

## Electronic Supplementary Information

for

# $^1J_{\text{CH}}$ couplings in Group14/IVA tetramethyls from the gas-phase NMR and DFT structural study: a search for the best computational protocol

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**Table S1.** Selected B3LYP/basis sets combinations tested (two steps considered)<sup>a</sup>

#	Geometry optimizations		<i>J</i> -coupling calculations		$R^2$ for $\nu_{\text{as}}(\text{CH}_3)$ $= f[\omega_{\text{as}}(\text{CH}_3)]$	$R^2$ for ${}^1J_{0,\text{CH}}$ $= f({}^1J_{\text{CH}}^{\text{theor}})$	Notes
	Basis set for the E atom	Basis set for C and H atoms	Basis set for the E atom	Basis set for C and H atoms			
1	<b>F</b>	<b>D</b>	<b>O</b>	<b>G</b>	0.9924	0.9650	b
2	<b>F</b>	<b>D</b>	<b>O</b>	<b>G</b>	0.9929	0.9658	
3	<b>A</b>	<b>D</b>	<b>L</b>	<b>G</b>	0.9987	0.9690	b
4	<b>A</b>	<b>D</b>	<b>L</b>	<b>G</b>	0.9973	0.9807	
5	<b>M</b>	<b>M</b>	<b>M</b>	<b>G</b>	0.9959	0.9783	
6	<b>A</b>	<b>C</b>	<b>L</b>	<b>G</b>	0.9982	0.9815	b, c
7	<b>A</b>	<b>C</b>	<b>M</b>	<b>I</b>	0.9994	0.9844	
8	<b>A</b>	<b>C</b>	<b>L</b>	<b>J</b>	0.9994	0.9845	
9	<b>A</b>	<b>C</b>	<b>L</b>	<b>G</b>	0.9994	0.9847	Protocol I
10	<b>B</b>	<b>C</b>	<b>M</b>	<b>I</b>	0.9998	0.9834	
11	<b>B</b>	<b>C</b>	<b>M</b>	<b>J</b>	0.9998	0.9840	
12	<b>B</b>	<b>C</b>	<b>M</b>	<b>G</b>	0.9998	0.9879	Protocol II
13	<b>B</b>	<b>D</b>	<b>M</b>	<b>G</b>	0.9970	0.9845	b
14	<b>B</b>	<b>D</b>	<b>M</b>	<b>G</b>	0.9967	0.9848	

<sup>a</sup> The gas-phase results for the all five species EMe<sub>4</sub>. <sup>b</sup> The six Cartesian *d* functions have been employed (6D option). <sup>c</sup> Without the keyword 'Int=UltraFine'.

Notation of all basis sets used in this work:

<b>A</b>	def2-TZVPP
<b>B</b>	def2-TZVPPD
<b>C</b>	6-31G( <i>d,p</i> )
<b>D</b>	6-31+G( <i>d,p</i> )
<b>E</b>	6-31+G(2 <i>df,p</i> )
<b>F</b>	aug-cc-pVTZ <i>or</i> aug-cc-pVTZ-PP (Sn, Pb)
<b>G</b>	IGLO-II
<b>H</b>	IGLO-III
<b>I</b>	aug-cc-pVTZ-J
<b>J</b>	pcJ-2
<b>K</b>	pcJ-3
<b>L</b>	def2-QZVPP
<b>M</b>	def2-QZVPPD
<b>N</b>	cc-pVQZ <i>or</i> cc-pVQZ-PP (Sn, Pb)
<b>O</b>	aug-cc-pVQZ <i>or</i> aug-cc-pVQZ-PP (Sn, Pb)

**Table S2.** *In vacuo* computed  $r_e$  vs. experimental  $r_g$  (from the GED data)<sup>a-e</sup> intramolecular distances in all five species EMe<sub>4</sub>, [Å]

	$r_g^{a-e}$	$r_e^f$	$r_{e,scal}^{f,g}$	$r_g - r_{e,scal}$	$r_{e,lit}^h$	$r_e - r_{e,lit}$
<b>C–C</b> <sup>a</sup>	1.537	1.536	1.540	-0.003	1.537	-0.001
C–H	1.114	1.096	1.103	0.011		
1,3 C··H	2.200	2.184	2.183	0.017		
C··C	2.508	2.508	2.505	0.003		
1,4 C··H	2.767	2.761	2.756	0.011		
1,4 C··H	3.480	3.474	3.463	0.017		
<b>Si–C</b> <sup>b</sup>	1.877	1.882	1.884	-0.007	1.896	-0.014
C–H	1.110	1.096	1.104	0.007		
Si··H	2.500	2.501	2.498	0.002		
C··C	3.065	3.074	3.066	-0.001		
1,4 C··H	3.293	3.294	3.285	0.008		
1,4 C··H	4.031	4.035	4.021	0.011		
<b>Ge–C</b> <sup>c</sup>	1.958	1.976	1.977	-0.019	1.969	0.007
C–H	1.111	1.094	1.102	0.009		
Ge··H	2.570	2.577	2.573	-0.003		
C··C	3.198	3.226	3.218	-0.020		
<b>Sn–C</b> <sup>d</sup>	2.144	2.168	2.168	-0.024	2.172	-0.004
C–H	1.118	1.094	1.101	0.017		
Sn··H	2.764	2.749	2.744	0.020		
<b>Pb–C</b> <sup>e</sup>	2.238	2.258	2.256	-0.018	2.256	0.002
C–H	1.083 <sup>i</sup>	1.092	1.100	-0.017		
Pb··H <sup>k</sup>	[2.721] <sup>j</sup>	[2.817]	[2.807]	[-0.086]		
C··C	3.656	3.687	3.675	-0.019		

<sup>a</sup> Ref. 1. <sup>b</sup> Ref. 2. <sup>c</sup> Ref. 3. <sup>d</sup> Ref. 4. <sup>e</sup> Ref. 5. <sup>f</sup> This work (protocol II). <sup>g</sup> Corrected (scaled)  $r_e$  values computed with the equation  $r_{e,scal} = (r_e + 0.01584)/1.0076$ ; see also Fig. S2. <sup>h</sup> B3LYP/RESC-derived E–C bond lengths, ref. 6. <sup>i</sup> This  $r_g$  distance seems to be underestimated, in the light of the C–H bond lengths in other species EMe<sub>4</sub>. <sup>j</sup> Most likely strongly underestimated value. <sup>k</sup> This distance was not used in the least squares regression analysis.

**Table S3.** *In vacuo* computed  $\omega_{as}(\text{CH}_3)$  vs. gas-phase experimental  $\nu_{as}(\text{CH}_3)$  (from IR spectra)<sup>a-c</sup> C–H vibrational stretching fundamentals for all five species EMe<sub>4</sub>, [cm<sup>-1</sup>]

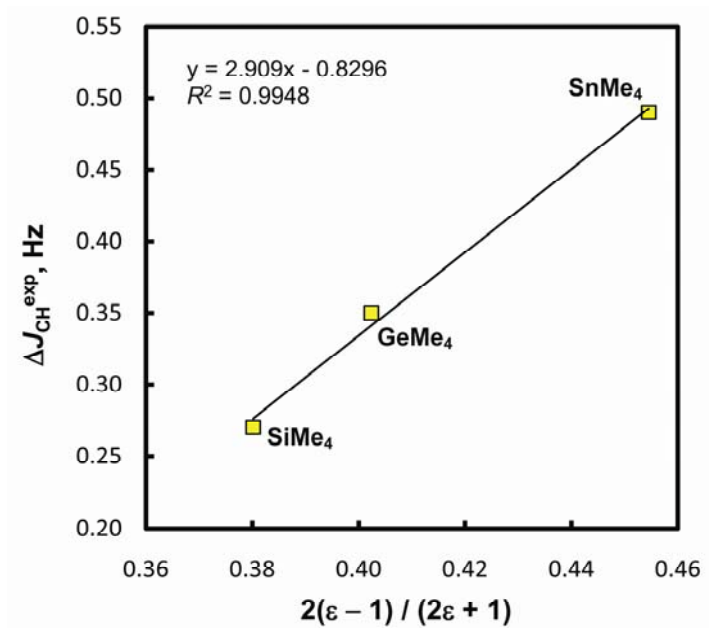
Compound	$\nu_{as}(\text{CH}_3)^a$	$\omega_{as}(\text{CH}_3)^d$	$\omega_{as}(\text{CH}_3)_{scal}^{d,e}$	$\nu_{as}(\text{CH}_3) - \omega_{as}(\text{CH}_3)_{scal}$	other $\nu_{as}(\text{CH}_3)$ s
CMe <sub>4</sub>	2960.7 <sup>f</sup>	3104.93	2960.71	0.0	2962, <sup>b</sup> 2959 <sup>c</sup>
SiMe <sub>4</sub>	2964.2	3109.12	2964.18	0.0	
GeMe <sub>4</sub>	2980.6	3128.63	2980.34	0.3	
SnMe <sub>4</sub>	2986.5	3136.49	2986.86	-0.4	
PbMe <sub>4</sub>	3005.0	3158.27	3004.91	0.1	

<sup>a</sup> Ref. 7. <sup>b</sup> Ref. 8. <sup>c</sup> Ref. 9. <sup>d</sup> This work (protocol II). <sup>e</sup> Corrected (scaled)  $\omega_{as}(\text{CH}_3)$  values computed applying the equation  $\omega_{as}(\text{CH}_3)_{scal} = [\omega_{as}(\text{CH}_3) + 468.34]/1.2069$ ; see also Fig. S3. <sup>f</sup> The second (?) value at 2967.5 cm<sup>-1</sup> has also been originally given for this fundamental frequency,<sup>a</sup> which was omitted in the current analysis.

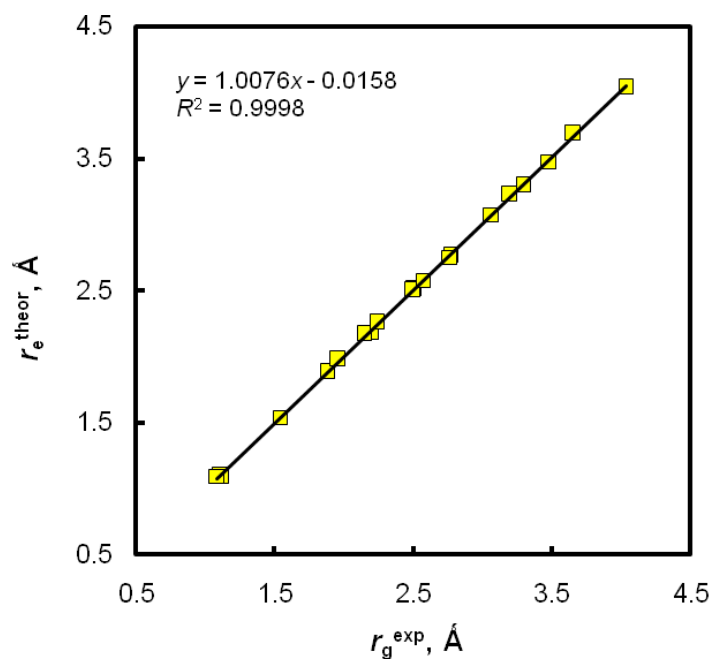
**Table S4.** Computed<sup>a</sup> vs. observed <sup>1</sup>J<sub>CH</sub> couplings for species EMe<sub>4</sub> in vacuum<sup>b</sup> and in CCl<sub>4</sub> or C<sub>6</sub>H<sub>6</sub> solution,<sup>c</sup> together with their decomposition into all four Ramsey terms, [Hz]

Compound	Medium	FC	SD	PSO	DSO	Total $J^{\text{theor}}$	$^1J_{\text{CH}}^{\text{b,c,d}}$
CMe <sub>4</sub>	gas (I)	119.67	0.19	0.92	0.73	121.50	123.93(4)
	gas (II)	119.70	0.18	0.92	0.73	121.52	
	CCl <sub>4</sub> (I)	119.65	0.19	0.92	0.73	121.48	124.0(2)
	CCl <sub>4</sub> (II)	119.67	0.18	0.92	0.73	121.50	
	C <sub>6</sub> H <sub>6</sub> (II)	119.67	0.18	0.92	0.73	121.50	
SiMe <sub>4</sub>	gas (I)	114.45	0.29	1.46	0.68	116.88	117.88(4)
	gas (II)	114.25	0.29	1.46	0.68	116.68	
	CCl <sub>4</sub> (I)	114.44	0.29	1.46	0.68	116.87	117.8(2)
	CCl <sub>4</sub> (II)	114.24	0.29	1.46	0.68	116.67	
	C <sub>6</sub> H <sub>6</sub> (II)	114.24	0.29	1.46	0.68	116.66	
GeMe <sub>4</sub>	gas (I)	120.84	0.33	1.13	0.98	123.27	124.05(1)
	gas (II)	120.70	0.33	1.13	0.98	123.13	
	CCl <sub>4</sub> (I)	120.82	0.33	1.13	0.98	123.25	124.6(2)
	CCl <sub>4</sub> (II)	120.67	0.33	1.13	0.98	123.10	
	C <sub>6</sub> H <sub>6</sub> (II)	120.67	0.33	1.13	0.98	123.10	
SnMe <sub>4</sub>	gas (I)	124.30	0.39	1.21	0.63	126.53	127.13(5)
	gas (II)	124.15	0.39	1.21	0.63	126.38	
	CCl <sub>4</sub> (I)	124.23	0.39	1.22	0.63	126.46	127.8(2)
	CCl <sub>4</sub> (II)	124.08	0.39	1.22	0.63	126.31	
	C <sub>6</sub> H <sub>6</sub> (II)	124.08	0.39	1.22	0.63	126.31	
PbMe <sub>4</sub>	gas (I)	130.67	0.44	1.10	0.57	132.79	133.29(3)
	gas (II)	130.51	0.44	1.10	0.57	132.62	
	CCl <sub>4</sub> (I)	130.57	0.44	1.11	0.57	132.69	134.3(2)
	CCl <sub>4</sub> (II)	130.41	0.44	1.11	0.57	132.53	
	C <sub>6</sub> H <sub>6</sub> (II)	130.41	0.44	1.11	0.57	132.53	

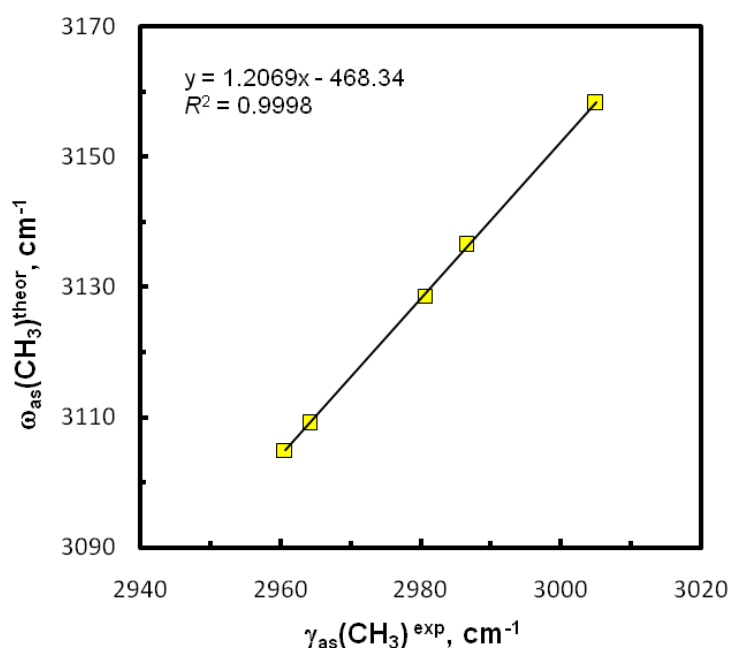
<sup>a</sup> Protocol I, II, I-CCl<sub>4</sub>, II-CCl<sub>4</sub>, and II-C<sub>6</sub>H<sub>6</sub> was applied, respectively. <sup>b</sup> The experimental <sup>1</sup>J<sub>0,CH,av</sub> values from Table 1 (in the main text) were used as *in vacuo* data. <sup>c</sup> The data for ~10% CCl<sub>4</sub> solution from <sup>1</sup>H NMR spectra, according to ref. 10. <sup>d</sup> The data for ~10% C<sub>6</sub>H<sub>6</sub> solution from <sup>13</sup>C{<sup>1</sup>H} NMR spectra, according to ref. 11.



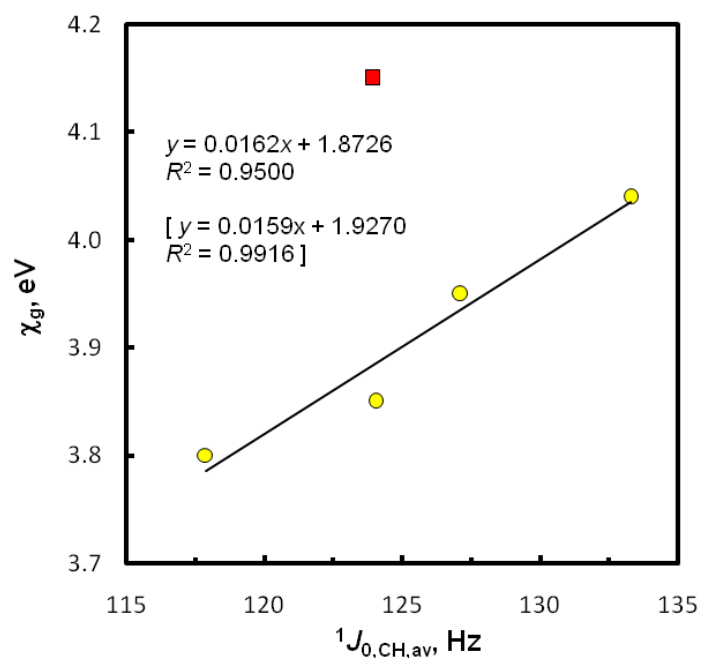
**Fig. S1.** Dependence of  $\Delta^1 J_{CH}^{exp} = {}^1 J_{CH}(\text{neat}) - {}^1 J_{0,CH,av}(\text{gas})$  on the reaction field function of relative permittivity  $\epsilon$  for the three normally liquid tetramethyls;  $J$  data from Table 1 (main text) and  $\epsilon$  values from ref. 12 were used.



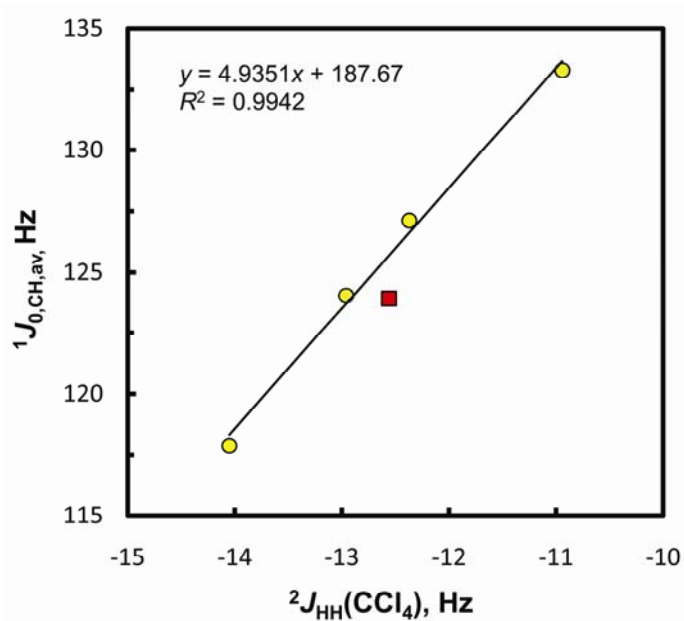
**Fig. S2.** Plot of computed (protocol II)  $r_e$  bond lengths vs. related experimental  $r_g$  distances for all five species  $EMe_4$ ; the numeral data from Table S2 were used.



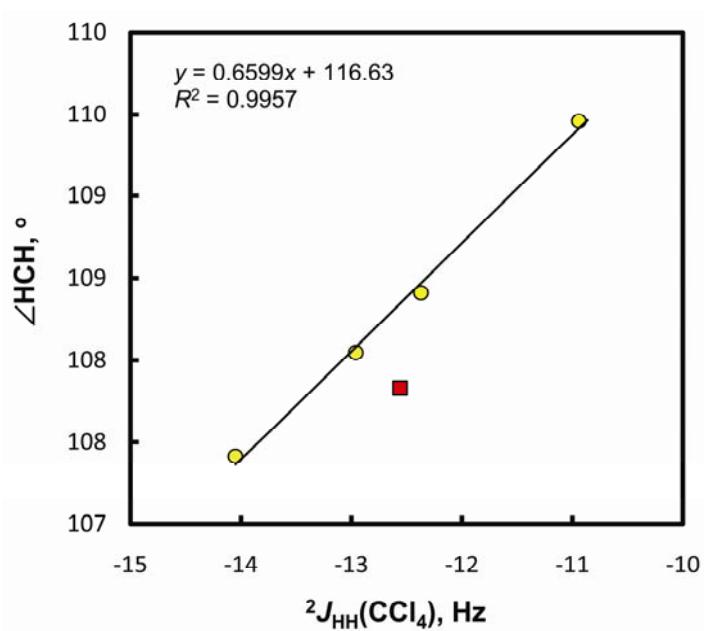
**Fig. S3.** Plot of *in vacuo* computed (protocol II) harmonic  $\omega_{\text{as}}(\text{CH}_3)$ s vs. experimental gas-phase frequencies,  $\nu_{\text{as}}(\text{CH}_3)$ s, for all five species  $\text{EMe}_4$ ; the data from Table S3 were applied.



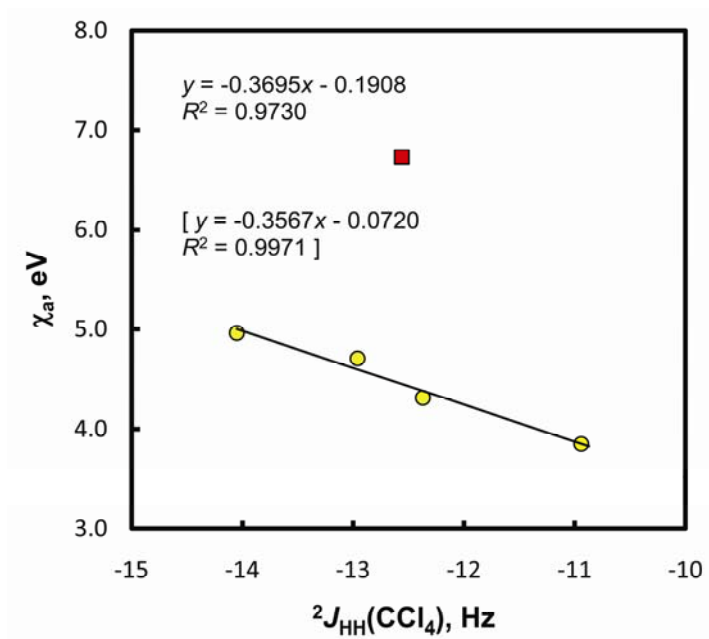
**Fig. S4.** The group electronegativity  $\chi_g$  vs. experimental  ${}^1J_{0,\text{CH,av}}(\text{gas})$  values; the  $\text{CMe}_4$  data point (■) was omitted. Statistics with the  $\chi_g$  corrected for  $\text{GeMe}_4$  (3.88 eV) are in the bracket. The numeral data from Tables 1 and 3 (main text) were used.



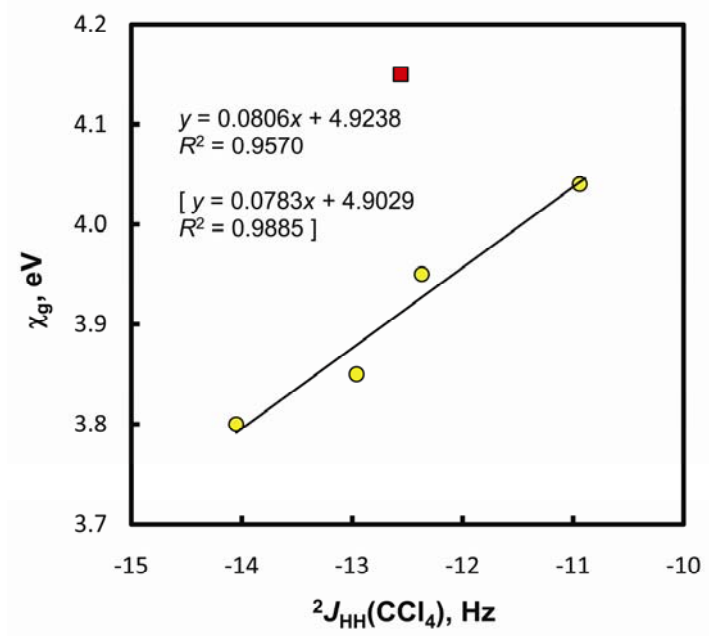
**Fig. S5.** Plot of experimental  ${}^1J_{0,\text{CH},\text{av}}(\text{gas})$  vs.  ${}^2J_{\text{HH}}(\text{CCl}_4)$  values; the  $\text{CMe}_4$  point (■) was omitted. The data from Tables 1 and 3 (main text) were applied.



**Fig. S6.** Plot of the computed (protocol II) HCH bond angles vs. experimental  ${}^2J_{\text{HH}}(\text{CCl}_4)$  couplings; the  $\text{CMe}_4$  point (■) was omitted. The data from Table 3 (main text) were used.



**Fig. S7.** The atom electronegativity  $\chi_a$  vs. experimental  ${}^2J_{\text{HH}}(\text{CCl}_4)$  couplings; the  $\text{CMe}_4$  point (■) was omitted. Statistics with the  $\chi_a$  corrected for Ge (4.54 eV) are in the bracket. The data from Table 3 (main text) were used.



**Fig. S8.** The group electronegativity  $\chi_g$  vs. experimental  ${}^2J_{\text{HH}}(\text{CCl}_4)$  couplings; the  $\text{CMe}_4$  data point (■) was omitted. Statistics with the  $\chi_g$  corrected for  $-\text{GeMe}_3$  (3.88 eV) are in the bracket. The data from Table 3 (main text) were used.



**Table S5.** Cartesian coordinates for **CMe<sub>4</sub>**[*In vacuo*, the protocol II<sup>‡</sup> used, N<sub>imag</sub> = 0, E(RB+HF-LYP)= -197.799809 Ha]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.886699	0.886699	0.886699
3	6	0	-0.886699	-0.886699	0.886699
4	6	0	-0.886699	0.886699	-0.886699
5	6	0	0.886699	-0.886699	-0.886699
6	1	0	1.531597	1.531597	0.279146
7	1	0	0.279146	1.531597	1.531597
8	1	0	1.531597	0.279146	1.531597
9	1	0	-1.531597	-1.531597	0.279146
10	1	0	-1.531597	0.279146	-1.531597
11	1	0	0.279146	-1.531597	-1.531597
12	1	0	-0.279146	-1.531597	1.531597
13	1	0	-1.531597	-0.279146	1.531597
14	1	0	-1.531597	1.531597	-0.279146
15	1	0	-0.279146	1.531597	-1.531597
16	1	0	1.531597	-0.279146	-1.531597
17	1	0	1.531597	-1.531597	-0.279146

<sup>‡</sup> B3LYP/6-31G(*d,p*)(C,H)def2-TZVPPD(E)**Table S6.** Cartesian coordinates for **SiMe<sub>4</sub>**[*In vacuo*, the protocol II used, N<sub>imag</sub> = 0, E(RB+HF-LYP)= -449.2407721 Ha]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.882286
3	6	0	1.774636	0.000000	-0.627429
4	6	0	-0.887318	-1.536880	-0.627429
5	6	0	-0.887318	1.536880	-0.627429
6	1	0	-1.020116	0.000000	2.283291
7	1	0	0.510058	-0.883446	2.283291
8	1	0	0.510058	0.883446	2.283291
9	1	0	1.812669	0.000000	-1.722872
10	1	0	-0.906335	-1.569817	-1.722872
11	1	0	-0.906335	1.569817	-1.722872
12	1	0	2.322727	0.883446	-0.280210
13	1	0	2.322727	-0.883446	-0.280210
14	1	0	-0.396277	-2.453264	-0.280210
15	1	0	-1.926450	-1.569817	-0.280210
16	1	0	-1.926450	1.569817	-0.280210
17	1	0	-0.396277	2.453264	-0.280210

**Table S7.** Cartesian coordinates for **GeMe<sub>4</sub>**[*In vacuo*, the protocol II used,  $N_{\text{imag}} = 0$ ,  $E(\text{RB+HF-LYP}) = -2236.7460606$  Ha]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	32	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.975809
3	6	0	1.862810	0.000000	-0.658603
4	6	0	-0.931405	-1.613241	-0.658603
5	6	0	-0.931405	1.613241	-0.658603
6	1	0	-1.022618	0.000000	2.365508
7	1	0	0.511309	-0.885613	2.365508
8	1	0	0.511309	0.885613	2.365508
9	1	0	1.889349	0.000000	-1.752636
10	1	0	-0.944675	-1.636224	-1.752636
11	1	0	-0.944675	1.636224	-1.752636
12	1	0	2.400658	0.885613	-0.306436
13	1	0	2.400658	-0.885613	-0.306436
14	1	0	-0.433366	-2.521837	-0.306436
15	1	0	-1.967292	-1.636224	-0.306436
16	1	0	-1.967292	1.636224	-0.306436
17	1	0	-0.433366	2.521837	-0.306436

**Table S8.** Cartesian coordinates for **SnMe<sub>4</sub>**[*In vacuo*, the protocol II used,  $N_{\text{imag}} = 0$ ,  $E(\text{RB+HF-LYP}) = -374.045353$  Ha]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	50	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	2.168123
3	6	0	2.044126	0.000000	-0.722708
4	6	0	-1.022063	-1.770265	-0.722708
5	6	0	-1.022063	1.770265	-0.722708
6	1	0	-1.024413	0.000000	2.551411
7	1	0	0.512207	-0.887168	2.551411
8	1	0	0.512207	0.887168	2.551411
9	1	0	2.064022	0.000000	-1.816296
10	1	0	-1.032011	-1.787495	-1.816296
11	1	0	-1.032011	1.787495	-1.816296
12	1	0	2.576228	0.887168	-0.367557
13	1	0	2.576228	-0.887168	-0.367557
14	1	0	-0.519804	-2.674663	-0.367557
15	1	0	-2.056424	-1.787495	-0.367557
16	1	0	-2.056424	1.787495	-0.367557
17	1	0	-0.519804	2.674663	-0.367557

**Table S9.** Cartesian coordinates for **PbMe<sub>4</sub>**

[In vacuo, the protocol II used, N<sub>imag</sub> = 0, E(RB+HF-LYP) = -352.5624235 Ha]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	82	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	2.257628
3	6	0	2.128512	0.000000	-0.752543
4	6	0	-1.064256	-1.843346	-0.752543
5	6	0	-1.064256	1.843346	-0.752543
6	1	0	-1.029569	0.000000	2.621891
7	1	0	0.514785	-0.891633	2.621891
8	1	0	0.514785	0.891633	2.621891
9	1	0	2.128753	0.000000	-1.844651
10	1	0	-1.064376	-1.843554	-1.844651
11	1	0	-1.064376	1.843554	-1.844651
12	1	0	2.643538	0.891633	-0.388620
13	1	0	2.643538	-0.891633	-0.388620
14	1	0	-0.549592	-2.735187	-0.388620
15	1	0	-2.093946	-1.843554	-0.388620
16	1	0	-2.093946	1.843554	-0.388620
17	1	0	-0.549592	2.735187	-0.388620

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