Chemistry of Heavy Carbene Analogues R_2M (M = Si, Ge, Sn). 16.[1] Reactions of Free Dimethylgermylene with Alkynes and Their Palladium Catalysis

Gilbert Billeb,[2] Hartmut Brauer,[3] Wilhelm P. Neumann,* and Markus Weisbeck

Department of Chemistry, University of Dortmund, Otto-Hahn-Strasse 6, D-4600 Dortmund 50, Germany

Received June 6, 1991

Free dimethylgermylene, Me_2Ge (1), reacts with alkynes RC≡CR′ (3) to give a multitude of four-, five-, and six-membered germaheterocycles 4–6, 8, containing one, two, or even three Ge atoms, or the acyclic 3-germapent-1-en-4-yne 7. The nature of R and R′ (H, alkyl, or aryl) determines whether 1,4-digermacyclohexa-2,5-dienes 4, 1-germacyclopenta-2,4-dienes 6, or 1,2,3-trigermacyclopent-4-enes 5 are formed. Hexafluoro-2-butyne gives the corresponding 1,2-digermacyclobut-3-ene 8. The mechanisms of product formation are discussed. Germirenes 11 or, in special cases, the digermene $Me_2Ge{=}GeMe_2$ (10) and the cyclotrigermane $(Me_2Ge)_3$ (12) are proposed as intermediates. A number of alkynes 3 which do not form isolable products with 1 give compounds 4 or 6 when catalytic amounts of $(Ph_3P)_4Pd$ are present.

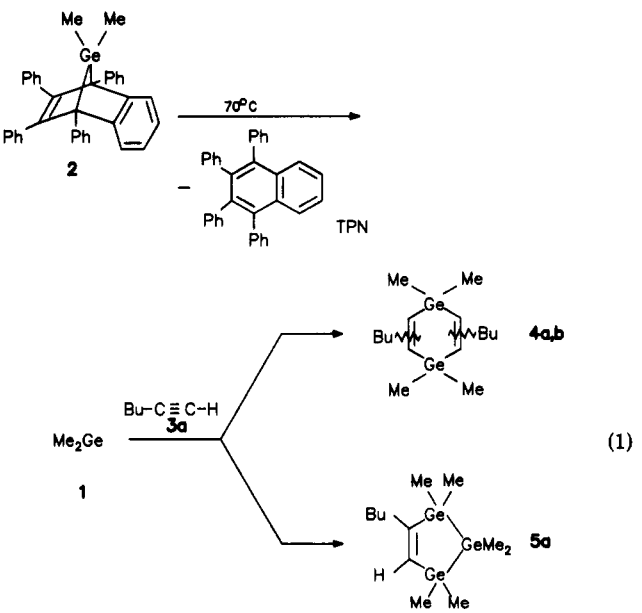
Introduction

In recent years, the heavy carbene analogues have received considerable, increasing interest.[4] For the corresponding germylenes, free dimethylgermylene, Me_2Ge (1), is a typical example, since its behavior is influenced neither by steric nor by additional electronic effects.[5] Its generation by mild thermal or photolytic cycloreversion from 2,3-benzo-7,7-dimethyl-7-germanorbornadiene (2) opened the way to numerous syntheses and mechanistic investigations. A multitude of (often cheletropic) cycloadditions to (1,4-disubstituted) 1,3-butadienes or (di-) hetero butadienes, giving (hetero-) germacyclopentenes, may be mentioned here, as well as the exclusive formation of 3,4-diphenylgermacyclopentanes on reaction with styrenes.[5] Competitive with all of these reactions of 1 is its very rapid polymerization to give $(Me_2Ge)_n$.[5] We have found that 1 inserts smoothly into the carbon–halogen bond of alkynes RC≡CX (X = Cl, Br) without an addition to the triple bond.[6]

We report here the results of our thorough studies of the reactions of terminal and internal alkynes, RC≡CR′ (3), with 1. Depending on R and R′, and on the reaction conditions, a surprising variety of germanium heterocycles containing one, two, or even three Me_2Ge units,[7] many of them novel, or acyclic germanium compounds were obtained as products, or nothing at all.

Results and Discussion

I. Reactions with Acetylene and Mono- and Disubstituted Alkynes. Me_2Ge (1), thermally generated from 2,[5] reacted with hexyne-1 (3a; 40-fold excess) to give a mixture of 2,6- and 2,5-dibutyl derivatives 4a,b in 50% yield. Apparently a sequence of reaction steps is involved, one of them not being regioselective.[7a] When a smaller excess of 3a was used, the 1,2,3-trigermacyclopentene 5a, a novel type of germanium heterocycle, was obtained as the only product (eq 1).



(1)

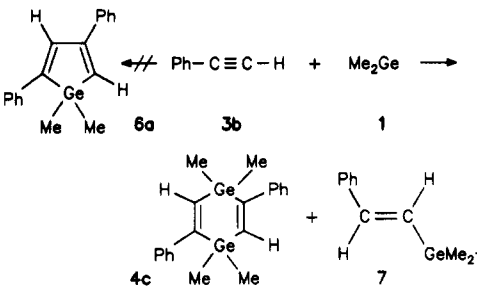
With phenylacetylene (3b) the 2,5-diphenyl derivative 4c was generated regioselectively, but not the 2,4-diphenyl derivative 6a, as had been concluded from preliminary results.[7a] Surprisingly, the other product had the same composition as 6a but was found to be the acyclic 3-germapent-1-en-4-yne 7 (eq 2). The 4c:7 ratio depends on the reactant stoichiometry, 4c being highly favored when a 1:1 molar ratio of 2 and 3b was used, whereas 7 was

Table I. Reaction between Me_2Ge and PhC≡CH (Eq 2)

	starting material		yield/%		
T/°C	[2]/mmol	[3b]/mmol	4c	7	overall yield/%
140	0.32	9.8	3	82	85
140	0.17	0.98	11	74	85
140	0.11	0.23	17	68	81
100	0.32	9.8	7	79	82
100	0.17	0.98	12	73	81
100	0.11	0.23	21	64	81
70	0.32	9.8	5	80	83
70	0.17	0.98	21	64	81
70	0.11	0.23	63	22	80
70	0.11	0.11	78	7	68

(1) Part 15: Billeb, G.; Bootz, K.; Neumann, W. P.; Steinhoff, G. *J. Organomet. Chem.* **1991**, *406*, 303.
(2) Billeb, G. Dr. rer. nat. Thesis, University of Dortmund, 1990.
(3) Brauer, H. Dr. rer. nat. Thesis, University of Dortmund, 1991.
(4) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, p 333.
(5) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311.
(6) Billeb, G.; Brauer, H.; Maslow, S.; Neumann, W. P. *J. Organomet. Chem.* **1989**, *373*, 11.
(7) Parts of our results have been reported in short, preliminary form: (a) Billeb, G.; Neumann, W. P.; Steinhoff, G. *Tetrahedron Lett.* **1988**, *29*, 5245. (b) Billeb, G.; Brauer, H.; Neumann, W. P. *Synlett* **1990**, 113. (c) Brauer, H.; Neumann, W. P. *Synlett* **1991**, 431.

0276-7333/92/2311-2069$03.00/0

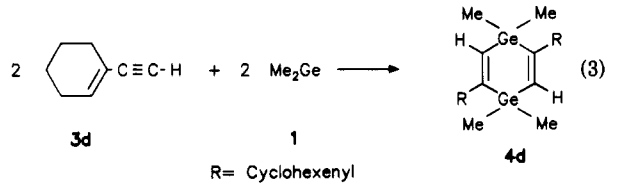


(2)

formed nearly exclusively when a large excess of **3b** was used (eq 2 and Table I).

Electron-releasing substituents in the alkyne retard the formation of cycloadducts **4**, which favors the polymerization of **1**. (4-Methylphenyl)acetylene (**3c**) gave neither a product of type **4**, as phenylacetylene does, nor the germacyclopentadiene **6** (eq 8). (4-Methoxyphenyl)-acetylene is completely unreactive, and only $(Me_2Ge)_n$ was formed. This provides further evidence for the nucleophilic character of **1** in such cycloadditions, as we had found in the case of 1,3-dienes.[8] An additional, even slight, steric hindrance as in (2-methylphenyl)acetylene also prevented any reaction with **1**.

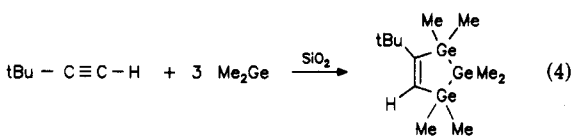
With 1-cyclohexenylacetylene (**3d**) an intermediate germirene might be expected to be stabilized (section II), but we could detect and isolate only **4d**, the product of a strictly regioselective reaction (eq 3).



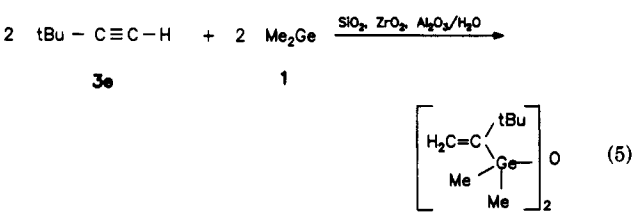
(3)

α,β-Unsaturated alkynes with a carbonyl or ester function adjacent to the triple bond, such as HC≡CCHO, HC≡CCOMe, or HC≡CCOOMe, gave no isolable products with **1**.

Under the usual conditions, neohexyne (**3e**) gave no detectable product with **1**. However, in the presence of a special, carefully dried silica gel, another member of the exotic trigermacyclopentenes, **5b**, was produced quantitatively (eq 4). Several other silica gels or ZrO_2 or Al_2O_3, none of which were anhydrous, however, produced a completely different reaction with participation of water (eq 5).[3,9]

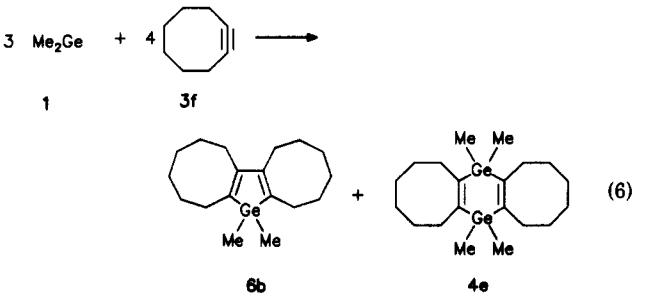


(4)

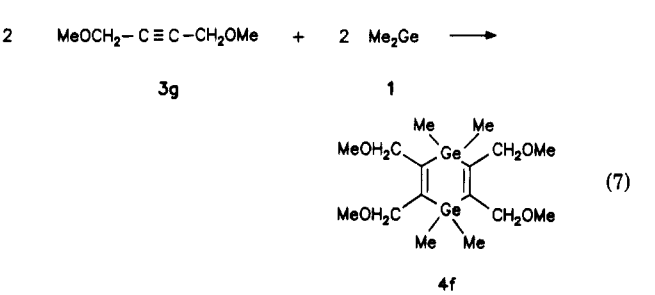


(5)

A number of disubstituted alkynes such as MeC≡CMe, PhC≡CMe, PhC≡CCO_2Me, PhC≡CCOMe, PhC≡CCOPh, PhC≡CCN, and MeC≡CCO_2Me did not yield stable adducts with **1**. However, the strained cyclooctyne **3f** did react, giving a mixture of **4e** and **6b** in good yield (eq 6). Also, the symmetrical methoxy-substituted alkyne **3g** reacted to give the cycloadduct **4f** (eq 7). The effect



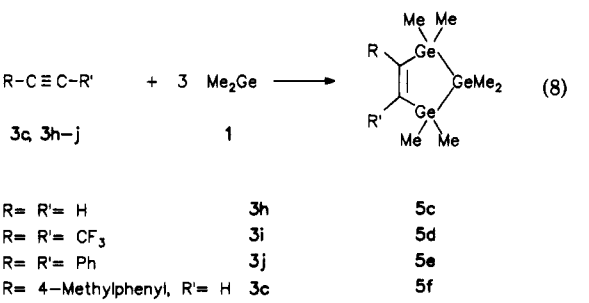
(6)



(7)

of the ether groups cannot involve simply an enhancement of the π-electron density of the triple bond, since such effects, as noted above, would lower the reactivity. We assume that in this case the lifetime of **1** is prolonged by complexation with the donor.[10]

Results with other alkynes **3c,h–j** are summarized in eq 8. Acetylene itself (**3h**) gave a good yield of the 1,2,3-



(8)

R= R'= H	3h	5c
R= R'= CF_3	3i	5d
R= R'= Ph	3j	5e
R= 4–Methylphenyl, R'= H	3c	5f

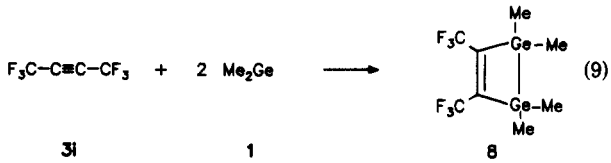
trigermacyclopentene **5c**, which is stable in C_6D_6 at room temperature. The strongly electron-deficient hexafluorobutyne-2 (**3i**) gave **5d**. With PhC≡CPh (**3j**) under these conditions, unexpectedly the trigermacyclopentene **5e** was formed,[11] whereas in earlier experiments under different conditions the 1,4-digermacyclohexadiene **4** was found.[12] (4-Methylphenyl)acetylene (**3c**) yielded, in contrast to phenylacetylene itself (eq 2), also the trigermacyclopentene **5f** (eq 8).

The high reactivity of **3i** no doubt results from the electron deficiency in the triple bond, the CF_3 substituent being one of the most electronegative groups. The Me group in MeC≡CMe (**3k**) has nearly the same steric requirements as the CF_3 group,[13] but as a +I effect donor, Me renders **3k** inert toward **1**. The germylene **1** is again a nucleophile here, as in other cases.[5,8]

The nature of the product formed on reaction of **1** with **3i** depends on the concentration of the latter. When **3i**

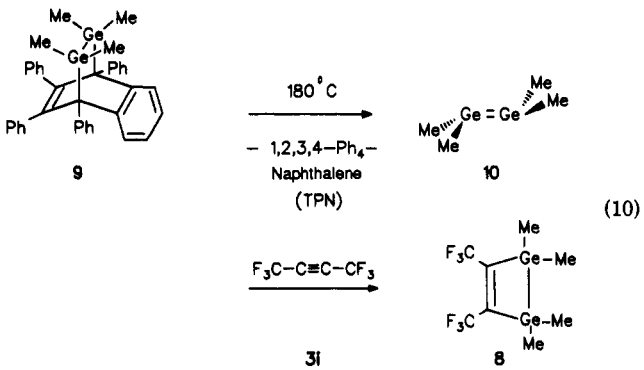
(8) Köcher, J.; Neumann, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 3861.
(9) (a) Neumann, W. P.; Sakurai, H.; Billeb, G.; Brauer, H.; Köcher, J.; Viebahn, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1028. (b) A detailed report will be given elsewhere: Brauer, H; Klein, B.; Neumann, W. P.; Wienken, S. Manuscript in preparation.
(10) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.
(11) Weisbeck, M. Diploma Thesis, University of Dortmund, 1991.
(12) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897.
(13) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284.

was used in large excess, the strained 1,2-digermacyclobutene 8 (eq 9) was produced rather than **5d**.



3i 1 8 (9)

II. Mechanistic Considerations. At first sight, it is difficult to understand the variety of products 4–8 (Scheme I). An insight is offered by the four-membered ring 8, generated only when a large excess of the alkyne **3i** was used. 8 did not insert 1 to give **5d**, when more 1 was generated in the presence of 8. On the other hand, **5d** did not extrude a Me_2Ge unit to give 8 under identical conditions. Therefore, 8 cannot be the precursor of **5d** and vice versa: Independent mechanisms are in operation when 1 and **3i** are reacted to give 8 or (if the formation of 8 is suppressed by lowering the concentration of **3i**) to give **5d** (Scheme I). 8 is stable under our conditions; it does not extrude a Me_2Ge unit. It is assumed, therefore, not to be a product of 1 itself (eq 9) but of tetramethyldigermene, $Me_2Ge{=}GeMe_2$ (**10**), generated by rapid dimerization of 1, and trapped by a very high concentration of **3i**. In fact, 8 has been formed by reaction of the independent, unequivocal digermene precursor **9**[14] and **3i** (eq 10). Moreover, **10** can be regarded as a nucleophile toward alkynes **3**, since no four-membered cyclic products such as 8 could be detected with **3c,h,j,k** (eq 8).



9 10 3i 8 (10)

This does not exclude a shortlived adduct of 1 to **3i** (Scheme I), **11**, which can be a germirene or a π–complex, prolonging the lifetime of 1. We have no direct evidence for **11**, but a sterically hindered germirene is stable.[15]

5d is not a product of 8 and, hence, not a product of $Me_2Ge{:}GeMe_2$ (**10**). It was formed only when the concentration of **3i** was much lower and, therefore, also the scavenging rate of **10** by **3i**. A consecutive product of **10** has to be considered as a precursor for **5d**. A reasonable one is the cyclotrigermane **12** (Scheme I), perhaps generated via reaction of **10** with additional 1. We have not been able to detect **12** directly so far. However, the formation of a stable cyclotrigermane has been established when it is strongly sterically hindered.[16] When **12** is not trapped by an alkyne **3**, it finally forms $(Me_2Ge)_n$.

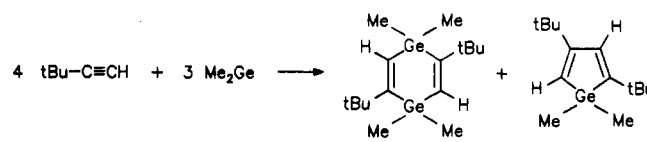
With a large excess of phenylacetylene (**3b**), the 3-germapent-1-en-4-yne **7** was found (eq 2 and Scheme I). This seems to be the product of an insertion of 1 into the H–alkyne bond, not observed so far, and a hydrogermylation of a second molecule of **3b**.[9b] When **2**, the precursor of 1, and **3b** were used in equimolar amounts (eq 2 and Table I), the six-membered-ring species **4c** has been found to be predominant between 70 and 140 °C. The less acidic alkynes **3a,d** exhibited no C–H reactivity under these conditions but yielded the product **4**, sometimes in competition with the formation of **5**. The sterically hindered alkynes (2-methylphenyl, tBu in **3e**) gave no products under the same conditions. Only in the presence of a special silica gel (eq 4) has **3e** produced **5b**.

It is reasonable to assume the common intermediate **11**, which dimerizes to give **4a–f**. On the other hand, **11** inserts into **3**, when available and highly reactive, to give a germacyclopentadiene (eq 6). The latter process resembles the 1,2-insertion of unsaturated compounds into silylene adducts of alkenes or alkynes.[17]

Each arrow in Scheme I indicates a specific rate constant depending on R and R′ in the alkyne **3**. Thus, for example, 1-hexyne (**3a**) only when it is in large excess can scavenge Me_2Ge (1) to give **4a,b** (via **11**), whereas lower concentrations of **3a** favored the di- and trimerization of 1, and the (assumed) cyclotrigermane **12** finally reacts to give **5a**. Electron-deficient alkynes in general are more reactive than others. n- or π-Donor substituents such as MeO or aryl in the substrate can form an intermediate complex with 1 via donation into the vacant p orbital of the latter,[5,10] thus lowering the polymerization rate of 1. This can increase the product formation in cases of slower additions.

These mechanistic considerations clearly are not a closed case, because of the reasons indicated. Additional investigations are needed. However, Scheme I is, at this point of development, a reasonable presentation of what happens. It is in accordance with all the facts we have at hand, and no contradiction is found.

III. Palladium Catalysis. Many alkynes gave no detectable products with 1; the polymerization of the latter won the competition. One example is neohexyne (**3e**), which formed no stable product with 1 spontaneously. In the presence of a special, carefully preheated silica gel, **3e** yielded **5b** (eq 4). However, when we added catalytic amounts of $Pd(PPh_3)_4$ to **3e**, and generated 1 from **2** in the mixture, a good yield of **4g** and **6c** could be isolated (eq 11). **4g**, the main product, is formed regioselectively; no



3e 1 4g 6c

ratio 4 : 1 (11)

2,6-$(tBu)_2$ isomer could be detected. This is an additional argument for the origin of products **4** from the transient precursor **11** via dimerization (Scheme I). **6c** is also the only isomer; 2,5- and 3,4-disubstituted germacyclopentadienes have not been detected.

The other alkynes we investigated form exclusively compounds **6** (eq 12). Again, the 2,4-disubstituted ring is obtained regioselectively. Only with **3a** (R = Bu) have the other isomers **6e,f** been found in small amounts.

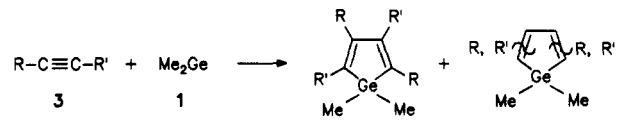
The only example of a Pd-catalyzed addition of the germylene R_2Ge (R = mesityl, nBu) to an alkyne we found

(14) Bleckmann, P.; Maly, H.; Minkwitz, R.; Neumann, W. P.; Watta, B.; Olbrich, G. *Tetrahedron Lett.* **1982**, *23*, 4655.

(15) (a) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083. (b) Egorov, M. P.; Kolesnikow, S. P.; Struchkov, Yu. T.; Anitipin, M. Yu.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27.

(16) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem.* **1991**, *103*, 916; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902 and references therein.

(17) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5.



R= Bu, R'= H	3a	6d	6e, 6f
R= 2-Methylphenyl, R'= H	3l	6g	
R= CO_2Me, R'= Me	3m	6h	
R= CO_2Et, R'= Ph	3n	6i	
R= R'= Ph	3j	6j	

(12)

in the literature concerns acetylene itself.[18]

Mechanistic considerations of the Pd catalysis may be discussed in terms of Scheme II. Routes a and b have been proposed[18] and are reasonable, because both enhance the chance of 1 to form stable products.

If we take into account the corresponding platinum–alkyne complexes,[19] an activation of the alkyne also by the Pd catalyst can be envisaged as a third possibility 1 is captured more effectively then by the complexed alkyne, 3 being more electron deficient now.

This surprising catalytic activity of Pd might be, as in other important fields of synthesis,[20] useful also for other germylene reactions.

Experimental Section

General Comments. The solvents were dried and distilled under dry argon. All reactions were carried out under dry argon. ^1H NMR spectra were taken on a 60-MHz EM-360A (Varian) or 300-MHz AM 300 spectrometer (Bruker); ^{13}C and ^{19}F NMR spectra were run with an AM 300 or AM 200 instrument (Bruker). Chemical shifts were measured against Me_4Si (^{19}F NMR, F11). Mass spectra were obtained on MAT 8230 and ITD 800 instruments (Finnigan-Mat), and elemental analyses were measured on a Carlo Erba MOD 1106 device. For preparation of 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorborna-2,5-diene (2) see ref 5. In a typical procedure 1.0 g (1.9 mmol) of 2, the alkyne 3, and 10 mL of benzene are heated at 70 °C for 4 h. After the volatiles are removed at 15 Torr/40 °C, 1,2,3,4-tetraphenylnaphthalene is precipitated by addition of 10 mL of pentane. The products are purified by Kugelrohr distillation.

Preparation of 1,1,4,4-Tetramethyl-2,5-dibutyl-1,4-digermacyclohexa-2,4-diene (4a) and 1,1,4,4-Tetramethyl-3,5-dibutyl-1,4-digermacyclohexa-2,5-diene (4b). The reactions were carried out without any solvent: 1.0 g (1.9 mmol) of 2, 10.0 mL (85.0 mmol) of **3a**, T = 70 °C, t = 4 h; bp 70–80 °C/0.01 Torr, yield 170 mg (50%), ratio 1:1 **4a:4b**; ^1H NMR (C_6H_6) δ −0.30 (s, 6 H, GeMe), −0.23 (s, 12 H, GeMe), −0.10 (s, 6 H, GeMe), 0.30–0.50 (m, 12 H, Me), 0.5–1.0 (m, 16 H, CH_2), 1.5–1.9 (m, 8 H, CH_2); ^{13}C NMR ($CDCl_3$) δ −1.5, −1.1, 1.8 ($GeMe_2$), 13.9 (CH_3), 22.4, 30.8, 31.0, 40.9 (CH_2), 138.3 (CH), 138.9 (CH), 161.7 (C=C), 162.1 (C=C); MS m/e (relative intensity) 370 (12, M^+), 355 (100, M^+ − Me), 104 (15, $GeMe_2$), 89 (10, GeMe). Anal. Calcd for $C_{16}H_{32}Ge_2$: C, 52.0; H, 8.66. Found: C, 51.8; H, 8.5.

Preparation of 1,1,2,2,3,3-Hexamethyl-4-butyl-1,2,3-trigermacyclopent-4-ene (5a): 1.0 g (1.9 mmol) of 2, 89 μL (0.80 mmol) of **3a**, 10 mL of benzene, T = 75 °C, t = 3 h; bp 100 °C/0.02 Torr, yield 120 mg (50%); ^1H NMR ($CDCl_3$) δ 0.28, 0.31, 0.38 (each s, each 6 H, GeMe), 0.89 (m, 3 H, Me), 1.35 (m, 4 H, CH_2), 2.39 (m, 2 H, CH_2), 6.75 (m, 1 H, HC=); ^{13}C NMR ($CDCl_3$) δ −7.45, −2.34, −2.17 (GeMe), 14.04 (Me), 22.58, 31.39, 39.31 (CH_2), 142.61 (HC=), 165.79 (C=, Cq); MS m/e (relative intensity) 390 (94, M^+), 375 (100, M^+ − Me), 308 (70, Ge_3Me_6), 207 (19, Ge_2Me_4). Anal. Calcd for $C_{12}H_{28}Ge_3$: C, 36.9; H, 7.2. Found: C, 37.0; H, 7.1.

Preparation of 1,1,4,4-Tetramethyl-2,5-diphenyl-1,4-digermacyclohexa-2,5-diene (4c): 1.0 g (1.9 mmol) of 2, 160 μL (2.0 mmol) of **3b**, 10 mL of benzene, T = 70 °C, t = 4 h; bp 150–180 °C/0.02 Torr; ^1H NMR (CCl_4) δ 0.48 (s, 6 H, GeMe), 6.9 (s, 1 H, HC=), 7.3 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ −0.24 ($GeMe_2$), 128.29 (CH, Ph), 128.84 (CH, Ph), 130.50 (CH, Ph), 144.02 (Cq, Ph), 145.57 (CH), 160.02 (C=C); MS m/e (relative intensity) 410 (7, M^+), 395 (9, M^+ − Me), 104 (19, $GeMe_2$), 77 (25, Ph); HRMS (EI) m/e calcd for M^+ ($C_{20}H_{24}Ge_2$) 410.0909, found 410.0911.

Preparation of (*E*)-3,3-Dimethyl-1,5-diphenyl-3-germapent-1-en-4-yne (7): 1.0 g (1.9 mmol) of 2, 6.1 mL (57 mmol) of **3b**, T = 140 °C, t = 2 h; ^1H NMR (300 MHz, $CDCl_3$) δ 0.59 (s, 6 H, $GeMe_2$), 6.66 (d, ^2J = 18.6 Hz, 1 H, CH), 7.06 (d, ^2J = 18.6 Hz, 1 H, CH), 7.29–7.35 (m, 5 H, Ph), 7.46–7.52 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ −1.0 ($GeMe_2$), 92.45 (C=C, 105.26 (C=C), 123.31 (Cq, Ph), 126.46, 126.60 (CH, Ph), 128.10, 128.14, 128.25, 128.49 (CH, Ph), 131.92 (CH), 137.73 (Cq, Ph), 143.97 (CH); HRMS (EI) m/e calcd for M^+ ($C_{18}H_{18}Ge$) 307.0555, found 307.0548.

Preparation of 1,1,4,4-Tetramethyl-2,5-bis(1-cyclohexenyl)-1,4-digermacyclohexa-2,5-diene (4d): 1.0 g (1.9 mmol) of 2, 0.42 g (4.0 mmol) of **3d**, T = 72 °C, t = 4 h, 5 mL of benzene; bp 125 °C/0.01 Torr, yield 170 mg (43%); ^1H NMR ($CDCl_3$) δ 0.45 (s, 12 H, GeMe), 1.67 (m, CH_2, 8 H), 2.20 (m, CH_2, 8 H), 5.77 (m, 2 H, HC=), 6.53 (m, 2 H, HC=); ^{13}C NMR ($CDCl_3$) δ −2.11 ($GeMe_2$), 22.42, 23.20, 26.26, 27.25 (CH_2), 127.77 (CH), 139.83 (C=C), 142.05 (CH), 164.48 (C=C); MS m/e (relative intensity) 418 (100, M^+), 403 (55, M^+ − Me), 316 (97, M^+ − $GeMe_2$). Anal. Calcd for $C_{20}H_{32}Ge_2$: C, 57,5; H, 7.7. Found: C, 57.7; H, 7.8.

Preparation of 1,1,2,2,3,3-Hexamethyl-4-*tert*-butyl-1,2,3-trigermacyclopent-4-ene (5b): 1.0 g (1.9 mmol) of 2, 2.0 mL (16.2 mmol) of **3e**, 10 mL of benzene, 1.0 g of SiO_2 (silica gel 545, Nagel & Co.), SiO_2 was pre-heated five times at 150 °C/0.001 Torr, T = 70 °C, t = 4 h, bp 110–130 °C/0.01 Torr, yield 170 mg (68%); ^1H NMR (C_6D_6) δ −0.75, −0.03, 0.68 (each s, each 6 H, GeMe), 0.71 (s, 9 H, tBu), 6.42 (s, 1 H, HC=); ^{13}C NMR ($CDCl_3$) δ −7.66 ($GeMe_2$), −2.15 ($GeMe_2$), 1.42 ($GeMe_2$), 31.32 (CH_3, tBu), 40.55 (Cq, tBu), 139.84 (CH), 173 (C=C); GC–MS m/e (relative intensity) 390 (37, M^+), 375 (30, M^+ − Me), 206 (16, Ge_2Me_4). Anal. Calcd for $C_{12}H_{28}Ge_3$: C, 36.9; H, 7.2. Found: C, 37.1; H, 7.2.

Preparation of 1,1-Dimethyl-2,3:4,5-bis(hexamethylene)-1-germacyclopenta-2,4-diene (6b) and 1,1,4,4-Tetramethyl-2,3:5,6-bis(hexamethylene)-1,4-digermacyclohexa-2,5-diene (4e): 1.0 g (1.9 mmol) of 2, 0.4 mL (4.6 mmol) of **3f**, T = 70 °C, t = 4 h, 20 mL of benzene bp 160–180 °C/0.02 Torr, yield 0.2 g (54%), ratio 3:7 **6b:4e**; ^1H NMR (CCl_4) δ 0.21 (s, 12 H, GeMe), 0.28 (s, 6 H, GeMe), 1.47 (m, 32 H, CH_2), 2.4 (m, 16 H, CH_2); ^{13}C NMR ($CDCl_3$) δ **6b** −4.11 ($GeMe_2$), 25.6, 26.3, 27.0, 29.0, 29.5, 30.7 (CH_2), 139.1, 149.1 (C=C), **4e** −1.3 (GeMe), 26.6, 29.7, 30.0 (CH_2), 152.8 (C=C); GC–MS m/e (relative intensity) **6b** 320 (14, M^+), 305 (24, M^+ − Me), 91 (100, $GeMeH_2$), **4e** 422 (2, M^+), 407 (54, M^+ − Me), 119 (100, $GeMe_3$).

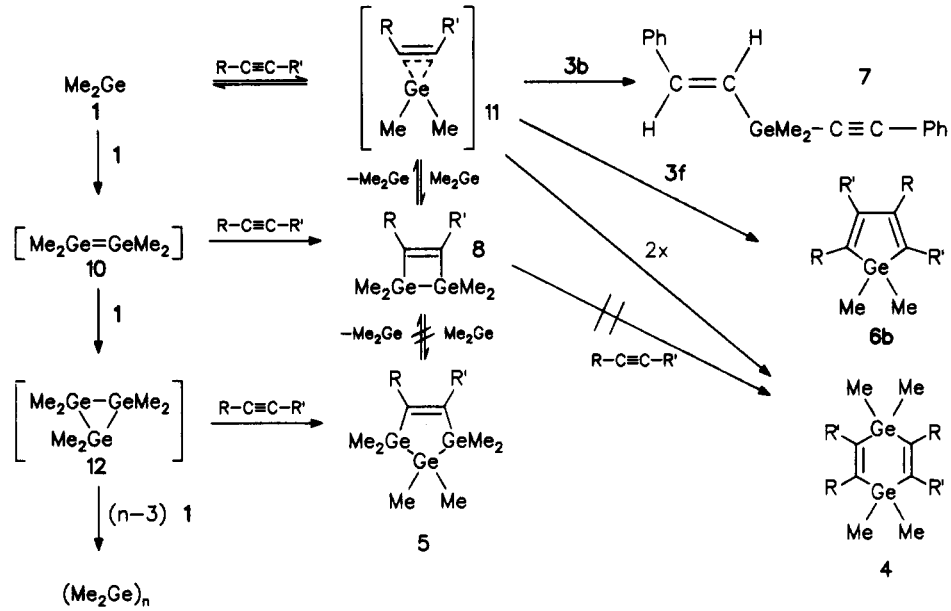
Preparation of 1,1,4,4-Tetramethyl-2,3,5,6-tetramethoxy-1,4-digermacyclohexa-2,5-diene (4f): 1.0 g (1.9 mmol) of 2, 0.45 mL (2.5 mmol) of **3g**, 15 mL of benzene, T = 70 °C, t = 4 h, bp 250 °C/0.05 Torr, yield 0.2 g (49%); ^1H NMR ($CDCl_3$) δ 0.31 (s, 12 H, GeMe), 3.23 (s, 12 H, OMe), 4.06 (s, 8 H, CH_2); ^{13}C NMR ($CDCl_3$) δ −0.48 (GeMe), 58.0 (OMe), 71.5 (CH_2), 152.3 (C=C); IR 2820 cm^{-1} (s, O–Me stretch), 1105 (vs, vb, C—O); Raman 1590 (m, C=C); MS m/e (relative intensity) 419 (30, M^+ − Me), 402 (9, M^+ − OMe), 135 (100, Me_3GeO). Anal. Calcd for $C_{16}H_{32}O_4Ge_2$: C, 44.2; H, 7.4. Found: C, 44.4; H, 7.5.

Preparation of 1,1,2,2,3,3-Hexamethyl-1,2,3-trigermacyclopent-4-ene (5c): 1.0 g (1.9 mmol) of 2, 1.2 bar of **3h**, 10 mL of benzene, T = 72 °C, t = 4 h, bp 50 °C/0.02 Torr, yield 270 mg (42%); ^1H NMR (300 MHz, C_6D_6) δ 0.38 (s, 6 H, $GeMe_2$), 0.41 (s, 3 H, $GeMe_2$), 7.15 (s, 2 H, CH); ^{13}C NMR (C_6D_6) δ −8 ($GeMe_2$), −2.2 ($GeMe_2$), 152.9 (CH=CH); GC–MS m/e (relative intensity) 334 (48, M^+), 319 (57, M^+ − Me), 119 (100, $GeMe_3$) (an analogous product has been found by reaction of 7.7-dibutyl substituted 7-germanorbornadiene with acetylene).[18] Anal. Calcd for $C_8H_{20}Ge_3$: C, 28.8; H, 5.9. Found: C, 29.0; H, 5.9.

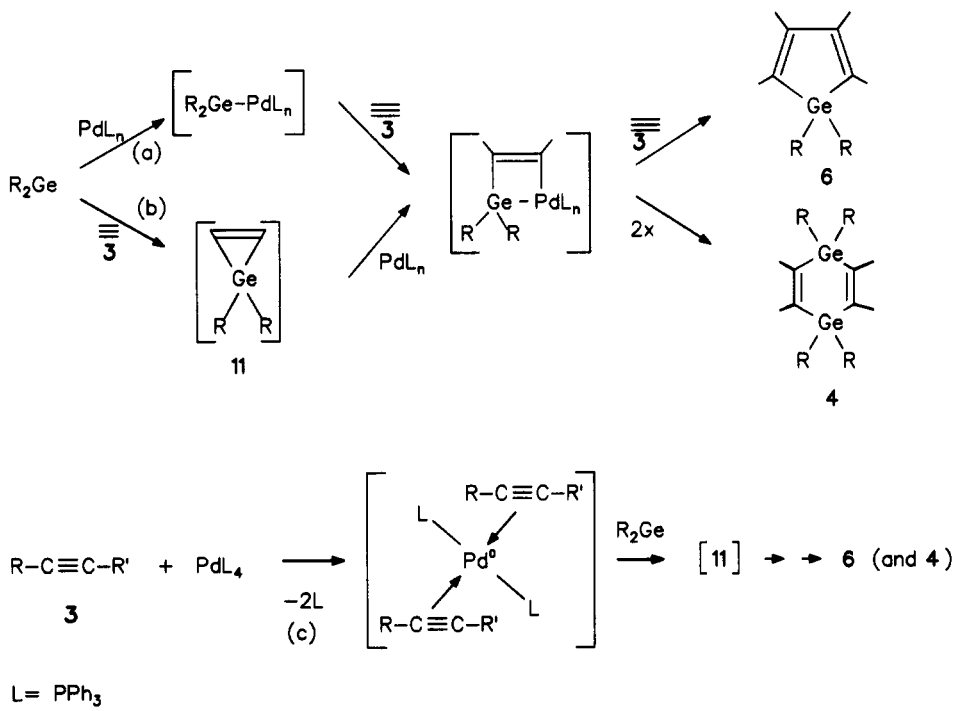
Preparation of 1,1,2,2,3,3-Hexamethyl-3,4-bis(trifluoromethyl)-1,2,3-trigermacyclopent-4-ene (5d) (sealed tube): 1.0

(18) Tsumuraya, T.; Ando, W. *Organometallics* **1990**, *9*, 869.
(19) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.
(20) (a) Fujiwara, Y.; Jintoku, T.; Takaki, K. *CHEMTECH* **1990**, 636. (b) Tsuji, J. *Synthesis* **1990**, 739.

Scheme I



Scheme II



g (1.9 mmol) of **2**, 0.16 g (1.0 mmol) of **3i**, 1 mL of benzene, T = 72 °C, t : 4 h, bp 30 °C/0.01 Torr, yield 120 mg (40%); ^{1}H NMR ($CDCl_3$) δ 0.47 (s, 12 H, GeMe), 0.54 (s, 6 H, GeMe); ^{13}C NMR ($CDCl_3$) δ -7.82, -1.03 (GeMe), 124.05 (CF_3, $^1J(^{13}C-^{19}F)$ = 281.9 Hz), 160.87 (Cq, $^2J(^{13}C-^{19}F)$ = 37.8 Hz); ^{19}F NMR ($CDCl_3$) δ -53.63 (s, CF_3); GC–MS m/e (relative intensity) 470 (20, M^+), 349 (13, M1+ - $GeMe_2F$), 119 (100, $GeMe_3$). Anal. Calcd for $C_{10}H_{18}Ge_3F_6$: C, 25.6; H, 3.8. Found: C, 25.7; H, 3.9.

Reaction between 1 and 3j To Give 1,1,2,2,3,3-Hexamethyl-3,4-diphenyl-1,2,3-trigermacyclopent-4-ene (5e): 1.0 g (1.9 mmol) of **2**, 0.72 g (4.0 mmol) of **3j**, 6 mL of C_6H_5Cl, T = 125 °C, t = 1 h; ^{1}H NMR (C_6D_6) δ 0.1 (s, 6 H, GeMe), 0.22 (s, 3 H, GeMe), 6.7 (m, 10 H, Ph); MS m/e (relative intensity) 486 (48, M^+), 471 (10, M^+ - Me), 308 (84, Ge_3Me_6), 119 (100, $GeMe_3$); Raman ν_s(Ge–Ge) = 242 cm^{-1}, ν_{as}(Ge–Ge) = 308 cm^{-1}.[11]

Preparation of 1,1,2,2,3,3-Hexamethyl-4-(4-methylphenyl)-1,2,3-trigermacyclopent-4-ene (5f): 1.0 g (1.9 mmol) of **2**, 0.45 g (3.8 mmol) of **3c**, 10 mL of benzene, T = 80 °C, t = 3 h, bp 130 °C/0.05 Torr, yield 80 mg (30%); ^{1}H NMR (300 MHz, C_6D_6) δ 0.44 (s, 6 H, $GeMe_2$), 0.45 (s, 6 H, $GeMe_2$), 0.51 (s, 6 H, $GeMe_2$), 2.14 (s, 3 H, CH_3), 7.02, 7.04 (d, ^2J = 7.8 Hz, 2 H, Ph), 7.26 (s, 1 H, CH), 7.31, 7.34 (d, ^2J = 7.8 Hz, 2 H, Ph); ^{13}C NMR (C_6D_6) δ -7.26 ($GeMe_2$), -2.03 ($GeMe_2$), -1.13 ($GeMe_2$), 21.10 (CH_3), 126.80 (CH, Ph), 129.29 (CH, Ph), 136.09 (Cq, Ph), 143.47 (Cq, Ph), 147.49 (CH), 164.92 (C=C); MS m/e (relative intensity) 424 (52, M^+), 308 (58, Ge_3Me_6), 119 (100, $GeMe_3$), 89 (22, GeMe); HRMS (EI) m/e calcd for M^+ ($C_{15}H_{26}Ge_3$) 424.0393, found 424.0382. Anal. Calcd for $C_{15}H_{26}Ge_3$: C, 42.5; H, 6.1. Found: C, 42.6; H, 6.0.

Preparation of 1,1,2,2-Tetramethyl-3,4-bis(trifluoromethyl)-1,2-digermacyclobut-3-ene (8) (sealed tube): 1.0 g (1.9 mmol) of **2**, 1.0 g (6.3 mmol) of **3i**, 3 mL of benzene, T = 74 °C, t : 4 h (1.0 g (1.5 mmol) of **9**, 1.0 g (6.3 mmol) of **3i**, 1 mL of benzene, T = 180 °C, t = 18 h), bp 23 °C/0.01 Torr, yield 210 mg (30%); ^{1}H NMR (C_6D_6) δ -20 (s, GeMe); ^{1}H NMR ($CDCl_3$) δ 0.73 (s, GeMe); ^{13}C NMR ($CDCl_3$) δ -1.82 (GeMe), 121.48 (CF_3, $^1J(^{13}C-^{19}F)$ = 275.5 Hz), 158.4 (Cq, $^2J(^{13}C-^{19}F)$ = 39.4 Hz); GC–MS m/e (relative intensity) 353 (100, M^+ - Me), 207 (27, Ge_2Me_4).

Anal. Calcd for $C_6H_{12}F_6Ge_2$: C, 26.2; H, 3.2. Found: C, 26.6; H, 2.9.

Preparation of 1,1,4,4-Tetramethyl-2,5-di-*tert*-butyl-1,4-digermacyclohexa-2,5-diene (4g) and 1,1-Dimethyl-2,4-di-*tert*-butyl-1-germacyclopenta-2,4-diene (6c): 1.0 g (1.9 mmol) of **2**, 0.47 g (5.7 mmol) of **3e**, 0.3 g (0.26 mmol) of $Pd(PPh_3)_4$, 10 mL of benzene, T = 72 °C, t = 4 h, bp 140 °C/0.01 Torr, ratio 8:2 **4g:6c**; **6c** ^{1}H NMR ($CDCl_3$) δ 0.40 (s, $GeCH_3$, 6 H), 1.08, 1.10 (each s, tBu, each 9 H), 5.48 (s, HC=, 1 H), 5.73 (s, HC=, 1 H), GC-MS (relative intensity) m/e 268 (21, M^+), 149 (100, M^+ - $GeMe_3$). **4g** ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 12 H, $GeCH_3$), 1.07 (s, tBu, 18 H), 6.37 (s, HC=, 2 H), ^{13}C NMR ($CDCl_3$) δ 2.61 ($GeCH_3$), 30.28 (CH_3, tBu), 39.76 (Cq, tBu), 137.26 (HC=), 168.82 (C=, Cq), GC-MS (relative intensity) m/e 370 (20, M^+), 355 (100, M^+ - Me).

Preparation of the Germoles 6d-j: 1.0 g (1.9 mmol) of **2**, 5.7 mmol of **3a,m,n**; 4.0 mmol of **3l**, 6.0 mmol of **3j**, 0.3 g (0.26 mmol) of $Pd(PPh_3)_4$, 10 mL of benzene, ratio **6d:6e,f** (>90% **6d**); **6d** bp 100 °C/0.02 Torr, ^{1}H NMR ($CDCl_3$) δ 0.43 (s, $GeCH_3$, 6 H), 1.02 (m, CH_3, 6 H), 1.50 (m, CH_2, 8 H), 2.35 (m, CH_2, 4 H), 5.67 (m, HC=, 1 H, ^4J(H-H) = 1.2 Hz), 6.33 (m, HC=, 1 H, ^4J(H-H) = 1.2 Hz), GC-MS (relative intensity) m/e 268 (43, M^+), 121 (100, C_9H_{13}); **6e,f** GC-MS m/e 268 (69, M^+), 105 (100, $GeMe_2H$), 269 (100, M^+); **6g** bp 130 °C/0.01 Torr, ^{1}H NMR ($CDCL_3$) δ 0.55 (s, 6 H, $GeCH_3$), 2.35 (s, 6 H, CH_3), 6.23 (d, 1 H, HC:, ^4J(H-H) = 1.2 Hz), 6.83 (d, 1 H, HC=), 7.17 (m, 8 H, Ph), ^{13}C NMR ($CDCl_3$) -2.83 ($GeCH_3$), 20.49, 21.43 (CH_3), 125.59, 125.65, 126.04, 127.16, 128.32, 129.50, 129.73, 130.19, 130.36, 132.01 (CH, Ph), 135.00, 140.01, 140.91, 141.59, 141.68, 155.90 (Cq), GC-MS m/e (relative intensity) 336 (83, M^+), 89 (100, GeMe); **6h** bp 130 °C/0.02 Torr, ^{1}H NMR ($CDCl_3$) 0.56 (s, 6 H, $GeCH_3$), 2.13, 2.40 (each s, each 3 H, CH_3), 3.78, 3.93 (each s, CH_3, each 3 H), ^{13}C NMR ($CDCl_3$) δ -4.38 ($GeCH_3$), 16.86, 17.53 (CH_3), 51.15, 51.52 ($COCH_3$), 128.24, 144.21, 154.57, 160.17 (Cq), 167.77, 167.97 (CO, Cq), GC-MS (relative intensity) m/e 300 (63, M^+), 105 (100, GeMeO); **6i** bp 200 °C/0.01 Torr, ^{1}H NMR ($CDCl_3$) δ 0.73 (s, 6 H, $GeCH_3$), 0.82, 1.09 (each t, each 3 H, CH_3, ^3J(H-H) = 7.2 Hz), 3.82, 4.03 (each q, each 2 H, CH_2), 7.30 (m, Ph, 10 H), ^{13}C NMR ($CDCl_3$) δ -3.12 ($GeCH_3$), 13.28, 13.80 (CH_3), 59.68, 60.42 (CH_2), 126.87, 127.04, 127.28, 127.50, 128.19, 128.32 (CH, Ph), 137.42, 137.57, 137.82, 143.28, 151.94, 159.78 (Cq), 166.33, 167.29 (CO, Cq), GC-MS (relative intensity) m/e 407 (29, M^+ - OEt), 105 (100, GeMeO); **6j** ^{1}H NMR ($CDCl_3$) δ 0.60 (s, 6 H, $GeCH_3$), 6.78 (m, 10 H, Ph), HRMS (EI) m/e calcd for M^+ ($C_{30}H_{26}Ge$) 460.1279, found 460.1260, mp 178 °C (179-180 °C).[21] Anal. Calcd for $C_{30}H_{26}Ge$: C, 78.4; H, 5.7. Found: C, 78.5; H, 5.7.

Acknowledgment. This research has been supported by the Fonds der Chemischen Industrie. We thank Dr. H. Hillgärtner and Mr. P. Urschel for skillful help in complicated MS and HRMS measurements and Professor Dr. J. Broekaert and Mr. M. Hüffner for special attention to and patience with elemental analyses.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for **5a,c,f** and **7** and ^{13}C NMR spectra for **4a,b** (9 pages). Ordering information is given on any current masthead page.

OM910324J

(21) Hota, N. K.; Willis, C. J. *J. Organomet. Chem.* **1968**, *15*, 89.

Chelate Control of Diphosphines around Platinum(II): η^2-Cyclenphosphoranide-Promoted Formation of Heterobimetallics

Dilip V. Khasnis, Michael Lattman,* Upali Siriwardane,[1] and Hongming Zhang

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275

Received December 5, 1991

The presence of the three-membered ring (containing nitrogen, phosphorus, and platinum) in (η^2-cyclenP)Pt square-planar complexes inhibits chelation of another small-bite bidentate ligand. Thus, (η^2-cyclenP)Pt(Cl)PPh_3 (**1**) reacts with dppe to form the bisbidentate derivative [(η^2-cyclenP)Pt(η^2-$Ph_2P(CH_2)_2PPh_2$)]Cl (**2a**), while previous work showed that reaction with dppm yielded (η^2-cyclenP)Pt(Cl)$Ph_2PCH_2PPh_2$ (**3**), where only one end of dppm is coordinated. Displacement of chloride from **3** by addition of $NaBPh_4$ leads to a mixture of compounds, one of which does appear to be the bischelate species [(η^2-cyclenP)Pt(η^2-$Ph_2PCH_2PPh_2$)]BPh_4 (**4**). Treatment of **3** with HBF_4 results in cleavage of the three-membered ring to give pure [(H_2cyclenP)Pt(Cl)(η^2-$Ph_2PCH_2PPh_2$)]$(BF_4)_2$ (**5**) in which dppm is bidentate. Restricting dppm to monodentate is useful in the formation of bridged heterobimetallic complexes with direct metal-metal bonds as shown by the reaction of **3** with Na[$Co(CO)_4$], which leads to (η^2-cyclenP)Pt[$Co(CO)_3$](μ-$Ph_2PCH_2PPh_2$) (**6**). X-ray data for **5**: $C_{33}H_{40}N_4P_3ClPt\cdot 2BF_4\cdot CH_3CN$, a = 16.113 (4) Å, b = 13.194 (5) Å, c = 20.500 (8) Å, β = 109.82 (3)°, monoclinic $P2_1/n$, Z = 4. X-ray data for **6**: $C_{36}H_{38}N_4O_3P_3CoPt\cdot C_6H_6$, a = 12.119 (4) Å, b = 24.840 (8) Å, c = 13.919 (4) Å, β = 103.20 (2)°, monoclinic $P2_1/n$, Z = 4.

Diphosphines, $R_2P(CH_2)_nPR_2$, are very common and important chelating and bridging ligands in transition-metal chemistry. The ability to initially restrict binding of these ligands to only one donor atom is potentially useful in the design of heterobimetallics. Thus far, coordination of only one end of a diphosphine has been accomplished by (1) using excess ligand to displace one end of the chelating diphosphine, (2) incorporating nonlabile ligands onto the metal, and (3) constraining the metal to undergo trans substitution only.[2] Our investigations into the chemistry of η^2-cyclenP square-planar complexes[3] suggest that an-

(1) Present address: Louisiana Tech University.

(2) See, for example: (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *99*. (b) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

0276-7333/92/2311-2074$03.00/0