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Computational Study on reactivity of cyclic organometallic dienes containining silicon, germanium and tin

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Table S1. Total energies of reactants obtained by B3LYP/LANL2DZ (a.u.)

		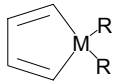			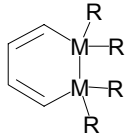
		R=H			*R=H*
	M				
1	C	-194.07159	**9**	C	-233.38217
2	Si	-159.84304	**10**	Si	-164.93178
3	Ge	-159.72211	**11**	SiGe	-164.81509
4	Sn	-159.31171	**12**	Ge	-164.69876
		R=CH₃			*R=CH₃*
5	C	-272.68522	**13**	C	-390.60631
6	Si	-238.49574	**14**	Si	-322.22849
7	Ge	-238.37146	**15**	SiGe	-322.10858
8	Sn	-237.96086	**16**	Ge	-321.98912
					
		-307.318396			

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Table S2. Total energies of transition state structures obtained by B3LYP/LANL2DZ (a.u.)

		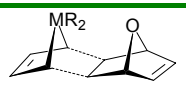	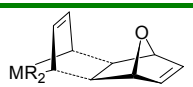			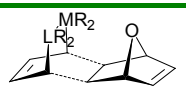	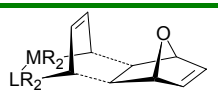
		R=H				*R=H*	
TS	**M**	*exo,exo-*	*exo,endo-*	**TS**	**M, L**	*exo,exo-*	*exo,endo-*
1	C	-501.357423	-501.358543	**9**	C	-540.660915	-540.664334
2	Si	-467.123108	-467.128282	**10**	Si	-472.210795	-472.212928
3	Ge	-467.001281	-467.007756	**11**	Si Ge	-472.094589	-472.097039
4	Sn	-466.593379	-466.596111	**12**	Ge	-471.977300	-471.979142
		R=CH$_3$				*R=CH$_3$*	
5	C	-579.948321	-579.963009	**13**	C	-697.862793	-697.872781
6	Si	-545.767487	-545.778962	**14**	Si	-629.502953	-629.507157
7	Ge	-545.645691	-545.654342	**15**	Si Ge	-629.383999	-629.387827
8	Sn	-545.238981	-545.243176	**16**	Ge	-629.266276	-629.268057

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Table S3. B3LYP/LANL2DZ total energies of products (in a.u.)

		Product *Exo,exo-*	Product *Exo,endo-*				Product *Exo,exo-*	Product *Exo,end-o*	
TS	**M**	*R=H*		*ΔΔE*	**TS**	**M, L**			*ΔΔE*
1	C	-501.43989	-501.43377	16.1	**9**	C	-540.76359	-540.76069	7.4
2	Si	-467.21245	-467.20798	11.8	**10**	Si	-472.31716	-472.31409	8.1
3	Ge	-467.09545	-467.09039	13.3	**11**	Si Ge	-472.20251	-472.199286	8.5
4	Sn	-466.69184	-466.68199	25.9	**12**	Ge	-472.08799	-472.08494	8.0
		R=CH₃							
5	C	-580.04993	-580.04232	32.5	**13**	C	-697.97353	-697.97224	22.9
6	Si	-545.85841	-545.85653	2.9	**14**	Si	-629.60994	-629.60842	4.0
7	Ge	-545.73936	-545.73843	2.4	**15**	Si Ge	-629.49237	-629.49034	5.3
8	Sn	-545.33764	-545.33019	19.6	**16**	Ge	-629.37539	-629.37276	6.9

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Table S4. Total energies of reactants obtained by B3LYP/LANL2DZ* // B3LYP/LANL2DZ (a.u.)

	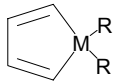			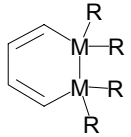	
	R=H				*R=H*
	M				
1	C	-194.12427	**9**	C	-233.445586
2	Si	-159.91135	**10**	Si	-165.02132
3	Ge	-159.77634	**11**	SiGe	-164.764495
4	Sn	-159.35969	**12**	Ge	-164.892518
	R=CH₃				*R=CH₃*
5	C	-272.76089	**13**	C	-233.445367
6	Si	-238.57861	**14**	Si	-165.02104
7	Ge	-238.43831	**15**	SiGe	-164.76431
8	Sn	-238.01917	**16**	Ge	-164.89225
					
	-307.39839				

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Table S5. Total energies of transition state structures obtained by B3LYP/LANL2DZ*//B3LYP/LANL2DZ (a.u.)

			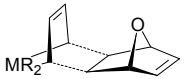			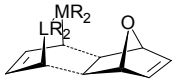	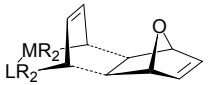
		R=H				*R=H*	
TS	**M**	*exo,exo-*	*exo,endo-*	**TS**	**M, L**	*exo,exo-*	*exo,endo-*
1	C	-501.50347	-501.50543	**9**	C	-540.81767	-540.82109
2	Si	-467.28650	-467.29371	**10**	Si	-472.39615	-472.39933
3	Ge	-467.15087	-467.15731	**11**	Si Ge	-472.26706	-472.27022
4	Sn	-466.73275	-466.73819	**12**	Ge	-472.13923	-472.14168
		R=CH₃				*R=CH₃*	
5	C	-580.11923	-580.13319	**13**	C	-698.06450	-698.07401
6	Si	-545.94572	-545.95765	**14**	Si	-629.71801	-629.72375
7	Ge	-545.80664	-545.81696	**15**	Si Ge	-629.45239	-629.45778
8	Sn	-545.38999	-545.39678	**16**	Ge	-629.58447	-629.59059

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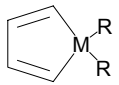
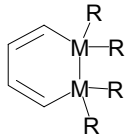
Table S6. Total energies of reactants obtained by B3LYP/LANL2DZ* (a.u.)

					
		R=H			*R=H*
	M				
1	C	-194.12427	**9**	C	-233.44559
2	Si	-159.91135	**10**	Si	-165.02132
3	Ge	-159.77634	**11**	SiGe	-164.89252
4	Sn	-159.35969	**12**	Ge	-164.764495
		R=CH₃			*R=CH₃*
5	C	-272.76126	**13**	C	-390.71506
6	Si	-238.57926	**14**	Si	-322.35076
7	Ge	-238.43858	**15**	SiGe	-322.21682
8	Sn	-238.01952	**16**	Ge	-322.08378

-307.400098

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Table S7. Total energies of transition state structures obtained by B3LYP/LANL2DZ* (a.u.)

		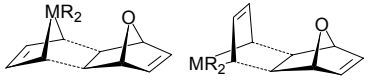				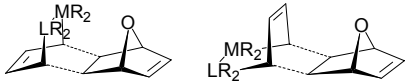	
		R=H				*R=H*	
TS	**M**	*exo,exo-*	*exo,endo-*	**TS**	**M, L**	*exo,exo-*	*exo,endo-*
1	C	-501.50726	-501.51015	**9**	C		-540.82549
2	Si	-467.29035	-467.29754	**10**	Si		-472.40249
3	Ge	-467.15429	-467.16042	**11**	Si Ge		-472.27431
4	Sn	-466.73714	-466.74195	**12**	Ge		-472.14435
		R=CH₃				*R=CH₃*	
5	C	-580.12279	-580.13728	**13**	C		-698.08006
6	Si	-545.94981	-545.96186	**14**	Si	-629.72307	-629.72835
7	Ge	-545.81091	-545.82028	**15**	Si Ge	-629.58953	-629.59514
8	Sn	-545.39429	-545.40061	**16**	Ge	-629.45749	

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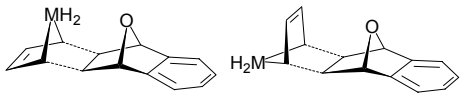
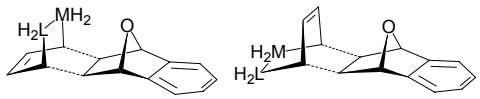
Table S8. AM1 activation energies in $kJmol^{-1}$





TS	M	*exo,exo-*	*exo,endo-*	TS		*exo,exo-*	*exo,endo-*
1	C	138.7	134.6	**9**	M=L=C	143.5	138.1
2	Si	179.0	149.3	**10**	M=L=Si	186.3	166.6
3	Ge	140.9	135.4	**11**	M=Si,L=Ge	166.1	149.6
4	Sn	174.7	157.5	**12**	M=L=Ge	146.6	137.9

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Table S9. B3LYP/LANL2DZ reactions' energies ΔH_{rxn} (in kJmol^{-1})

		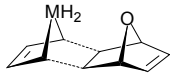	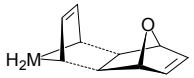				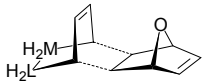
		R=H				R=H	
TS	**M**	*exo,exo-*	*exo,endo-*	**TS**	**M, L**	*exo,exo-*	*exo,endo-*
1	C	-131.0	-114.9	**9**	C	-165.5	-158.1
2	Si	-133.9	-122.1	**10**	Si	-175.9	-167.8
3	Ge	-144.3	-131.0	**11**	Si Ge	-181.2	-172.8
4	Sn	-136.2	-110.3	**12**	Ge	-185.9	-177.9
		$R=CH_3$				$R=CH_3$	
5	C	-121.6	-89.1	**13**	C	-128.2	-105.3
6	Si	-116.2	-113.3	**14**	Si	-165.5	-161.5
7	Ge	-129.9	-127.5	**15**	Si Ge	-171.9	-166.6
8	Sn	-153.3	-133.7	**16**	Ge	-178.2	-168.3

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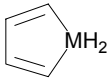
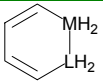
Table S10. B3LYP/LANL2DZ FMO orbital energies in eV

							
	M	HOMO	LUMO			HOMO	LUMO
		R=H					
1	C	-5.91	-0.56	**9**	M=L=C	-5.71	-0.73
2	Si	-6.35	-1.53	**10**	M=L=Si	-6.49	-1.67
3	Ge	-6.36	-1.50	**11**	M=Si,L=Ge	-6.49	-1.65
4	Sn	-6.35	-1.53	**12**	M=L=Ge	-6.49	-1.64
		R=CH₃					
5	C	-5.83	-0.63	**13**	M=L=C	-5.69	-0.73
6	Si	-6.09	-1.31	**14**	M=L=Si	-6.14	-1.37
7	Ge	-6.09	-1.27	**15**	M=Si,L=Ge	-6.12	-1.35
8	Sn	-6.08	-1.30	**16**	M=L=Ge	-6.10	-1.33

I=$HOMO_{(diene)}$-$LUMO_{(alkene)}$; II=$HOMO_{(alkene)}$-$LUMO_{(diene)}$

7oxaNBD: HOMO=-6.19, LUMO= -0.95 eV

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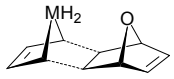
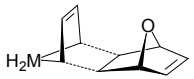
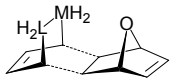
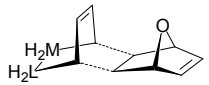
Table S11. B3LYP/LANL2DZ quantum of charge transfer from diene to dienophile[a]

							
		R=H				R=H	
TS	**M**	*exo,exo-*	*exo,endo-*	**TS**	**M, L**	*exo,exo-*	*exo,endo-*
1	C	-0.071	-0.067	**9**	C	-0.090	-0.054
2	Si	0.017	0.128	**10**	Si	0.045	0.035
3	Ge	0.005	0.009	**11**	Si Ge	0.049	0.055
4	Sn	0.030	0.002	**12**	Ge	0.040	0.041
		R=CH₃				*R=CH₃*	
5	C	-0.072	-0.071	**13**	C	-0.082	-0.080
6	Si	0.009	0.007	**14**	Si	0.003	0.001
7	Ge	0.007	0.007	**15**	Si Ge	0.010	0.024
8	Sn	0.018	0.028	**16**	Ge	0.004	0.011

[a]Negative numbers = electron transfer from diene to dienophile (normal el. demand)

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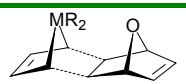
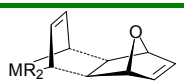
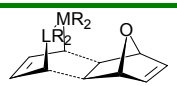
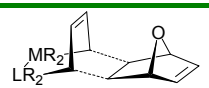
Table S12.Comparison of the length of the forming bond lengths (in Å) in **TS1-16** calculated with the B3LYP/LANL2DZ and AM1 methods.

											
		R=H						*R=H*			
TS	**M**	*exo,exo-*		*exo,endo-*		**TS**	**M,L**	*exo,exo-*		*exo,endo-*	
		B3LYP	AM1	B3LYP	AM1			B3LYP	AM1	B3LYP	AM1
1	C	2.310; 2.347	2.155; 2.155	2.296; 2.298	2.141; 2.142	**9**	C	2.360; 2.361	2.171; 2.172	2.344; 2.345	2.161; 2.161
2	Si	2.353; 2.356	2.155; 2.156	2.324; 2.325	2.131; 2.135	**10**	Si	2.385; 2.392	2.181; 2.183	2.345; 2.386	2.166; 2.167
3	Ge	2.301; 2.414	2.161; 2.163	2.323; 2.332	2.143; 2.146	**11**	Si, Ge	2.377; 2.398	2.076; 2.312	2.324; 2.434	2.121; 2.228
4	Sn	2.371; 2.402	2.167; 2.168	2.324; 2.327	2.153; 2.155	**12**	Ge	2.385; 2.400	2.186; 2.188	2.365; 2.391	2.177; 2.178
		R=CH$_3$						*R=CH$_3$*			
5	C	2.326; 2.337	2.165; 2.170	2.325; 2.339	2.151; 2.155	**13**	C	2.336; 2.409	2.183; 2.195	2.311; 2.404	2.168; 2.177
6	Si	2.326; 2.405	2.123; 2.140	2.133; 2.333	2.133; 2.146	**14**	Si	2.401; 2.402	2.178; 2.190	2.360; 2.397	2.168; 2.168
7	Ge	2.361; 2.378	2.161; 2.163	2.339; 2.342	2.143; 2.144	**15**	Si Ge	2.300; 2.463	2.087; 2.301	2.338; 2.419	2.119; 2.230
8	Sn	2.370; 2.400	2.167; 2.176	2.334; 2.348	2.158; 2.159	**16**	Ge	2.403; 2.403	2.187; 2.190	2.384; 2.388	2.174; 2.176