4/1 hexane/Et_2O): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.91−1.01 (m, 9H), 1.94−2.42 (m, 12H), 5.77 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.38, 13.43, 13.80, 22.88, 23.03, 23.65, 25.74, 30.27, 37.40, 127.37, 136.00, 137.98, 166.12, 199.83; IR (neat) 1706 cm^{-1}; HRMS calcd for $C_{14}H_{22}O$, 206.1669; found, 206.1666.

1,2-Diethylspiro[4,5]deca-1-en-7-one (7b). To a solution of 2,3-diethylzirconacyclopentene (1 mmol), prepared in situ from zirconocene dichloride (292 mg, 1 mmol), EtMgBr (2 mol), and 3-hexyne (82 mg, 1 mmol) in THF (5 mL), were added 3-iodo-2-cyclohexen-1-one **2a** (244 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) at room temperature. After the same workup described above, column chromatography on silica gel (4/1 hexane/Et_2O) afforded **7b** as a colorless liquid (83 mg, 40%): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.97 (q, J = 7.4 Hz, 6H), 1.45−2.40

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[15] Perlmutter, P. *Conjugate Addition Reactions*; Pergamon Press: Oxford, 1992; pp 41−43 and references therein.

[16] For general Experimental Section, see our recent paper: Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672−1680.

(m, 16H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.75, 15.33, 17.65, 21.64, 23.15, 31.49, 33.36, 34.77, 41.13, 50.63, 56.15, 138.36, 141.00, 212.07; IR (neat) 1703 cm^{-1}; HRMS calcd for $C_{14}H_{22}O$, 206.1669; found, 206.1666.

(1*R,4*R**)-Spiro[bicyclo[3.3.0]octane-3,1′-cyclohexan-3′-one] (9a).** 3-Iodo-2-cyclohexen-1-one **2a** (244 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) were sequentially added to a reaction mixture at 20 °C contaning 3-zirconabicyclo[3.3.0]-octane, prepared in situ from zirconocene dichloride (292 mg, 1 mmol), *n*-BuLi (2 mol), and 1,6-heptadiene (96 mg, 1 mmol) (1 mmol) in THF (5 mL). After the same workup, the title compound was isolated by column chromatography on silica gel (4/1 hexane/Et_2O) as a colorless liquid (155 mg, 80%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.94−1.09 (m, 4H), 1.54−2.02 (m, 12H), 2.24−2.32 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.14, 26.20 (2C), 28.91, 39.08, 39.95, 41.01, 41.22, 52.25, 52.52, 54.13, 55.60, 211.50; IR(neat) 1725 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O$: C, 81.20%; H, 10.48%. Found: C, 81.09%; H, 10.48%.

(1′*R,6′*S**)-Spiro[3-cyclohexanone-1,8′-(3′,4′-diphenylbicyclo[4.3.0]-non-3-ene)] (9c).** To a solution of 3,4-diphenyl-8-zirconabicyclo[4.3.0]non-3-ene in situ prepared from zirconocene dichloride (292 mg, 1 mmol), *n*-BuLi (2 mol), and 4,5-diphenyl-1,4,7-octatriene (260 mg, 1 mmol) in THF (5 mL) were added 3-iodo-2-cyclohexen-1-one **2a** (244 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) at 20 °C. After stirring at the same temperature for 1 h, the reaction mixture was quenched with 3 N HCl. After the same workup, a colorless solid of **9c** (200 mg, 56%) was obtained by column chromatography on silica gel (4/1 hexane/Et_2O): mp 148−149 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.25−1.30 (m, 2H), 1.69−1.93 (m, 6H), 2.28−2.34 (m, 6H), 2.53−2.68 (m, 4H), 6.98−7.14 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.00, 34.55, 35.80 (2C), 36.35 (2C), 41.19, 44.65 (2C), 46.87, 54.67, 125.75 (2C), 127.68 (4C), 128.82 (4C), 135.87 (2C), 143.26 (2C), 211.57; IR(neat) 1726 cm^{-1}; HRMS calcd for $C_{26}H_{28}O$, 356.2139; found, 356.2136.

3-Butylcyclohexenone (9f). To a solution of zirconacyclopentane, prepared in situ from zirconocene dichloride (292 mg, 1 mmol), *n*-BuLi (2 mol), and ethylene in THF (5 mL), were added 3-iodo-2-cyclohexen-1-one **2a** (244 mg, 1.1 mmol) and CuCl (198 mg, 2 mmol) at 20 °C. Quenching of the reaction mixture with 3 N HCl, extraction with hexane, washing with a saturated solution of NaCl, drying ($MgSO_4$), and concentration in vacuo after additional stirring at the same temperature for 1 h was followed up by column chromatography on silica gel (4/1 hexane/Et_2O) that afforded the title compound as a colorless liquid (76 mg, 50%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.87 (t, $J = 7.2$ Hz, 3H), 1.29 (q, $J = 7.4$ Hz, 2H), 1.43 (q, $J = 7.4$ Hz, 2H), 1.93 (m, 2H), 2.16 (t, $J = 7.5$ Hz, 2H), 2.24 (t, $J = 6.0$ Hz, 2H), 2.30 (t, $J = 6.6$ Hz, 2H), 5.82 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.70, 22.23, 22.65, 28.97, 29.58, 37.26, 37.65, 125.54, 166.56, 199.74; HRMS calcd for $C_{10}H_{16}O$, 152.1200; found, 152.1206.

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Supporting Information Available: Characterization of a series of derivatives of **4**; experimental details, structures, tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for **4** and **5i**; and ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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