PREPARATION OF Sn-, Ge-, AND Si-HETEROCYCLES FROM ZIRCONACYCLES

Yasuyuki Ura, Yanzhong Li, Fu-Yu Tsai, Kiyohiko Nakajima,† Martin Kotora, and Tamotsu Takahashi*

Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo 060-0811 Japan and CREST, Science and Technology Corporation (JST), Sapporo 060-0811 Japan

†Department of Chemicstry, Aichi University of Education, Igaya, Kariya, 448-8542, Japan and CREST, Science and Technology Corporation (JST), Igaya, Kariya , 448-8542, Japan

Abstract - Stannacycles such as stannacyclopentanes, stannacyclopentenes and stanacyclopentadienes were prepared from the corresponding zirconacycles. The effect of addition of CuCl on the reaction of zirconacycles with tin halides is remarkable. In the case of germanium and silicon halides, the remarkable effect of CuCl addition was not observed. Symmetrical or unsymmetrical germa- and silacycles were prepared by the reaction of silicon or germanium halides with dilithio compounds prepared from the corresponding zirconacycles. Several heterocyclic compounds containing two metalloatoms were also prepared.

Group 14 (Si, Ge, Sn) heterocycles are attractive for application in medicinal chemistry as well as in material science.[1] Different procedures leading to their preparation are known; however, the number of general procedures is limited. A synthetically attractive approach to heterocycles would be the one based on the transmetallation of metallacycles prepared by the reductive coupling of alkenes or alkynes on the reduced metal. Generally, this approach may be classified into the following three categories (Scheme 1):

I. The first such procedure, developed by Fagan and Nugent, is based on "metallacycle transfer" of the carbon fragment from five-membered zirconacycle to a halide of main group elements. Nonetheless,

---

Dedicated to Prof. Teruaki Mukaiyama of Science University of Tokyo on the occasion of his 73rd birthday.

in some cases, the reaction with halides of main group elements was very sluggish and prolonged reaction time was needed to achieve reasonable yields of products (Sn) or, despite all efforts, the yields of products were rather low (Si).[2] Moreover, the procedure requires isolation of the metallacycles prior to the reaction with the corresponding halides.

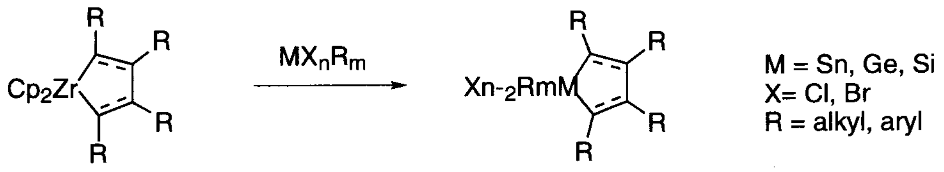
II. The second approach, preliminarily and recently reported by our group, is based on the reaction of zirconacycles with tin halides in the presence of CuCl, which facilitates the metallacycle transfer. This method is a one-pot reaction with overall reaction periods several times shorter than those of method I.[3]

III. The last approach is based on the reaction of dilithio compounds, which were prepared from zirconacycles by an iodination-lithiation sequence, with silicon and germanium halides as was reported by a number of groups[4] as well as us.[5] The synthetic applicability of this aproach has increased since we developed a very efficient procedure for the preparation of symmetrical and unsymmetrical 1,4-diiodo-1,3-butadiene derivatives.[5]

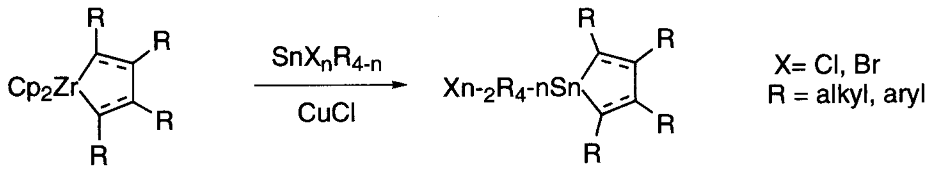
In this paper, we would like to report full details of a preparative method of group 14 element (Sn, Ge, Si) heterocycles (both mono- and bicyclic) from zirconacycles.

Scheme 1

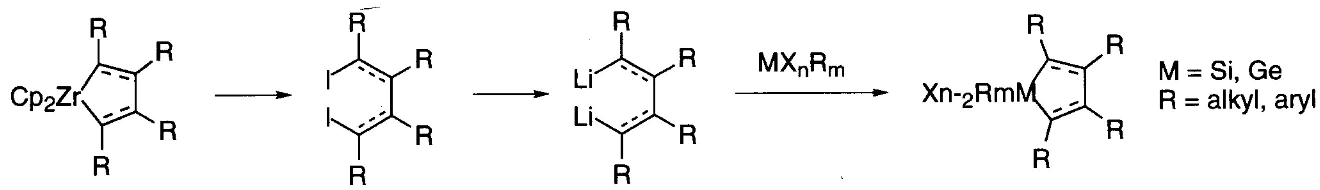
Method I. *Metallacycle Transfer*



Method II. *One-pot Metallacycle Transfer in the Presence of CuCl*



Method III. *Reaction of Dilithio Compounds with Si and Ge Halides*



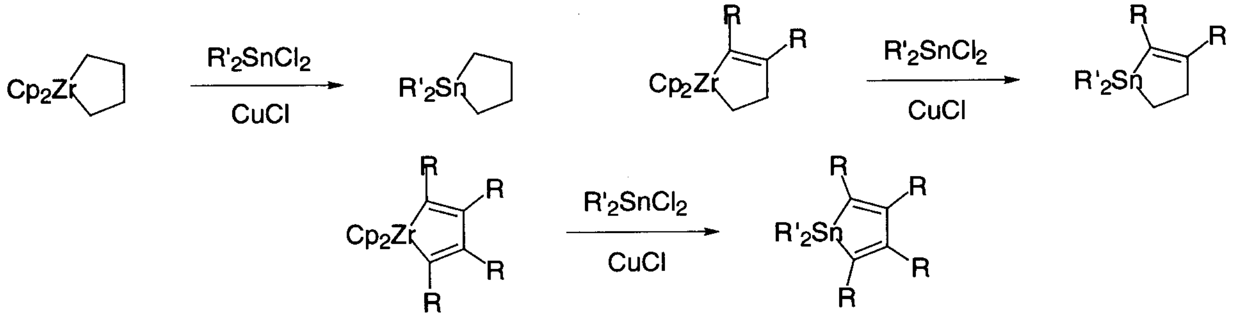
Results and discussion

The aim of this paper is to present a general strategy for the preparation of heterocyclic compounds (stanna-, germa, and silacycles) from zirconacycles. The zirconacycles are easily prepared *"in situ"* from alkenes and alkynes.[6-8] The preparation is divided into two phases according to the experimental procedure: the former includes preparation of stannacycles by Method II and the latter includes preparation of germa- and silacycles by Method III.

Preparation of Stannacycles

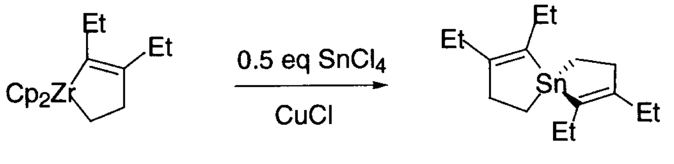
All stannacycles were conveniently prepared in high yields directly by the reaction of zirconacyclopentanes, -pentenes, and -pentadienes with R_2SnCl_2 in the presence of a stoichiometric or catalytic amount of CuCl (Scheme 2). The clear-cut advantage of this method over a simple reaction of zirconacycles with an appropriate tin halide is clearly demonstrated by the examples given in Tables 1 and 2.

Scheme 2



In Table 1 are given typical examples of the reaction of zirconacyclopentanes and -pentenes with tin halides. All zirconacyclopentanes, mono- (Entry 1) as well as bicyclic (Entries 2,3), reacted with tin halides in the presence of a stoichimetric amount of CuCl to give high yields (80-98%) of the corresponding stannacycles in 1-3h. This method also enabled preparation of bimetallic silastannabicyclooctane (Entries 3) in high yields (80%). Although the reaction proceeded in the absence of CuCl, ten times longer reaction time was required (12 h) and the yields of the products were rather low. Similar effect was observed for the reactions of both mono- (Entries 4-6) as well as bicyclic zirconacyclopentenes(Entries 7,8). In the presence of CuCl (1 eq), they afforded the corresponding stannacycles in high yields (90-99%) in 1-3 h. The reaction of a zirconacyclopentene (Entry 9) with 0.5 eq of tin tetrachloride resulted, as expected, in the formation of a spirostannacycle in good yield (74%) (Scheme 3).

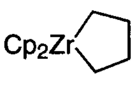
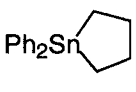
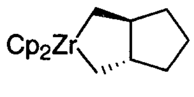
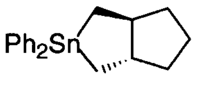
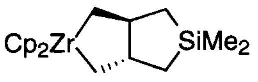
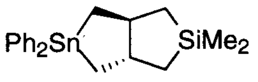
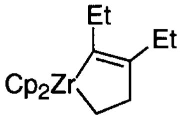
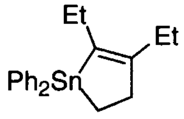
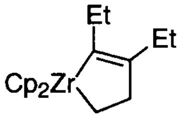
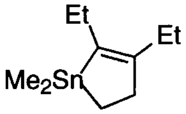
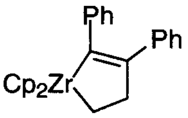
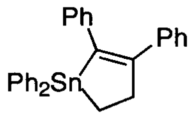
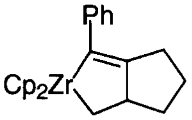
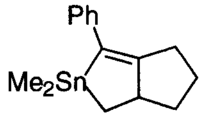
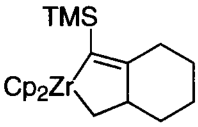
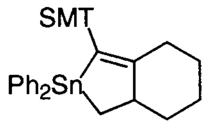
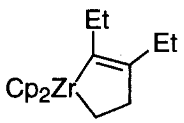
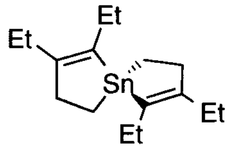
Scheme 3



Stannacycle (**6**) was obtained as crystals suitable for X-Ray analysis and its structure is shown in Figure 1. In contrast to the reactions of zirconacyclopentanes, the zirconacyclopentenes, in many cases, did not react with tin halides in the absence of CuCl (Entries 4,6,9) or it required prolonged reaction time but the yields were low.

In Table 2 are given typical examples of the reaction of zirconacyclopentadienes with tin halides. In contrast to the reaction of zirconacyclopentanes and -pentenes, the successful course of the reactions required only a catalytic amount of CuCl (10 mol%). In all cases (Entries 1-7) stannacyclopentadienes

Table 1. Reaction of zirconacyclopentanes and -pentenes with R_2SnCl_2 in the presence of a stoichiometric amount of CuCl.

Entry	Zirconacycles	R_2SnCl_2	Time (h)	Product	Yields (%)[a]
1		Ph_2SnCl_2	1 12^b	 (1)	96 (69) 81
2		Ph_2SnCl_2	1 12^b	 (2)	98 (74) 45 (30)
3		Ph_2SnCl_2	3 12^b	 (3)	80 (64) 55 (36)
4		Ph_2SnCl_2	3 48^b	 (4)	99 (53) 0
5		Me_2SnCl_2	3 72^b	 (5)	99 (80) 20
6		Ph_2SnCl_2	3 48^b	 (6)	90 (56) 0
7		Me_2SnCl_2	1 18^b	 (7)	95 (76) 92
8		Ph_2SnCl_2	1 48^b	 (8)	94 (78) 77
9		$SnCl_4$	3 48^b	 (9)	74 (68) 0

[a] ^1H NMR yields. Isolated yields are given in parentheses. [b] Without CuCl.

were obtained in good to high yields usually in 1-3 h. The use of suitable starting material enabled preparation of bimetallic metallacycles such as a distannabicycle (Entry 5) and a stannagermabicycle (Entry 6). The reaction of 1 eq of zirconacyclopentadiene with 0.5 eq of $SnCl_4$ (Entry 7) resulted in the formation of spirostannacyclopentadiene in high yield (Scheme 4). In the absence of CuCl, the completion of reactions required a long reaction time and the yields were low. In some cases, the formation of the products was not observed at all (Entries 1, 2, 7).

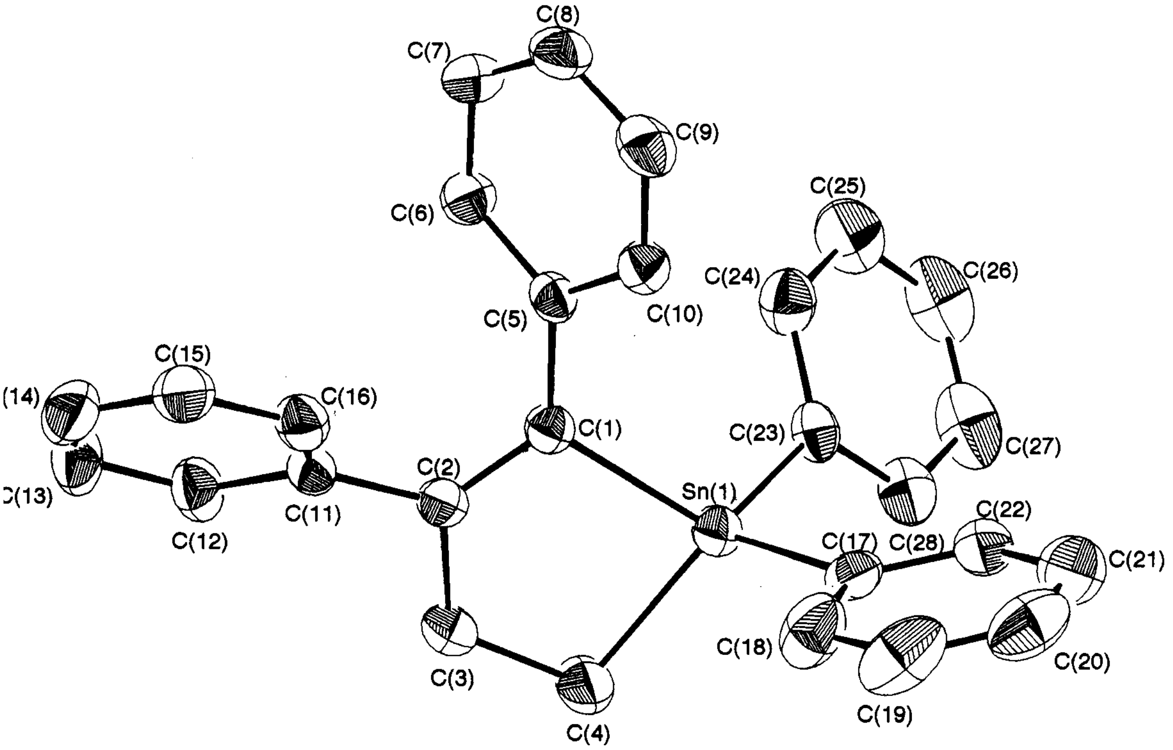
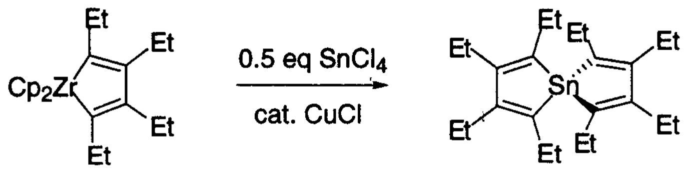


Figure 1. Structure of compound (**6**). Selected distances (Å) and angles (°) are as follows. n(1)-C(1) : 2.136(3), Sn(1)-C(4) : 2.137(6), C(1)-C(2) : 1.347(4), C(2)-C(3): 1.525(5), C(3)-C(4) : .513(5), C91)-Sn(1)-C(4): 85.9(1), Sn(1)-C(1)-C(2): 109.5(2), Sn(1)-C(4)-C(3): 105.7.

Scheme 4



general conclusion regarding these data clearly shows that the reaction in the presence of CuCl resulted higher yields and considerably shorter reaction time when compared with the reaction conducted ithout CuCl. In some cases, reaction without CuCl did not proceed at all. The positive effect of the resence of CuCl is easily explained by the transmetallation of the Zr-C bonds to the Cu-C bonds[9] at reacted with tin halides (Scheme 5).

Scheme 5

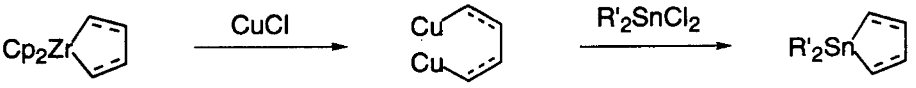
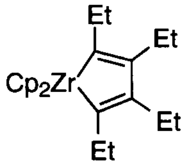
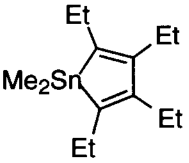
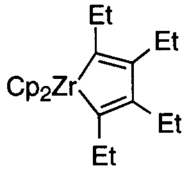
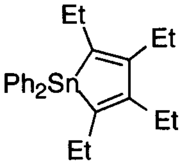
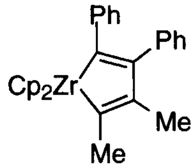
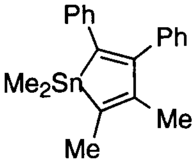
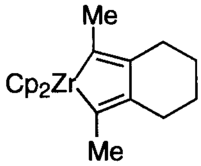
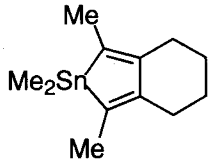
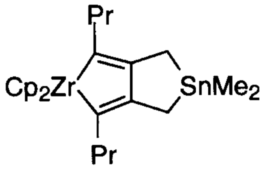
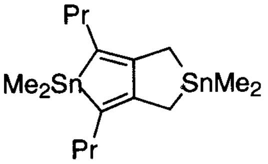
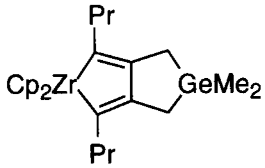
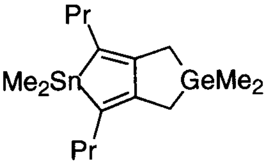
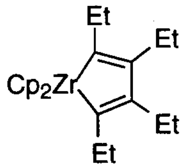
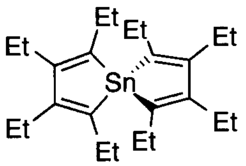


Table 2. Reaction of zirconacyclopentadienes with R_2SnX_2 in the presence of a catalytic amount of CuCl (10 mol%).

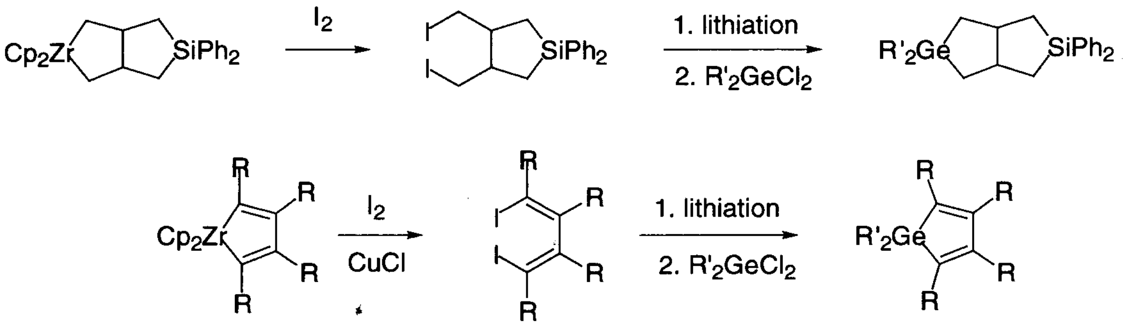
Entry	Zirconacycles	R_2SnX_2	Time (h)	Product	Yields (%)[a]
1		Me_2SnCl_2	1 48[b]	 **(10)**	84 (73) 0
2		Ph_2SnCl_2	3 48[b]	 **(11)**	- (72) 0
3		Me_2SnCl_2	1 48[b]	 **(12)**	83 (68) 40
4		Me_2SnBr_2	3 48[b]	 **(13)**	99 (87) 99[c]
5		Me_2SnCl_2	1 48[b]	 **(14)**	65 (48) <5
6		Me_2SnCl_2	12 48[b]	 **(15)**	- (86) <5
7		$SnCl_4$	3 48[b]	 **(16)**	- (86) 0

[a] ^{1}H NMR yields. Isolated yields are given in parentheses. [b] Without CuCl. [c] See ref. 2a.

Preparation of Germacycles

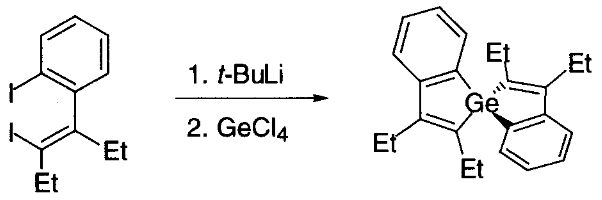
It was reported that zirconacyclopentadienes reacted readily with $GeCl_4$ to give the corresponding germacyclopentadienes[2]; however, dialkyl- or diphenylgermanium dihalides did not react either in the presence or absence of CuCl. To achieve the formation of germacycles using dialkyl- or diphenylgermanium halides, the conventional Method III is appropriate. This procedure was based on the preparation of diiodides from zirconacycles followed by lithiation and, finally, reaction with the corresponding germanium halide (Scheme 6).

Scheme 6



Iodination of zirconacyclopentanes is well known and process as usual to give high yields of the corresponding diiodides.[10] As for diiodination of zirconacyclopentadienes, we used our previously published method that enables preparation of both symmetrically and unsymmetrically substituted diiodobutadienes in high yields.[5] The lithiation of the corresponding diiodides was achieved by the reaction with *t*-BuLi in Et_2O (Method A).

Scheme 7



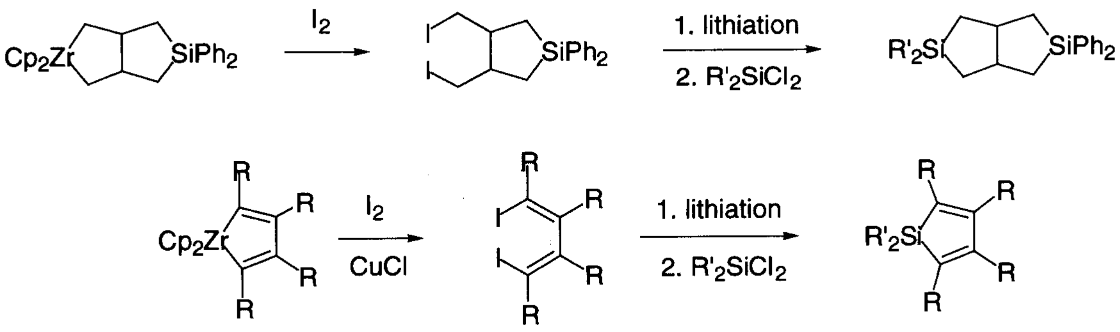
In Table 3 are given some typical examples of the preparation of germacycles. The reaction of di(lithiomethyl)cyclopentanes with dimethyl- or diphenylgermyl dichlorides afforded the corresponding germasilabicyclooctanes (Entries 1,2) in good yields. Also, the reaction of dilithiobutadiene with dimethylgermyl dichloride afforded the corresponding germacyclopentadiene in high yield (Entry 3). It is noteworthy that the reaction of 1 eq of dilithio compound with 0.5 eq of $GeCl_4$ (Entry 4) afforded germa-1,1'-spirobisindene in high yield (Scheme 7). It was reported that the reaction of zirconacyclopentadiene with $GeCl_4$ afforded only germacyclopentadiene.[2a]

Preparation of Silacycles

As far as the formation of silacycles is concerned, the behaviour of zirconacycles to silicon halides is similar to that of germanium halides. The only reported direct transformation of zirconacycle to silacycle was the reaction of zirconacyclopentadiene with $SiBr_4$ at 150 °C to give the corresponding silacyclopentadiene in low yield (28%) after two days.[2a] In order to obtain silacycles in high yield, the same method as for the formation of germacycles was used. In this instance, the lithiation of the corresponding diiodides was achieved either by the reaction with *t*-BuLi in Et_2O (Method A) or *t*-BuLi in

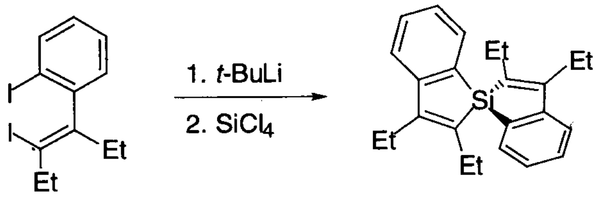
THF (Method B).

Scheme 8



In Table 3 are given some typical examples of the formation of silacycles. The reaction of dilithio compounds with dimethyl- or diphenylsilyl dichloride afforded disilabicyclooctanes (Entries 5,6) and in good yields. The reaction of 1,4-dilithiobutadienes with dimethylsilyl dichloride afforded the corresponding silacyclopentadiene (Entry 7) and silaindene (Entry 8) in excellent yields. Similarly to the case of germyl tetrachloride, the reaction of 1 eq of dilithio compound with 0.5 eq of $SiCl_4$ (Entry 9) yielded sila-1,1'-spirobisindene in high yield (Scheme 9).

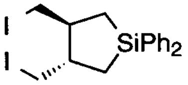
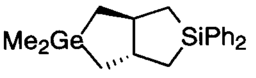
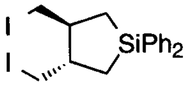
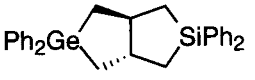
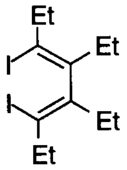
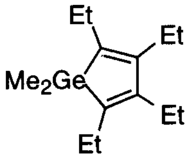
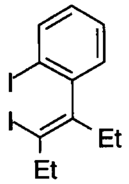
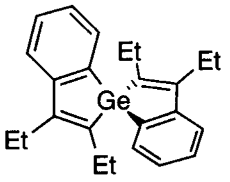
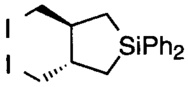
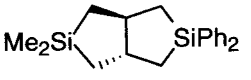
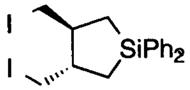
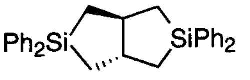
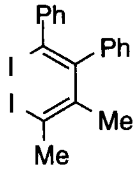
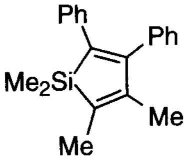
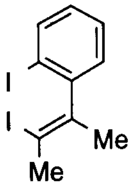
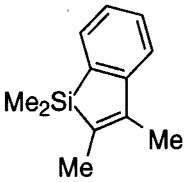
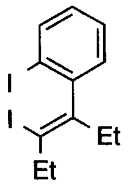
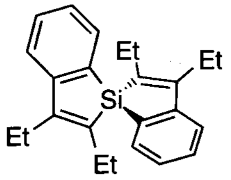
Scheme 9



Formation of Bimetallic Heterocycles

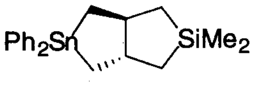
It is noteworthy that both methods offer a simple and efficient method for the preparation of bimetallic bicycles. Thus, bimetallic bicycles containing Sn, Si (**3**), Sn, Sn (**14**), or Sn, Ge (**15**) could be easily prepared by the reaction of zirconacycles with tin halides in the presence of CuCl. Bicycles containing Ge, Si (**17**, **18**) and Si, Si (**21**, **22**) could be effectively prepared by the reaction of dilithio compounds with the corresponding silyl or germyl halides.

Table 3. Preparation of germa- and silacycles from 1,4-dilithio compounds.

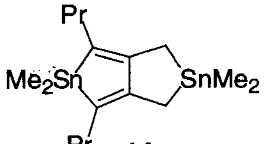
Entry	Zirconacycles	Method[a]	R_2MCl_2	Product	Yields (%)[b]
1		A	Me_2GeCl_2	 (**17**)	68 (46)
2		A	Ph_2GeCl_2	 (**18**)	- (53)
3		A	Me_2GeCl_2	 (**19**)	82 (74)
4		A	$GeCl_4$	 (**20**)	- (83)
5		A	Me_2SiCl_2	 (**21**)	- (45)
6		A	Ph_2SiCl_2	 (**22**)	- (67)
7		B	Me_2SiCl_2	 (**23**)	- (95)
8		B	Me_2SiCl_2	 (**24**)	- (98)
9		A	$SiCl_4$	 (**25**)	- (84)

---

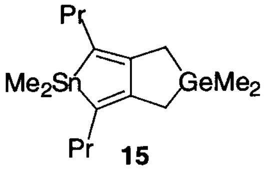
[a] Method A: *t*-BuLi/Et_2O. Method B: *t*-BuLi/ THF. [b] ^1H NMR yields. Isolated yields are given in parentheses.



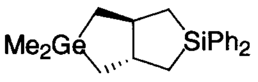
3



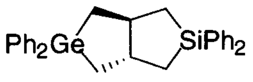
14



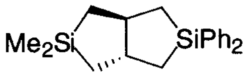
15



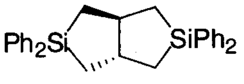
17



18



21

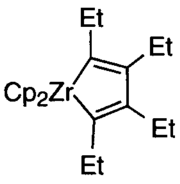


22

Conclusion

In the case of Method II (one-pot metallacycle transfer) the effect of CuCl on the reaction is essential as can be clearly seen from Table 2. In Table 4 is given a comparison of the reaction of tetraethylzirconacyclopentadiene with different group 14 halides in the absence or presence of CuCl. Whereas the presence of CuCl does not have any influence on the reaction with Si and Ge halides, the reaction with tin halides is significantly influenced. Firstly, the presence of CuCl accelerates the overall reaction rate ($SnCl_4$, Me_2SnCl_2) and, secondly, enables the reaction to proceed in the cases where a zirconacyclopentadiene alone does not react with tin halide.

Table 4. Reaction of tetraethylzirconacyclopentadiene with silicon, germanium, and tin halides and the effect of the added CuCl on the reaction.[a]

		Effect of Added CuCl
$SiCl_4$	n.g.	no influence
Me_2SiCl_2	n.g.	no influence
$GeCl_4$	reaction[b]	no influence
Me_2GeCl_2	n.g.	no influence
$SnCl_4$	n.g.	86%[c]
Me_2SnCl_2	n.g.	84%

[a] n.g. : no reaction or very low yield.

[b] Germacyclopentadiene (1:1 reaction product) was obtained. See ref. 2a.

[c] Stannaspirocyclopentadiene (1:2 reaction product) was formed.

As far as the preparation of sila- and germacycles is concerned, Method III offers the best pathway.

EXPERIMENTAL

General information. Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions were run under a slightly positive pressure of dry N_2. THF and hexane were refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Zirconocene dichloride was purchased from Aldrich Chemical Company, Inc. or TCI. Ethylmagnesium bromide (THF solution), n-butyllithium (hexane solution), *t*-butyllithium (pentane solution) and $SnCl_4$ were purchased from Kanto Chemicals Co., Ltd. Me_2SnCl_2 and Ph_2SnCl_2 were purchased from TCI Co., Ltd. CuCl was purchased from Wako. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker-400 NMR spectrometer. GC analysis was performed on a gas chromatograph equipped with a flame ionization detector using a capillary column (CBP1-M25-025).

Zirconacycles[6-8] and diiodides[4,10] were prepared according to previously published procedures.

A General Procedure for the Formation of Stannacyclopentanes and -pentenes from Zirconacyclopentanes and -pentenes in the Presence of CuCl. To a solution of zirconacycle (1 mmol) in THF (5 mL) were added R_2SnCl_2 (1 mmol) and CuCl (2 mmol, 198 mg) at rt. The reaction mixture was stirred at rt for 1 h, then the solvent was removed under reduced pressure. The residue was extracted with hexane (2 x 5 mL), filtered, and concentrated under the reduced pressure. Column chromatography on silica gel (hexane) afforded the pure products.

1,1-Diphenylstannacyclopentane (1). Isolated as a colorless solid (69%): mp 106 – 108 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90-1.4 (m, 4H), 1.6-2.0 (m, 4H), 7.2-7.8 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 9.94 (satellites, J_{SnC} = 358, 340 Hz, 2C), 29.77 (satellites, J_{SnC} = 20.1 Hz, 2C), 128.39 (4C), 128.68 (2C), 136.81 (satellites, J_{SnC} = 36.2 Hz, 4C), 139.28 (2C). IR (neat) 2955, 2920, 2853, 1462, 1429, 1377, 725, 698 cm^{-1}. Anal. Calcd for $C_{16}H_{18}Sn$: C, 58.41; H, 5.51. Found: C, 57.90; H, 5.56.

(1*R,5*R**)-3,3-Diphenyl-3-stannabicyclo[3.3.0]octane (2).** Isolated as a colorless liquid (74%). ^{1}H and ^{13}C NMR characteristics were in agreement with the previously published data.[2a] IR (neat) 2944, 2903, 2862, 1429, 1377, 1074, 725, 698 cm^{-1}.

(1*R,5*R**)-3,3-Dimethyl-7,7-diphenyl-3-sila-7-stannabicyclo[3.3.0]octane (3).** Isolated as a colorless solid (64%): mp 95 – 96°C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.11 (s, 6H), 0.25-0.40 (m, 2H), 0.70-0.85 (m, 2H), 1.10-1.20 (m, 2H), 1.40-1.55 (m, 2H), 1.70-1.85 (m, 2H), 7.30-7.40 (m, 6H), 7.45-7.65 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.63 (satellites, J_{SiC} = 48.9 Hz, 2C), 20.76 (satellites, J_{SnC} = 314, 329 Hz, 2C), 25.14 (satellites, J_{SnC} = 62 Hz, J_{SiC} = 50 Hz, 2C), 51.30 (satellites, J_{SnC} = 12 Hz, 2C), 128.38 (satellites,

J_{SnC} = 48.6 Hz, 4C), 128.63 (satellites, J_{SnC} = 10.9 Hz, 2C), 136.72 (satellites, J_{SnC} = 40 Hz, 4C), 140.02 (satellites, J_{SnC} = 424, 443 Hz, 2C). IR (neat) 2953, 2926, 2855, 1460, 1427, 1377, 1250, 1175, 1088, 841, 818, 727, 696 cm^{-1}. Anal. Calcd for $C_{20}H_{26}SiSn$: C, 58.13; H, 6.34. Found: C, 57.78; H, 6.40.

1,1-Diphenyl-2,3-diethyl-1-stannacyclopent-2-ene (4). Isolated as a colorless liquid (53%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.01 (t, J = 7.5 Hz, 3H), 1.04 (t, J = 7.6 Hz, 3H), 1.10-1.30 (m, 2H), 2.23 (q, J = 7.6 Hz, 2H), 2.41 (q, J = 7.5 Hz, satellites, J_{SnH} = 54 Hz, 2H), 2.69-2.92 (m, 2H). 7.30-7.65 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 4.74 (satellites, J_{SnC} = 352, 337 Hz), 13.58, 17.63 (satellites, J_{SnC} = 17 Hz), 25.19 (satellites, J_{SnC} = 56 Hz), 25.59 (satellites, J_{SnC} = 65 Hz), 36.35 (satellites, J_{SnC} = 25 Hz), 128.39 (satellites, J_{SnC} = 98 Hz, 4C), 128.59 (satellites, J_{SnC} = 12 Hz, 2C), 136.82 (satellites, J_{SnC} = 38 Hz, 4C), 138.82, 140.92 (satellites, J_{SnC} = 463 Hz, 443 Hz, 2C), 157.03 (satellites, J_{SnC} = 115, 110 Hz). IR (neat) 3050, 2963, 2903, 1603, 1564, 1462, 1429, 1377, 1074, 997, 727, 698 cm^{-1}. Anal. Calcd for $C_{20}H_{24}Sn$: C, 62.70; H, 6.31. Found: C, 62.61; H, 6.35.

1,1-Dimethyl-2,3-diethyl-1-stannacyclopent-2-ene (5). Isolated as a colorless liquid (80%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.29 (s, satellites, J_{SnH} = 53 Hz, 6H), 0.80-1.21 (m, 8H), 2.00-2.20 (m, 2H), 2.40 (q, J = 7.5 Hz, 2H), 2.73 (t, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -7.45 (satellites, J_{SnC} = 303, 289 Hz, 2C), 5.17 (satellites, J_{SnC} = 337, 322 Hz), 14.21, 18.04 (satellites, J_{SnC} = 17 Hz), 25.89 (satellites, J_{SnC} = 60 Hz), 26.08 (satellites, J_{SnC} = 56 Hz), 37.67 (satellites, J_{SnC} = 21 Hz), 140.51, 154.60 (satellites, J_{SnC} = 107 Hz). IR (neat) 2945, 2933, 2855, 1462, 1452, 1377, 764 cm^{-1}. Anal. Calcd for $C_{10}H_{20}Sn$: C, 46.38; H, 7.78. Found: C, 46.76; H, 7.60.

1,1,2,3-Tetraphenyl-1-stannacyclopent-2-ene (6). Isolated as a colorless solid (56%): mp 135-136 °C'; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.40-1.61 (m, 2H), 3.25-3.45 (m, 2H), 6.85-7.70 (m, 20H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 5.89 (satellites, J_{SnC} = 344 Hz), 39.83 (satellites, J_{SnC} = 14 Hz), 124.73, 126.59, 127.88 (2C), 127.98 (2C), 128.51 (2C), 128.61 (2C), 128.63 (satellites, J_{SnC} = 50 Hz, 4C), 129.03 (satellites, J_{SnC} = 12 Hz, 2C), 136.81 (satellites, J_{SnC} = 39 Hz, 4C), 139.87 (2C), 141.43, 142.27, 143.57, 156.75. IR (neat) 2949, 2932, 2855, 1593, 1462, 1427, 1377, 1073, 752, 727, 698 cm^{-1}. Anal. Calcd for $C_{28}H_{24}Sn$: C, 70.18; H, 5.05. Found: C, 70.00; H, 5.27.

3,3-Dimethyl-2-phenyl-3-stannabicyclo[3.3.0]oct-1(2)-ene (7). Isolated as a colorless liquid (76%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.31 (s, satellites, J_{SnH} = 53 Hz, 3H), 0.41 (s, satellites, J_{SnH} = 53 Hz, 3H), 0.60-0.70 (m, 1H), 1.05-1.20 (m, 1H), 1.40-1.50 (m, 1H), 1.70-1.83 (m, 1H), 1.9-2.1 (m, 2H), 2.30-2.40 (m, 1H), 2.50-2.60 (m, 1H), 2.85-3.00 (m, 1H), 7.00-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -8.04, -6.00, 14.15 (satellites, J_{SnC} = 336, 322 Hz), 25.62, 28.73 (satellites, J_{SnC} = 49 Hz), 36.11 (satellites, J_{SnC} = 41

Hz), 53.00 (satellites, J_{SnC} = 14 Hz), 124.75, 128.05 (2C), 128.09 (2C), 134.72, 144.12, 163.32; IR (neat) 2913, 2901, 2889, 1462, 1454, 1377, 1188, 725, 669 cm^{-1}. HRMS calcd. for $C_{15}H_{20}Sn$ 320.0586, found 320.0599.

3,3-Diphenyl-2-trimethylsilyl-3-stannabicyclo[4.3.0]non-1(2)-ene (8). Isolated as a colorless solid (78%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.09 (s, 9H), 0.75 (dd, J = 13.5, 3.5 Hz, 1H), 1.10-1.70 (m, 4H), 1.70-2.00 (m, 2H), 2.00-2.30 (m, 2H), 2.80-3.10 (m, 2H), 7.10-7.90 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.70 (satellites, J_{SiC} = 52 Hz, 3C), 13.73 (satellites, J_{SnC} = 316 Hz), 27.39, 29.40, 38.04 (satellites, J_{SnC} = 106 Hz), 41.03 (satellites, J_{SnC} = 19.4 Hz), 51.05 (satellites, J_{SnC} = 46 Hz), 128.35 (2C), 128.38 (2C), 128.47, 128.53, 129.58, 136.70 (satellites, J_{SnC} = 38.6 Hz, 2C), 136.81 (satellites, J_{SnC} = 37.8 Hz, 2C), 141.07, 141.50, 177.92; IR (neat) 2945, 2929, 2855, 1457, 1450, 1429, 1377, 1246, 930, 853, 727, 698 cm^{-1}. HRMS calcd. for $C_{23}H_{30}SiSn$ 454.1137, found 454.1141.

1,2,6,7-Tetraethyl-5-stannaspiro[4.4]nona-1,6-diene (9). Isolated as a colorless liquid (68%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.80-1.40 (m, 16H), 2.00-2.20 (m, 4H), 2.30-2.55 (m, 4H), 2.60-2.90 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 5.21, 13.65, 17.46, 25.70, 25.74, 36.68, 140.87, 154.70; IR (neat) 2966, 2911, 2861, 1603, 1461, 1453, 1316, 1045, 656 cm^{-1}. HRMS calcd. for $C_{16}H_{28}Sn$ 340.1212, found 340.1205.

A General Procedure for the Formation of Stannacyclopentadienes from Zirconacyclopentadienes in the Presence of a Catalytic Amount of CuCl. To a solution of zirconacyclopentadiene (1 mmol) in THF (5 mL) were added R_2SnCl_2 (1 mmol) and CuCl (0.1 mmol, 10 mg) at rt. The reaction mixture was stirred at rt for 1 h, then the solvent was removed under reduced pressure. The residue was extracted with hexane (2 x 5 mL) and filtered. Distillation by galss tube oven under a reduced pressure afforded the product.

1,1-Dimethyl-2,3,4,5-tetraethylstannacyclopentadiene (10). Isolated as a colorless liquid (73%): bp 78 °C (1 mmHg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.31 (s, satellites, J_{SnH} = 53 Hz, 6H), 0.99 (t, J = 7.5 Hz, 6H), 1.07 (t, J = 7.5 Hz, 6H), 2.28 (q, J = 7.5 Hz, 4H), 2.38 (q, J = 7.5 Hz, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -8.65 (satellites, J_{SnC} = 296 and 310 Hz), 14.88 (satellites, J_{SnC} = 10 Hz), 17.54 (satellites, J_{SnC} = 21 Hz), 22.10 (satellites, J_{SnC} = 61 Hz), 25.56 (satellites, J_{SnC} = 55 Hz), 142.71, 151.56 (satellites, J_{SnC} = 89 Hz); IR (neat) 2961, 2928, 2870, 1455, 1373, 1308, 1184, 1046, 775, 741 cm^{-1}. HRMS calcd for $C_{14}H_{26}Sn$ 314.1055, found 314.1056.

1,1-Diphenyl-2,3,4,5-tetraethylstannacyclopentadiene (11). This compound could not be distilled. Filtration and evaporation gave a colorless liquid (72%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.03 (t, J = 7.5 Hz, 6H), 1.05 (t, J = 7.5 Hz, 6H), 2.37 (q, J = 7.5 Hz, 4H), 2.46 (q, J = 7.5 Hz, 4H), 7.31-7.59 (m, 10H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 14.96 (satellites, J_{SnC} = 10 Hz), 17.88 (satellites, J_{SnC} =19 Hz), 22.46, 25.65 (satellites, J_{SnC} = 54 Hz), 128.50, 128.65, 137.08, 139.88, 141.20, 153.70; HRMS calcd for $C_{24}H_{30}Sn$ 438.1368, found 438.1367. IR (neat) 2961, 2930, 2870, 1577, 1530, 1480, 1455, 1429, 1373, 1310, 1188, 1074, 1022, 997, 727, 698 cm^{-1}.

1,1,2,3-Tetramethyl-4,5-diphenyl-1-stannacyclopentadiene (12). Isolated as a colorless liquid (68%): Decomp. 62 – 70 °C (1 mmHg); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.44 (s, satellites, J_{SnH} = 54 and 57 Hz, 6H), 1.62 (s, satellites, J_{SnH} = 8 Hz, 3H), 2.10 (s, satellites, J_{SnH} = 47 and 48 Hz, 3H), 6.75-7.24 (m, 10H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ -8.99 (satellites, J_{SnC} = 309 and 324 Hz), 16.82, 18.95, 124.54, 126.02, 127.60, 127.84, 128.69 (satellites, J_{SnC} = 20 Hz), 129.57, 136.62 , 141.27, 142.15, 143.44, 147.65, 154.15. IR (liquid paraffin) 2953, 2926, 2855, 1597, 1590, 1528, 1462, 1443, 1377, 1073, 795, 756, 733, 700, 693 cm^{-1}. Anal. Calcd for $C_{20}H_{22}Sn$: C, 63.03; H, 5.82. Found: C, 62.86; H, 5.85.

2*H*-4,5,6,7-Tetrahydro-1,2,2,3-tetramethyl-2-stannaindene (13). Isolated as a colorless liquid (87%). bp 71 °C (1 mmHg); ^{1}H and ^{13}C NMR characteristics were in agreement with the previously published data.[2a] IR (neat) 2921, 2857, 2847, 1451, 1429, 1250, 775, 741. cm^{-1}

3,3,7,7-Tetramethyl-2,4-dipropyl-3,7-distannabicyclo[3.3.0]octa-1(2),4-diene (14). Isolated as a yellow liquid (48%): bp 140 °C (1 mmHg); ^{1}H NMR (C$_6$D$_6$, Me$_4$Si) δ 0.26 (s, satellites, J_{SnH} = 56, 54 Hz, 6H), 0.29 (s, satellites, J_{SnH} = 54, 53 Hz, 6H), 0.93 (s, J = 7.3 Hz, 6H), 1.40-1.50 (m, 4H), 1.80 (s, satellites, J_{SnH} = 45, 15 Hz, 4H), 2.37 (s, J = 7.6 Hz, 4H); ^{13}C NMR (C$_6$D$_6$, Me$_4$Si) δ -10.26 (satellites, J_{SnC} = 319, 306 Hz), -8.26 (satellites, J_{SnC} = 303, 289 Hz), 13.52 (satellites, J_{SnC} = 306, 293, 57 Hz), 14.56, 26.28 (satellites, J_{SnC} = 17 Hz), 36.91 (satellites, J_{SnC} = 56 Hz), 139.65 (satellites, J_{SnC} = 443, 423, 47 Hz), 154.15 (satellites, J_{SnC} = 87 Hz); IR (neat) 2957, 2919, 2870, 1462, 1453, 1377, 1269, 1192, 1086, 1061, 756 cm^{-1}. HRMS calcd for $C_{16}H_{30}Sn_2$ 462.0391, found 462.0401.

3,3,7,7-Tetramethyl-6,8-dipropyl-3-germa-7-stannabicyclo[3.3.0]octa-1(8),5-diene (15). Isolated as a colorless liquid (86%); bp 98°C (1 mmHg); ^{1}H NMR (C$_6$D$_6$, Me$_4$Si) δ 0.29 (s, satellites, J_{SnH} = 55, 53 Hz, 6H), 0.30 (s, 6H), 0.92 (s, J = 7.3 Hz, 6H), 1.41-1.48 (m, 4H), 1.72 (s, satellites, J_{SnH} = 15 Hz, 4H), 2.33 (t, J = 7.6 Hz, 4H); ^{13}C NMR (C$_6$D$_6$, Me$_4$Si) δ -8.31 (satellites, J_{SnC} = 301, 288 Hz), -2.47, 14.46, 18.45 (satellites, J_{SnC} = 53 Hz), 26.12 (satellites, J_{SnC} = 16 Hz), 35.85 (satellites, J_{SnC} = 57 Hz), 139.25 (satellites, J_{SnC} = 445, 426 Hz), 153.72 (satellites, J_{SnC} = 89 Hz); IR (neat) 2961, 2928, 2915, 2872, 1462, 1455, 1377, 1237, 1103, 828, 808, 741, 606, 579 cm^{-1}. HRMS calcd for $C_{16}H_{30}GeSn$ 416.0589, found 416.0574.

1,2,3,4,6,7,8,9-Octaethyl-5-stannaspirononatetraene (16). In this case zirconacyclopentadiene (1 mmol) and $SnCl_4$ (0.13 g, 0.5 mmol) were used; otherwise, the procedure was the same. Filtration and evaporation gave a pure colorless liquid liquid (86%): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7.4 Hz, 12H), 0.92 (t, J = 7.5 Hz, 12H), 2.25 (q, J = 7.5 Hz, 8H), 2.31 (q, J = 7.5 Hz, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.66, 17.44, 22.29, 25.83, 141.39, 151.83 (satellites, J_{SnC} = 87.0 Hz); IR (neat) 2969, 2930, 2870, 1456, 1373, 1308, 1183, 1047 cm^{-1}. HRMS calcd. for $C_{24}H_{40}Sn$ 448.2150, found 448.2151.

Synthesis of Sila- and Germacycles

Method A: To a solution of diiodide (1.0 mmol) in Et_2O (5 mL) was added *t*-BuLi (4.0 mmol) at -78°C and stirred for 1 h. Then Me_2SiCl_2 (0.13 g, 1 mmol) was added and the reaction mixture was warmed up to rt and stirred for additional 1 h. All of the volatile materials were removed under reduced pressure, the product was extracted with hexane and quickly filtered over a short pad silica gel.

Method B: To a solution of diiodide (1.0 mmole) in THF (5 mL) was added *t*-BuLi (4.0 mmol) at -78°C and stirred for 1 h. After that $GeCl_4$ or $SiCl_4$ (0.5 mmol) was added and the reaction mixture was warmed up to rt and stirred for additional 12 h. Workup procedure was the same as for Method A.

(1*R,5*R**)-3,3-Diphenyl-7,7-dimethyl-3-sila-7-germabicyclo[3.3.0]octane (17).** Isolated as a colorless liquid (46%): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.27 (s, 6H), 0.40-0.46 (m, 2H), 0.74-0.80 (m, 2H), 1.32 (dd, J = 12.0, 5.1 Hz, 2H), 1.54-1.61 (m, 4H), 7.27-7.34 (m, 6H), 7.51-7.54 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.39 (2C), 21.61 (satellites, J_{SiC} = 51.2 Hz, 2C), 24.30 (2C), 50.84 (2C), 127.84 (4C), 129.14 (2C), 134.61 (4C), 137.36 (satellites, J_{SiC} = 64.4 Hz, 2C); HRMS calcd for $C_{20}H_{26}GeSi$ 368.1047, found 368.1023. IR (neat) 3020, 2935, 2885, 1427, 1273, 1118, 953, 814, 793, 728, 698, 630 cm^{-1}.

(1*R,5*R**)-3,3,7,7-Tetraphenyl-3-sila-7-germabicyclo[3.3.0]octane (18).** Isolated as a yellow solid (53%): mp 189 – 191 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.85-0.91 (m, 2H), 0.93-0.99 (m, 2H), 1.67-1.70 (m, 2H), 1.83-1.86 (m, 4H), 7.34-7.36 (m, 12H), 7.50-7.55 (m, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.60 (satellites, J_{SiC} = 51.9 Hz, 2C), 22.97 (2C), 51.21 (2C), 127.89 (4C), 128.16 (4C), 128.72 (2C), 129.27 (2C), 134.08 (4C), 134.61 (4C), 137.04 (satellites, J_{SiC} = 66.1 Hz, 2C), 138.98 (2C); HRMS calcd. for $C_{30}H_{30}GeSi$ 492.1327, found 492.1336. IR (neat) 3065, 1429, 1113, 797, 694 cm^{-1}.

1,1-Dimethyl-2,3,4,5-tetraethylgermacyclopentadiene (19). Isolated as a colorless liquid (74%): bp 65 °C (1 mmHg); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.36 (s, 6H), 0.98 (t, J =7.5 Hz, 6H), 1.05 (t, J =7.5 Hz, 6H), 2.24 (q, J =7.5 Hz, 4H), 2.35 (q, J =7.5 Hz, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -2.59, 14.93, 15.68, 20.89, 23.40, 140.73, 149.51; IR (neat) 2963, 2932, 2874, 1462, 1455, 1373, 1314, 1229, 1204, 1061, 1047, 860, 829, 804, 745, 596, 581 cm^{-1}. HRMS calcd. for $C_{14}H_{26}Ge$ 268.1254, found 268.1262.

2,2',3,3'-Tetraethyl-1,1'-germaspirobisindene (20). Isolated as a colorless viscous oil (83%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.93 (s, 6H), 2.16 (s, 6H), 7.14 (dt, *J* = 6.7, 2.1 Hz, 2H), 7.32-7.39 (m, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.96, 15.66, 121.67, 126.42, 129.63, 132.44, 133.34, 133.44, 146.70, 151.09; HRMS calcd. for $C_{20}H_{20}Ge$ 334.0776, found 334.0776. IR (neat) 3054, 2963, 2934, 2872, 1584, 1441, 1375, 1235, 1123, 1051, 862, 770, 733 cm^{-1}.

(1*R,5*R**)-3,3-Diphenyl-7,7-dimethyl-3,7-disilabicyclo[3.3.0]octane (21).** Isolated as a colorless liquid (45%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.11 (s, 6H), 0.26-0.33 (m, 2H), 0.73-0.79 (m, 2H), 1.10 (dd, *J* = 12.0, 4.7 Hz, 2H), 1.52-1.59 (m, 4H), 7.30-7.34 (m, 6H), 7.52-7.54 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -0.73 (satellites, J_{SiC} = 48.8 Hz, 2C), 21.75 (satellites, J_{SiC} = 51.9 Hz, 2C), 23.15 (satellites, J_{SiC} = 48.8 Hz, 2C), 49.89 (2C), 127.84 (4C), 129.15 (2C), 134.63 (4C), 137.36 (satellites, J_{SiC} = 65.1 Hz, 2C); HRMS calcd. for $C_{20}H_{26}Si_2$ 322.1572, found 322.1573. IR (neat) 3069, 2936, 2887, 1427, 1271, 1248, 1117, 1065, 951, 815, 791, 729, 698 cm^{-1}.

(1*R,5*R**)-3,3,7,7-Tetraphenyl-3,7-disilabicyclo[3.3.0]octane (22).** Isolated as a pale yellow solid (67%): mp 190 – 192 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.82-0.93 (m, 4H), 1.68 (dd, *J* = 14.7, 4.9 Hz, 4H), 1.81-1.88 (m, 2H), 7.33-7.38 (m, 12 H), 7.53-7.55 (m, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.76 (satellites, J_{SiC} = 50.9 Hz, 4C), 50.39 (2C), 127.89 (8C), 129.26 (4C), 134.63 (8C), 137.01 (satellites, J_{SiC} = 66.1 Hz, 4C); HRMS calcd. for $C_{30}H_{30}Si_2$ 446.1884, found 446.1886. IR (neat) 3063, 2973, 2841, 1462, 1377, 1117, 799, 735, 698 cm^{-1}.

1,1,2,3-Tetramethyl-4,5-diphenylsilacyclopentadiene (23). Isolated as a pale yellow liquid (95%): bp 143 – 145 °C/1.0 mmHg; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.30 (s, 6H), 1.64 (s, 3H), 1.91 (s, 3H), 6.80-7.30 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -4.63 (2C), 13.50, 15.27, 125.04, 126.45, 127.77 (2C), 128.03 (2C), 128.57 (2C), 129.23 (2C), 134.48, 138.43, 140.13, 140.39, 148.34, 155.02; HRMS calcd for $C_{22}H_{18}Si$ 290.1490, found 290.1474. IR (neat) 3058, 3024, 2959, 2913, 1597, 1493, 1441, 1250, 1073, 1010, 841, 774, 698 cm^{-1}.

1,1,2,3-Tetramethyl-1-silaindene (24). Isolated as a colorless liquid (98%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.00 (s, 6H), 1.69 (s, 3H), 1.78 (s, 3H), 6.91-7.40 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -4.74 (2C), 12.36, 13.44, 120.60, 125.59, 129.63, 131.13, 136.63, 137.68, 146.69, 151.43. IR (neat) 3054, 2990, 2909, 1586, 1441, 1246, 1130, 1051, 843, 745, 669 cm^{-1}; HRMS calcd for $C_{12}H_{16}Si$ 188.1020, found 188.1021.

2,2',3,3'-Tetraethyl-1,1'-silaspirobisindene (25). Isolated as a colorless solid (84%): ^{1}H NMR ($CDCl_3$,

Me_4Si) δ 1.83 (s, 6H), 2.21 (s, 6H), 7.16 (dt, *J* =7.0, 1.3 Hz, 2H), 7.26-7.45 (m, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.02, 13.73, 120.69, 126.21, 130.40, 130.76, 130.78, 132.51, 151.94, 153.47; HRMS calcd for $C_{20}H_{20}Si$ 288.1333, found 288.1311.

X-Ray structural analysis of 1,1,2,3-tetraphenyl-1-stannacyclopent-2-ene (6). A colorless prismatic crystal with dimensions of 0.20 x 0.25 x 0.30 mm was selected and mounted on a glass fiber with epoxy resin. The diffraction intensities were collected with graphite-monochromated Mo *K*α radiation (λ = 0.71069 Å) using a Rigaku AFC7R diffractometer. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout the data collection and no decay correction was applied. Absorption correction was applied to the data by a numerical integration method from the crystal shape. The Laue symmetry was shown to be 2/m, and the space group was determined from systematic absences unambiguously to be $P2_1/n$. The cell parameters were obtained from the least-squares refinement of the setting angles of 25 carefully centered reflections with 2θ in the range 29.6 - 30.0 °. The structure was solved by direct methods (SHELXS-86),[11] which revealed the position of the Sn atom. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses and refinments using the Xtal 3.2[12] software package. All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters. The hydrogen atoms were located from difference Fourier maps and refined isotropically. The full-matrix least-squares refinements (358 parameters) on 3933 independent reflections with $|Fo|>3\sigma(|Fo|)$ converged at R = 0.028 and R_w = 0.034.

Table 5. Crystallographic data of compound (**6**).

Compound	**6**
Formula	$C_{28}H_{24}Sn$
M	479.21
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
a, (Å)	14.361(1)
b, (Å)	9.993(2)
c, (Å)	17.197(1)
β, (°)	113.77(1)
Z	4
V, (Å^3)	2258.6(5)
μ(Mo *K*α), (cm^{-1})	11.4
Transm factor	0.749-0.8144
Crystal color	colorless
Crystal habit	prismatic
Crystal size, (mm^3)	0.20x0.25x0.30
D_{calcd}, (g cm^{-3})	1.41
F(000)	968

Diffractometer	Rigaku AFC7R
λ(Mo $K\alpha$), (cm^{-1})	0.71069
T, (K)	298
Scan range, (°)	$1.680+0.30\tan\theta$
Scan mode	ω-2θ
Scan speed, (° min^{-1})	8
$2\theta_{max}$, (°)	60
Reflections measd	$0\leq h\leq 18$
	$-14\leq k\leq 0$
	$-22\leq l\leq 22$
No. of reflections measd	5654
No. of reflections obsd [$\|Fo\|>3\sigma(\|Fo\|)$]	3933
No. of parameters refined	358
R	0.028
R_w	0.034
S, goodness of fit	1.43
$(\Delta/\delta)_{max}$	0.41
Largest diff peak, (e $Å^{-3}$)	0.42
Largest diff hole, (e $Å^{-3}$)	-0.50

$R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$,
$R_w=[\Sigma w||Fo|-|Fc||^2/\Sigma w|Fo|^2]^{1/2}$, $w=[\sigma^2(Fo)+\{0.015(Fo)\}^2]^{-1}$.
$S=[\Sigma w||Fo|-|Fc||^2/(m-n)]^{1/2}$ (m=no. of used reflections, n=no. of refined parameters).

ACKNOWLEDGMENT

A part of this study was supported by the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

1. (a) J. Dubac, A. Laporterie, and G. Manuel, *Chem. Rev.*, 1990, **90**, 215. (b) E. Colomer, R. J. P. Corriu, and M. Lheureux, *Chem. Rev.*, 1990, **90**, 265.
2. (a) P. J. Fagan, W. A. Nugent, and J. C. Calabrese, *J. Am. Chem. Soc.*, 1994, **116**, 1880; (b) P.J. Fagan and W. A. Nugent, *J. Am. Chem. Soc.*, 1988, **110**, 2310. See also (c) S Kim and K.H. Kim, *Tetrahedron Lett.*, 1995, **36**, 3725.
3. Y. Ura, Y. Li, Z. Xi, and T. Takahashi, *Tetrahedron Lett.*, 1998, **39**, 2787.
4. (a) A. J. Ashe III, J. W. Kampf, S. Pilotek, and R. Rousseau, *Organometallics*, 1994, **13**, 4067. (b) U. Bankwitz, H. Sohn, D. R. Powell, and R. West, *J. Organomet. Chem.*, 1995, **449**, C7. (c) W. P. Freeman, T. D. Tilley, O. M. Liable-Sands, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1996, **118**, 10457. (d) U. M. Dzhemilev, R. M. Sultanov, and R. G. Gaimaldinov, *J. Organomet. Chem.*, 1995, **491**, 1.
5. C. Xi, S. Huo, T. A. Affifi, R. Hara, and T. Takahashi, *Tetrahedron Lett.*, 1997, **38**, 4099.
6. Zirconacyclopentanes: E. Negishi, D. R. Swanson, and T. Takahashi, *Tetrahedron Lett.*, 1986, **27**, 2829.

7. Zirconacyclopentenes: (a) T. Takahashi, M. Kageyama, V. Denisov, R. Hara, and E. Negishi, *Tetrahedron Lett.*, 1993, **34**, 687. (b) See also ref. 8c.

8. Zirconacyclopentadienes: (a) see ref. 6a. (b) E. Negishi, S. J. Holms, J. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson, and T. Takahashi, *J. Am. Chem. Soc.*, 1989, **111**, 3336. (c) Z. Xi, R. Hara, and T. Takahashi, *J. Org. Chem.*, 1995, **60**, 4444.

9. The presence of CuCl is known to facilitate various reactions of zirconacycles with electrophiles, see: (a) T. Takahashi, M. Kotora, K. Kasai, and N. Suzuki, *Tetrahedron Lett.*, 1994, **35**, 5685. (b) T. Takahashi, M. Kotora, K. Kasai, and N. Suzuki, *Organometallics*, 1994, **13**, 4183. (c) K. Kasai, M. Kotora, N. Suzuki, and T. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1995, 109. (d) T. Takahashi, M. Kotora, and Z. Xi, *J. Chem. Soc., Chem. Commun.*, 1995, 361. (e) T. Takahashi, M. Kotora, and Z. Xi, *J. Chem. Soc., Chem. Commun.*, 1995, 1503. (f) B. H. Lipshutz and M. Segi, *Tetrahedron,* 1995, **51**, 4407. (g) T. Takahashi, R. Hara, Y. Nishihara, and M. Kotora, *J. Am. Chem. Soc.*, 1996, **118**, 5154. (h) T. Honda and M. Mori, *Organometallics,* 1996, **15**, 5464. (i) T. Takahashi, Z. Xi, M. Kotora, C. Xi, and K. Nakajima, *Tetrahedron Lett.*, 1996, **37**, 7521. (j) F. Dekura, T. Honda, and M. Mori, *Chem. Lett.*, 1997, 825. (l) T. Takahashi, Y. Nishihara, R. Hara, S. Huo, and M. Kotora, *Chem. Commun.*, 1997, 1599. (m) M. Kotora, C. Umeda, T. Ishida, and T. Takahashi, *Tetrahedron Lett.*, 1997, **38**, 8355. (n) T. Takahashi, Z. Xi, A. Yamazaki, Y. Liu, and M. Kotora, *J. Am. Chem. Soc.*, 1998, **120**, 1672. (o) M. Kotora, C. Xi, and T. Takahashi, *Tetrahedron Lett.*, 1998, **39**, 4321. (p) T. Takahashi, W. -H. Sun, Y. Liu, K. Nakajima, and M. Kotora, *Organometallics,* 1998, **17**, 3841.

10. (a) C. J. Rousset, D. R. Swanson, F. Lamaty, and E. Negishi, *Tetrahedron Lett.*, 1989, **30**, 5105. (b) D. R. Swanson, C. J. Rousset, E. Negishi, T. Takahashi, T. Seki, M. Saburi, and Y. Uchida, *J. Org. Chem.*, 1989, **54**, 6521. (c) T. Takahashi, T. Seki, Y. Nitto, M. Saburi, C. J. Rousset, and E. Negishi, *J. Am. Chem. Soc.*, 1991, **113**, 6266.

11. G. M. Sheldrick, *SHELXS-86, Program for Crystal Structure Determination*; University of Gottingen, Germany, 1986.

12. S. R. Hall, H. D. Flack and J.M. Stewart, *Xtal 3.2, Program for X-ray Crystal Structure Analysis*; Universities of Western Australia, Geneva, and Maryland, 1992.

Received, 23rd June, 1999