Diels-Alder cycloaddition reactions of 1,1-dichloro-2,3,4,5-tetraethylgermole and 1-chloro-2,3,4,5-tetraethylphosphole with maleic anhydride and maleimide

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Dedicated to Professor Ernst Anders on the Occasion of his 65th Birthday

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Abstract
The Diels-Alder reaction of 1-chloro-2,3,4,5-tetraethylphosphole with maleic anhydride and with maleimide yields 4-chloro-1,7,8,9-tetraethyl-4-oxa-10-phosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione (**1**) and 4-chloro-1,7,8,9-tetraethyl-4-aza-10-phosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione (**2**). The molecular structure of **1** confirms the formation of the endo-cyclo-adduct with the chlorine atom in an anti-position to the C=C double bond. In contrast to this chlorophosphole, 1,1-dichloro-2,3,4,5-tetraethylgermole reacts with two equivalents of the maleic derivatives to 1,4,7,8-tetraethylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid anhydride (**3**) as well as the aza-analogue **4**. The molecular structure of **3** shows the formation of an exo,exo-product. The 1,1-dichloro-2,5-bis(trimethylsilyl)-3,4-diorganylgermoles with R = Me (**5**), *n*Pr (**6**) and Ph (**7**) show no reactivity toward maleic acid derivatives.

Keywords: Diels-Alder reactions, phospholes, germoles, cycloaddition reactions

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Introduction

Germoles and phospholes (germa- and phosphacyclopentadienes) belong to a substance class of unsaturated heterocycles which gained tremendous interest as such as well as their anions during the last decades. Due to the diagonal relationship the similarity of the CH and P units seemed to suggest a comparison of the cyclopentadienes with the phospholes regarding the structures and chemical and physical properties. Furthermore, comparisons are undertaken for cyclopentadienes with their heavier homologous metalloles. The first preparative procedures include the metathesis reaction of the halides of phosphorus and germanium with 1,4-dilithiobutadienes.[1, 2] Later a procedure starting from 1,1-cyclopentadienyl-1-zirconacyclopenta-2,4-dienes was developed.[3, 4] Thereafter numerous considerations concerning the aromaticity of these germoles as well as their anions were published.[5-12] Synthesis and chemical behaviour of germoles[13, 14] and phospholes[15-17] are summarized in several review articles.

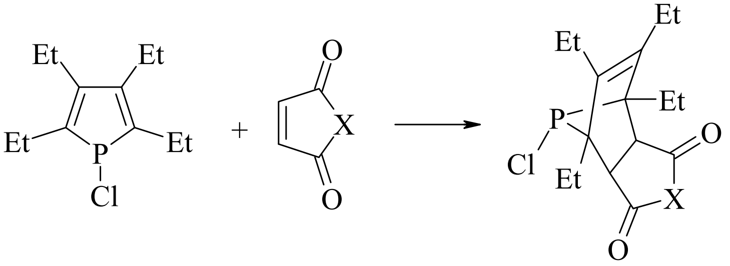
Germoles and phospholes readily undergo [4+2] cycloaddition Diels-Alder reactions with a wide variety of multiple bonds such as alkenes, alkynes or butadienes. Therefore, dimerization of phospholes can also be observed[18-21] and was investigated by quantum chemical methods.[22, 23] 1-Arylphospholes react with maleic anhydride as well as with N-phenylmaleimide to the corresponding cycloaddition products.[24] Furthermore, also 1-aryl-thioxophospholes undergo Diels-Alder reactions.[25] A reduction of these phosphole sulfides with nickelocene and a [4+2] cycloaddition with N-phenylmaleimide also lead to the formation of the appropriate product.[26] Further examples are summarized in review articles[15-17] as well as in the literature cited therein.

The investigations on germoles are far less extensive. The reaction of aryl and alkyl substituted germoles with maleic anhydride also yields the Diels-Alder products.[27-30] The [4+2] cycloaddition Diels-Alder reactions of germoles with tetracyanoethylene lead to the formation of 2,2,3,3-tetracyano-7-germa[2.2.1]hept-5-enes.[31-33]

Results and Discussion

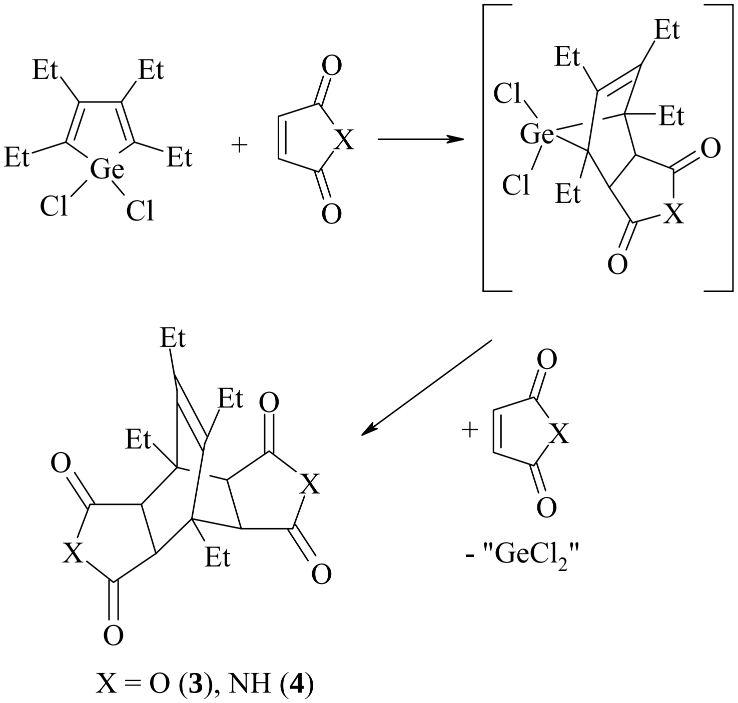
Synthesis

1-Chloro-2,3,4,5-tetraethylphosphole reacted at room temperature in a solvent mixture of 1,2-dimethoxyethane (DME) and THF with maleic anhydride (X = O) as well as with maleimide (X = NH) according to equation (1) to the cycloaddition products **1** and **2**, respectively. These compounds precipitated at -20°C in the shape of orange crystals. In contrast to the starting chlorophosphole, no reaction of bis(2,3,4,5-tetraethylphospholyl) (Et_4C_4P-PC_4Et_4) with maleic anhydride or with maleimide was observed.



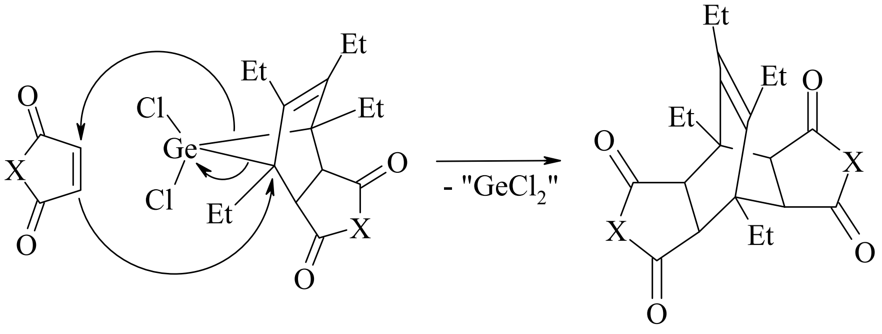
X = O (**1**), NH (**2**)

In a similar procedure, 1,1-dichloro-2,3,4,5-tetraethylgermole was reacted with an equimolar amount of maleic anhydride (X = O) and maleimide (X = NH). Already the NMR spectroscopic characterization of the reaction showed that the cycloaddition reactions followed a 1:2 stoichiometry. Whereas half of the amount of the dichlorogermole was still present in the reaction mixture, the maleic acid substrates were already converted into the cycloaddition products (Scheme 1). After cooling of the concentrated solutions colorless single crystals of **3** or oily **4** were isolated.



Scheme 1

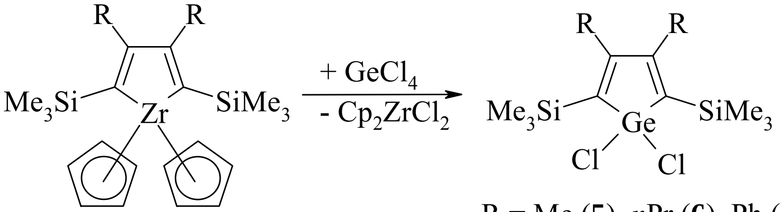
Surprisingly, the “simple” 1:1 Diels-Alder cycloaddition product was not detected as for the reaction of the chlorophosphole with the maleic acid derivatives. Instead, a second maleic anhydride attacked the germanorbornene, a mechanistic proposal is represented in equation (2). The first Diels-Alder cycloaddition reaction step is very slow for the chlorophosphole and for the dichlorogermole. Therefore, a complete reaction was achieved after approximately one day (X = O) and two days (X = NH). The second reaction has to be much faster and therefore, we were unable to see the germanorbornene intermediate. The eliminated germanium(II) chloride was not stable under these reaction conditions and underwent subsequent decomposition reactions. These rather complex decomposition reactions were already studied during the warm-up procedure of matrix isolated $GeCl_2$.



X = O (**3**), NH (**4**)

In contrast to our observations, the 1,1-dimethylgermoles form the Diels-Alder products with maleic anhydride and with maleimide, regardless whether the carbon atoms are substituted by hydrogen or phenyl groups.[30] Therefore, we repeated the reaction of maleic anhydride with the less bulky 1,1,-dichloro-2,3,4,5-tetramethylgermole. However, the same reaction mechanism was observed and the already well-known[34] 1,4,7,8-tetramethyl-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid anhydride was obtained. Criegee et al.[34] isolated this compound after the reaction of 3,4-diiodo-1,2,3,4-tetramethylcyclobutene with two equivalents of maleic anhydride in the presence of mercury.

In order to extend the reactivity investigations, germoles with trimethylsilyl substituents in 2,5-positions were prepared according to equation (3). The 1,1-bis(cyclopentadienyl)zirconacyclopenta-2,4-dienes were prepared from zirconocene dichloride, n-butyllithium and the appropriate alkynes Me_3Si-C≡C-R with R = Me, *n*Pr and Ph at low temperatures (see experimental section for the preparation of 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-di(*n*-propyl)-1-zirconacyclopenta-2,4-diene). The reaction of these zirconacyclopentadienes with $GeCl_4$ yielded the corresponding 1,1-dichloro-2,5-bis(trimethylsilyl)-3,4-methyl- (**5**), -3,4-di(n-propyl)- (**6**) and -3,4-diphenylgermole (**7**).



R = Me (**5**), *n*Pr (**6**), Ph (**7**)

The molecular structures of **5**, **6** and **7** are very similar and therefore, only the molecular structures of the n-propyl (**6**, Fig. 1) and phenyl derivatives (**7**, Fig. 2) are shown. Selected structural parameters are summarized in table 1. The molecule of **5** lies on a mirror plane, whereas the molecule of **7** shows crystallographic C_2 symmetry.

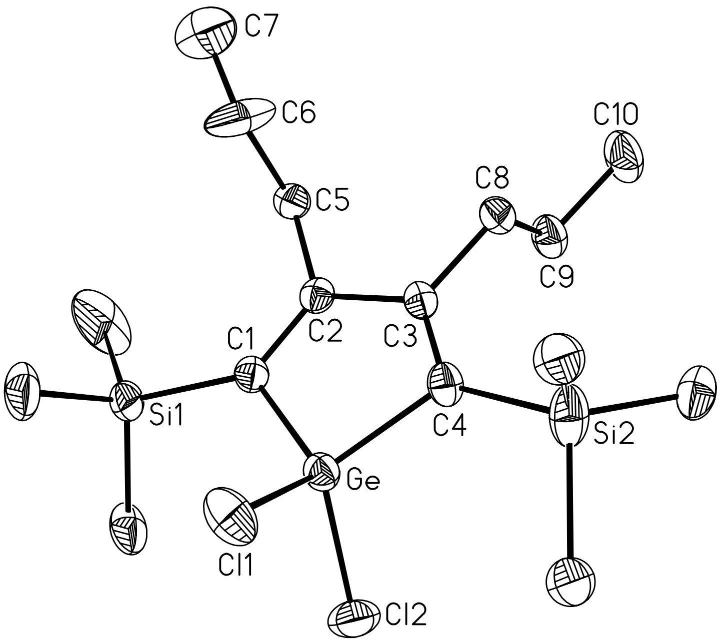


Figure 1. Molecular structure and numbering scheme of **6**. The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons.

Table 1. Comparison of selected bond lengths (Å) of the 1,1-dichlorogermoles **5**, **6** and **7**

	5 (R = Me)	**6** (R = *n*Pr)	**7** (R = Ph)
Ge-Cl1	2.1552(9)	2.160(1)	2.1459(7)
Ge-Cl2		2.148(1)	
Ge-C1	1.925(4)	1.927(3)	1.934(2)
Ge-C4	1.918(4)	1.925(3)	
C1-C2	1.331(6)	1.352(5)	1.338(3)
C2-C3	1.532(7)	1.528(4)	1.545(4)
C3-C4	1.343(6)	1.345(5)	
C1-Si1	1.870(4)	1.870(3)	1.874(2)
C4-Si2	1.869(5)	1.870(4)	
C2-C_R	1.528(6)	1.517(5)	1.491(3)
C3-C_R	1.515(6)	1.516(4)	

As expected there is no delocalization of the double bond character within the GeC_4 ring. Therefore, these compounds could react as dienes in the Diels-Alder reaction. However, the trimethylsilyl groups reduce the electron density at the α-carbon atom by hyperconjugation (back donation) of electron density from the p_z(C) orbital into a σ*(Si-C) bond of the trimethylsilyl group. This so-called α-silyl effect seems to reduce the reactivity of the 2,5-bis(trimethylsilyl)-

substituted 1,1-dichlorogermoles and no Diels-Alder cycloaddition reactions occurred with maleic acid derivatives.

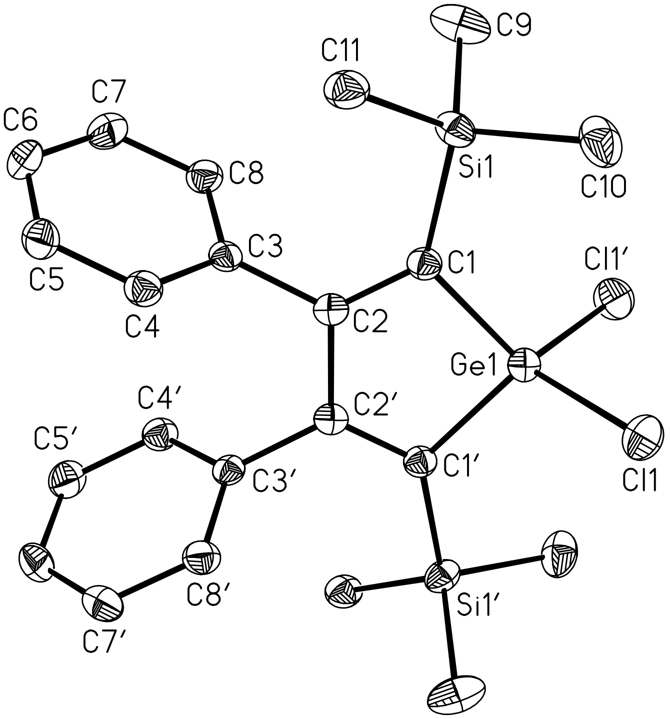


Figure 2. Molecular structure and numbering scheme of 1,1-dichloro-2,5-bis(trimethylsilyl)-3,4-diphenylgermole (**7**). The ellipsoids represent a probability of 40%, H atoms are not shown due to clarity reasons. Symmetry-related atoms (-x, y, -z+1.5) are marked with apostrophes.

Molecular Structures of 1 and 3

The Diels-Alder product **1** as well as its numbering scheme is shown in Figure 3. During the [4+2] cycloaddition reaction the *endo*-isomer is formed. The phosphorus atom is in a pyramidal environment and the chlorine substituent at the phosphorus atom is in an anti-position to the C=C double bond. A similar stereochemistry was observed for example for the cycloaddition reactions of 1-phenyl-3,4-dimethylphosphole with N-phenylmaleimide.[26] 1-(2,4,6-trialkylphenyl)-3-methylphospholes yielded with maleic acid derivatives a mixture of endo- and exo-products, however, the P-bound group was always in a trans-position to the C=C fragment.[24] The reaction of 3,4-dimethyl-2H-phosphole with maleic anhydride gave the endo-Diels-Alder cyclo-adduct but the phosphorus atom is the bridge head atom of the heterocycle of 3,4-dimethyl-1-phospha-2-norbornene-5,6-dicarboxylic acid anhydride.[35]

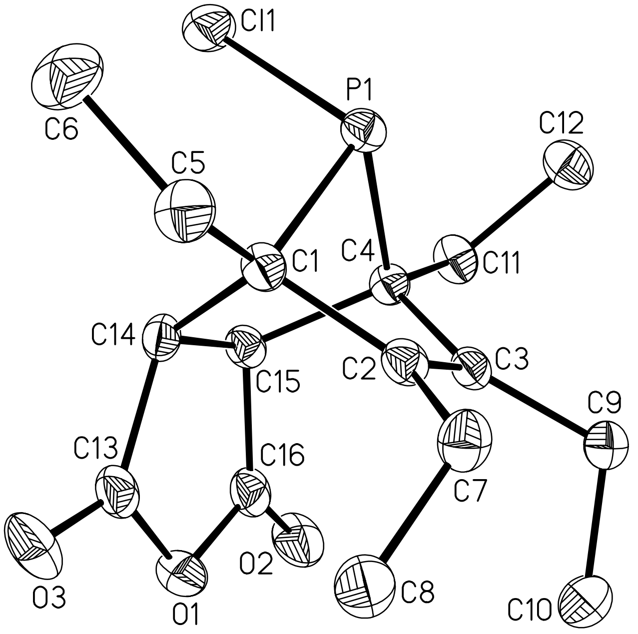


Figure 3. Molecular structure an numbering scheme of **1**. The ellipsoids represent a probability of 40%, H atoms are omitted for clarity reasons. Selected bond lengths (Å): P1-Cl1 2.0971(8), P1-C1 1.872(2), P1-C4 185.5(2), C1-C2 1.520(3), C1-C5 1.527(3), C1-C14 155.8(3), C2-C3 1.359(3), C2-C7 1.499(3), C3-C4 1.529(3), C3-C9 1.508(3), C4-C11 1.528(3), C4-C15 1.557(3), C14-C15 1.521(3), C13-C14 1.508(3), C15-C16 1.497(3), C13-O11.384(3), C13-O3 1.185(3), C16-O1 1.383(3), C16-O2 1.186(3).

The structural parameters are in accordance to the characteristic values. The deviations of the carbon atoms C2 and C3 of the C=C double bond from a trigonal planar environment are negligible, even though pyramidalization of these carbon atoms due to a heteroatom substitution has attracted considerable interest.[36] However, usually no deviation from planarity of the C=C fragment of norbornenes was observed for the substitution of the methylene moiety by heavier main group elements.[30]

Compound **3** crystallized with two crystallographically independent molecules A and B in the asymmetric unit. In Figure 4 molecule A is represented with its numbering scheme. The bond lengths correspond very well to those of the organic backbone of **1**. This structure shows that the stereochemistry of the first [4+2] cycloaddition step follows the same principle as observed for **1** and that the endo-isomer was formed. The cycloaddition under loss of the $GeCl_2$ fragment leads to an isomer with the second carboxylic acid anhydride in a *syn* position to the C=C double bond as shown in equation (3).

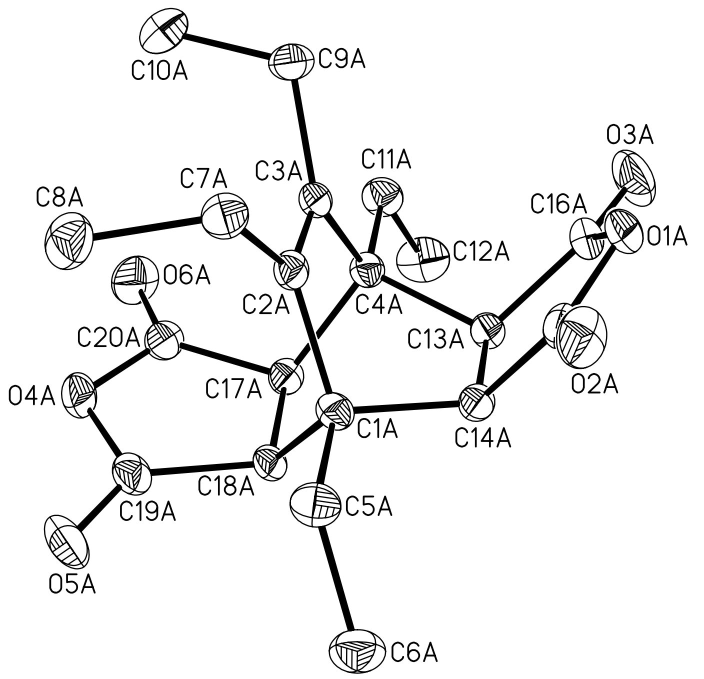


Figure 4. Molecular structure and numbering scheme of **3**. The ellipsoids represent a probability of 40%, the hydrogen atoms are omitted for clarity reasons. Only molecule A is shown. Selected bond lengths (Å): C1A-C2A 1.538(4), C2A-C3A 1.349(4), C3A-C4A 1.535(4), C1A-C14A 1.555(4), C13A-C14A 1.528(4), C4A-C13A 1.567(4), C1A-C18A 1.562(4), C17A-C18A 1.526(4), C4A-C17A 1.555(4).

In **3** the ethylene fragment C2A=C3A is strictly planar despite the steric strain induced by the ethyl groups. The bulky ethyl groups and the ring strain lead to slight distortions of the environment of these carbon atoms, however, no deviation from planarity is observed [C3A-C2A-C7A 124.0(2), C3A-C2A-C1A 115.1(2), C7A-C2A-C1A 120.8(2), C2A-C3A-C9A 123.8(2), C2A-C3A-C4A 115.5(2), C9A-C3A-C4A 120.7(2)].

Scope of these reactions

Whereas the Diels-Alder cycloaddition reactions of the phospholes are intensively investigated, the chemistry of the germoles remained somewhat ignored. The expectation that the germoles would react similarly to the phospholes was confirmed for the first reaction step. However, during a subsequent reaction of the intermediate 4,4-dichloro-1,7,8,9-tetraethyl-4-oxa-10-germatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione mith maleic anhydride, the $GeCl_2$ moiety is eliminated. Due to the α-silyl effect germoles with trimethylsilyl groups in 2,5-positions show no reactivity toward maleic acid derivatives.

Experimental Section

General Procedures. All reactions were performed in an argon atmosphere using standard Schlenk techniques. All solvents were dried and thoroughly deoxygenated according to standard procedures prior to use. The NMR spectra were recorded at r.t. in [D$_6$]benzene solutions. IR spectra were recorded in Nujol suspensions between KBr windows. All compounds are moisture sensitive and handling under unaerobic conditions is necessary. Low carbon values of the elemental analysis resulted from carbonate formation during combustion of the compounds.

4-Chloro-1,7,8,9-tetraethyl-4-oxa-10-phosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione (1). 1-Chloro-2,3,4,5-tetraethylphosphole (0.69 g, 3.0 mmol) was dissolved in 20 ml of DME. At r.t. 0.29 g of maleic anhydride (3.0 mmol) was added at once. After one day of stirring, the volume of the solution was reduced to a third of the original volume. After storage at -20°C, 0.81 g of orange crystals of **1** (2.47 mmol, 82%) were collected. M.p. 73°C. ^{1}H NMR: δ = 0.78 (t, 6H, Me), 0.98 (t, 6H, Me), 1.91 (m, 4H, CH$_2$), 2.24 (q, 4H, CH$_2$), 3.69 (s, 2H, CH). ^{13}C{^{1}H} NMR: δ = 11.2 (d, Me, ^{3}J(C,P) = 9.2 Hz), 13.9 (d, Me, ^{4}J(C,P) = 3.1 Hz), 19.2 (s, CH$_2$), 21.2 (d, CH$_2$, ^{2}J(C,P) = 8.1 Hz), 135.4 (s), 143.2 (d, ^{1}J(C,P) = 25.1 Hz), 171.0 (d, CO, ^{3}J(C,P) = 2.0 Hz). ^{31}P{^{1}H} NMR: δ = 58.6 (s). IR: 1855 vs, 1819 s, 1782 vs, 1718 m, 1700 m, 1687 w, 1653 vw, 1473 m, 1439 m, 1384 s, 1346 vw, 1316 vw, 1296 w, 1261 s, 1244 s, 1216 s, 1177 m, 1159 m, 1134 w, 1128 w, 1104 m, 1072 s, 1060 s, 999 m, 960 w, 950 m, 915 vs, 850 m, 834 vw, 815 vw, 758 vw, 726 vw, 695 m, 617 m, 604 w, 557 m, 536 w, 504 vw, 449 s, 419 m, 376 m, 333 vw, 303 vw. Elemental analysis ($C_{16}H_{22}ClO_3P$, 328.76): calcd.: C 58.45, H 6.75; found: C 58.25, H 6.95.

4-Chloro-1,7,8,9-tetraethyl-4-aza-10-phosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione (2). 1-Chloro-2,3,4,5-tetraethylphosphole (0.69 g, 3.0 mmol) was dissolved in a mixture of 15 ml of DME and 5 ml of THF. At r.t. 0.29 g of maleimide (3.0 mmol) was added at once. After 2 days the solution was concentrated to a few milliliters. At -20°C 0.71 g of orange crystals of **2** (2.16 mmol, 72%) precipitated. M.p. 107 °C. ^{1}H NMR: δ = 0.84 (t, 6H, Me), 1.04 (t, 6H, Me), 1.99 (m, 4H, CH$_2$), 2.06 (m, 4H, CH$_2$), 3.54 (s, 2H, CH). ^{13}C{^{1}H} NMR: δ = 11.2 (d, Me, ^{3}J(C,P) = 10.0 Hz), 13.8 (d, Me, ^{4}J(C,P) = 3.3 Hz), 19.3 (s, CH$_2$), 21.6 (d, CH$_2$, ^{2}J(C,P) = 9.5 Hz), 134.5 (s), 142.4 (d, ^{1}J(C,P) = 25.8 Hz), 177.2 (d, CO, ^{3}J(C,P) = 1.4 Hz). ^{31} P{^{1}H} NMR: δ = 59.7 (s). IR: 1770 m, 1723 s, 1711 s, 1473 m, 1440 m, 1384 m, 1370 m, 1350 m, 1295 w, 1275 m, 1245 m, 1229 m, 1187 m, 1143 m, 1108 m, 1100 m, 1082 m, 1062 m, 1049 m, 1009 w, 980 w, 963 w, 940 w, 916 w, 835 m, 778 w, 722 w, 686 w, 677 w, 633 w, 614 w, 599 w, 581 w, 556 vw, 529 vw, 511 vw, 495 vw, 476 vw, 448 m, 413 m, 402 s, 376 s. Elemental analysis ($C_{16}H_{23}ClNO_2P$, 327.77): calcd.: C 58.63, H 7.07, N 4.27; found: C 57.70, H 7.20, N 4.20.

1,4,7,8-Tetraethylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid anhydride (3). Maleic anhydride (0.57 g, 5.8 mmol) was added at r.t. to a solution of 1.79 g of 1,1-dichloro-2,3,4,5-tetraethylgermol (5.8 mmol) in 10 ml of DME. The reaction mixture slowly turned red. After 1 day the precipitate was removed and the solution concentrated to a few milliliters. Cooling of this solution to 5°C afforded 0.92 g of crystalline **3** (2.57 mmol, 89%). Dec. above 165 °C. ^{1}H NMR: δ = 0.86 (t, 6H, Me), 1.21 (t, 6H, Me), 2.09 (q, 4H, CH_2), 2.48 (q, 4H, CH_2), 3.37 (s, 2H, CH). $^{13}C\{^1H\}$ NMR: δ = 8.1 (s, Me), 14.2 (s, Me), 20.6 (s, CH_2), 20.8 (s, CH_2), 44.8 (s, C_q), 45.5 (s, CH), 142.0 (s, C=C), 170.6 (s, CO). IR: 1855 vw, 1778 s, 1709 w, 1562 vw, 1459 s, 1377 m, 1261 w, 1217 m, 1085 m, 1022 w, 938 m, 814 m, 763 vw, 729 vw. Elemental analysis ($C_{20}H_{24}O_6$, 360.39): calcd. C 66.65, H 6.71; found: C 65.22, H 6.78.

1,4,7,8-Tetraethylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid diimide (4). To a solution of 1.74 g of 1,1-dichloro-2,3,4,5-tetraethylgermol (5.65 mmol) in 10 ml of DME 0.54 g of maleimide (5.65 mmol) was added at once. The solution turned dark red. After 2 days all solids were removed and the volume of the solution reduced to a few milliliters. A brown oily substance of NMR spectroscopically pure **4** (0.76 g, 2.12 mmol, 75%) remained in the Schlenk flask. ^{1}H NMR: δ = 0.94 (t, 6H, Me), 1.03 (t, 6H, Me), 2.21 (q, 4H, CH_2), 2.41 (q, 4H, CH_2), 3.57 (s, 2H, CH). $^{13}C\{^1H\}$ NMR: δ = 7.8 (s, Me), 13.5 (s, Me), 19.6 (s, CH_2), 20.3 (s, CH_2), 45.0 (s, C_q), 45.2 (s, CH), 139.4 (s, C=C), 178.3 (s, CO). IR: 1772 vw, 1709 m, 1458 m, 1376 w, 1182 vw, 814 w, 722 vw.

1,1-Dichloro-2,5-bis(trimethylsilyl)-3,4-dimethylgermole (5). $GeCl_4$ (2.51 ml, 22.0 mmol) was added to a solution of 9.81 g of 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethyl-1-zirconacyclopenta-2,4-diene (22.0 mmol) in 150 ml of THF. The solution turned brown immediately. After 3 hours all volatile materials were removed in vacuo and the residue dissolved in 50 ml of pentane. Now all solids were removed. After reduction of the volume of the solution to a few milliliters 7.5 g of colorless crystals of **5** (20 mmol, 93%) precipitated at 5°C. M.p. 118°C. ^{1}H NMR: δ = 0.21 (s, 9H, SiMe), 2.12 (s, 3H, Me). $^{13}C\{^1H\}$ NMR: δ = -0.4 (s, SiMe), 19.6 (s, Me), 132.6 (s, C2/C5), 162.3 (s, C3/C4). IR: 1591 s, 1570 m, 1520 vw, 1459 s, 1433 s, 1406 s, 1345 w, 1237 m, 1121 s, 1046 vs, 1007 vs, 958 m, 896 m, 865 vs, 817 m, 752 vs, 729 s, 629 w, 613 w. Elemental analysis ($C_{12}H_{24}Cl_2GeSi_2$, 368.01): calcd. C 39.17, H 6.57; found: C 38.78, H 6.58.

1,1-Bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-di(n-propyl)-1-zirconacyclopenta-2,4-diene. Zironocene dichloride (5.20 g, 18.0 mmol) and 6.66 ml of 1-trimethylsilyl-1-pentyne (35 mmol) are dissolved in 25 ml of THF and cooled to -78 °C. At this temperature, 14.3 ml of a 2.5M solution of *n*BuLi in hexane was added dropwise. After complete addition, the solution was stirred at -78°C for additional 15 min and then warmed to r.t. thereafter, all volatile materials were removed in vacuum and the residue dissolved in 50 ml of pentane. After removal of all solids by filtration, the volume of the solution was reduced. After cooling to 5°C 7.11 g of colorless 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-di(*n*-propyl)-1-zirconacyclopenta-2,4-diene (14.0 mmol, 78%) precipitated. M.p. 106 °C. ^{1}H NMR: δ = 0.14 (s, 9H, SiMe), 0.92 (t, 3H, Me), 1.36 (m, 2H, CH_2), 2.12 (m, 2H, CH_2), 5.97 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR: δ = 2.9 (s, SiMe), 14.4 (s, Me), 24.7 (s, CH_2), 41.0 (s, CH_2), 110.7 (s, Cp), 148.4 (s, C2/C5), 201.6 (s, C3/C4). $^{29}Si\{^1H\}$ NMR: δ = -17.5 (s). IR: 1780 vw, 1686 vw, 1584 vw, 1498 w, 1475 vw, 1465 w, 1444 m, 1401 vw, 1372 vw, 1292 vw, 1256 s, 1245 vs, 1181 vw, 1114 w, 1084 w, 1079 w, 1046 s, 1021 s, 1016 s, 893 m, 884 s, 842 vs, 786 vs, 753 s, 738 m, 676 s, 628 s, 532 vw, 482 w, 445 vw. Elemental analysis ($C_{26}H_{42}Si_2Zr$, 501.99): calcd. C 62.20, H 8.43; found: C 60.16, H 8.69.

X-ray structure determination of 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-di(n-propyl)-1-zirconacyclopenta-2,4-diene: triclinic, *P* 1, T = 200(2) K, a = 8.5446(2), b = 9.5581(2), c = 16.9258(4) Å, α = 96.539(1)°, β = 91.523(1)°, γ = 93.9770(9)°, V = 1369.20(5) Å^3, Z = 2, d_{calc} = 1.218 g cm^{-3}, μ = 0.499 mm^{-1}, 18158 measured reflections, 4786 independent reflections, wR_2 = 0.1028 (on all data on F^2), R_1 = 0.0430 (on 3679 observed data with $I > 2\sigma(I)$), s = 1.040, residual electron density 0.34/-0.52 e Å^{-3}; selected bond lengths (Å): Zr-C1 223.5(3), Zr-C4 224.4(3), C1-C2 136.2(4), C2-C3 152.3(4), C3-C4 135.5(4), C1-Si1 186.9(3), C4-Si2 186.2(3); selected bond angles (°):C1-Zr-C4 83.4(1), Zr-C1-Si1 131.2(2), Zr-C4-Si2 131.4(2), Zr-C1-C2 105.9(2), C1-C2-C3 121.5(3), C2-C3-C4 122.7(3), C3-C4-Zr 105.3(2). The structure is very similar to 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethyl-1-zirconacyclopenta-2,4-diene.[37]

1,1-Dichloro-2,5-bis(trimethylsilyl)-3,4-di(n-propyl)germole (6). $GeCl_4$ (1.60 ml, 14.0 mmol) was added to a solution of 7.11 g of 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-di(*n*-propyl)-1-zirconacyclopenta-2,4-diene (14.0 mmol) in 50ml of THF. The solution slowly turned yellow. After 12 hours all volatile materials were removed in vacuo and the residue dissolved in 20 ml of pentane. After removal of all solid materials the volume of the solution was reduced to a few milliliters and 4.4 g of colorless crystals of **6** (10.4 mmol, 74%) precipitated at -20°C. M.p. 89 °C. ^{1}H NMR: δ = 0.32 (s, 9H, SiMe), 0.82 (t, 3H, Me), 1.24 (m, 2H, CH_2), 2.30 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR: δ = 0.5 (s, SiMe), 14.2 (s, Me), 24.8 (s, CH_2), 35.1 (s, CH_2), 131.9 (s, C2/C5), 165.0 (s, C3/C4). IR: 1561 m, 1499 m, 1466 s, 1405 w, 1378 w, 1337 vw, 1250 vs, 1139 m, 1088 s, 1030 w, 901 s, 866 vs, 839 vs, 759 s, 688 w, 634 m, 535 w, 479 m. Elemental analysis ($C_{16}H_{32}Cl_2GeSi_2$, 424.09): calcd. C 45.31, H 7.54; found: C 43.15, H 7.25.

1,1-Dichloro-2,5-bis(trimethylsilyl)-3,4-diphenylgermole (7). $GeCl_4$ (1.14 ml, 10.0 mmol) was added to a solution of 5.28 g of 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-zirconacyclopenta-2,4-diene (9.28 mmol) in 15 ml of THF. The solution turned red immediately and finally the color changed to brown. After 3 hours all volatile materials were removed in vacuo and the residue dissolved in 20 ml of toluene. After removal of all solids and reduction of the volume to a few milliliters 3.9 g of colorless crystals of **7** (8.0 mmol, 86%) precipitated at 5°C. M.p. 122°C. ^{1}H NMR: δ = 0.18 (s, 9H, SiMe), 6.52-7.01 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR: δ = 0.6 (s, SiMe), 126.7, 128.7, 129.8, 132.2 (Ph), 136.2 (s, C2/C5), 164.3 (s, C3/C4). IR: 1600 vw, 1575 vw, 1559 vw, 1512 vw, 1489 w, 1474 vw, 1466 vw, 1457 vw, 1442 w, 1409 w, 1378 vw, 1288 vw, 1261 s, 1250 vs, 1232 vw, 1220 vw, 1177 vw, 1155 vw, 1090 m, 1074 m, 1060 m, 1012 s, 995 m, 965 vw, 945 m, 915 w, 901 w, 865 vs, 842 vs, 803 s, 774 s, 760 vs, 731 w, 700 vs, 673 m, 645 vw, 627 vw, 538 vw, 496 vw, 398 vs. Elemental analysis ($C_{22}H_{28}Cl_2GeSi_2$, 492.11): calcd. C 53.69, H 5.73; found: C 52.06, H 5.44.

Crystal structure determinations. Data was collected on a STOE-IPDS diffractometer and on a Siemens P4 diffractometer with a CCD area detector with graphite-monochromated Mo-K_α

radiation using oil-coated rapidly cooled single crystals. Crystallographic parameters, details of data collection and refinement procedures are summarized in Table 2.

The structures were solved by direct methods with the program SIR-97[38] and refined with software package SHELXL-97.[39] Neutral scattering factors were taken from *Cromer* and *Mann*[40] and for the hydrogen atoms from *Stewart* et al.[41] The non-hydrogen atoms were refined anisotropically. The H atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms, however, the N-bound hydrogen atoms were refined isotropically.

Table 2. Crystallographic parameters and details of data collection and refinement details

Compound	**1**	**3**	**5**	**6**	**7**
formula	$C_{16}H_{22}ClO_3P$	$C_{20}H_{24}O_6$	$C_{12}H_{24}Cl_2GeSi_2$	$C_{16}H_{32}Cl_2GeSi_2$	$C_{22}H_{28}Cl_2GeSi_2$
fw ($g\cdot mol^{-1}$)	328.76	360.39	368.01	424.09	492.11
T/K	193(2)	183(2)	200(2)	183(2)	193(2)
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$ (Nr. 19)	$P2_1$/c (Nr. 14)	$P2_1$/m (Nr. 11)	*P*bca (Nr. 61)	*C*2/c (Nr. 15)
a/Å	8.623(2)	7.6555(2)	8.3088(4)	14.7935(3)	20.418(4)
b/Å	11.915(3)	29.0377(6)	10.2098(4)	14.3293(3)	10.492(2)
c/Å	15.628(3)	15.8767(5)	11.6219(5)	21.0459(4)	11.465(2)
α/°	90	90	90	90	90
β/°	90	93.515(1)	106.597(2)	90	99.86(3)
γ/°	90	90	90	90	90
V/Å^3	1605.7(6)	3522.7(2)	944.82(7)	4461.3(2)	2419.9(8)
Z	4	8	2	8	4
σ ($g\cdot cm^{-3}$)	1.360	1.359	1.293	1.263	1.351
μ (mm^{-1})	0.345	0.100	2.013	1.714	1.591
measured data	7232	19577	8496	30207	6184
data with $I > 2\sigma(I)$	2148	5068	1377	3615	1724
unique data (R_{int})	2295	7994	1577	5099	2751
wR_2 (all data, F^2)$^{a)}$	0.0669	0.2008	0.0862	0.1482	0.0546
R_1 ($I > 2\sigma(I)$)$^{a)}$	0.0263	0.0753	0.0338	0.0485	0.0305
$s^{b)}$	1.068	1.014	1.075	1.028	0.830
res. dens./e·Å^{-3}	0.171/-0.138	0.496/-0.399	0.427/-0.390	1.780/-0.619	0.284/-0.268
CCDC No.	-614063	-614064	-614065	-614066	-614067

$^{a)}$ Definition of the R indices: $R_1 = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$ $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

$^{b)}$ $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

Supporting Information Available

X-ray crystallographic files in CIF format. These crystallographic data can be obtained free of charge on application to the Cambridge Crystallographic Data Centre {12 Union Road, Cambridge, CB2 1EZ, U.K. [fax (internat.) + 44(0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk}.

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