High-Pressure Assisted Synthesis of Fused Norbornenes Containing Two 7-Metallonorbornene Units

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The high-pressure synthesis of new rod-like and U-shaped polycyclic compounds containing two 7-metallonorbornene (silicon or germanium) units fused to the 7-oxanorbornene rings is described. In addition, the structural features of adduct **9** established by X-ray structure determination and DFT calculations of model compounds are discussed.

Introduction

High pressure has emerged in the past decades as an extremely attractive and unique tool for the synthesis of complex polycyclic molecules from simple and diverse building blocks.[1] Representative examples of these studies include the preparation of linear and cyclic semirigid supramolecular systems made up of norbornene, 7-oxanorbornene and diazabicyclo[2.2.2] units. A variety of novel compounds with important properties – such as beltanes,[2] trinacrenes,[3] molecular tweezers,[4] molecular clefts[5] and ribbons[6] – have been prepared in this way.

Much less effort has been put into the synthesis of polycyclic molecules containing 7-metallonorbornene rings, in spite of their potential interest for study of the mechanisms of thermal and photochemical rearrangements of 7-metallonorbornene rings embedded in geometrically fixed environments. They also provide an appealing set of molecules for exploration of the roles of heteronuclear bridges with low-lying virtual orbitals in transmitting long-range π–π interactions. A synthesis of adducts of this type, containing a 7-silanorbornene ring condensed with various 7-oxanorbornene derivatives, was recently developed in one of our research groups.[7–11]

In this work we report on the synthesis of more complex molecules containing two 7-sila- or 7-germanorbornene moieties. Two types of bis-dienophiles – the 1,4:5,8-diepoxy-1,4,5,8-tetrahydronaphthalene derivatives **4**[12] and **5**[13] and the *syn*-1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene **6**[14] and its dimethyl derivative **7**[14] – were selected for this purpose (Scheme 1). The first type of dienophiles would be expected to allow the formation of rod-like adducts, whilst the presence of the annelated benzene rings in dienophiles **6** and **7** on the other hand causes curvature of the rigid framework, resulting in a U-cavity shaped molecule.[5] In the first part of the paper we describe the synthesis and molecular structures of these compounds' homonuclear bis-adducts with siloles **1** and **2** and 1,1-dimethyl-2,3,4,5-tetraphenylgermole (**3**). In the second part, results of experiments designed for the preparation of the corresponding heteronuclear bis-metalloid systems are discussed.

Results and Discussion

A summary of the reactions employed in the preparation of homonuclear bis-metalloid adducts is given in Scheme 1 and Table 1.

We first examined the possibility of preparing bis-adduct **8** by heating 1,4:5,8-diepoxy-1,4,5,8-tetrahydronaphthalene-4a,8a-anhydride (**4**) with two equivalents of 1,1-dimethyl-2,3,4,5-tetraphenylsilole (**1**) at normal pressure (0.1 MPa; Entries 1 and 2, Table 1). In none of these experiments was the desired cycloadduct **8** formed. Moreover, in the experiments carried out at the higher temperature (Entry 2) decomposition of the starting material was observed. When the same reaction was carried out under high pressure (Entries 3 and 4, Table 1), **8** was the only product that could be isolated, but in very poor yield. Finally, by conducting the reaction in the presence of an excess of **1** and with prolongation of the reaction time to 7 days, the *exo,endo* adduct **8** was formed as the sole product in 81% yield (Entry 5, Table 1). The product was purified by column chromatography (see Experimental Part for details) and

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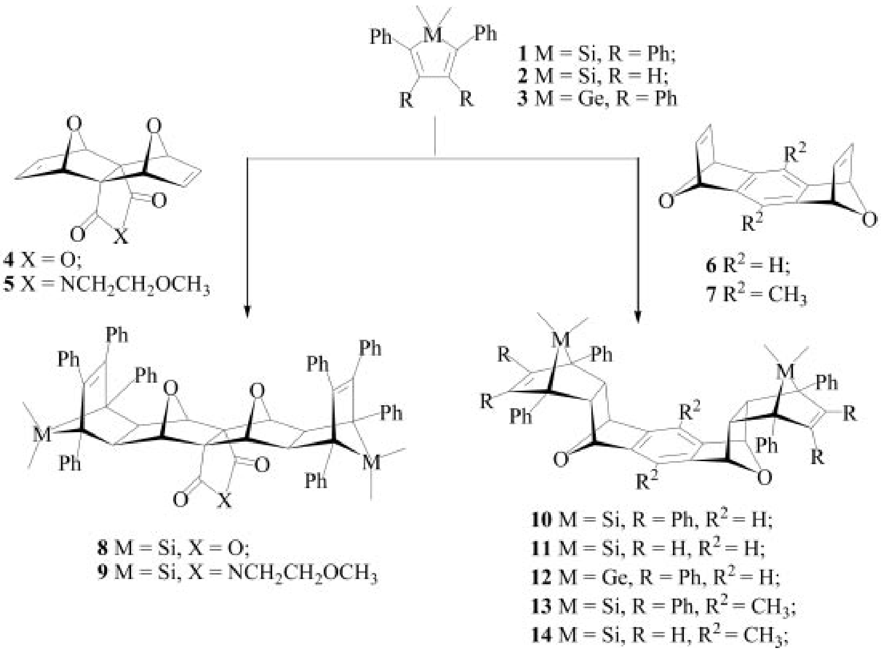


Scheme 1. Synthesis of molecules **8**–**14**.

Table 1. Synthesis of adducts **8**–**14**.[a]

Entry	Reactants	Mol. ratio	Reaction conditions	Product	Yield (%)
1	**1 + 4**	2:1	80 °C, 0.1 MPa, 3 d, toluene	–	–
2	**1 + 4**	2:1	120 °C, 0.1 MPa, 3 d, toluene	–	–
3	**1 + 4**	2:1	25 °C, 1 GPa, 3 d, CH_2Cl_2	**8**	14
4	**1 + 4**	2:1	60 °C, 1 GPa, 3 d, CH_2Cl_2	**8**	16
5	**1 + 4**	4:1	25 °C, 1 GPa, 7 d, CH_2Cl_2	**8**	81
6	**1 + 5**	2:1	70 °C, 0.8 GPa, 3 d, CH_2Cl_2	**9**	57
7	**1 + 6**	3:1	50 °C, 1 GPa, 5 d, CH_2Cl_2	**10**	79
8	**2 + 6**	3:1	50 °C, 1 GPa, 5 d, CH_2Cl_2	**11**	74
9	**3 + 6**	3:1	80 °C, 1 GPa, 6 d, CH_2Cl_2	**12**	85
10	**1 + 7**	3:1	70 °C, 0.8 GPa, 3 d, CH_2Cl_2	**13**	66
11	**2 + 7**	3:1	70 °C, 0.8 GPa, 3 d, CH_2Cl_2	**14**	72

[a] 0.1 GPa = 1 kbar.

fully characterized by spectroscopic methods. In particular, 1D and 2D ^{1}H NMR spectral analysis in combination with NOE experiments provided firm evidence for the *exo,endo* stereochemistry of the bis-adduct formed.[15]

Under similar reaction conditions we also prepared the adduct **9**, through the reaction between **1** and **5** (Entry 6, Table 1). It is interesting to note that replacement of the anhydride moiety on the central dipolarophile bond with an amide did not have any significant influence on the reaction outcome, while the chromatographic properties and the isolation of adduct **9** were greatly improved. Moreover, we were able to prepare a single crystal of **9**, suitable for X-ray analysis, providing additional confirmation of the stereochemistry of adducts **8** and **9** (Figure 1). To the best of our knowledge this is the first crystal structure of a bis-metallated cycloadduct so far reported in the literature. Details of its molecular structure are discussed in the next section.

Like **4** and **5**, bis-dienophile **6** was found to undergo double cycloaddition with siloles **1** and **2**, to afford the bis-adducts **10** and **11**, each containing two 7-silanorbornene subunits separated by a benzene spacer (Entries 7 and 8, Table 1), in reasonably good yields. Under similar conditions the structurally related bis-germyl adduct **12** was also prepared through the reaction between the tetraphenyl germole **3** and dienophile **6**. Finally, bis-adducts **13** and **14** were obtained by treatment of dienophile **7** with siloles **1** and **2**, respectively, in fair yields (Entries 10 and 11). The stereochemistry of adducts **10–14** was established by 1D and 2D ^{1}H NMR spectroscopy (combining correlations obtained by 1H-1H-COSY and 1H-1H-NOESY experiments).

Molecular Structures of Bis-adducts 9 and 10

We shall commence this section with a brief discussion of the X-ray structure of molecule **9**.[16] A molecule of **9**

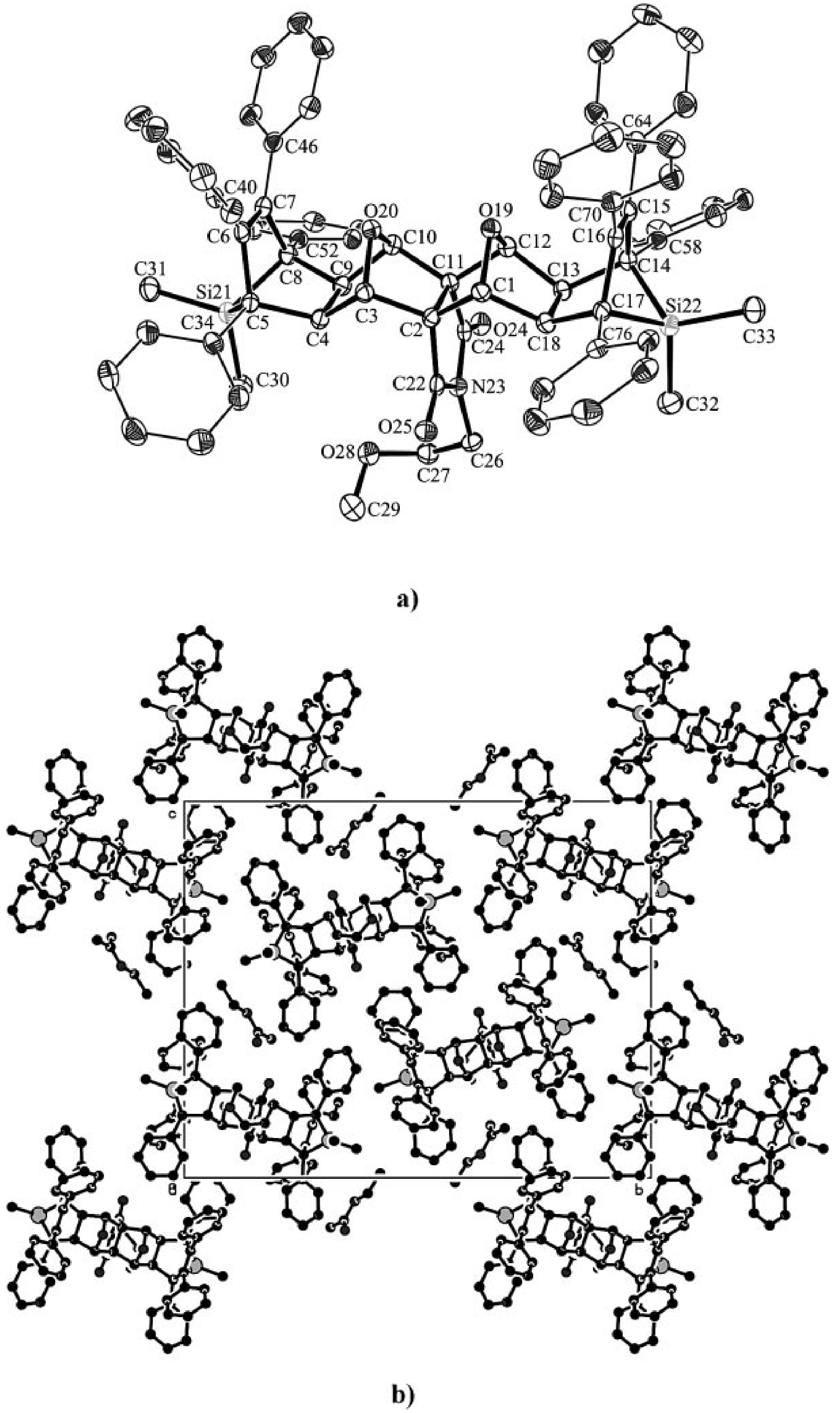


Figure 1. a) ORTEP plot of molecule **9** (50% probability displacement ellipsoids). Phenyl moieties are shown in grey and H atoms are omitted for clarity. b) The crystal packing of **9**·EtOAc.

Table 2. Selected geometrical parameters of the X-ray structure of **9** and B3LYP/6-31G* structures of **9a** and **10a**.[a]

d [Å]	**9** X-ray	**9a**	*d* [Å]	**10a**
C(1)–C(2), C(2)–C(3), C(10)–C(11), C(11)–C(12)	1.550(3)–1.560(3)[b]	1.570	C(1)–C(2)	1.567
C(1)–C(18), C(3)–C(4), C(12)–C(13), C(9)–C(10)	1.535(3)–1.552(3)[b]	1.554	C(2)–C(19)	1.579
C(1)–O(19), C(3)–O(20), C(12)–O(19), C(10)–O(20)	1.436(3)–1.448(3)[b]	1.432	C(1)–C(22)	1.516
C(2)–C(11)	1.545(3)	1.560	C(1)–Si(23)	1.935
C(4)–(C9), C(13)–C(18)	1.562(3)–1.566(3)[b]	1.579	C(21)–C(22)	1.345
C(4)–C(5), C(8)–C(9), C(13)–C(14), C(17)–C(18)	1.560(3)–1.568(3)[b]	1.569	C(2)–C(3)	1.565
C(5)–C(6), C(7)–C(8), C(14)–C(15), C(16)–C(17)	1.533(3)–1.549(3)[b]	1.515	C(3)–C(4)	1.524
C(6)–C(7), C(15)–C(16)	1.347(3)–1.357(3)[b]	1.346	C(4)–C(5)	1.349
C(5)–Si(21), C(8)–Si(21), C(14)–Si(22), C(17)–Si(22)	1.908(2)–1.923(2)[b]	1.936	C(4)–C(17)	1.405
Si(21)–Si(22)	10.116(11)	10.162	C(3)–O(24)	1.441
			Si(23)–Si(26)	9.987
θ [°]			θ [°]	
C(1)–O(19)–C(12), C(3)–O(20)–C(10)	97.02(14)–97.10(15)[b]	97.70	C(1)–Si(23)–C(20)	86.9
C(5)–Si(21)–C(8), C(14)–Si(22)–C(17)	82.42(10)–82.51(10)[b]	80.5	C(3)–O(24)–C(18)	80.5
ψ [°]			ψ [°]	
C(14)–C(15)–C(16)–C(70)	0.3(2)	1.8	C(1)–C(22)–C(21)–C(21′)	2.0
C(17)–C(16)–C(15)–C(64)	6.8(2)	1.8		
C(5)–C(6)–C(7)–C(46)	12.5(2)	1.8		
C(8)–C(7)–C(6)–C(40)	1.3(2)	1.8		

[a] Butterfly bendings (ψ) defined as in ref.[18] and bond angles (θ). [b] Range of values.

crystallizes with a molecule of ethyl acetate, thus forming the solvate **9**·EtOAc. The molecular structure and the crystal packing are shown in Figure 1 and selected structural parameters are listed in Table 2.

The bond lengths and bond angles of **9** are similar to those found in structurally related molecules.[10,17] The double bonds in both 7-silanorbornene moieties deviate slightly from planarity (as indicated by the butterfly bendings;[18] Table 2), a feature observed in most 2,3-diphenylnorbornene and 2,3-diphenyl-7-metallonorbornene derivatives.[19] Molecules of **9** form voids occupied by the ethyl acetate molecules. Hydrophobic interactions and weak C–H···π[20,21] and C–H···O hydrogen bonds are the only packing interactions observed.

An interesting feature of bis-cycloadducts **8–14**, as mentioned above, concerns the presence of the cavity within the molecular framework. Unfortunately, all attempts to grow X-ray-quality crystals of these adducts, which would allow detailed analysis of their molecular structures and thus better characterization of the shape of the cavity, have so far failed. We therefore optimized the geometry of the model compound **10a** (derived by replacing the phenyl groups in **10** with hydrogen atoms) by the B3LYP/6-31G* method.[22] To validate the computational results we also carried out calculations for the model compound **9a** (obtained by replacing the phenyl groups in **9** with hydrogen atoms).

The calculated key structural parameters for both molecules are listed in Table 2. Without going into details we can conclude that there is a good agreement between the calculated geometry (B3LYP/6-31G*) of the structure of the model compound **9a** and the X-ray structure of its tetraphenyl-substituted derivative **9**. The experimentally determined Si–Si distance, for instance, is 10.10 Å, while the calculated value is 10.162 Å. Furthermore, the Si–C distances were found to lie within the 1.908–1.923 Å range, as compared to the B3LYP value of 1.936 Å. Moreover, the X-ray determined C(5)–Si(21)–C(8) angles are 97.0°, and the calculated value 97.70°. We can therefore safely conclude that the employed computational model represents a reasonable tool for study of the geometrical and spatial details of the molecules under consideration. This in turn allows us to analyse the shape of the cavity in **10**. It appears that the calculated structure indicates the presence of a host cavity, but that this is rather shallow, as illustrated by the space-filling model of the model compound **10a** shown in Figure 2. This implies that the host–guest interactions might be observable experimentally only with difficulty.

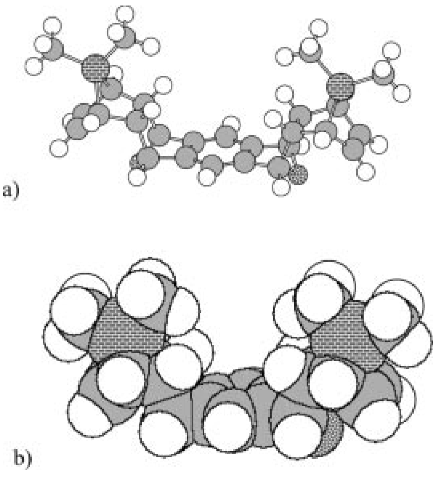


Figure 2. a) B3LYP/6-31G* optimized geometry of bis-adduct **10a**, and b) space-filling model (phenyl substituents are omitted for clarity).

This conclusion is further corroborated by the calculation of the AM1 electrostatic potential surface of the B3LYP/6-31G*-optimised structure of the bis-adduct **10a** (Figure 3, a), which indicates that there is little possibility for electrostatic interactions between the aromatic ring and the aromatic host within the host cavity.[23] Instead, the most negative electron density is, not surprisingly, located on the bridgehead oxygen atoms on the outer walls of the molecule (Figure 3, b).

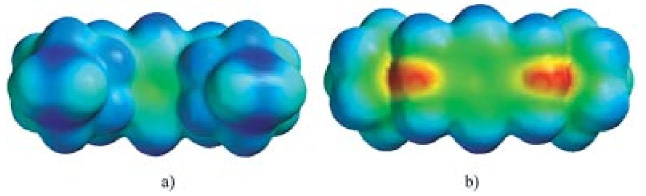
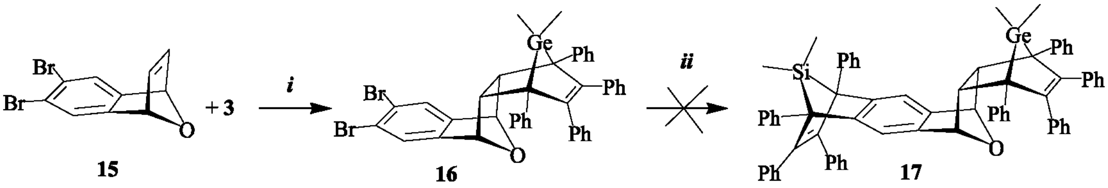


Figure 3. AM1 electrostatic potential mapped on the electron density surface (isovalue = 0.002) of the B3LYP/6-31G* optimised structure of bis-adduct **10a**: a) top view, b) bottom view. The colour code spans from –25 (red) to 25 kcal mol^{-1} (blue).

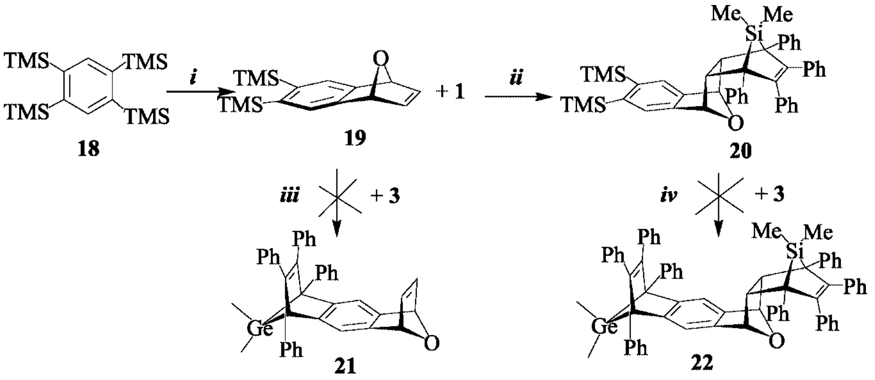
Synthetic Studies Towards Heteronuclear Bis-metallated Systems

The synthesis of the corresponding heteronuclear bis-metallated systems proved to be a more difficult task. Several synthetic routes were investigated for this purpose (Schemes 2, 3 and 4), but none afforded the desired products. We first investigated the possibility of preparing the adducts by addition of diene **1** to the benzyne intermediate (formed in situ) containing the mono-metallated adduct **16**.[24] Thus, treatment of the 6,7-dibromo-1,4-epoxy-1,4-dihydronaphthalene/germole adduct **16** (Scheme 2) with *n*BuLi in THF at low temperature and a subsequent attempt to trap the formed intermediate with silole **1** resulted in complete decomposition of the reactants and the formation of an intractable tar (Scheme 2).

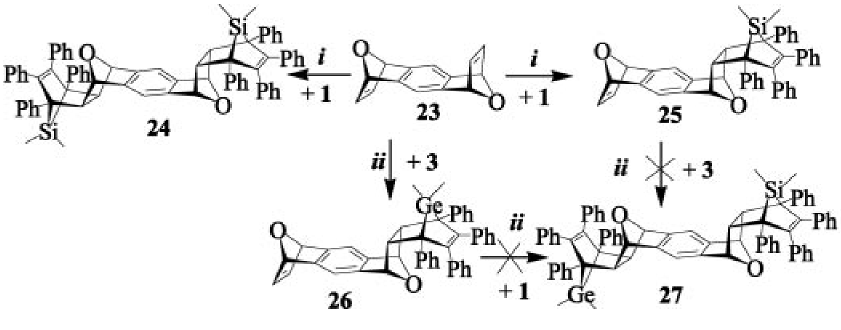
A milder method of benzyne generation, starting from 1,4-epoxy-6,7-bis(trimethylsilyl)-1,4-dihydronaphthalene adduct **20**[25] with use of the hypervalent iodine reagent iodobenzene diacetate [PhI(OAc)$_2$[26]], was therefore employed (Scheme 3). The adduct **20** was prepared in two-step fashion from 1,2,4,5-tetrakis(trimethylsilyl)benzene **18**.[27] In the first step, **18** was treated with PhI(OAc)$_2$, tetrabutylammonium fluoride and furan at room temperature, followed by high-pressure treatment with silole **1**. Attempts to generate



Scheme 2. Reagents and conditions. *i*) 0.8 GPa, 70 °C, 3 d, DCM. *ii*) *n*BuLi, –80 °C, THF, 3 h.



Scheme 3. Reagents and conditions. *i*) a) PhI(OAc)$_2$/DCM, 0 °C, TfOH, b) (*i*Pr)$_2$NH/DCM, 0 °C, c) furan, *n*Bu$_4$NF/THF, R.T. 20 min. *ii*) 0.8 GPa, 70 °C, 1 d, DCM. *iii*) a) PhI(OAc)$_2$/DCM, 0 °C, TsOH, b) (*i*Pr)$_2$NH/DCM, 0 °C, c) *n*Bu$_4$NF/THF, room temp. 20 min. *iv*) a) PhI(OAc)$_2$/DCM, 0 °C, TfOH, b) (*i*Pr)$_2$NH /DCM, 0 °C, *n*Bu$_4$NF/THF, room temp. 20 min.



Scheme 4. Reagents and conditions i) 0.8 GPa, 70 °C, 1 d, DCM. *ii*) 0.8 GPa, 70 °C, 3 d, DCM.

benzyne from **20** under reaction conditions identical to those used for the preparation of **19** and subsequent trapping with silole **1** or germole **3** resulted ultimately in cleavage of the organometallic bridges.

Finally, an attempt to prepare the heteronuclear bis-metalloid adducts by the two-step cycloadditions outlined in Scheme 4 under high pressure was made. When two equivalents of silole **1** were used together with *anti*-1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene **23**, a single product, the symmetrical 2:1 adduct **24,** was obtained in 38% yield. Accordingly, high-pressure treatment of equimolar amounts of diene **23** and silole **1** or germole **3** afforded 1:1 adducts **25** and **26** in 64% and 25% yields, respectively. However, when these 1:1 adducts were subjected to second high-pressure Diels–Alder reactions with metalloles **1** or **3**, complex mixtures of products were formed, as indicated by proton NMR spectroscopy. Successive chromatographic separations did not produce a pure sample of the desired adduct **27**, although HRMS of the crude reaction mixture indicated the presence of its molecular ion. Essentially the same outcome resulted when 1:1 adducts of imide **5** with **1** and **3** were subjected to the second high-pressure reaction.

Conclusion

High-pressure conditions have been shown to be beneficial for the reactions between siloles or germoles and oxanorbornenes. Addition of metalloles enabled the preparation of novel bis-metallic polynorbornenes with rigid and well defined geometrical separation of metal centres. All cycloaddition reactions with metalloles studied exhibited high stereospecificity resulting in exclusive formation of the *exo,endo* adducts. The synthetic methods employed in this work did not give bis-metallated cycloadducts.

Experimental Section

All reagents were used as purchased from commercial suppliers without further purification. Dry THF used in air-sensitive experiments was dried and distilled from sodium/calcium hydride under nitrogen prior to use. The 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (**1**),[28] 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene (**2**)[29] and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**3**)[30] were prepared according to the literature. Compounds **4**[31] and **5**[32] were available from our previous work. NMR spectra were recorded in $CDCl_3$ solutions containing tetramethylsilane as internal standard on a Bruker Avance 300 NMR spectrometer fitted with a gradient probe. The high-resolution mass spectra were obtained on a Micromass Autospec instrument, with electron impact (EI), chemical ionisation (CI) or electrospray (ES) ionisation. Melting point determinations were measured on a Kofler ENH apparatus and are uncorrected. Radial chromatography was carried out with a Chromatotron[33] model No. 79245T on 1-mm plates with Merck silica gel 60 PF_{254} as the stationary phase and with ethyl acetate/petroleum ether 40–60 °C mixture as eluent. Analytical thin layer chromatography was conducted on Merck silica gel 60 aluminium-backed plates. High pressure reactions were performed with the high-pressure piston-cylinder apparatus, in Teflon cells and with pentane as piezotransmitter liquid.[34]

The X-ray data were collected at 100(1) K with use of ω-scans on an Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystal data for **9**·EtOAc: $C_{75}H_{67}NO_5Si_2 \cdot C_4H_8O_2$, M_r = 1206.58, monoclinic $P2_1/n$ (No. 14), a = 9.8146(13) Å, b = 28.296(3) Å, c = 23.120(2) Å, β = 99.453(10)°, V = 6333.5(11) Å^3, Z = 4, $\rho_{calcd.}$ = 1.265 Mg m^{-3}3, μ = 0.115 mm^{-1}, $2\theta_{max}$ = 50°, 54067 measured reflections, 11100 independent reflections, 8770 reflections with $I > 2\sigma(I)$, 809 parameters refined, R_1 = 0.0555 [$F2 > 2\sigma(F2)$] and 0.0792 (all data), wR_2 = 0.1326 [$F2 > 2\sigma(F2)$] and 0.1458 (all data), S = 1.154, the largest difference peak and hole 0.403 and –0.291 e Å^{-3}. Data reduction (including intensity integration, background, Lorentz and polarization corrections) was performed by use of the CrysAlis software package.[35] The structure was solved by direct methods (SHELXS)[36] and refined by the full-matrix, least-squares method based on $F2$ against all reflections (SHELXL).[37] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and were refined by use of the riding model. Geometry calculations were carried out by use of PLATON[38] and PARST,[39] and the structure drawings were prepared by use of ORTEP[40] from the WinGX software system.[41]

(1α,2β,3α,4β,5β,8β,9β,10α,11β,12α,13β,14β,17β,18β)-21,21,22,22-Tetramethyl-5,6,7,8,14,15,16,17-octaphenyl-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-diene-22,24-dione (8): A solution of silacyclopentadiene **1** (166 mg, 0.4 mmol) and dienophile **4** (23 mg, 0.1 mmol) in dichloromethane (1.5 mL) was pressurized at 1 GPa and heated at 80 °C for 6 days. Solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) to afford colourless crystals (86 mg, 81%, m.p. 218–222 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.17 (s, 6 H, 23-H, 26-H), 0.61 (s, 6 H, 24-H, 25-H), 3.62 (s, 4 H, 4-H, 9-H, 13-H, 18-H), 5.39 (s, 4 H, 1-H, 3-H, 10-H, 12-H), 6.75–7.23 (m, 40 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –7.1 (C23, C26), –3.2 (C24, C25), 29.7 (C2, C11), 52.0 (C4, C9, C13, C18), 53.3 (C5, C8, C14, C17), 84.7 (C1, C3, C10, C12), 125.2, 125.7, 127.1, 128.2, 128.5, 130.1, 137.9, 139.3, 139.9, 169.3 (C22, C24) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): 39.5 ppm. HRMS (m/z): calcd. for $C_{72}H_{60}O_5Si_2$: 1060.3979; found 1060.3982.

(1α,2β,3α,4β,5β,8β,9β,10α,11β,12α,13β,14β,17β,18β)-23-(2-Methoxyethyl)-21,21,22,22-tetramethyl-5,6,7,8,14,15,16,17-octaphenyl-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-diene-22,24-dione (9): A solution of silacyclopentadiene **1** (100 mg, 0.242 mmol) and dienophile **5** (35 mg, 0.121 mmol) in dichloromethane (1.5 mL) was pressurized at 0.8 GPa and heated at 70 °C for 3 days. Solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford colourless crystals (49 mg, 57%, m.p. 229–232 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 6 H, 29-H, 31-H), 0.65 (s, 6 H, 28-H, 30-H), 3.25 (s, 3 H, 27-H), 3.54 (s, 4 H, 4-H, 9-H, 13-H, 18-H), 3.67 (t, J = 5.3 Hz, 2 H, 25-H), 3.85 (t, J = 5.3 Hz, 2 H, 26-H), 5.39 (s, 4 H, 1-H, 3-H, 10-H, 12-H), 6.85–7.25 (m, 40 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –11.2 (C29, C31), –8.1 (C28, C30), 33.1 (C2, C11), 46.7 (C4, C9, C13,C18), 48.6 (C5, C8, C14, C17), 53.3 (C27), 63.8 (C25), 69.2 (C26), 79.8 (C1, C3, C10, C12), 123.0, 123.2, 123.5, 124.1, 125.1, 128.3, 134.6 (q, C6, C7, C15, C16), 136.4 (q), 138.0 (q), 171.6 (C11, C24) ppm. HRMS (m/z): calcd. for $C_{75}H_{67}O_5N_2Si_2$: 1131.4588, $C_{75}H_{67}O_5N_2Si_2Na$: 1154.4486; found 1154.4494.

(1α,2β,3α,7α,8β,9α,12α,13β,14α,18α,19β,20α-23,23,26,26)-Tetramethyl-1,9,10,11,12,20,21,22-octaphenyl-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): A solution of silacyclopentadiene **1** (497 mg, 1.2 mmol) and dienophile **6** (84 mg, 0.4 mmol) in dichloromethane (1.5 mL) was pressurized at 1 GPa and heated at 50 °C for 5 days. Solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) to afford colourless crystals (328 mg, 79%, m.p. >300 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 6 H, 27-H, 30-H), 0.62 (s, 6 H, 28-H, 29-H), 3.36 (s, 4 H, 2-H, 8-H, 13-H, 19-H), 5.70 (s, 4 H, 3-H, 7-H, 14-H, 18-H), 6.77–7.30 (m, 42 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –6.9 (C27, C30), –3.3 (C28, C29), 51.6 (C1, C9, C12, C20), 52.9 (C2, C8, C13, C19), 82.1 (C3, C7, C14, C18), 110.2 (C5, C16), 124.9, 125.4, 127.0, 127.9, 128.9, 130.2, 138.8, 139.9, 141.5, 146.7 ppm. HRMS (FAB, *m/z*): calcd. for $C_{74}H_{62}O_2Si_2$: 1038.4288, $C_{74}H_{62}O_2Si_2Na$: 1016.4186; found 1016.4164.

(1α,2β,3α,7α,8β,9α,12α,13β,14α,18α,19β,20α)-23,23,26,26-Tetramethyl-1,9,12,20-tetraphenyl-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): A solution of silacyclopentadiene **2** (79 mg, 0.3 mmol) and dienophile **6** (21 mg, 0.1 mmol) in dichloromethane (1.5 mL) was pressurized at 1 GPa and heated at 50 °C for 5 days. Solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) to afford colourless crystals (54 mg, 74%, m.p. >300 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 6 H, 27-H, 30-H), 0.16 (s, 6 H, 28-H, 29-H), 3.49 (s, 4 H, 2-H, 8-H, 13-H, 19-H), 5.30 (s, 4 H, 3-H, 7-H, 14-H, 18-H), 6.43 (s, 4 H, 10-H, 111-H, 21-H, 22-H), 7.18–7.48 (m, 22 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –9.1 (C27, C30), –3.3 (C28, C29), 50.1 (C1, C9, C12, C20), 51.9 (C2, C8, C13, C19), 82.0 (C3, C7, C14, C18), 109.6 (C5, C16), 124.7, 125.8, 128.7 (C10, C11, C21, C22), 133.8, 142.9, 145.6 ppm. HRMS (*m/z*): calcd. for $C_{50}H_{46}O_2Si_2$: 734.3036; found 734.3052.

(1α,2β,3α,7α,8β,9α,12α,13β,14α,18α,19β,20α)-23,23,26,26-Tetramethyl-1,9,10,11,12,20,21,22-octaphenyl-24,25-dioxa-23,26-digermanoheptacyclo$[18.2.1.1^{3,18}.1^{7,14}.1^{9,12}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}]$hexacosa-4,6,10,16,21-pentaene (12): A solution of germacyclopentadiene **3** (137 mg, 0.3 mmol) and dienophile **6** (21 mg, 0.1 mmol) in dichloromethane (1.5 mL) was pressurized at 1 GPa and heated at 80 °C for 6 days. Solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) to afford colourless crystals (96 mg, 85%, m.p. 298–301 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.35 (s, 6 H, 27-H, 30-H), 0.67 (s, 6 H, 28-H, 29-H), 3.46 (s, 4 H, 2-H, 8-H, 13-H, 19-H), 5.68 (s, 4 H, 3-H, 7-H, 14-H, 18-H), 6.75–7.23 (m, 42 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –6.3 (C27, C30), –0.8 (C28, C29), 53.8 (C2, C8, C13, C19), 55.7 (C1, C5, C8, C14), 82.3 (C3, C7, C14, C18), 110.2 (C5, C16), 124.7, 125.2, 126.9, 127.8, 128.7, 130.1, 139.0, 139.6, 142.1, 146.4 ppm. HRMS (*m/z*): calcd. for $C_{74}H_{62}O_2Ge_2$: 1130.3173, $C_{74}H_{62}O_2Ge_2Na$: 1153.3071; found 1153.3092.

(1α,2β,3α,7α,8β,9α,12α,13β,14α,18α,19β,20α)-5,16,23,23,26,26-Hexamethyl-1,9,10,11,12,20,21,22-octaphenyl-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 (13): A solution of silacyclopentadiene **1** (621 mg, 1.5 mmol) and dienophile **7** (119 mg, 0.5 mmol) in dichloromethane (1.5 mL) was pressurized at 0.8 GPa and heated at 70 °C for 3 days. Solvent was removed in vacuo and the residue was purified by radial chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford colourless crystals (350 mg, 66%, m.p. >300 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 6 H, 27-H, 30-H), 0.63 (s, 6 H, 28-H, 29-H), 2.43 (s, 6 H, 31-H, 32-H), 3.32 (s, 4 H, 2-H, 8-H, 13-H, 19-H), 5.76 (s, 4 H, 3-H, 7-H, 14-H, 18-H), 6.81–7.21 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –6.8 (C27, C30), –3.4 (C28, C29), 15.4 (C31, C32), 51.5 (C1, C9, C12, C20), 52.3 (C2, C8, C13, C19), 81.1 (C3, C7, C14, C18), 117.5 (C5, C16), 124.9, 125.4, 127.0, 127.9, 128.8, 130.2, 138.8, 138.4, 141.7, 145.7 ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): 41.7 ppm. HRMS (*m/z*): calcd. for $C_{76}H_{66}O_2Si_2$: 1066.4601, $C_{76}H_{66}O_2Si_2Na$: 1089.4499; found 1089.4514.

(1α,2β,3α,7α,8β,9α,12α,13β,14α,18α,19β,20α)-5,16,23,23,26,26-Hexamethyl-1,9,12,20-tetraphenyl-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 (14): A solution of silacyclopentadiene **2** (393 mg, 1.5 mmol) and dienophile **7** (119 mg, 0.5 mmol) in dichloromethane (1.5 mL) was pressurized at 0.8 GPa and heated at 70 °C for 3 days. Solvent was removed in vacuo and the residue was purified by radial chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford colourless crystals (283 mg, 72%, m.p. >300 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, 6 H, 27-H, 30-H), 0.14 (s, 6 H, 28-H, 29-H), 2.33 (s, 6 H, 31-H, 32-H), 3.49 (s, 4 H, 2-H, 8-H, 13-H, 19-H), 5.29 (s, 4 H, 3-H, 7-H, 14-H, 18-H), 6.41 (s, 4 H, 10-H, 11-H, 21-H, 22-H), 7.19–7.44 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –9.4 (C27, C30), –3.8 (C28, C29), 15.1 (C31, C32), 50.0 (C1, C9, C12, C20), 51.0 (C2, C8, C13, C19), 80.9 (C3, C7, C14, C18), 124.7, 125.6, 128.7, 133.5, 134.1, 143.1, 145.6 ppm. HRMS (*m/z*): calcd. for $C_{52}H_{50}O_2Si_2$: 762.3349, $C_{52}H_{50}O_2Si_2Na$: 785.3247; found 785.3421.

6,7-Bis(trimethylsilyl)-1,4-dihydronaphthalene 1,4-Epoxide (19): A solution of iodobenzene diacetate (5.32 g, 16.5 mmol) in DCM (50 mL) was cooled to 0 °C, and triflic acid (3.1 mL, 36.3 mmol) was slowly added dropwise. After stirring for 1 hour at room temperature, the reaction mixture was again cooled to 0 °C and a solution of 1,2,4,5-tetrakis(trimethylsilyl)benzene (**18**, 3.96 g, 10.9 mmol) and diisopropylamine (3.0 mL, 21.5 mmol) in DCM (30 mL) was slowly added dropwise. The reaction mixture was warmed to room temperature for 15 min and furan (10 mL) was added, followed by a solution of tetrabutylammonium fluoride (5.83 g, 18.5 mmol) in THF (20 mL). After 20 min, water (200 mL) was added and the reaction mixture was stirred for 30 min. The organic phase was separated and the aqueous layer was extracted with DCM (3 × 50 mL). The combined organic layers were washed with water and dried (Na_2SO_4), and the solvent was removed in vacuo to yield the product as a black, oily solid. The product was purified by radial chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford **19** as a light yellow solid (2.40 g, 76%, m.p. 127–129 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.34 (s, 18 H, SiMe), 5.69 (s, 2 H, oxa), 7.00 (s, 2 H, Ar), 7.58 (s, 2 H).

(1α,2α,3β,10β,11α,12α)-15,15-Dimethyl-1,12,13,14-tetraphenyl-6,7-bis(trimethylsilyl)-16-oxa-15-silaheptacyclo$[10.2.1^{3,10}.1^{1,12}.0^{2,11}.0^{4,9}]$hexacosa-4,6,8,13-tetraene (20): A solution of silacyclopentadiene **1** (82 mg, 0.198 mmol) and dienophile **19** (57 mg, 0.198 mmol) in dichloromethane (1 mL) was pressurized at 0.8 GPa and heated at 70 °C for 1 day. Solvent was removed in vacuo and the residue was purified by radial chromatography on silica gel (petroleum ether/ethyl acetate 20:1) to afford **19** as colourless crystals (43 mg, 31%, m.p. 184–186 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.16 (s, 3 H, 17-H), 0.43 (s, 18 H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H), 0.66 (s, 3 H, 18-H), 3.38 (s, 2 H, 2-H, 11-H), 5.75 (s, 2 H, 3-H, 10-H), 6.83–7.23 (m, 20 H), 7.67 (s, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –7.5 (C17), –1.9 (C18), 1.23 (C19, C20, C21, C22, C23, C24), 50.0 (C1, C12), 51.8 (C2, C11), 81.3 (C3, C10), 123.8, 124.5, 125.9, 126.4, 126.9, 127.8, 129.4, 137.9, 138.5, 140.5, 143.7, 146.1 (C5, C8) ppm. HRMS (*m*/*z*): calcd. for $C_{46}H_{50}OSi_3$: 702.3169; found 702.3181.

(1α,2β,3α,7β,8α,9β,12β,13α,14β,18α,19β,20α)-23,23,26,26-Tetramethyl-1,9,10,11,12,20,21,22-octaphenyl-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 (24): A solution of silacyclopentadiene **1** (100 mg, 0.241 mmol) and dienophile **23** (28 mg, 0.133 mmol) in dichloromethane (1.5 mL) was pressurized at 0.8 GPa and heated at 70 °C for 1 day. Solvent was removed in vacuo and the residue was purified by radial chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford colourless crystals (49 mg, 38%, m.p. 247–248 °C). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.18 (s, 6 H, H-27, H-29), 0.66 (s, 6 H, H-28, H-30), 3.40 (s, 4 H, H-2, H-8, H-13, H-19), 5.74 (s, 4 H, H-3, H-7, H-14, H-18), 6.82–7.26 (m, 42 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = –3.2 (C27, C29), –1.1 (C28, C30), 51.7 (C1, C9, C12, C20), 53.0 (C2, C8, C13, C19), 82.1 (C3, C7, C14, C18), 110.2 (C5, C16), 124.8, 125.3, 126.9, 127.9, 128.9, 130.1, 138.7, 139.3, 141.4, 146.6 ppm. HRMS (*m*/*z*): calcd. for $C_{74}H_{62}O_2Si_2$: 1038.4288, $C_{74}H_{62}O_2Si_2Na$: 1061.4186; found 1061.4173.

(1α,5β,6α,7β,10β,11α,12β,16α)-21,21-Dimethyl-7,8,9,10-tetraphenyl-19,20-dioxa-21-silapentacyclo[14.2.1.1^{5,12}.1^{7,10}.0^{2,15}.0^{4,13}.0^{6,11}]henicosa-2,4,8,14-tetraene (25): A solution of silacyclopentadiene **7** (100 mg, 0.109 mmol) and dienophile **23** (14 mg, 0.067 mmol) in dichloromethane (1.5 mL) was pressurized at 0.8 GPa and heated at 70 °C for 1 day. Solvent was removed in vacuo and the residue was purified by radial chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford colourless crystals (51 mg, 64%, m.p. 291–293 °C). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.03 (s, 3 H, 23-H), 0.57 (s, 3 H, 22-H), 3.17 (s, 2 H, 6-H, 11-H), 5.59 (s, 2 H, 5-H, 12-H), 5.67 (s, 2 H, 1-H, 16-H), 6.87–7.21 (m, 22 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = –6.6 (C23), –4.4 (C22), 51.6 (C7, C10), 52.8 (C6, C11), 81.9 (C5, C12), 82.3 (C1, C18), 112.2 (C3, C14), 124.7, 125.2, 126.9, 127.8, 128.7, 130.1, 138.8, 139.4, 141.3, 143.1 (C17, C18), 145.4, 148.6 ppm. HRMS (*m*/*z*): calcd. for $C_{44}H_{36}O_2Si$: 624.2484; found 624.2471.

(1α,5β,6α,7β,10β,11α,12β,16α)-21,21-Dimethyl-7,8,9,10-tetraphenyl-19,20-dioxa-21-germanopentacyclo[14.2.1.1^{5,12}.1^{7,10}.0^{2,15}.0^{4,13}.0^{6,11}]henicosa-2,4,8,14-tetraene (26): A solution of germacyclopentadiene **7** (50 mg, 0.109 mmol) and dienophile **23** (13 mg, 0.055 mmol) in dichloromethane (1.5 mL) was pressurized at 0.8 GPa and heated at 70 °C for 3 days. Solvent was removed in vacuo and the residue was purified by radial chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford colourless crystals (16 mg, 25%, m.p. 239–242 °C). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.27 (s, 3 H, 23-H), 0.76 (s, 3 H, 22-H), 3.31 (s, 3 H, 6-H, 11-H), 5.60 (s, 3 H, 5-H, 12-H), 5.72 (s, 3 H, 11-H, 16-H), 6.76–7.29 (m, 22 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = –6.6 (C23), –0.9 (C22), 53.7 (C6, C11), 55.6 (C7, C10), 82.1 (C5, C12), 82.3 (C1, C16), 112.2 (C3, C14), 124.6, 125.1, 126.9, 127.8, 128.6, 130.2, 139.2, 139.8, 142.1, 143.1 (C17, C18), 145.4, 148.6 ppm. HRMS (*m*/*z*): calcd. for $C_{44}H_{36}O_2Ge$: 670.1927; found 670.1934.

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