Organometallics **1990**, *9*, 3001-3003 3001

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Registry No. $CpMoCo(CO)_7$, 62015-65-0; $CpWCo(CO)_7$, 62015-64-9; $CpMoCo(CO)_5(PhC{\equiv}CPh)$, 129540-85-8; $CpMoCo(CO)_5(HC{\equiv}CH)$, 129540-86-9; $CpMoCo(CO)_5(MeOC(O)C{\equiv}CC(O)OMe)$, 129540-87-0; $CpMoCo(CO)_5(Me_3SiC{\equiv}CH)$, 129540-88-1; $CpMoCo(CO)_5(Me_3SiC{\equiv}CSiMe_3)$, 129540-89-2; $CpWCo(CO)_5(PhC{\equiv}CPh)$, 119705-21-4; $CpWCo(CO)_5(MeOC(O)C{\equiv}CC(O)OMe)$, 129540-90-5; $CpWCo(CO)_5(MeOC(O)C{\equiv}CH)$, 129540-91-6; $CpMoCo(CO)_4(HC{\equiv}CH)_2$, 129540-92-7; $CpMoCo(CO)_4(PhC{\equiv}CPh)_2\cdot CH_2Cl_2$, 129540-94-9; $CpMoCo(CO)_4(MeOC(O)C{\equiv}CH)_2$, 129540-95-0; $CpWCo(CO)_4(MeOC(O)C{\equiv}CC(O)OMe)_2$, 129540-96-1; $CpWCo(CO)_4(HC{\equiv}CH)_2$, 129540-97-2; $CpMoCo(CO)_4(PhC{\equiv}CPh)(MeOC(O)C{\equiv}CH)$, 129540-98-3; $CpMoCo(CO)_4(MeOC(O)C{\equiv}CC(O)OMe)(MeOC(O)C{\equiv}CH)$, 129540-99-4; $CpMoCo(CO)_4(PhC{\equiv}CPh)_2$, 129540-93-8; $PhC{\equiv}CPh$, 501-65-5; $HC{\equiv}CH$, 74-86-2; $MeOC(O)C{\equiv}CC(O)Me$, 762-42-5; $Me_3SiC{\equiv}CH$, 1066-54-2; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $MeOC(O)C{\equiv}CH$, 922-67-8.

Supplementary Material Available: A listing of anisotropic thermal parameters (1 page); a table of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

C-Methylated (Germacyclopentadienyl)lithium

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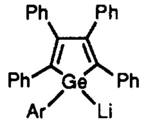
Summary: (1-Phenyl-2,3,4,5-tetramethyl-1-germacyclopentadienyl)lithium (**4**) was prepared by reaction of 1-phenyl-2,3,4,5-tetramethylgermole with *n*-butyllithium in THF/hexane at −70 °C and chemically identified by electrophilic silylation and stannylation. A ^{13}C NMR suggests that the negative charge in **4** is strongly localized on the germanium atom.

The characterization of silabenzenes[1,2] and anions derived from silacyclopentadienes,[3-5] compounds having Hückel π systems, represents important work in the area of p_π–p_π multiple bonding of the heavier main-group elements.

In the case of the silacyclopentadienide anion, the theoretical approach reveals a pyramidal ground-state structure and very low resonance energy.[6] Three silyl anions derived from C-phenylated siloles or dibenzosiloles have been characterized in solution,[3-5] but the synthesis of a C-methylated species failed.[7] Therefore, it appears that the stability of these ions requires phenyl group substituents on the ring carbon atoms. Until now, the same result has been observed for germanium chemistry; only C-phenylated derivatives of (germacyclopentadienyl)lithium (**1a–c**) were known.[8,9]



1

Ar = phenyl (**1a**),[8] tolyl (**1b**), *p*-(dimethylamino)phenyl (**1c**)[9]

We report here the characterization of the first C-methylated group 14 metallacyclopentadienide, (1-phenyl-2,3,4,5-tetramethyl-1-germacyclopentadienyl)lithium (4).

Experimental Section

The starting germole 2 has been prepared from bis(cyclopentadienyl)zirconium dichloride, 2-butyne, and germanium tetrachloride.[10]

Ether and tetrahydrofuran were freshly distilled from sodium wire and benzophenone. All manipulations were carried out under argon by using conventional Schlenk-tube techniques.

Proton and carbon NMR spectra (200 and 50.32 MHz) were recorded on a Bruker AC 200 spectrometer (δ in ppm from TMS).

1-Phenyl-2,3,4,5-tetramethylgermole (3). To 100 mL of a cooled (−70 °C) solution of 2 g (7.95 mmol) of germole 2 in dry Et_2O was added 50 mL of phenylmagnesium bromide (7.95 mmol) in Et_2O. The solution, warmed to room temperature, was stirred for 2 h and slowly added to a cooled (0 °C) suspension of 0.3 g (7.95 mmol) of $LiAlH_4$ in 20 mL of Et_2O. The mixture was stirred for 5 h. After hydrolysis and extractions (Et_2O), the organic solution was concentrated. Distillation gave 3 (1.65 g) in 80% yield: bp 102 °C (0.52 mmHg); ^1H NMR (C_6D_6) δ 1.98 and 1.80 (2 s, CMe), 5.82 (s, GeH), 7.21 and 7.55 (aromatic protons); ^{13}C NMR, see Table I; IR 2031 cm^{-1} (ν(Ge–H)); GC/MS (70 eV; *m/e*, ^{74}Ge) M^+ 260 (24), $(M - Ph)^+$ 183 (13), $(GePh)^+$ 151 (100), $(M - Ph - C_2Me_2)^+$ 129 (24). Anal. Calcd for $C_{14}H_{18}Ge$: C, 64.95; H, 7.00. Found: C, 65.0; H, 7.1.

(1-Phenyl-2,3,4,5-tetramethyl-1-germacyclopentadienyl)lithium (4) and 1-Deuterio-1-phenyl-2,3,4,5-tetramethylgermole (5). A solution of 6.4 mmol of *n*-butyllithium (1.6 M in hexane) was added dropwise to a stirred solution of 1.65 g (6.4 mmol) of hydrogermole 3 in THF (10 mL) cooled to −70 °C. A bright yellow color appeared upon initial addition of butyllithium. The mixture was stirred at −70 °C for 1 h. A solution of 4, prepared from 2 mmol of 3, in THF-d_8 was analyzed by using carbon NMR spectroscopy at −60 °C (Table I).

Deuteriolysis of an aliquot of the THF solution of 4 gives the 1-deuteriogermole 5: ^1H NMR (C_6D_6) δ 2.04 and 1.87 (2 s, CMe), 7.27 and 7.58 (aromatic protons); IR 1459 cm^{-1} (ν(Ge–D)); GC/MS (70 eV; *m/e*, ^{74}Ge) M^+ 261 (72), $(M - Ph)^+$ 184 (17), $(GePh)^+$ 151

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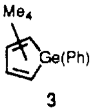
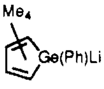
Table I. ^{13}C NMR Spectra of (Arylgermyl)lithiums Compared with Those of Neutral Arylgermanes[a,b]

	phenyl C				ethylenic ring C		
	ipso	ortho	meta	para	C_α	C_β	ref
 3	130.0	135.8	129.6	130.2	128.2	148.9	this work
 4	159.6	136.4	127.3	124.3	138.7	151.5	this work
Ph_3GeH	136.4	135.8	129.1	129.8			13
Ph_3GeLi	159.4	136.9	127.1	124.5			14b
Ph_2GeH_2	135.0	136.1	129.4	130.1			14c
Ph_2GeHLi	159.4	137.6	127.0	124.1			14a,c

[a] δ (ppm) from TMS, ν_0 = 50.32 MHz, solvent THF-d_8. [b] Like **1**, **4** is unstable at room temperature; its spectrum has been obtained at −60 °C.

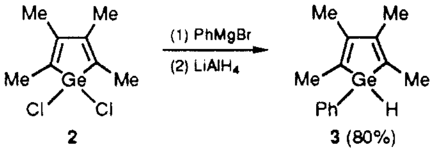
(100), $(M - Ph - C_2Me_2)^+$ 130 (19).

1-(Trimethylsilyl)-1-phenyl-2,3,4,5-tetramethylgermole (6). To a solution of **4** prepared from 0.83 g (3.2 mmol) of the hydrogermole **3** was added 1 equiv (0.35 g) of chlorotrimethylsilane in THF (2 mL). The yellow solution was decolorized and was stirred 1 h at room temperature. After removal of the solvent, pentane was added and lithium chloride eliminated by filtration. The solvent was stripped off in vacuo, and **6** (0.8 g) was obtained as a colorless liquid in 75% yield: ^1H NMR (CD_3COCD_3) δ 0.25 (s, SiMe), 1.85 and 1.99 (2 s, CMe), 7.29 and 7.42 (aromatic protons); GC/MS (70 eV; *m/e*, ^{74}Ge) M^+ 332 (36), $(M - Me)^+$ 317 (51), $(GePh)^+$ 151 (57), $(Me_3Si)^+$ 73 (100). Anal. Calcd for $C_{17}H_{26}SiGe$: C, 61.67; H, 7.91. Found: C, 61.5; H, 7.7.

1-(Trimethylstannyl)-1-phenyl-2,3,4,5-tetramethylgermole (7). By the same process as for **6**, from 0.57 g (2.2 mmol) of **3** and *n*-butyllithium (2.2 mmol), using 1 equiv of trimethyltin chloride, we obtained 0.55 g (60% yield) of stannylgermole **7** as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.42 (s, SnMe), 1.92 and 2.18 (2 s, CMe), 7.28 and 7.50 (aromatic protons). Anal. Calcd for $C_{17}H_{26}GeSn$: C, 48.42; H, 6.21. Found: C, 48.3; H, 6.1.

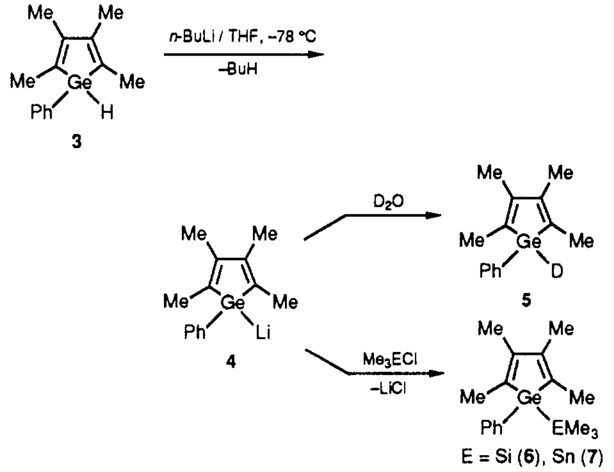
Results and Discussion

The transmetalation reaction between group 4 metallacyclopentadienes $Cp_2EC_4R_4$ (E = Ti, Zr, Hf; R = Ph, Me) and various halogermanes[10,11] leads to the corresponding germoles having germanium–halogen bonds. The precursor germole 1-phenyl-2,3,4,5-tetramethylgermole (**3**) was obtained from 1,1-dichloro-2,3,4,5-tetramethylgermole (**2**), synthesized by the reaction of $GeCl_4$ with the 1,1-bis(cyclopentadienyl)-2,3,4,5-tetramethylzirconacyclopentadiene or -hafnacyclopentadiene.[10,11] The reaction of **2** with 1 equiv of a Grignard reagent, followed by reduction, allows the synthesis of the corresponding monosubstituted derivative. While the monomethylation failed,[11] the monophenylation gave the expected germole **3** (eq 1) in good yield (80%).



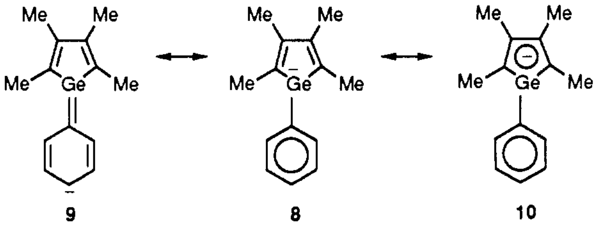
(1)

The treatment with D_2O, at the same temperature, of the yellow solution obtained gives 1-deuterio-1-phenyl-2,3,4,5-tetramethylgermole (**5**). The reaction of a THF solution of **4**, at −70 °C, with chlorotrimethylsilane or chlorotrimethylstannane leads to 1-(trimethylsilyl)-1-phenyl-2,3,4,5-tetramethylgermole (**6**) or 1-(trimethylstannyl)-1-phenyl-2,3,4,5-tetramethylgermole (**7**) in 75% and 60% yields, respectively (eq 2).



(2)

^{13}C NMR spectroscopic studies show that the delocalization of charge in phenylsilyl[12] and phenylgermyl anions[13,14] is significantly less than that found in phenyl carbanions. Therefore, a similar study of **4** would yield information on its charge distribution. Three possible forms can be envisioned: the negative charge could be localized at germanium (**8**), or it could be delocalized either at the phenyl substituent (**9**) or at the five-membered ring (**10**). The results of this study are shown in Table I.



With regard to the carbon shifts of the phenyl substituent, they are nearly the same as those observed for the phenylgermanes and their anions.[13,14] The ipso carbon resonance shifts to lower field strength (Δδ = 29.6 ppm), resulting in a decrease of electron density at this carbon atom, probably caused by the high negative charge

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localized on the germanium atom.[13] The shifts for ortho ($\Delta\delta$ = 0.6 ppm) and meta carbons ($\Delta\delta$ = −2.3 ppm) are weak. The shielding of the para carbon ($\Delta\delta$ = −5.9 ppm) has been interpreted as an increase in π-electron density at this position corresponding to the resonance form **9** or to a polarization of the phenyl ring by the negatively charged germanium.[13]

Moreover, the deshielding of five-membered-ring carbons C_α ($\Delta\delta$ = 10.5 ppm) and C_β ($\Delta\delta$ = 2.6 ppm) do not correspond to a delocalization of the negative charge onto the ring. The increase of the π-electron density on the ethylenic carbons in the cyclopentadienide anion, with regard to those of cyclopentadiene, leads to an important shielding ($\Delta\delta \simeq -30$ ppm).[15] The high electronic cyclic delocalization within phospholyllithiums gives a double-bond character to the ring phosphorus–carbon bonds and a shielding of the C_β ring carbons ($\Delta\delta$ = −20 ppm).[16]

Consequently, the field effect of the negatively charged germanium atom in **7** is clearly accentuated on the three neighboring carbons.

Our results demonstrate that the presence of phenyl groups on the ring carbons is not necessary to stabilize the germacyclopentadienide anion and that the negative charge is localized on the germanium atom.

Registry No. **2**, 113111-20-9; **3**, 127932-68-7; **4**, 129466-89-3; **5**, 129466-90-6; **6**, 129466-91-7; **7**, 129466-92-8; chlorotrimethylstannane, 1066-45-1.

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Formal C–C Triple-Bond Splitting in an Organopalladium Compound[1]

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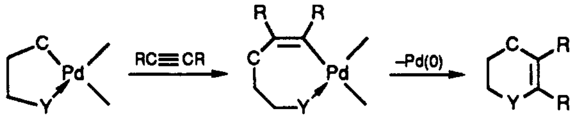
Summary: The cationic cyclopalladated compound derived from cyclometalated 2-benzylpyridine affords a heterocyclic compound containing a benzo[*b*]quinolizinium unit upon reaction with ethyl 3-phenylpropiolate through an overall C–C triple-bond cleavage of the alkyne.

It is known that the reaction between alkynes and cyclopalladated compounds can afford new synthetic pathways to heterocyclic compounds after depalladation of the organometallic intermediate.[2] This is indeed the case when one alkyne has been inserted into the Pd–C bond of the starting material, which then leads to six- or seven-membered heterocyclic rings, depending upon the size of the cyclopalladated ring. The following scheme summarizes this reaction sequence:



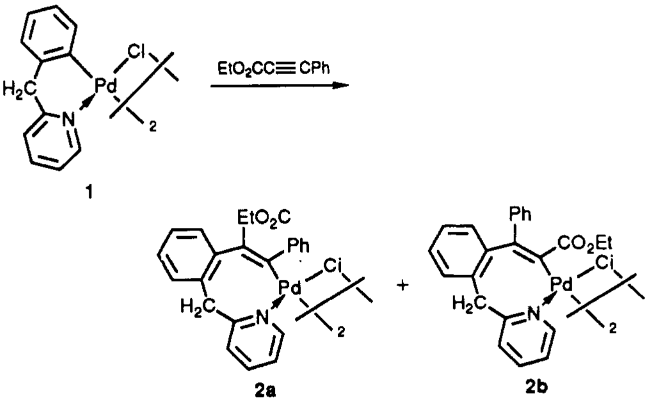
Herein we wish to report a reaction in which it is the vinyl carbon β to the palladium atom that is linked to the nitrogen, and hence, this result might shed some light on the depalladation process of the reaction described above.

Table I. Selected Bond Lengths (Å) for Compound 4[a]

N-C1	1.454 (7)	C7-C8	1.424 (8)	B-F2	1.347 (7)
N-C5	1.446 (7)	C7-C12	1.385 (7)	B-F3	1.368 (7)
N-C13	1.429 (7)	C8-C9	1.322 (8)	B-F4	1.333 (7)
C1-C2	1.348 (7)	C9-C10	1.406 (8)	C14-C15	1.374 (7)
C2-C3	1.391 (8)	C10-C11	1.340 (7)	C14-C19	1.375 (6)
C3-C4	1.338 (9)	C11-C12	1.368 (7)	C15-C16	1.386 (7)
C4-C5	1.413 (8)	C12-C13	1.336 (6)	C16-C17	1.358 (8)
C5-C6	1.383 (8)	C13-C14	1.492 (7)	C17-C18	1.350 (8)
C6-C7	1.365 (7)	B-F1	1.346 (7)	C18-C19	1.364 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

We previously reported[3] that the cyclopalladated 2-benzylpyridine **1** leads to ring-expanded compounds when treated with internal alkynes. In contrast to related examples, the reaction with ethyl 3-phenylpropiolate afforded two isomers, **2a** and **2b**, in a 97/3 ratio:



1

2a **2b**

The reaction between the iodide derivative of **1** and alkynes allowed isolation (in low yield, however) of seven-membered heterocyclic cations, this being the result of C–N bond formation between the palladated vinyl group and the nitrogen atom of intermediates analogous to **2a**.

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