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High Pressure Assisted Synthesis of Fused Norbornenes containing two 7-Metallonorbornene Units

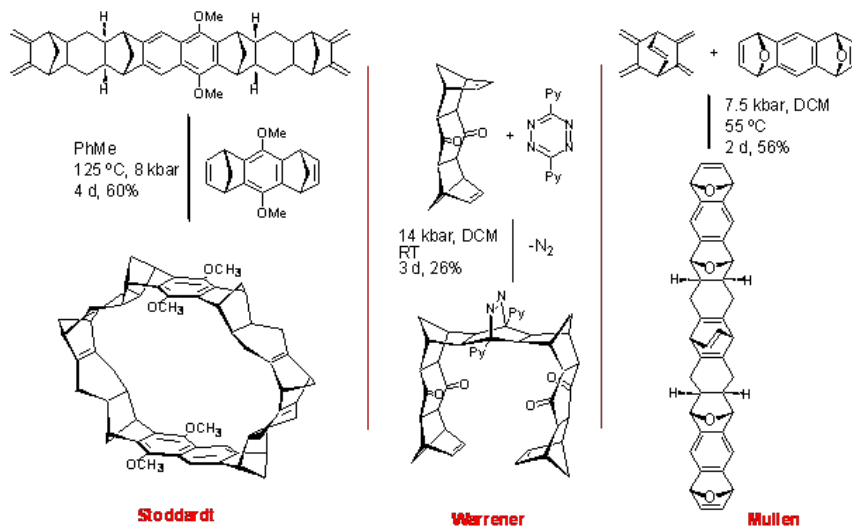
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Abstract. High pressure synthesis of new polynorbornene compounds containing two silicon or germanium atoms is described. In addition, the structural features based on DFT calculations of model compounds are discussed.

Introduction. Synthetic work of Stoddardt[1], Klöner[2], Warrenner[3] and Müllen[4] on rigid polycycles containing benzonorbornenes based on multistep Diels-Alder reactions are the most outstanding examples of this type of work. Preparation of novel linear and cyclic semi-rigid superstructures based on norbornene chemistry and single-pot multi-cycloaddition protocols was greatly facilitated by the use of high pressure (Scheme 1). In such a way, beltanes, trinacrenes, molecular tweezers, molecular clefts and ribbons were prepared.



Scheme 1

All previously reported polycyclic molecules contain norbornane, oxanorbornane or diazabicyclo[2.2.2]octane units, while compounds with a hetero-atom positioned at a bridgehead were not studied. In continuation to our research program in cycloaddition chemistry, here we explore synthetic strategies for organic molecules possessing silicon and germanium atoms incorporated in the polycyclic skeleton. Work described in this note utilizes [4p+2p] cycloaddition methodology based on 1-sila-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene, 1-sila-2,5-diphenyl-1,1-dimethyl-2,4-cyclopentadiene, and 1-germa-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene as reactive dienes. So far, our work on the synthesis of mono-sila and mono-germanorbornenes using this protocol has been published. It was established that these cycloadditions are p-face selective[5] and stereospecific, giving a single isomer possessing *exo,endo*- geometry.[6] This synthetic technique opened a route to a novel

class of compounds possessing 7-sila- (and 7-germa-) norbornene ring moieties.[7,8] In our preliminary work, it was found that the 7-oxanorbornene p bond is the only reactive norbornene bond, while norbornene or benzonorbornene were found to be not reactive due to the steric and electronic reasons. Therefore, for the work reported here covering the synthesis of more complex systems, we have chosen reactive \diamond bis-dienophiles 1,4:5,8-diepoxy-1,4,5,8-tetrahydronaphthalene amide **4**,[9] 1,4:5,8-diepoxy-1,4,5,8-tetrahydronaphthalene anhydride **5**[10] and *syn*-1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene **6**[11].

Results and discussion. All Diels-Alder cycloaddition reactions of 1,1-dimethyl-2,3,4,5-tetraphenyl- and 1,1-dimethyl-2,5-diphenyl- metalloles with bis-dienophiles were carried out under high pressure. Products and stereochemical outcomes of the reactions were analysed by NMR spectroscopy.

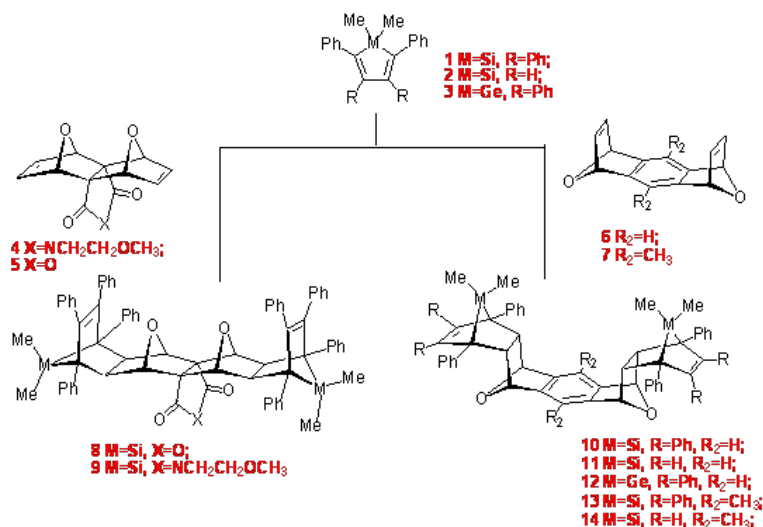


Table 1

Entry	Reactants	Mol. ratio	Conditions	Product	Yield (%)
1	1+5	2 : 1	80 °C, 1 bar 3 d, toluene	-	-
2	1+5	2 : 1	120 °C, 1 bar 3 d, toluene	-	-
3	1+5	2 : 1	60 °C, 10 kbar 3 d, CH ₂ Cl ₂	8	16
4	1+5	2 : 1	25 °C, 10 kbar 3 d, CH ₂ Cl ₂	8	14
5	1+5	4 : 1	25 °C, 10 kbar 7 d, CH ₂ Cl ₂	6	81
6	1+7	3 : 1	50 °C, 10 kbar 5 d, CH ₂ Cl ₂	10	79
7	2+7	3 : 1	50 °C, 10 kbar 5 d, CH ₂ Cl ₂	11	74
8	3+7	3 : 1	80 °C, 10 kbar 6 d, CH ₂ Cl ₂	12	85
9	1+4	2 : 1	70 °C, 8 kbar 3 d, CH ₂ Cl ₂	9	57
11	1+6	3 : 1	80 °C, sealed tube, 4 d, CCl ₄	13	78
12	3+6	3 : 1	80 °C, sealed tube, 4 d, CCl ₄	14	98

A summary of the reactions studied is shown in **Scheme 2** and **Table 1**. Reaction of *syn*-1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene, **6** with two equivalents of 1,2-dimethyl-2,3,4,5-tetraphenyl silole **1** gave the 2:1 *exo,endo*- adduct **8** as a single product in 16 % yield (10 kbar, 60 °C, DCM, 3 days, Entry 3). It was found that temperature is not a critical factor for reaction conducted at high pressure (entries 3 and 4 have essentially identical yields). A much better yield was achieved by use of the silole in great excess. When the same reaction was performed in the presence of four equivalents of **1**, and the reaction time extended, the symmetrical di-silicon adduct **6** was formed in 81 % yield. Reactions conducted thermally at normal pressure \diamond in \diamond toluene did not yield products (entries 1 and 2). Replacement of the anhydride moiety on the central dipolarophile bond with an amide does not have a big influence on the reaction outcome, but rather improves the chromatographic properties and the isolation of adduct **9** (Entry 9).

Bis-dienophile **7** readily undergoes double cyclisation with 1,2-dimethyl-2,3,4,5-tetraphenyl silole **1** and 1,2-dimethyl-2,5-diphenyl silole **2** to give bis-adducts **10** and **11** (in 79 and 74 % yields, respectively, entries 6 and 7). Reaction conditions were the following: 10 kbar, 80 °C, 5 days in dichloromethane as solvent. In another experiment, reaction of dienophile **7** with 1,2-dimethyl-2,3,4,5-tetraphenyl germole **3** under high pressure reaction conditions was explored (10 kbar, 80 °C, 6 days, dichloromethane). Thus, the germanium counterpart **12** of the silicon *exo,endo*- bis-adduct **10** was prepared in 55 % yield (entry 8). Finally, the bis-adducts **13** and **14** which include aromatic rings were obtained by heating **1** with **4** (or **5**) (at 80 °C, 4 days, in carbon tetrachloride) in 78 and 98% yields respectively (entries 11 and 12).

Elucidation of the stereochemistry of adducts **8-14** was obtained by using standard 1D and 2D 1H-NMR spectroscopy (combining correlations obtained by 1H-1H-COSY and 1H-1H-NOESY experiments). The key products were also submitted for X-ray structural analysis.

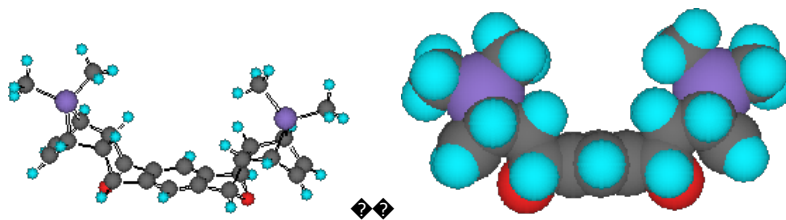


Figure 1. B3LYP/6-31G* optimized structure of bis-adduct **10** and space filling model (phenyl substituents are omitted for clarity)

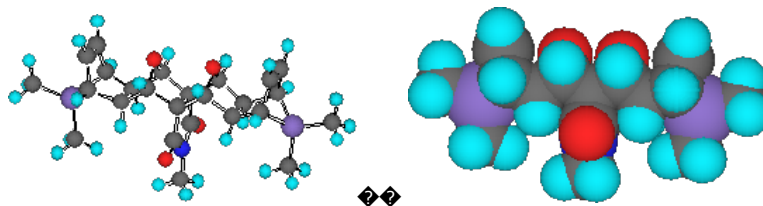
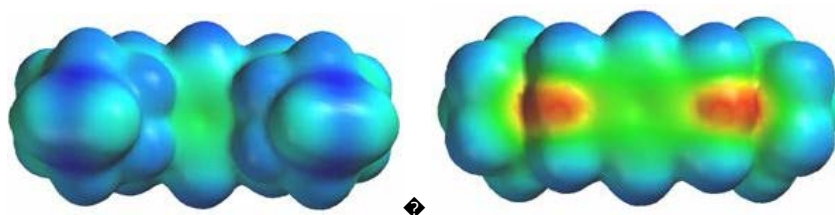


Figure 2. B3LYP/6-31G* optimized structure of adduct **9** and space filling model (phenyl substituents are omitted for clarity)

Adducts **8-14** are among the first examples of organometallic polynorbornene compounds containing two metal atoms at the bridgehead positions. Gaussian 98[12] was used for the B3LYP/6-31G* modelling of the molecular structure of adduct **10** (Figure 1, phenyl substituents are omitted for sake of clarity) which has shown that the spatial separation between the two metal atoms is 10.1 Å. Space fillings model shows that there is a cavity for possible host-guest interactions; however it is very shallow, indicating that there is not much chance to observe them experimentally. Bis-adduct **9** has an almost identical metal-metal separation estimated to be 10.16 Å (Figure 2), but without a cavity formed within polycyclic framework. Furthermore, semiempirically calculated (AM1) electrostatic potential surface of B3LYP/6-31G* optimised structure of bis-adduct **10** (Figure 3), indicates that there is small possibility for electrostatic interactions between aromatic ring and aromatic host within a host cavity.[13] Instead, the most negative electron density is located on the bridgehead oxygen atoms on the outer walls of molecule (Figure 3b).



a  b

Figure 3. Semiempirically calculated (AM1) electrostatic potential surface of B3LYP/6-31G* optimised structure of bis-adduct **10**: a) top view, b) bottom view

EXPERIMENTAL - Selected spectroscopic data

(1a,2b,3a,4b,5b,8b,9b,10a,11b,12a,13b,14b,17b,18b)-5,6,7,8,14,15,16,17-octaphenyl-21,21,22,22-tetramethyl-19,20,23-trioxa-21,22-disilanonacyclo[10.6.3^{2,11}.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]pentacosa-6,15-dien-22,24-dione (**8**)
¹H (CDCl₃), d/ppm: 0.17 (6H, s), 0.61 (6H, s), 3.62 (4H, s), 5.39 (4H, s), 6.75-7.23 (40H, m).

(1a,2b,3a,4b,5b,8b,9b,10a,11b,12a,13b,14b,17b,18b)-23-(2-methoxyethyl)-5,6,7,8,14,15,16,17-octaphenyl-21,21,22,22-tetramethyl-23-aza-19,20-dioxa-21,22-disilanonacyclo[10.6.3^{2,11}.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]pentacosa-6,15-dien-22,24-dione (**9**)
¹H (CDCl₃), d/ppm: 0.11 (6H, s), 0.65 (6H, s), 3.25 (3H, s), 3.54 (4H, s), 3.67 (2H, t, *J*=5.3 Hz), 3.85 (2H, t, *J*=5.3 Hz), 5.39 (4H, s), 6.85-7.25 (40H, m).

23,23,26,26-tetramethyl-1,9,10,11,12,20,21,22-octaphenyl-1a,2b,3a,7a,8b,9a,12a,13b,14a,18a,19b,20a-24,25-dioxa-23,26-disilaheptacyclo[18.2.1.1^{3,18}.1^{7,14}.1^{9,12}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}]hexacosa-4,6,10,16,21-pentaene (**10**)
¹H (CDCl₃), d/ppm: 0.14 (6H, s), 0.62 (6H, s), 3.36 (4H, s), 5.70 (4H, s), 6.77-7.30 (42H, m).

23,23,26,26-tetramethyl-1,9,12,20-tetraphenyl-1a,2b,3a,7a,8b,9a,12a,13b,14a,18a,19b,20a-24,25-dioxa-23,26-disilaheptacyclo[18.2.1.1^{3,18}.1^{7,14}.1^{9,12}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}]hexacosa-4,6,10,16,21-pentaene (**11**)

¹H (CDCl₃), d/ppm: 0.14 (6H, s), 0.16 (6H, s), 3.49 (4H, s), 5.30 (4H, s), 6.43 (4H, s), 7.18-7.48 (22H, m).

23,23,26,26-tetramethyl-1,9,10,11,12,20,21,22-octaphenyl-1a,2b,3a,7a,8b,9a,12a,13b,14a,18a,19b,20a-24,25-dioxa-23,26-digermanoheptacyclo

◆[18.2.1.1^{3,18,17,14,19,12,02,19,04,17,06,15,08,13}] hexacosa-4,6,10,16,21-pentaene (**12**)

¹H (CDCl₃), d/ppm: 0.35 (6H, s), 0.67 (6H, s), 3.46 (4H, s), 5.68 (4H, s), 6.75-7.23 (42H, m).

5,16,23,23,26,26-hexamethyl-1,9,10,11,12,20,21,22-octaphenyl-1a,2b,3a,7a,8b,9a,12a,13b,14a,18a,19b,20a-24,25-dioxa-23,26-disilaheptacyclo

◆[18.2.1.1^{3,18,17,14,19,12,02,19,04,17,06,15,08,13}] hexacosa-4,6,10,16,21-pentaene (**13**)

¹H (CDCl₃), d/ppm: 0.14 (6H, s), 0.63 (6H, s), 2.43 (6H, s), 3.32 (4H, s), 5.76 (4H, s), 6.81-7.21 (20H, m).

5,16,23,23,26,26-hexamethyl-1,9,12,20-tetraphenyl-1a,2b,3a,7a,8b,9a,12a,13b,14a,18a,19b,20a-24,25-dioxa-23,26-disilaheptacyclo

◆[18.2.1.1^{3,18,17,14,19,12,02,19,04,17,06,15,08,13}] hexacosa-4,6,10,16,21-pentaene (**14**)

¹H (CDCl₃), d/ppm: 0.08 (6H, s), 0.14 (6H, s), 2.33 (6H, s), 3.49 (4H, s), 5.29 (4H, s), 6.41 (4H, s), 7.19-7.44 (20H, m).

Conclusion. High pressure conditions were proven to be beneficial for the reaction of siloles and germales with oxanorbornenes. Addition of metalloles enables preparation of novel bis-metallic polynorbornenes with rigid and well defined geometrical separation of metal centres. All studied cycloaddition reactions with metalloles exhibit high stereospecificity resulting in exclusive formation of the *exo,endo*- adducts.

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