The Multiple Bonding in Heavier Group 14 Element Alkene Analogues is Stabilized Mainly by Dispersion Force Effects

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Supporting Information

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Table S1. Calculated binding energies (kcal mol^{-1}) of E_2R_4 (E = Ge or Sn; R = $CH(SiMe_3)_2$) with a *syn*,*anti* configuration for the ER_2 units and H-C-E-C angles set at experimental values.

$[E\{CH(SiMe_3)_2\}_2]_2 \rightarrow 2E\{CH(SiMe_3)_2\}_2$				
	E = Ge		E = Sn	
	B3PW91	B3PW91-D3	B3PW91	B3PW91-D3
ΔE^a	5.6 (-2.3)	40.2 (28.7)	12.0 (2.1)	38.5 (26.3)
$\Delta E^{a,b}$	14.0 (6.5)	50.4 (39.4)	13.3 (3.1)	40.5 (28.8)
[a] Binding energy. In parentheses are values with ZPE and BSSE corrections. [b] The Ge and Sn monomers are optimized by fixing the (H-C-E-C) torsion angles at experimental values: 2° for GeR2; 15° for SnR2.				

Table S2. Calculated structural data for the Ge_2R_4 and Sn_2R_4 (R = $CH(SiMe_3)_2$) dimers with the GeR_2 and SnR_2 units within the dimers in *syn*,*syn* configuration.

	Ge_2R_4			Sn_2R_4		
	B3PW91	B3PW91-D3	B97-D3	B3PW91	B3PW91-D3	B97-D3
E-E (Å)	2.428	2.377	2.452	2.842	2.765	2.855
E-C (Å)	2.034 (av.)	2.012 (av.)	2.051 (av.)	2.239 (av.)	2.210 (av.)	2.267 (av.)
C-E-C (°)	98.7 (av.)	98.1 (av.)	97.7 (av.)	96.3 (av.)	96.0 (av.)	95.3 (av.)
C-E-E (°)	122.6 (av.)	121.0 (av.)	120.2 (av.)	121.2 (av.)	119.2 (av.)	118.6 (av.)
C-E-E-C (°)	-51.6 (av.) 164.0 (av.)	-56.3 (av.) 167.2 (av.)	-58.7 (av.) 167.4 (av.)	-58.7 (av.) 168.7 (av.)	-62.9 (av.) 163.4 (av.)	-65.2 (av.) 166.9 (av.)
Trans-bent angle (°)	34.3 (av.)	38.0 (av.)	40.1 (av.)	39.0 (av.)	43.4 (av.)	44.8 (av.)

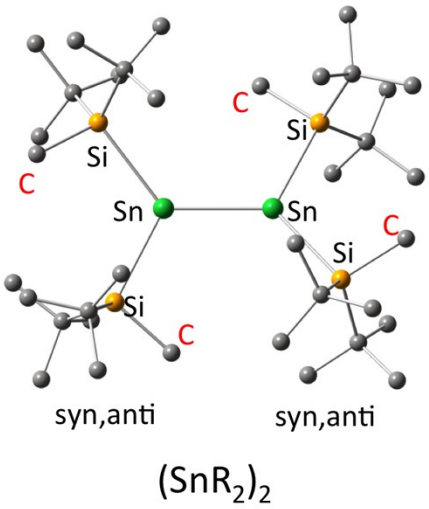
Table S3. Calculated binding energies (kcal mol^{-1}) of the E_2R_4 dimers (E = Ge or Sn; R = $CH(SiMe_3)_2$) with each ER_2 unit within the dimer in a *syn*,*syn* configuration.

$[E\{CH(SiMe_3)_2\}_2]_2 \rightarrow 2E\{CH(SiMe_3)_2\}_2$						
	E = Ge			E = Sn		
	B3PW91	B3PW91-D3	B97-D3	B3PW91	B3PW91-D3	B97-D3
ΔE^a	-4.6	30.3 (29.6)	24.8	6.3	33.7 (34.0)	28.9
ΔE^b	-14.1	18.9		-3.8	20.0	
ΔH^c $-T\Delta S^c$ ΔG^c	-13.5 -18.5 -32.0	20.0 -20.7 -0.7		-3.6 -16.6 -20.2	21.2 -21.5 -0.3	
[a] Binding energy. In parentheses are MP2 values. [b] With ZPE and BSSE corrections. [c] At 25℃ (298 K) and 1atm.						

Table S4. Calculated and experimental structural parameters for the dimetallene Pb_2R_4 (R = $CH(SiMe_3)_2$), in which the $Pb\{CH(SiMe_3)_2\}_2$ units have the *syn*,*anti* configuration.

$[Pb\{CH(SiMe_3)_2\}_2]_2$				
	B3PW91	B3PW91-D3	B97-D3	X-ray[a]
E-E (Å)	3.202	2.956	3.073	4.129(1)
E-C (Å)	2.384(avg.)	2.345(avg.)	2.395(avg.)	2.313(5), 2.323(5)
C1-E-C2 (°)	106.3	106.6	106.4	93.4(2)
C-E-E (°)	108.7 121.7	108.3 116.7	107.4 119.4	
[a] Ref. 11.				

Table S5. Calculations on the dissociation of $(SnR_2)_2 \rightarrow 2SnR_2$ ($R = SiMe^tBu_2$).



$(SnR_2)_2$

Unit: kcal/mol	Monomer: SnR_2 ($R = SiMe^tBu_2$)	
	B3PW91	B3PW91-D3
Singlet state	0.0	0.0
Triplet state	4.5	6.8
$(SnR_2)_2 \rightarrow 2\ SnR_2$ ($R = SiMe^tBu_2$)		
ΔE (dissociation)	36.4	59.5
ΔE (BSSE + ZPE)	25.8	46.8
(BSSE,25°C, 1.0 atm)		
ΔH	25.9	47.3
-TΔS	-17.6	-20.8
ΔG	8.3	26.5

	Dimer: $(SnR_2)_2$ (syn, anti)		
	B3PW91	B3PW91-D3	Exp.
Sn-Sn (Å)	2.702	2.647	2.668
Sn-Si (Å)	2.665	2.597	2.660 (av.)
Sn-Sn-Si (°)	124.6	124.3	113.8 (av.)
Si-Sn-Si (°)	110.9	111.4	111.7 (av.)
Trans-bending angle θ (°)	0.0	0.0	1.2
Torsion angle τ (°) (between Sn planes)	40.9	43.6	44.6