

Supporting Information S1–S7 for

Synthesis, Structure, and a Nucleophilic Coordination Reaction of Germanetellurones

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I. Crystal data collection and structural refinement details

Table 1s. For compounds **1**, **2**, **4**, and **5**

	1	2	4^b	5₂
formula	C ₃₄ H ₄₆ GeN ₂	C ₈₂ H ₁₀₀ Fe ₂ Ge ₂ N ₄	C ₃₄ H ₄₆ GeN ₂ Te	C ₈₂ H ₁₀₀ Fe ₂ Ge ₂ N ₄ Te ₂
fw	555.32	1398.54	682.92	1653.74
cryst syst	Monoclinic	Triclinic	Orthorhombic	Monoclinic
space group	<i>P2₁/n</i>	<i>P</i> -1	<i>Pna2₁</i>	<i>P2₁/c</i>
<i>a</i> /Å	13.4531(5)	14.148(3)	16.739(3)	12.8840(5)
<i>b</i> /Å	16.6254(5)	17.098(3)	9.7212(19)	18.4790(13)
<i>c</i> /Å	14.7792(5)	17.556(4)	20.247(4)	31.6633(14)
<i>α</i> /deg		107.85(3)		
<i>β</i> /deg	110.700(4)	110.20(3)		90.677(4)
<i>γ</i> /deg		97.91(3)		
<i>V</i> /Å ³	3092.17(18)	3650.4(13)	3294.6(11)	7538.0(7)
<i>Z</i>	4	2	4	4
$\rho_{\text{calcd}}/\text{g}\cdot\text{cm}^{-3}$	1.193	1.272	1.377	1.457
μ/mm^{-1}	1.014	1.250	1.821	1.971
<i>F</i> (000)	1184	1472	1392	3360
crystal size/mm ³	0.45×0.40×0.20	0.49×0.20×0.16	0.40×0.40×0.10	0.30×0.20×0.12
θ range/deg	2.82–26.00	2.99–27.47	3.15–26.00	2.71–26.00
	−16 ≤ <i>h</i> ≤ 16	−18 ≤ <i>h</i> ≤ 18	−20 ≤ <i>h</i> ≤ 18	−15 ≤ <i>h</i> ≤ 15
index ranges	−20 ≤ <i>k</i> ≤ 17	−22 ≤ <i>k</i> ≤ 22	−11 ≤ <i>k</i> ≤ 11	−22 ≤ <i>k</i> ≤ 22
	−18 ≤ <i>l</i> ≤ 11	−22 ≤ <i>l</i> ≤ 22	−24 ≤ <i>l</i> ≤ 24	−39 ≤ <i>l</i> ≤ 38
collected data	13154	57128	25512	44382
unique data	6062	16498	6445	14765
	(<i>R</i> _{int} = 0.0238)	(<i>R</i> _{int} = 0.0630)	(<i>R</i> _{int} = 0.0402)	(<i>R</i> _{int} = 0.0904)
completeness to θ (%)	99.6	98.6	99.8	99.8
data/restraints/params	6062/0/344	16498/942/931	6445/426/329	14765/380/875
GOF on <i>F</i> ²	1.027	1.095	1.047	0.999
final <i>R</i> indices [<i>I</i> > 2 (<i>I</i>)]	<i>R</i> ₁ = 0.0309 <i>wR</i> ₂ = 0.0727	<i>R</i> ₁ = 0.0375 <i>wR</i> ₂ = 0.0821	<i>R</i> ₁ = 0.0404 <i>wR</i> ₂ = 0.0982	<i>R</i> ₁ = 0.0657 <i>wR</i> ₂ = 0.0831
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0391	<i>R</i> ₁ = 0.0654	<i>R</i> ₁ = 0.0528	<i>R</i> ₁ = 0.1233

	$wR_2 = 0.0755$	$wR_2 = 0.1029$	$wR_2 = 0.1049$	$wR_2 = 0.0972$
Largest diff peak/hole ($e \cdot \text{\AA}^{-3}$)	0.311/-0.288	0.955/-0.779	0.751/-0.719	0.850/-0.845

^a All data were collected at 173(2) K using Mo K_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation. $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$. ^b The data recorded here for **4** is corresponding to structure **4a** (Figure 2s). The data for structure **4b** are slightly changed after final refinements ($wR_2 = 0.0983$ and largest diff peak/hole ($e \cdot \text{\AA}^{-3}$) is 0.753/-0.714. The others are the same).

Table 2s. For compounds **6–9**^a

	6-0.5n-hexane	7^c	8	9
formula	C ₄₀ H ₅₃ GeN ₂ Te	C ₃₄ H ₄₆ Cl ₂ Ge ₂ N ₂ Te	C ₃₆ H ₄₄ AuF ₅ GeN ₂ S	C ₃₆ H ₄₄ AuF ₅ GeN ₂ S e
fw	762.03	826.41	901.35	948.25
cryst syst	Monoclinic	Monoclinic	Triclinic	Triclinic,
space group	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P-1</i>	<i>P-1</i>
<i>a</i> /\AA	12.9507(8)	9.7181(7)	10.1603(4)	10.224(2)
<i>b</i> /\AA	18.5924(10)	18.7331(13)	12.8671(7)	12.966(3)
<i>c</i> /\AA	17.3739(9)	19.6618(12)	15.0468(9)	15.085(3)
α /deg			66.571(5)	66.54(3)
β /deg	92.59(3)	90.562(6)	74.778(4)	74.75(3)
γ /deg			84.434(4)	84.32(3)
<i>V</i> /\AA ³	4091.5(4)	3579.3(4)	1741.55(16)	1770.0(6)
<i>Z</i>	4	4	2	2
ρ_{calcd} /g·cm ⁻³	1.237	1.534	1.719	1.779
μ /mm ⁻¹	1.474	2.652	5.185	1.779
<i>F</i> (000)	1564	1656	892	928
crystal size/mm ³	0.30×0.30×0.10	0.15×0.10×0.02	0.40×0.20×0.10	0.15×0.10×0.03
θ range/deg	3.10–26.00	3.02–26.00	2.69–26.00	3.00–25.00
index ranges	-15 ≤ <i>h</i> ≤ 14 -21 ≤ <i>k</i> ≤ 22 -12 ≤ <i>l</i> ≤ 21	-11 ≤ <i>h</i> ≤ 11 -11 ≤ <i>k</i> ≤ 23 -14 ≤ <i>l</i> ≤ 24	-12 ≤ <i>h</i> ≤ 12 -15 ≤ <i>k</i> ≤ 15 -18 ≤ <i>l</i> ≤ 18	-12 ≤ <i>h</i> ≤ 12 -15 ≤ <i>k</i> ≤ 15 -17 ≤ <i>l</i> ≤ 17
collected data	17544	14585	20968	13709
unique data	8008 ($R_{\text{int}} = 0.0551$)	7008 ($R_{\text{int}} = 0.0998$)	6838 ($R_{\text{int}} = 0.0982$)	6137 ($R_{\text{int}} = 0.1559$)
completeness to θ (%)	99.7	99.7	99.9	98.6
data/restraints/params	8008/5/436	7008/0/370	6838/0/426	6137/12/421
GOF on <i>F</i> ²	0.990	0.999	1.010	1.054
final <i>R</i> indices [<i>I</i> > 2 (<i>I</i>)]	$R_1 = 0.0604$ $wR_2 = 0.1272$	$R_1 = 0.0798$ $wR_2 = 0.1018$	$R_1 = 0.0574$ $wR_2 = 0.1016$	$R_1 = 0.1095$ $wR_2 = 0.2437$
<i>R</i> indices (all data)	$R_1 = 0.1016$ $wR_2 = 0.1423$	$R_1 = 0.1561$ $wR_2 = 0.1195$	$R_1 = 0.0799$ $wR_2 = 0.1099$	$R_1 = 0.1803$ $wR_2 = 0.3055$
Largest diff peak/hole ($e \cdot \text{\AA}^{-3}$)	0.713/-0.393	0.876/-1.169	1.736 / -1.275	2.288/-4.812

^a All data were collected at 173(2) K using Mo K_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation. $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$. ^c The data recorded here for **7** is corresponding to structure **7a** (Figure 3s). The data for structure **7b** are not changed after final refinements.

II. Crystal structures of Cp-bonded compounds 1, 4 and 7

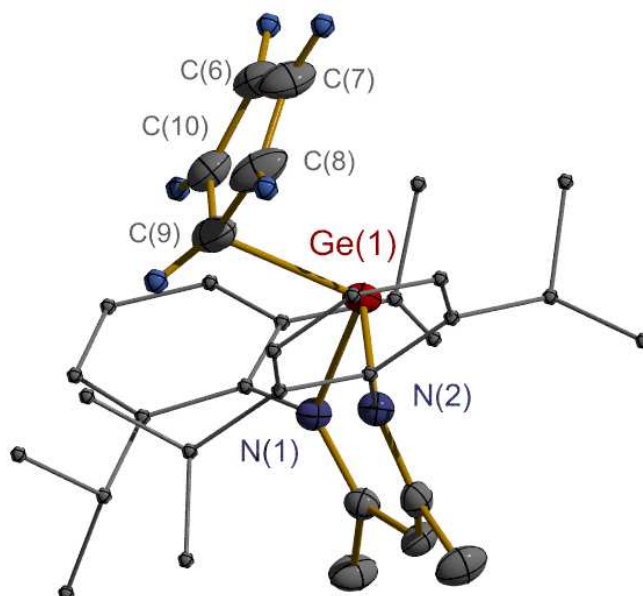


Figure 1s. X-ray crystal structure of **1**. Thermal ellipsoids are drawn at 50% probability level. H atoms at the Cp group are enhanced for clarity.

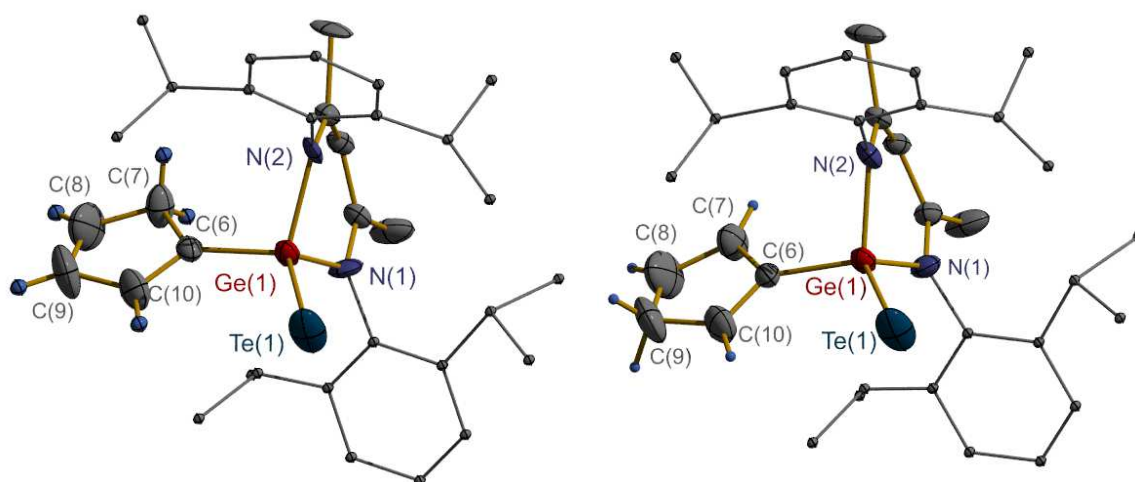


Figure 2s. X-ray crystal structures of **4** with two different hydrogen addition modes over the Cp ring corresponding to isomeric structures **4a** (left) and **4b** (right) shown in the text. Thermal ellipsoids are drawn at 50% probability level.

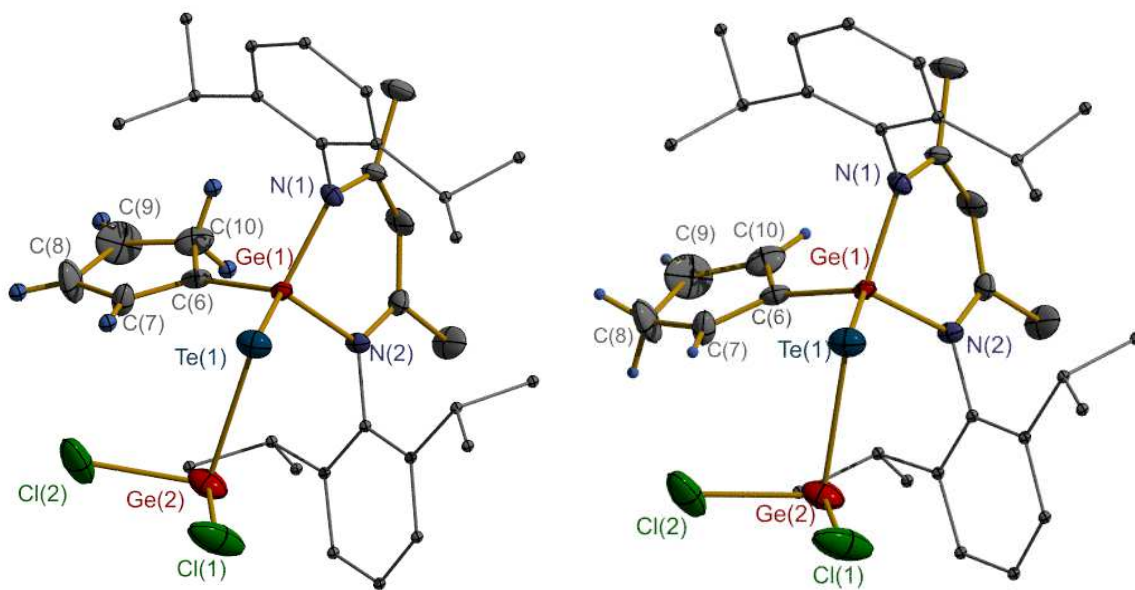


Figure 3s. X-ray crystal structures of **7** with two different hydrogen addition modes over the Cp ring corresponding to isomeric structures **7a** (left) and **7b** (right). Thermal ellipsoids are drawn at 50% probability level.

III. Variable temperature (25–80 °C) ^1H NMR spectral studies of compound **4**

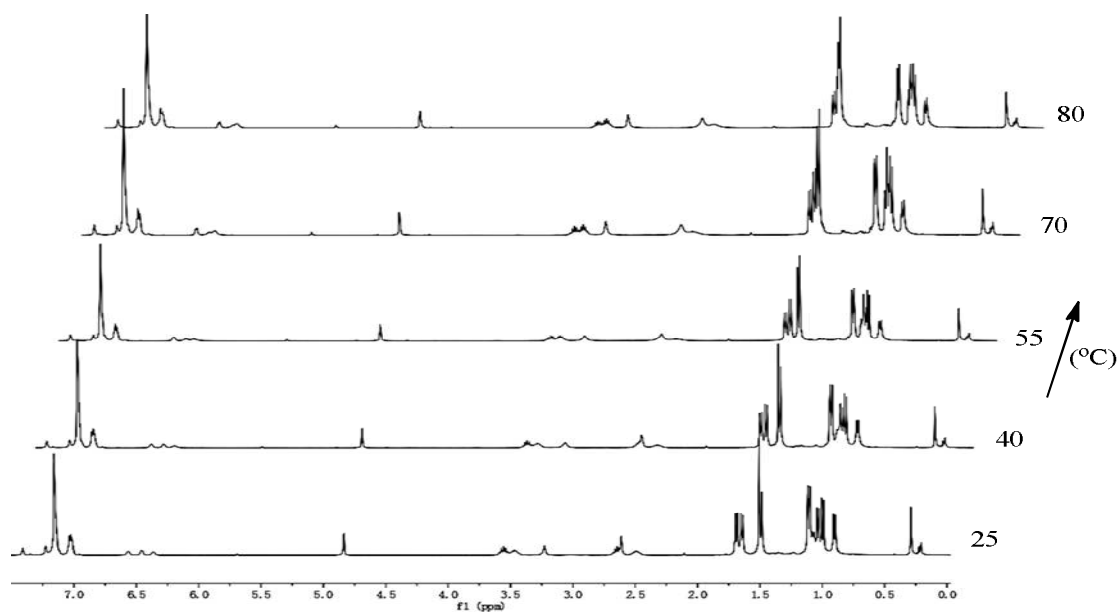


Figure 4s. Exhibition of a series of ^1H NMR spectra of compound **4** recorded in C_6D_6 at elevated temperatures.

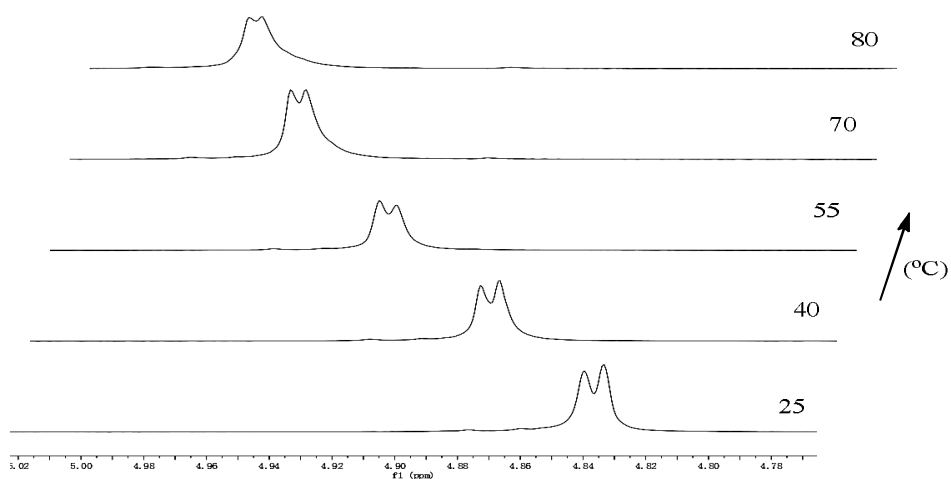


Figure 5s. Exhibition of the enhanced resonances for the L ligand backbone γ -CH proton of compound **4** at δ 4.77–5.02 ppm in Figure 4s.

IV. UV-vis spectra of compounds **1** and **2**

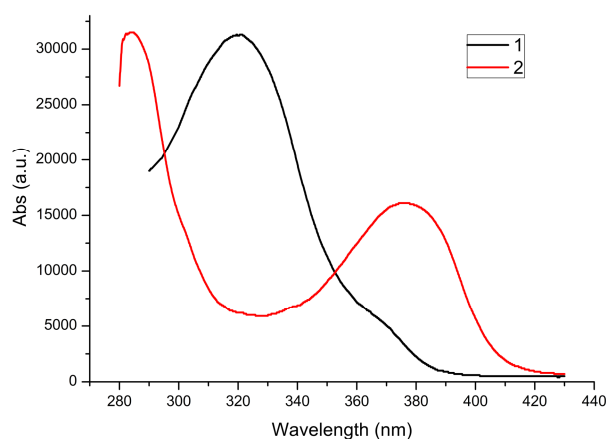
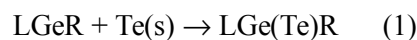


Figure 6s. UV-vis spectra of compounds **1** (black, λ_{\max} (peak), 320, 366 nm) and **2** (red, λ_{\max} (peak), 287, 344 nm) recorded in toluene at room temperature (1×10^{-5} mol/L).

IV. DFT calculations

Computational details: All quantum-chemical calculations were carried out by using the Gaussian 09 program.¹ Geometry optimization for compound LGeR (R = Cp, C \equiv CH) was performed by using B3LYP/6-31+G(d)²⁻⁶ and that for LGe(Te)R (R = Cp, C \equiv CH) was adopted on Stuttgart RSC 1997 ECP (to simplify the calculation, we use the H group instead of the Fc and Ph group).⁷ Vibrational frequencies were calculated to ensure the optimized structure. Charge analyses were performed by using the natural bond orbital (NBO) program.⁸ Computationally, it seems too difficult to directly calculate the enthalpies of reaction of LGeR with Te to form germanetellurone (eq (1)) because Te is

used as a solid powder. But, the bond disassociation energy (BDE) of Ge=Te could be calculated on considering the Te atom (the standard enthalpy value, 47.1 kcal/mol, has been experimentally determined⁹) according to eq (2) and (3).



$$\text{BDE}_{\text{Ge=Te}} = \Delta H_{\text{LGe(Te)R}} - \Delta H_{\text{LGeR}} - \Delta H_{\text{Te atom}} \quad (3)$$

$$\Delta H_{\text{rxn}} = \text{BDE}_{\text{Ge=Te}} + \Delta H_{\text{f}}^{\circ}(\text{Te atom}) \quad (4)$$

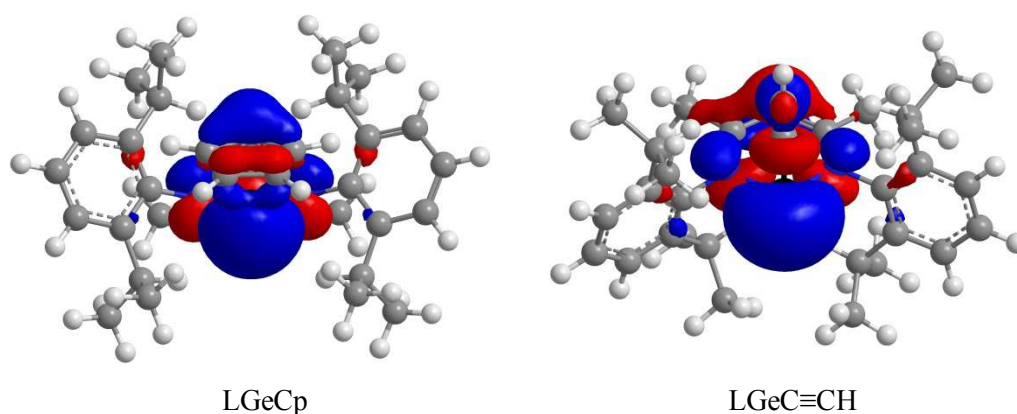
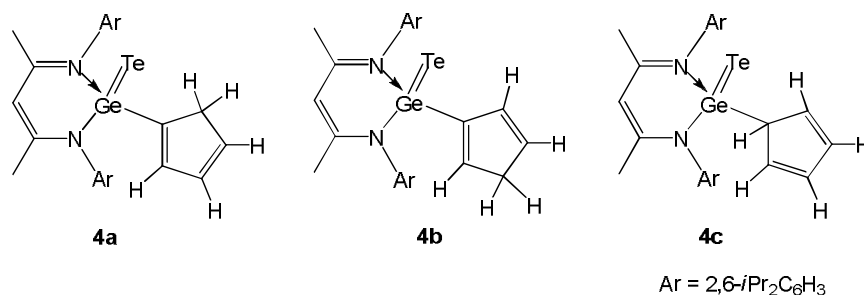


Figure 7s. HOMO orbital picture of LGeR



Scheme 1s. Three possible isomeric structures of compound **4** (Relative energies (kcal/mol), -2.5 for isomer **4a**, -1.0 for **4b**, and 0.0 for **4c**)

Table 3s. NBO analysis for LGeR (L = HC[C(Me)N-2,6-*i*Pr₂C₆H₃]₂)

R	NBO Charge of Ge	Characteristics of lone pair of Ge			
		Occupation	Composition (%)		
			s	p	d
Cp	+1.047	1.967	86.5	13.5	0.0
C≡CH	+0.983	1.943	77.5	22.5	0.0

Table 4s. NBO analysis of LGe(Te)R (L = HC[C(Me)N-2,6-*i*Pr₂C₆H₃]₂)

R	NBO charge		HOMO-LUMO gap (eV)	Characteristics of the Ge–Te bond		
	Ge	Te		Occupation	Contributions (%)	Composition (%) s p d
Cp	+1.385	-0.543	2.73	1.932	Ge: 51.2 Te: 48.8	44.3 55.3 0.4 11.1 88.9 0.0
C≡CH	+1.280	-0.454	2.80	1.944	Ge: 54.7 Te: 45.3	51.4 48.3 0.3 10.6 89.4 0.0

Table 5s. Calculated enthalpies for reactions of LGeR with Te to LGe(Te)R

R	Bond disassociation energy (Ge=Te, kcal/mol)	ΔH_{rxn} (kcal/mol)
Cp	47.1	0.0
C≡CH	50.2	-3.1

References

- 1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A. 02, Gaussian, Inc., Wallingford, CT 200 (2009).
- 2 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
- 3 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
- 4 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- 5 C. T. Lee, W. T. Yang and R.G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
- 6 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
- 7 M. Dolg, H. Stoll, H. Preuss and R. M. Pitzer, *J. Phys. Chem.*, 1993, **97**, 5852 and these basis sets and ECPs correspond to Revision: Fri Jun 27 1997 of the Stuttgart/Dresden groups.
- 8 A. E. Reed and F. Weinhold, *J. Chem. Phys.* 1983, **78**, 4066.
- 9 Experimental value taken from <http://www.wiredchemist.com/chemistry/data/enthalpies>.