Computational study on reactivity of cyclic organometallic dienes containing silicon, germanium and tin†

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Results of DFT (B3LYP/LANL2DZ) quantum-chemical study of reactivity of penta- and hexacyclic metalloles (Si, Ge and Sn) in Diels–Alder cycloaddition reactions are described. It was found that computational method employed correctly predicted the experimentally observed stereochemical outcome of the related reactions, which are governed by steric interactions in the transition states.

Introduction

Siloles, such as 1-sila-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene[1] and 1-sila-2,5-diphenyl-1,1-dimethyl-2,4-cyclopentadienes are reactive dienes, which readily undergo [4π + 2π] cycloadditions with activated alkynes or alkenes to give 7-silanorbornadiene and 7-silanorbornene derivatives, respectively.[2] Work on cycloaddition of germoles[3] has been also reported[4–8] while stannole cycloadducts are known to be thermally unstable.[9] In recent years we have been interested in exploring cycloadditions of siloles and germoles to 7-oxanorbornene derivatives under high-pressure conditions.[10–12] This synthetic approach[13] opened an avenue to a novel class of compounds possessing a 7-sila (7-germa) norbornene ring fused to the 7-oxanorbornene moiety.[14–17] Typical compounds, prepared in the course of these studies are shown in Fig. 1.

All studied reactions exhibited high stereospecificity leading to the *exo*,*endo*-adduct as a single product.[18] In order to get an insight into the origin of the observed stereospecificity we have also calculated activation energies for the related model reactions using the semiempirical AM1 method.[19] Since it is known that accuracy of the computed activation energies of Diels–Alder reactions (DA) strongly depends upon the method used for calculations[20–22] we decided to address this issue using the more reliable density functional (DFT) method. Herewith we present the most important results of this study. In addition to pentacyclic dienes **1–8**, the reactivity of a series of hexacyclic dienes (**9–16**) was calculated (Fig. 2).

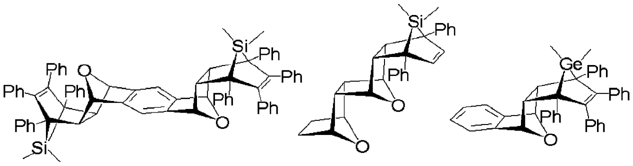

Fig. 1 Organometallic polynorbornene analogues.

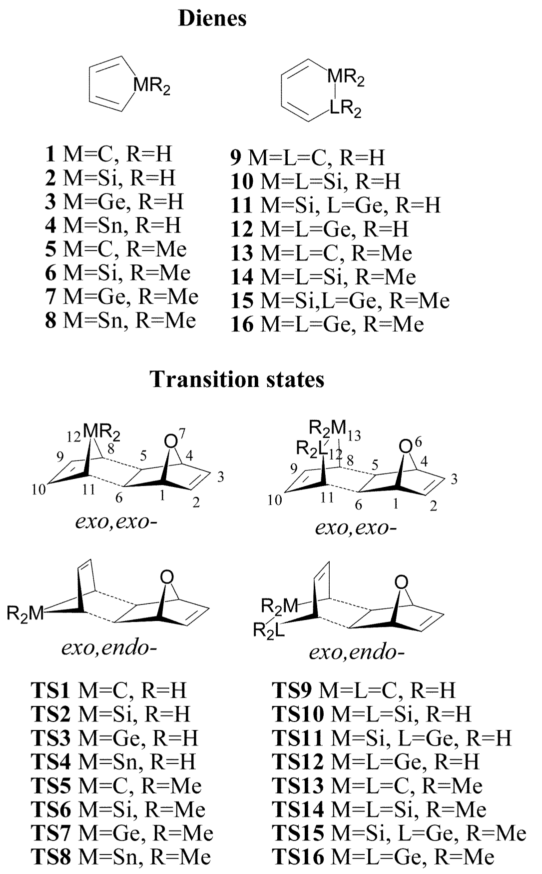

Fig. 2 Dienes and transition states studied in this work.

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† Electronic supplementary information (ESI) available: B3LYP/LANL2DZ calculated electronic energies for all reactants and products studied in this work (Tables S1–S3), results of single point B3LYP/LANL2DZ*//B3LYP/LANL2DZ and B3LYP/LANL2DZ* are given in Tables S4 and S5 and Tables S6 and S7, as well as the results of the relevant AM1 calculations[19] (Table S8), results of reaction energies (Table S9), FMO energies (Table S10), quantum of charge transfer (Table S11) and comparison of the B3LYP/LANL2DZ and AM1 calculated forming bond lengths in all transition structures (Table S12). Cartesian coordinates for all calculated structures are available on request from authors. See DOI: 10.1039/b515810a

Results and discussion

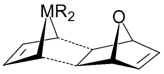
Due to the lack of parametrization for tin in the 6-31G* basis set, which is generally accepted to provide reliable relative energies and geometries for pericyclic reactions in conjunction with the hybrid B3LYP functional, all calculations were performed using the smaller LANL2DZ basis set. In order to test the performance of the LANL2DZ basis set for this type of reaction we first calculated the activation energy for the Diels–Alder reaction of cyclopentadiene and ethene which has been studied extensively both experimentally and computationally.[22] The computed activation energy of 96.2 kJ mol^{-1} (not including vibrational zero-point energies) was found to compare well with the experimental value[23] (99.2 kJ mol^{-1}). Correction of the electronic energies by ZPVEs increases this value to 106.2 kJ mol^{-1}, indicating that the LANL2DZ basis set, likewise 6-31G*,[22] overestimates the reaction barrier for this reaction.

Moreover, comparison of this value with results of previously published computational studies[24–27] for the same reaction revealed that the performance of the B3LYP/LANL2DZ method is close to that of the most accurate approaches used so far (B3LYP/6-31G*, MP3/6-31G* and CCSD(T)/6-31G*).[28,29] In the next step, we applied the same method to calculate activation energy for reaction of silole and ethylene. The resulting value of 98.5 kJ mol^{-1} was found to be in moderate agreement with that of the highest level calculations for this reaction reported so far.[25] In addition, in order to check the possible role of polarization functions, we also calculated the activation energy for both reactions with the same basis set supplemented by polarization functions at all atoms for the geometries optimized at the B3LYP/LANL2DZ level of theory (hereafter denoted as LANL2DZ*). These calculations afforded lower activation energies as compared to those obtained without polarization functions by 8.9 and 13.8 kJ mol^{-1} for reaction of cyclopentadiene and silole with ethylene, respectively. This in turn leads to reversal of reactivity ordering of cyclopentadiene and silole relative to the prediction obtained by the B3LYP/LANL2DZ method. However, due to a lack of experimental results for the latter reaction it is, unfortunately, not possible to conclude which of two approaches is more accurate. Therefore, in calculating activation energies of the reactions considered in this work we decided to apply both computational methods.

The results of these calculations are summarized in Table 1. In Table 2 the frontier molecular orbital (FMO) energies of the cyclic dienes are listed, while Table 3 summarizes C···C forming bond lengths in transition states calculated with the B3LYP/LANL2DZ method. Selected transition state structures optimized at the same level of theory are depicted in Fig. 3 and 5. The calculated electronic energies of the reactants, transition structures and products, as well as reaction energies obtained by B3LYP/LANL2DZ method are given in the ESI† (Tables S1–S3), while results of a single point B3LYP/LANL2DZ*//B3LYP/LANL2DZ and B3LYP/LANL2DZ* are given in Tables S4 and S5 and Tables S6 and S7, respectively. Table S8 summarizes relevant results of the AM1 calculations, for the sake of completeness.

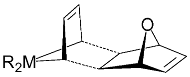
We shall commence discussion by comparing the calculated activation barriers for reactions of dienes **1–4** with 7-oxanorbornadiene.[30] It is well known that *endo*-approach to the norbornene π-bond in cycloaddition reactions is highly unlikely to occur.[31,32] Hence, we considered in detail only the reactions which take place through the *exo*-approach to the π-bond of 7-oxanorbornadiene. This premise was justified by calculations of activation barriers for all possible modes of addition of silole **2** to 7-oxanorbornadiene. Specifically, for the *exo*,*endo*-, *exo*,*exo*-, *endo*,*exo*- and *endo*,*endo*-diene

Table 1 B3LYP/LANL2DZ and B3LYP/LANL2DZ* activation energies (in parentheses)[a]



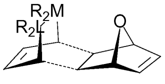
exo,exo-

TS R = H	M	ΔE_a I	 II	$\Delta\Delta E_a$
1	C	85.4 (50.4)	82.4 (45.2)	3.0 (5.2)
2	Si	100.8 (61.0)	87.0 (42.1)	13.8 (18.9)
3	Ge	102.9 (62.6)	86.2 (45.7)	16.7 (16.9)
4	Sn	96.2 (66.5)	89.1 (52.2)	7.1 (14.3)



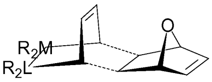
exo,endo-

TS R = CH_3	M	ΔE_a I	 II	$\Delta\Delta E_a$
5	C	146.9 (104.9)	107.9 (68.5)	39.0 (36.4)
6	Si	122.6 (82.1)	92.5 (50.8)	30.1 (31.3)
7	Ge	115.9 (78.9)	93.3 (51.8)	22.6 (27.1)
8	Sn	114.2 (72.4)	94.6 (54.6)	19.6 (17.8)



exo,exo-

TS R = H	M, L	ΔE_a I	 II	$\Delta\Delta E_a$
9	C, C	104.2 (69.1)	95.0 (60.1)	9.2 (9.0)
10	Si, Si	103.3 (61.9)	97.9 (53.5)	5.4 (8.4)
11	Si, Ge	102.1 (65.4)	95.8 (55.3)	6.3 (10.1)
12	Ge, Ge	104.6 (67.2)	99.8 (56.6)	4.8 (10.6)



exo,endo-

TS R = CH_3	M, L	ΔE_a **I**	 **II**	$\Delta\Delta E_a$
13	C, C	162.8 (127.3)	136.4 (101.8)	26.4 (25.5)
14	Si, Si	115.5 (80.3)	104.2 (65.2)	11.3 (15.1)
15	Si, Ge	113.0 (77.6)	102.9 (63.4)	10.1 (14.2)
16	Ge, Ge	108.3 (79.4)	103.6 (63.5)	4.7 (15.9)

[a] In kJ mol^{-1}; reaction mode: I = *exo*,*exo*; II = *exo*,*endo*.

Table 2 B3LYP/LANL2DZ FMO energy differences (in eV)

R = H	M	E_N	E_I		M, L	E_N	E_I
1	C	4.96	5.63	**9**	C, C	4.76	5.46
2	Si	5.40	4.66	**10**	Si, Si	5.54	4.52
3	Ge	5.41	4.69	**11**	Si, Ge	5.54	4.54
4	Sn	5.40	4.66	**12**	Ge, Ge	5.54	4.55
R = CH_3							
5	C	4.88	5.56	**13**	M = L = C	4.74	5.46
6	Si	5.14	4.88	**14**	M = L = Si	5.19	4.82
7	Ge	5.13	4.92	**15**	M = Si, L = Ge	5.17	4.84
8	Sn	5.12	4.91	**16**	M = L = Ge	5.15	4.86

[a] $E_N = HOMO_{(diene)} - LUMO_{(7\text{-oxanorbornadiene})}$. [b] $E_I = HOMO_{(7\text{-oxanorbornadiene})} - LUMO_{(diene)}$.

approaches, B3LYP/LANL2DZ activation energies were calculated to be 87.0, 100.8, 105.5 and 137.9 kJ mol^{-1}, respectively. This implies that *exo*-approach of diene is more favourable, with the *exo*,*endo*-orientation.

In analogy to this, for all other pentacyclic dienes considered in this work, the *exo*,*endo*-mode of addition to 7-oxanorbornadiene was calculated to have lower activation energies than the *exo*,*exo*-addition, irrespective of the method used. On the other hand, for all studied reactions the *exo*,*exo*-product was found to be more thermodynamically stable (Table S9 in ESI†), indicating that reactions proceed under kinetic control. Analysis of results in Table 1 shows that according to the B3LYP/LANL2DZ calculations the reactivity ordering of the dienes **1–4** in the *exo*,*endo*-mode of addition decreases across the series **1** (CH_2) > **2** (SiH_2) > **3** (GeH_2) > **4** (SnH_2). It is also worth of nothing that the difference in reactivity between metalloles **2–4** lies in the range of only 6.7 kJ mol^{-1}. Addition of polarization functions to all atoms in calculating electronic energies leads to somewhat different prediction (Table 1). The most significant changes include pronounced reduction of all activation energies and reversal of the reactivity ordering between **1** (CH_2) and **2** (SiH_2).[33] Nevertheless, both sets of values suggest that cycloaddition reactivity of silole, germole and stannole should be comparable to that of cyclopentadiene. In other words, all these reactions should be experimentally feasible. This holds in particular, for cycloadditions conducted under extreme reaction conditions such as high pressure or microwave irradiation. As to the reaction energies, all studied reactions are predicted to be exothermic by ∼110–185 kJ mol^{-1} (Table S9 in ESI†).

Analysis of the calculated activation energies for the reaction of the six-membered cyclic dienes **9–12** with 7-oxanorbornadiene reveals that stereoselectivity of these compounds follows the same trend as observed for metalloles **1–4**. That is, the *exo*,*endo*-mode of addition tends to be energetically more favourable than the *exo*,*exo*-mode. Furthermore, similarly to pentacyclic dienes, the magnitude of activation energies, as well as the order of reactivity, are found to be dependent on the method used. Thus, while reactivity ordering predicted by LANL2DZ calculations decreases across the series **9** (CH_2CH_2) ≥ **11** (SiH_2GeH_2) > **10** (SiH_2SiH_2) > **12** (GeH_2GeH_2) reactivities predicted by the LANL2DZ* calculations follow the order: **11** (SiH_2GeH_2) > **10** (SiH_2SiH_2) > **9** (CH_2CH_2) ∼**12** (GeH_2GeH_2). It should be however emphasised that, similarly to the previously discussed set of molecules, the differences in calculated activation energies for the reactions of all considered metalloles are rather small.[34] We also note that in all reactions, activation energies for cycloadditions of hexacyclic dienes at both levels of theory are larger by *ca.* 10 kJ mol^{-1} than for their pentacyclic analogues. These results are in accordance with the experimental observation that cyclopentadiene **1** (CPD) is more reactive than

Table 3 B3LYP/LANL2DZ C···C (C_5–C_8 and C_6–C_{11}) forming bond lengths (in Å) in **TS17–32**

TS R = H	M			TS R = CH_3	M		
		I	II			I	II
17	C	2.310; 2.347	2.296; 2.298	**21**	C	2.326; 2.337	2.325; 2.339
18	Si	2.353; 2.356	2.324; 2.325	**22**	Si	2.326; 2.405	2.333; 2.333
19	Ge	2.301; 2.414	2.323; 2.332	**23**	Ge	2.361; 2.378	2.339; 2.342
20	Sn	2.371; 2.402	2.324; 2.327	**24**	Sn	2.370; 2.400	2.334; 2.348
TS R = H	M, L			TS R = CH_3	M, L		
		I	II			I	II
25	C	2.360; 2.361	2.344; 2.345	**29**	C	2.336; 2.409	2.311; 2.404
26	Si	2.385; 2.392	2.345; 2.386	**30**	Si	2.401; 2.402	2.360; 2.397
27	Si Ge	2.377; 2.398	2.324; 2.434	**31**	Si Ge	2.300; 2.463	2.338; 2.419
28	Ge	2.385; 2.400	2.365; 2.391	**32**	Ge	2.403; 2.403	2.384; 2.388

[a] Reaction modes: I = *exo*,*exo*; II = *exo*,*endo*.

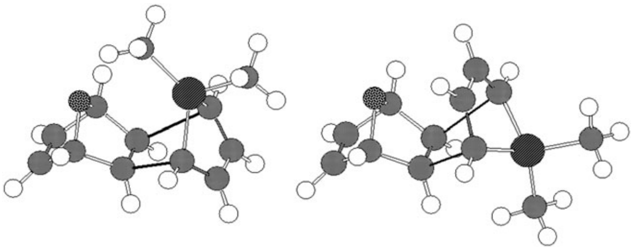


Fig. 3 B3LYP/LANL2DZ optimised *exo*,*exo*-**TS7** (left) and *exo*,*endo*-**TS7** (right) TS structures for reaction of diene **7** with 7-oxanorbornadiene. The forming bonds (denoted as C5–C8 and C6–C11 in Fig. 2) are shown as dashed lines.

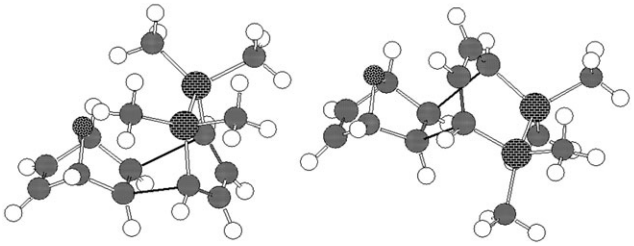


Fig. 5 B3LYP/LANL2DZ optimised *exo*,*exo*-**TS14** (left) and *exo*,*endo*-**TS14** (right) TS structures for reaction of diene **14** with 7-oxanorbornadiene. The forming bonds (denoted as C5–C8 and C6–C11 in Fig. 2) are shown as dashed lines.

cyclohexadiene **9** in Diels–Alder reactions with strained cyclic dienophiles and 2-substituted allylacetylenes,[35] as well as with results of previously reported calculations for reactions of **1** and **9** with ethylene.[36,37] Earlier, Henry *et al.*[38] ascribed this result to difference in distances in 1,4-diene reactive sites. In other words, in reactions with **9** the degree of orbital overlap between reacting sites in the transition structure is smaller than in case of **1** and consequently the contribution of the donor–acceptor interaction to the reaction barrier is smaller. Alternatively, the larger reactivity of **1** could be understood in terms of larger strain energy of the five-membered ring relative to **9**.[36] Since **1** is more strained than **9**, the energy of the DA transition state structure is expected to be closer to that of the reactants.

The effect of replacement of the hydrogen atoms within the MH_2 group in **1–4** and **9–12** with the methyl groups on activation barriers was also explored. Calculated activation energies are summarized in Table 1. Their analysis shows that for the methyl substituted dienes **5–8**, B3LYP/LANL2DZ calculations predict a larger *exo*,*endo*-/*exo*,*exo*-energy gap than for the corresponding unsubstituted metalloles (in some instances up to 39 kJ mol^{-1}). The most plausible explanation of this finding lies in an increase of steric hindrance for the *exo*,*exo*-diene approach, as illustrated by Fig. 3 for the *exo*,*exo*-addition of germole **7** to 7-oxanorbornadiene. This is corroborated by analysis of electrostatic density surfaces in the transition structures for the *exo*,*exo*-addition of pentacyclic dimethyl substituted dienes **5–8** to 7-oxanorbornadiene (*exo*,*exo*-**TS5–TS8**) (Fig. 4), which clearly shows that steric/electronic interactions between the oxygen lone pair and hydrogen atoms of the methyl groups, decreases on going from the *exo*,*exo*-**TS5** to the *exo*,*exo*-**TS8**. It seems reasonable to assume that this results from the increase of the metal–carbon bond lengths in the diene component across the considered series. On the other hand, steric hindrance for the *exo*,*exo*-approach of cyclic hexadienes **9–12** to 7-oxanorbornene is expected to be less sensitive to methylation than pentacyclic dienes, due to the fact that in these structures, the oxygen lone pair bisects M_{12}–M_{13} (C_9–C_{10}) bond, thus resulting in larger $O_7 \cdots M_{12}$ methyl hydrogen separation than in structures **TS1–TS8**. For instance, $O_7 \cdots M_{12}$ methyl hydrogen distances are 2.080 and 2.420 Å in the *exo*,*exo*-**TS6** and the *exo*,*exo*-**TS14**, respectively. For the same reason, less pronounced increase in the *exo*,*endo*-/*exo*,*exo*-energy gap is expected, as indeed observed (Table 1). This is also illustrated by comparison of the optimized TS structures of the *exo*,*exo*-**TS14** and the *exo*,*endo*-**TS14** in Fig. 5. Finally, it is important to stress that contribution of intramolecular hydrogen bonding to stability of TSs can be generally ruled out due to large distances between oxygen O_7 and hydrogen atom of approaching dienes.

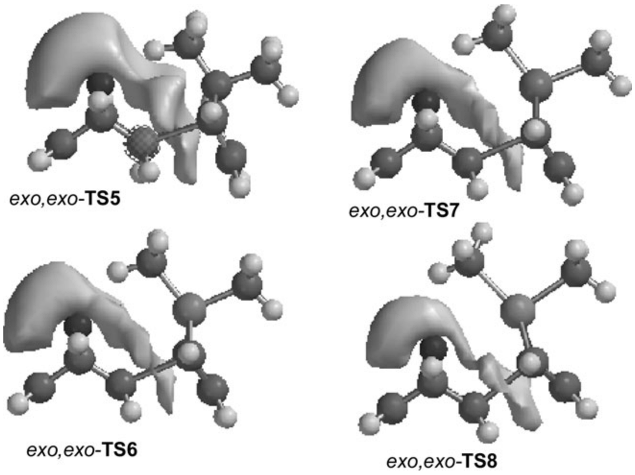


Fig. 4 Electrostatic potential (surface plotted at −20 kJ mol^{-1}) of B3LYP/LANL2DZ optimised *exo*,*exo*-TSs for reaction of dienes **5–8** with 7-oxanorbornadiene (*exo*,*exo*-**TS5–TS8**).

Following our interest in Diels–Alder reactivity of polysubstituted siloles,[15] we have also calculated activation energies for the model reaction of 7-oxanobornadiene with 1,1,2,3,4,5-hexamethyl-1-silacyclopentadiene, the latter acting as an acceptable model for the experimentally used 1,1-dimethyl-2,3,4,5-tetraphenylsilole. For this purpose only the LANL2DZ basis set was used. As expected on the basis of steric repulsions, the activation energy for the more favourable *exo*,*endo*-addition was found to be by 3 kJ mol^{-1} higher than activation energy for reaction of 1,1-dimethyl-1-silacyclopentadiene (90.2 kJ mol^{-1}). It is gratifying that this result is in agreement with the experimentally observed influence of ring substituents on the barrier heights in previously studied Diels–Alder reactions of siloles.[39] Specifically, experimentally determined activation energies for Diels–Alder reactions of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene and 1,1-dimethyl-3,4-diphenyl-1-silacyclopentadiene with maleic anhydride are

60.25, 39.33 and 34.73 kJ mol^{-1}, respectively. It is noteworthy that the latter values are close to those observed in addition of cyclopentadiene with maleic anhydride. This suggests that substitution at the silole 2,5-position increases barrier height, by similar steric and electronic effects[39] as reported earlier for reaction of furan and 2,5-dimethylfuran with dimethyl acetylene dicarboxylate.[40]

Finally, we shall briefly analyse reactivity ordering of the considered metalloles based on examination of their frontier molecular orbitals (FMO).[41] Closer inspection of the results presented in Table 2 and Table S10 in ESI† indicates that cycloaddition reactions of all-carbon containing dienes (**1**, **5**, **9** and **13**) studied in this work follow normal electron demand Diels–Alder reactions. On the other hand, reactions of all heterocyclic dienes are predicted to be inverse electron demand Diels–Alder reactions. Furthermore, based on FMO analysis, dienes **1** and **9** are predicted to be less reactive than their heteroatom analogues, thus being in contrast with the reactivity ordering calculated by the B3LYP/LANL2DZ method. The opposite trend is encountered for series **5–8** and **13–16**, although differences in the calculated E_{I} values across each of the series of dienes are quantitatively marginal. Calculations of quantum of charge transfer (*q*CT) from diene to dienophile lead to the same conclusion (see Table S11 in ESI†).

Although geometries of the considered molecules are not of primary concern in this paper, a few comments on geometries of transition state structures are warranted here. For this purpose we shall make use of geometries calculated at the B3LYP/LANL2DZ level of theory only, since addition of polarization functions to all atoms was found to have practically no effect on structural parameters. The most interesting aspect of the calculated geometries is the length of the newly formed bonds between the diene and 7-oxanorbornadiene (C···C (C_5–C_8 and C_6–C_{11}) forming bond lengths) in the TS structures (Table 3). Survey of the data shows that the calculated transition structures for most of the considered reactions of pentacyclic dienes are slightly asynchronous, with the difference in length of the two forming bonds being 0.001–0.009 Å (Table 3). The only exception is provided by **TS6**, in which the length of the newly forming bonds is found to be identical. On the other hand, reactions of all hexacyclic dienes studied in this work are found to proceed through highly asynchronous transition states with one notable exception: the **TS9** in which the difference in the two forming bonds is negligible (Table 3). As to the length of the forming bonds, we conclude that all the considered reactions proceed through the early TS.

It is also noteworthy that the B3LYP/LANL2DZ C···C forming bond lengths in TSs for two different approaches of dienes in TSs **11–16** are on average 0.037 Å longer in the *exo*,*exo*-than in the *exo*,*endo*-approach. On the other hand, there is no uniform trend in changes of the forming bond length upon replacing MH_2 with the $M(CH_3)_2$ groups. The same holds for substitution of the tetrahedral carbon with the other group 14 elements in the series.

Finally, we note that in the B3LYP/LANL2DZ calculated TS structures C···C forming bond lengths are on average by 0.190 Å longer than previously published AM1 values (Table S12 in ESI†).[19]

Conclusion

B3LYP quantum chemical calculations using the LANL2DZ basis set and the LANL2DZ basis set supplemented with polarization functions at all atoms were used to model cycloaddition reactions of penta- (**1–8**) and hexacyclic (**9–16**) metalloles with 7-oxanorbornadiene. The computational study correctly predicts experimentally observed *exo*,*endo*-stereospecificity of the studied reactions, which are governed by steric interactions in the transition states. The calculated activation energies, as well as the order of reactivity of the five-membered dienes is found to be dependent on the method used. Specifically, addition of polarization functions to all atoms is found to lead to pronounced lowering of all activation energies and reversal of the reactivity ordering between **1** (CH_2) and **2** (SiH_2). This, however, does not hold for their methylated analogues (**5–8**) in which the carbocyclic diene is found to be less reactive than its metallole analogues at both levels of theory. Therefore, thorough experimental studies of the considered reactions would be highly desirable in order to check these predictions. A similar trend was encountered for the hexacyclic dienes and their methylated analogues. Analysis of the optimized geometries of the transition states indicates that all reactions proceed through asynchronous transition states with the difference in the length of the forming bonds being more pronounced in reactions of hexacyclic dienes. The only exception is provided by **TS6** which was found to be synchronous.

Computational details

Initial geometries of all species obtained by AM1 method[42] were optimised using Becke's three-parameter method using the Lee, Young and Parr correlation functional (B3LYP),[43–45] with the LANL2DZ basis set (D95V on first row,[46] Los Alamos ECP[47,48] plus DZ for heavier elements). The energies of the selected structures were further refined by single point electronic energy calculations using the B3LYP/LANL2DZ method supplemented with polarization functions at all atoms at the geometries optimized by the B3LYP/LANL2DZ (B3LYP/LANL2DZ*//B3LYP/LANL2DZ method). Some of the structures were also optimised using the B3LYP/LANL2DZ method with polarization functions added to all atoms (B3LYP/LANL2DZ*), while energies were estimated by single point geometry optimizations carried out with the *Gaussian 03* suite of programs[49] on the Isabella computer cluster (24 dual processor HP ProLiant BLP20p nodes with Intel Xeon 2.8 GHz, 32 dual processor Dell 1850 1U nodes with Intel Xeon 3.4 GHz and 24 dual processor Pyramid GX28 nodes with AMD Opteron 248). Each transition structure was located using a standard routine within *Gaussian 03* and verified by the possession of only one imaginary frequency of vibration, corresponding to the motion of forming C···C bonds for concerted transition structures.[50]

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