Germanium(III) corrole complex: reactivity and mechanistic studies of visible-light promoted N–H bond activations

Huayi Fang,[†] Zhen Ling,[†] Ke Lang,[†] Penelope J. Brothers,[‖] Bas de Bruin*[,‡], Xuefeng Fu*[,†]

[†]Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

[‡]Homogeneous & Supramolecular Catalysis, van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam (UvA), Science Park 904, 1098 XH Amsterdam, The Netherlands

[‖]School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1042, New Zealand

Table of Contents

General Procedures.

All operations were performed using Schlenk techniques under dry argon or nitrogen. Solvents and liquid amines were dried over 4 Å molecular sieves and degassed prior to use. A 500 W high-pressure xenon lamp (CHF-XM35-500W, Beijing Trustech Co., Ltd.) with a 420 ~ 780 nm UV-cutoff filter in the light path was used as the source of visible light. The ^{1}H NMR spectra were recorded on Bruker Avance III 400M and 500M spectrometers and referenced to the residual protons in the solvent. The single-crystal X-ray diffraction data were collected on a Rigaku MM007HF Saturn724+ diffractometer. Mass spectra were recorded on Bruker Apex IV FTMS and Jeol JMS T100CS spectrometers. The starting material (TPFC)Ge–H was prepared according to our previously published method.[S1]

Synthesis of (TPFC)Ge(TEMPO).

40.0 mg (TPFC)Ge-H (0.047 mmol), 14.7 mg (7.0×10^{-3} mmol, 2.0 equiv) of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) were mixed in 2.0 mL toluene, in a Schlenk flask. After heating the mixture at 80 ^{o}C for 2 h, the product (TPFC)Ge(TEMPO) was produced quantitatively along with formation of one equivalent of TEMPOH. The solvent was removed under vacuum and the TEMPO*H* was removed by washing the residue with *n*-hexane (2 mL). Recrystallization using toluene/hexane gave deep red crystal suitable for single-crystal X-ray diffraction analysis. (TPFC)Ge(TEMPO) ^{1}H NMR (400 MHz, C_7D_8) δ (ppm): 9.11 (d, 2H, ^{3}J(H,H) = 4.0 Hz; β-pyrrole H), 8.85 (d, 2H, ^{3}J(H,H) = 3.7 Hz; β-pyrrole H), 8.71 (d, 2H, ^{3}J(H,H) = 3.8 Hz; β-pyrrole H), 8.67 (d, 2H, ^{3}J(H,H) = 4.0 Hz; β-pyrrole H), 0.15 (q, 2H, ^{3}J(H,H) = 5.7 Hz; *p*-CH_2), -0.04 (br, 4H; *m*-CH_2), -1.00 (br, 6H; *o*-CH_3), -2.24 (br, 6H; *o*-CH_3); HRMS (ESI) calcd for $C_{46}H_{27}F_{15}GeN_5O$ $[M+H]^+$ 1024.11879; found 1024.11814. UV/Vis ($CHCl_3$): λ_{max}(nm): 391.5, 412.0, 496.0, 534.5, 562.5, 578.0. 2,2,6,6-tetramethylpiperidin-1-ol ^{1}H NMR (400 MHz, C_7D_8) δ (ppm): 3.62 (br, 1H; OH), 1.37 (m, 4H; *m*-CH_2), 1.32 (m, 2H; *p*-CH_2), 1.10 (s, 12H; *o*-CH_3); HRMS (ESI) calcd for $C_9H_{20}NO$ $[M+H]^+$ 158.15394; found 158.15348.

UV-Vis spectrum of (TPFC)Ge(TEMPO) and (TPFC)Ge–H.

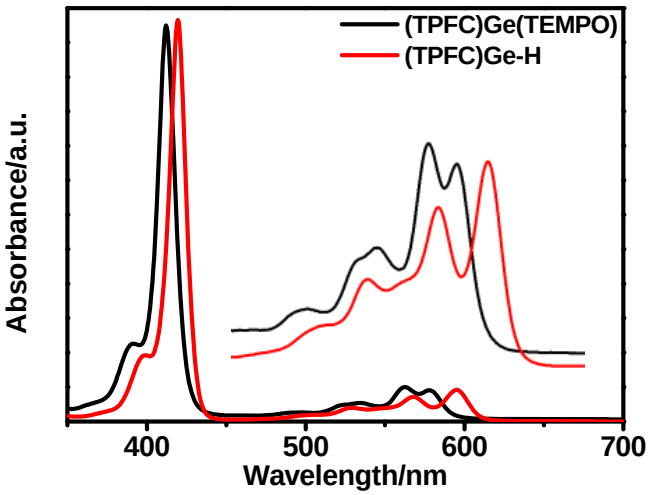


Figure S1. UV-Vis spectrum of (TPFC)Ge(TEMPO) and (TPFC)Ge–H.

Configuration transformation energy barrier calculation for (TPFC)Ge(TEMPO).

The kinetics of the configuration transformation of (TPFC)Ge(TEMPO) at different temperatures were simulated using DNMR package implanted in Bruker TopSpin 3.1 program based on the peaks assigned to *o*-CH_3 in the TEMPO ligand. And then the energy barrier was calculated using the Arrhenius equation.

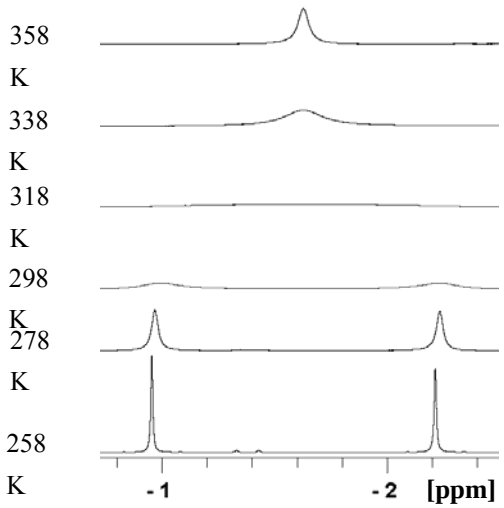


Figure S2. Resonances of the four methyl group at different temperature (258K~358K, left).

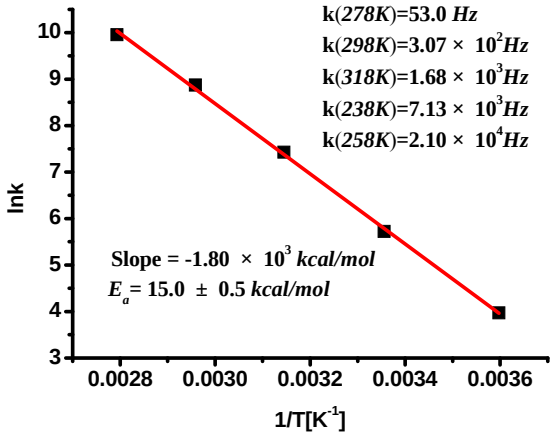


Figure S3. Measurement of apparent topomerization energy barrier using ^{1}H NMR.

Synthesis of (TPFC)Ge–OH.

To a solution of freshly prepared (TPFC)Ge(TEMPO) (37 mg, 0.036 mmol) in 3 mL toluene in Schlenk flask, 10 μl water was added (15 equivalent). The reaction was done without visible light irradiation at room temperature, after a reaction time of 5 hours, the TEMPO ligand was change to hydroxyl ligand quantitatively. The X-ray diffraction analysis suitable crystal was obtained by the concentration of the chloroform solution of (TPFC)Ge–OH.

(TPFC)Ge–OH (prepared using water; 5 hours; yield: >95%) ^{1}H NMR (400 MHz, C_7D_8) δ(ppm): 9.11 (d, 2H, ^3J(H,H)=4.0 Hz; *β*-pyrrole H), 8.89 (d, 2H, ^3J(H,H)=3.7 Hz; *β*-pyrrole H), 8.71 (t, 2H, ^3J(H,H)=3.9 Hz; *β*-pyrrole H), 8.69 (d, 2H, ^3J(H,H)=4.3 Hz; *β*-pyrrole H);

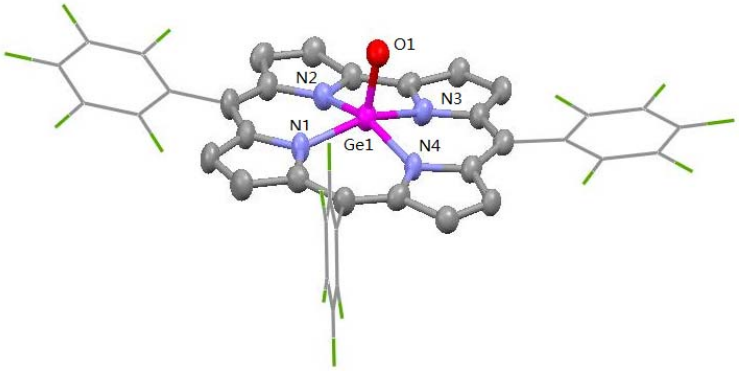


Figure S4. Solid state structure of complex **2** (hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge(1)–O(1) = 1.785(4), Ge(1)–N(1) = 1.918(4), Ge(1)–N(2) = 1.920(4), Ge(1)–N(3) = 1.903(4), Ge(1)–N(4) = 1.905(4), O(1)–Ge(1)–N(1) = 105.24(18), O(1)–Ge(1)–N(2) = 104.58(18), O(1)–Ge(1)–N(3) = 99.99(18), O(1)–Ge(1)–N(4) = 101.83(17), N(3)–Ge(1)–N(1) = 154.03(19), N(4)–Ge(1)–N(2) = 152.27(18).

General procedures for the reactions of (TPFC)Ge(TEMPO) with amines in dark.

For the reactions of (TPFC)Ge(TEMPO) with amines in the dark, excess amount of amines was added (calcd. 3 atm for ammonia gas and 10 equivalents for the liquid amines) to a solution of freshly prepared (TPFC)Ge(TEMPO) in 0.40 mL deuterated toluene (8.8 mmol L^{-1}) in a J. Young Valve NMR tube. After a reaction time ranging from 12 hours to several days at room temperature or elevated temperature (up to 110 ^{o}C) in the dark, the corrole germanium amide (TPFC)Ge–NR_1R_2 was formed.

General procedures for visible light promoted reactions of (TPFC)Ge(TEMPO) with amines.

To 0.40 mL deuterated toluene solution of freshly prepared (TPFC)Ge(TEMPO) (8.8 mmol L^{-1}) in a J. Young Valve NMR tube, excess amine was added. The J. Young Valve NMR tube was placed 50 cm away from the xenon lamp (the visible light irradiation power is 18 mW). After irradiation for a period of time (15 minutes up to 128 hours), the corrole germanium amide (TPFC)Ge–NR_1R_2 was formed.

(TPFC)Ge–NH_2 (**2**) ^{1}H NMR (400 MHz, C_7D_8) δ□(ppm): 9.12 (d, 2H, ^3J(H,H) = 4.3 Hz; β-pyrrole H), 8.88 (d, 2H, ^3J(H,H) = 4.7 Hz; β-pyrrole H), 8.71 (t, 2H, ^3J(H,H) = 4.2 Hz; β-pyrrole H), 8.68 (d, 2H, ^3J(H,H) = 4.7 Hz; β-pyrrole H), -5.45 (br, 2H, NH_2); HRMS (ESI) calcd for $C_{37}H_{11}F_{15}GeN_5$ $[M+H]^+$ 883.99893; found 883.99935. CSI-MS calcd for $C_{37}H_{11}F_{15}GeN_5$ $[M+H]^+$ 884.00; found 883.98.

$[(TPFC)Ge]_2NH$ (**3**) ^{1}H NMR (400 MHz, C_7D_8) δ□(ppm): 8.89 (d, 2H, ^3J(H,H) = 4.3 Hz; β-pyrrole H), 8.33 (d, 2H, ^3J(H,H) = 4.0 Hz; β-pyrrole H), 8.30 (d, 2H, ^3J(H,H) = 4.1 Hz; β-pyrrole H), 8.06 (d, 2H, ^3J(H,H) = 4.5 Hz; β-pyrrole H); CSI-MS calcd for $C_{74}H_{17}F_{30}Ge_2N_9$ $[M]^+$ 1747.97; found 1747.95.

(TPFC)Ge–$NHCH_2CH_2CH_3$ (**4**) ^{1}H NMR ^{1}H NMR (400 MHz, C_7D_8) δ□(ppm): 9.13 (d, 2H, ^3J(H,H) = 4.0 Hz; β-pyrrole H), 8.87 (d, 2H, ^3J(H,H) = 4.1 Hz; β-pyrrole H), 8.71 (d, 2H, ^3J(H,H) = 3.7 Hz; β-pyrrole H), 8.68 (d, 2H, ^3J(H,H) = 3.8 Hz; β-pyrrole H), -0.97 (t, 3H, ^3J(H,H) = 7.3 Hz; δ-CH_3), -1.62 (m, 2H; γ-CH_2), -1.89 (q, 2H, ^3J(H,H) = 6.8 Hz; β-CH_2), -5.17 (t, 1H, ^3J(H,H) = 6.9 Hz; NH).

(TPFC)Ge–NHCH(CH_3)$_2$ (**5**) ^{1}H NMR (500 MHz, C_7D_8) δ□(ppm): 9.14 (d, 2H, ^3J(H,H) = 4.1 Hz; β-pyrrole H), 8.87 (d, 2H, ^3J(H,H) = 4.2 Hz; β-pyrrole H), 8.72 (d, 2H, ^3J(H,H) = 3.8 Hz; β-pyrrole H), 8.67 (d, 2H, ^3J(H,H) = 4.3 Hz; β-pyrrole H), -1.75 (d, 6H, ^3J(H,H) = 6.3 Hz; γ-CH_3), -2.35 (m, 1H; β-CH), -5.25 (d, 1H, ^3J(H,H) = 8.6 Hz; NH).
(TPFC)Ge–NHC(CH_3)$_3$ (**6**) ^{1}H NMR (500 MHz, C_7D_8) δ□(ppm): 9.13 (d, 2H, ^3J(H,H) = 4.1 Hz; β-pyrrole H), 8.86 (d, 2H, ^3J(H,H) = 4.3 Hz; β-pyrrole H), 8.71 (d, 2H, ^3J(H,H) = 3.9 Hz; β-pyrrole H), 8.66 (d, 2H, ^3J(H,H) = 4.4 Hz; β-pyrrole H), -1.90 (s, 9H; γ-CH_3), -5.20 (s, 1H; NH).
(TPFC)Ge–NHC$_6$H$_5$ (**7**) ^{1}H NMR (400 MHz, C_7D_8) δ□(ppm): 9.09 (d, 2H, ^3J(H,H) = 4.2 Hz; β-pyrrole H), 8.86 (d, 2H, ^3J(H,H) = 4.4 Hz; β-pyrrole H), 8.70 (d, 2H, ^3J(H,H) = 4.1 Hz; β-pyrrole H), 8.65 (d, 2H, ^3J(H,H) = 4.5 Hz; β-pyrrole H), 5.91 (m, 3H; δ-CH and ε-CH), 2.79 (d, 1H, ^3J(H,H) = 2.4 Hz; γ-CH), 2.78 (d, 1H, ^3J(H,H) = 3.4 Hz; γ-CH), -2.97 (s, 1H; NH).
(TPFC)Ge–N(CH_2CH_3)$_2$ (**8**) ^{1}H NMR (400 MHz, C_7D_8) δ□(ppm): 9.12 (d, 2H, ^3J(H,H) = 4.2 Hz; β-pyrrole H), 8.85 (d, 2H, ^3J(H,H) = 4.3 Hz; β-pyrrole H), 8.71 (d, 2H, ^3J(H,H) = 3.9 Hz; β-pyrrole H), 8.67 (d, 2H, ^3J(H,H) = 4.4 Hz; β-pyrrole H), -1.76 (m, 10H; β-CH_2 and γ-CH_3).
(TPFC)Ge–N{$CH(CH_3)_2$}$_2$ (**9**) ^{1}H NMR (400 MHz, C_7D_8) δ□(ppm): 9.11 (d, 2H, ^3J(H,H) = 4.2 Hz; β-pyrrole H), 8.82 (d, 2H, ^3J(H,H) = 4.7 Hz; β-pyrrole H), 8.70 (d, 2H, ^3J(H,H) = 4.2 Hz; β-pyrrole H), 8.63 (d, 2H, ^3J(H,H) = 4.7 Hz; β-pyrrole H), -1.67 (m, 2H; β-CH), -1.76 (d, 12H, ^3J(H,H) = 6.1 Hz; γ-CH_3).

CSI-MS spectrum of (TPFC)Ge–NH_2 and [(TPFC)Ge]$_2$NH.

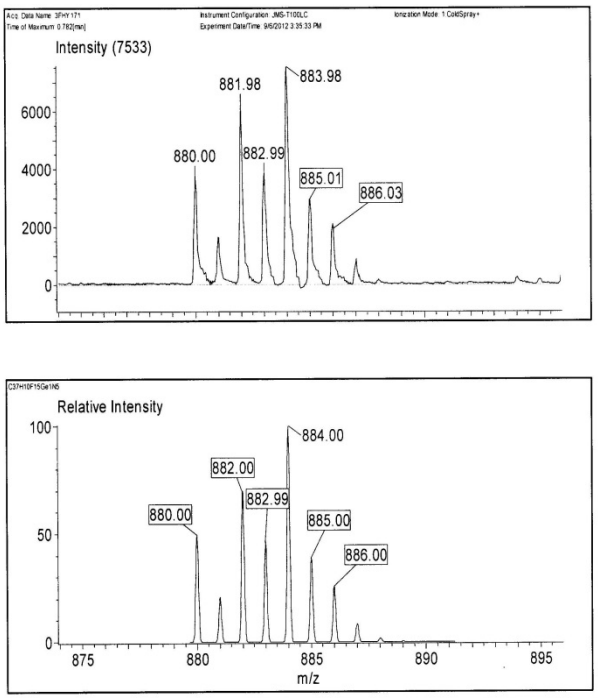


Figure S5. Experimental (top) and simulated (bottom) CS-MS spectrum of (TPFC)Ge–NH_2.

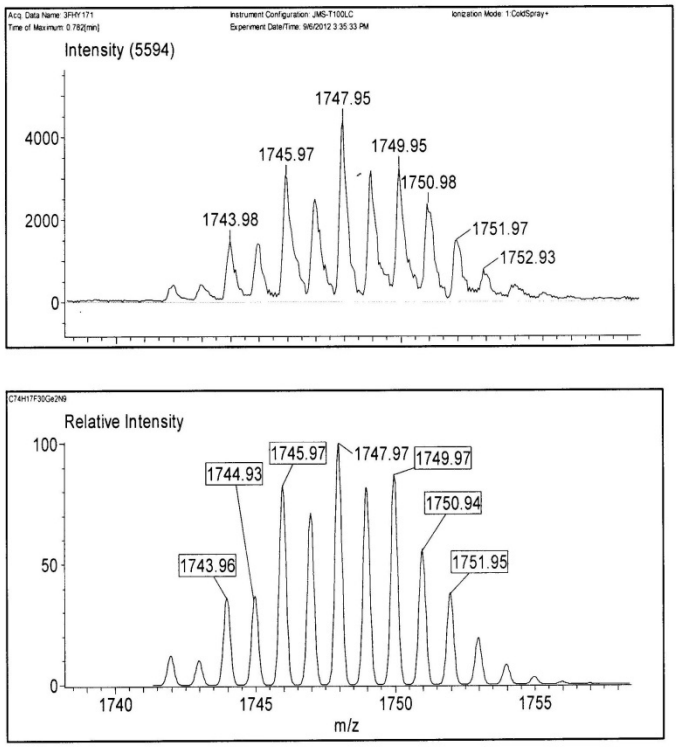


Figure S6. Experimental (top) and simulated (bottom) CS-MS spectrum of $[(TPFC)Ge]_2NH$.

EPR experiment of (TPFC)Ge(TEMPO) under visible light illumination.

3.6 mg (TPFC)Ge(TEMPO) (3.5×10^{-3} mmol) was dissolved in 0.40 mL toluene in a quartz tube suitable for the EPR experiment. A 500W mercury lamp with a <420nm UV-cutoff filter in the light path was used as the source of visible light in the irradiation experiment. The sample was about 1 m away from the mercury lamp. All the EPR spectrum was recorded at room temperature.

Experimental and simulation spectrum of dilute toluene solution of free TEMPO.

The EPR spectrum of toluene solution of TEMPO (0.20 mM) was recorded at 238K. Oxygen was removed from the sample before the measurement. The hyperfine coupling constants were obtained by simulation and are listed in Table S1.

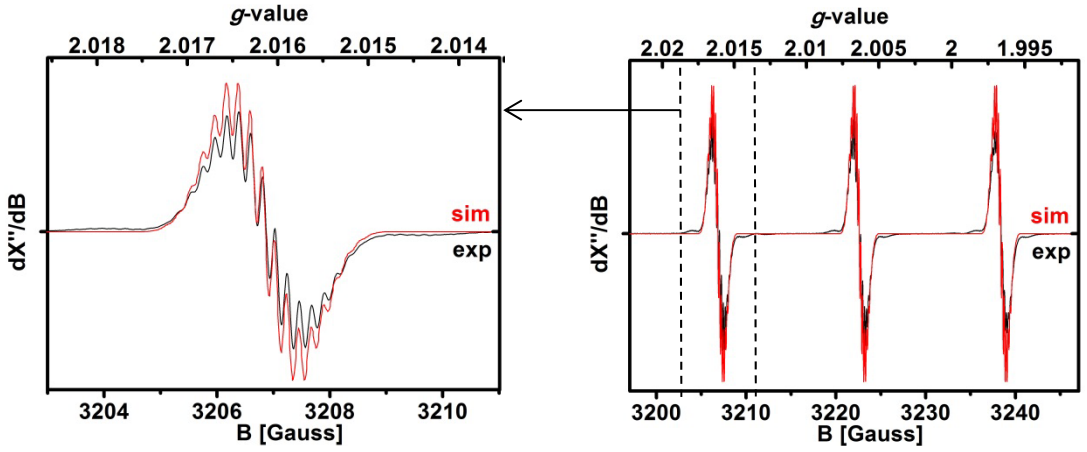
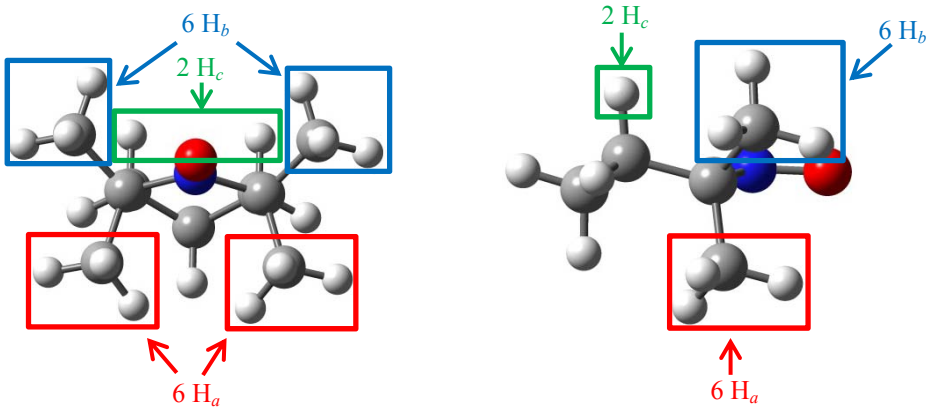


Figure S7. Experimental and simulated EPR spectrum of TEMPO in toluene solution (0.20 mM) at 238K (microwave frequency: 9.047345 GHz; microwave power: 1 mW)

Table S1. Hyperfine coupling constants of TEMPO

Atom	N	H_a	H_b	H_c [a]
Coupling constant/MHz	44.11	1.195	0.519	0.205

[a] Not resolved, based on line shape



Procedure for visible light promoted reaction of (TPFC)Ge(TEMPO) with ethylene.

To a solution of freshly prepared (TPFC)Ge(TEMPO) (3.6 mg, 3.5×10^{-3} mmol) in 0.40 mL deuterated toluene in a J. Young Valve NMR tube, calcd. 5 atm of ethylene was added. The J. Young Valve NMR tube was placed 20 cm away from the xenon lamp (the visible light irradiation power is 47.2 mW). After 70 hours irradiation at 80 °C, the alkyl germanium corrole products (TPFC)GeCH2CH2R (R=TEMPO) formed in a yields of 65%.

(TPFC)GeCH_2CH_2R (**10**) ^{1}H NMR (400 MHz, C_7D_8) δ (ppm): 9.11 (d, 2H, ^3J(H,H)=4.0 Hz; β-pyrrole H), 8.86 (d, 2H, ^3J(H,H)=4.1 Hz; β-pyrrole H), 8.70 (d, 2H, ^3J(H,H)=3.9 Hz; β-pyrrole H), 8.65 (d, 2H, ^3J(H,H)=4.0 Hz; β-pyrrole H), 0.82 (m, 6H; ζ-CH_2 and η-CH_2), 0.16 (s, 6H; ε-CH_3), -0.08 (s, 6H; ε-CH_3), -0.67 (t, 2H, ^3J(H,H)=9.0 Hz; β-CH_2), -4.12 (t, 2H, ^3J(H,H)=9.0 Hz; α-CH_2). HRMS (ESI) calcd for $C_{48}H_{31}F_{15}GeN_5O$ $[M+H]^+$ 1052.15068; found 1052.15077.

Procedure for axial ligand exchange reaction.

To a solution of freshly prepared (TPFC)Ge(TEMPO) (3.6 mg, 3.5×10^{-3} mmol) in 0.40 mL deuterated toluene in a J. Young Valve NMR tube, 2 equivalent of ^{OMe}TEMPO was added. The sample was irradiated by visible light at room temperature until the equilibrium (K_{eq} ~ 0.5) was reached. The reaction of (TPFC)Ge(^{OMe}TEMPO) with 2 equivalent of TEMPO under identical reaction condition also gave the same equilibrium constant.

(TPFC)Ge(^{OMe}TEMPO) ^{1}H NMR (400 MHz, C_7D_8) δ(ppm): 9.11 (d, 2H, ^3J(H,H)=4.2 Hz; β-pyrrole H), 8.85 (d, 2H, ^3J(H,H)=4.3 Hz; β-pyrrole H), 8.71 (d, 2H, ^3J(H,H)=4.2 Hz; β-pyrrole H), 8.67 (d, 2H, ^3J(H,H)=4.5 Hz; β-pyrrole H), 2.50 (s, 3H; OMe), 2.07 (m, 1H; p-CH), 0.55 (br, 2H; m-CH_2), -0.09 (br, 2H; m-CH_2), -1.01 (br, 6H; o-CH_3), -2.21 (br, 6H; o-CH_3); HRMS (ESI) calcd for $C_{47}H_{29}F_{15}GeN_5O_2$ $[M+H]^+$ 1054.12991; found 1054.13059.

4-methyl-2,2,6,6-tetramethylpiperidin-1-ol ^{1}H NMR (400 MHz, C_7D_8) δ(ppm): 3.51 (br, 1H; OH), 3.32 (tt, 1H, ^3J(H,H)=10.3 Hz, ^3J(H,H)=4.1 Hz; p-CH), 3.13 (s, 3H; OMe), 1.84 (m, 2H; m-CH_2), 1.46 (dd, 2H, ^2J(H,H)=11.7 Hz, ^3J(H,H)=11.7 Hz; m-CH_2), 1.12 (s, 6H; o-CH_3), 1.09 (s, 6H; o-CH_3); HRMS (ESI) calcd for $C_{10}H_{22}NO_2$ $[M+H]^+$ 188.16451; found 188.16381.

Kinetic study of the light promoted reaction of (TPFC)Ge(TEMPO) with n-propylamine.

To a solution of freshly prepared (TPFC)Ge(TEMPO) (3.6 mg, 3.5×10^{-3} mmol) in 0.40 mL deuterated toluene in a J. Young Valve NMR tube, 10 equivalent of *n*-propylamine was added. Another two samples were prepared using similar method, but with one and two equivalent of TEMPO respectively. The samples were irradiated at room temperature. ^{1}H NMR spectra was recorded at 0/1/2/3/4/5/6/8/10 minutes. The yield of (TPFC)GeNH^{n}Pr product was calculated based on (TPFC)Ge(TEMPO). The kinetic study showed that the reaction of (TPFC)Ge(TEMPO) with n-propylamine under visible light irradiation was zero-ordered for the concentration of (TPFC)Ge(TEMPO) and independent on the concentration of free TEMPO, in accordance with that the photo-cleavage of the Ge–O bond in (TPFC)Ge(TEMPO) is the rate determining step of N–H bond activation process.

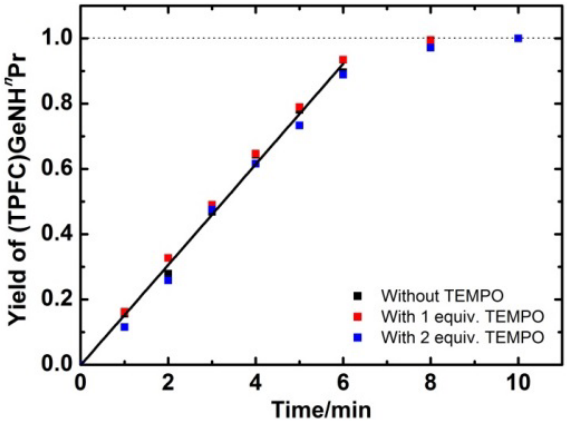


Figure S8. Dependence of the yield of (TPFC)GeNH^{n}Pr on the reaction time

The HOMO and LUMO of (TPFC)Ge(TEMPO).

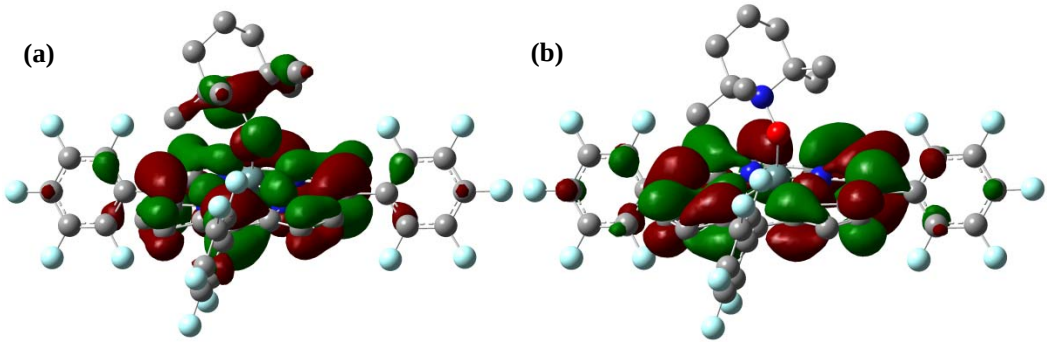


Figure S9. HOMO (a) and LUMO (b) orbitals of complex **1** (isovalue=0.02). H atoms have been omitted for clarity.

The SOMO of [(TPFC)Ge]$^{\bullet}$.

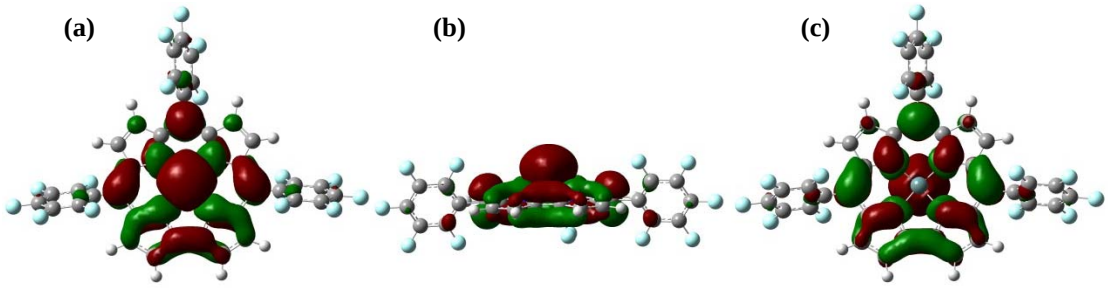


Figure S10. Top view (a), side view (b) and bottom view (c) of the SOMO of [(TPFC)Ge]$^{\bullet}$ (isovalue = 0.02).

Optimized structure coordination for the DFT study of the homolysis of Ge–O bond.

(TPFC)Ge(TEMPO)
E=-5692.10056974

Ge	-0.05583600	-0.72916600	-0.29215200
F	-4.90503100	-2.35741800	0.89593800
F	-7.59288600	-2.61083500	0.80904500
F	-9.02430100	-1.35740100	-1.14652700
F	-7.74200900	0.14899500	-3.02548500
F	-5.05401600	0.39633500	-2.96336500
F	0.73208700	4.64325100	-2.06830700
F	0.75782100	7.27433700	-1.44980400
F	0.04403900	8.10026700	1.04998100
F	-0.69151600	6.27075600	2.93597100
F	-0.71047300	3.63666600	2.33495100
F	4.88095700	0.16956400	-3.03528200
F	7.56099100	-0.10182900	-3.20385400
F	8.91943100	-1.51243400	-1.30441500
F	7.57050700	-2.64663700	0.77918800
F	4.89231700	-2.36927500	0.97248900
O	-0.34169600	-0.77862300	1.50124000
N	-1.27943700	-1.99683100	-1.10716600
N	1.17549300	-2.07910100	-0.94168300
N	1.36000300	0.56926200	-0.59474200
N	-1.42990100	0.61632000	-0.57683600
N	0.31487000	-1.67290100	2.44112700
C	-0.77253900	-3.21811200	-1.46805300
C	-1.84875900	-4.05829000	-1.84594100
H	-1.76762300	-5.07976900	-2.19044700
C	-3.01100000	-3.31622800	-1.69435300
H	-4.01885700	-3.63972600	-1.91369500
C	-2.64327300	-2.01461100	-1.23269800

C	-3.40375100	-0.86046500	-0.97757700
C	-2.80466700	0.37335200	-0.68274700
C	-3.48258000	1.61836600	-0.48325600
H	-4.55424500	1.74811600	-0.51578100
C	-2.54227900	2.58902700	-0.27391700
H	-2.71415900	3.64425100	-0.12085400
C	-1.25538800	1.96700900	-0.33142800
C	-0.00790000	2.59501100	-0.21007200
C	1.21830100	1.93473600	-0.37695300
C	2.51918000	2.52639000	-0.35883100
H	2.71985900	3.57755600	-0.21537800
C	3.43453500	1.53153300	-0.56634500
H	4.50834400	1.63682100	-0.61281200
C	2.73135900	0.29537900	-0.71152000
C	3.31337300	-0.96426600	-0.91903700
C	2.53823100	-2.12548800	-1.07569100
C	2.87734000	-3.43272200	-1.54155800
H	3.87884600	-3.77886800	-1.75495500
C	1.69674200	-4.13415400	-1.73605900
H	1.59058600	-5.13887900	-2.12071800
C	0.63743900	-3.26380300	-1.38039200
C	1.10022500	-0.81522800	3.39690800
C	1.68235100	-1.74301400	4.49067300
H	2.43651600	-2.39133300	4.02649200
H	2.20870300	-1.11288300	5.21703600
C	0.63755300	-2.61982400	5.17523700
H	1.11962200	-3.28412200	5.90236000
H	-0.07281900	-2.00732500	5.74277500
C	-0.08475400	-3.43967900	4.11029200
H	-0.86429500	-4.06895800	4.55554600
H	0.63739700	-4.11567000	3.63425400
C	-0.74614600	-2.58005400	3.00737800
C	0.31689000	0.36070600	4.02414700
H	1.02024500	1.02402500	4.53937600
H	-0.42557400	0.04419500	4.75779800
H	-0.18825600	0.94252300	3.25047500
C	2.29249300	-0.22669900	2.62585700
H	1.97186200	0.53942100	1.91978600
H	2.83168400	-1.00967800	2.08692200
H	2.98691200	0.24568400	3.32928400
C	-2.00822500	-1.86507200	3.54274200
H	-1.85539600	-1.38270500	4.50939300
H	-2.81204800	-2.59845100	3.66830800
H	-2.34800300	-1.11242100	2.82867600

C	-1.19024500	-3.54095200	1.89209100
H	-1.83508200	-3.04500700	1.16646300
H	-1.76458100	-4.36534100	2.32824700
H	-0.32215500	-3.96084500	1.37745700
C	-4.88682700	-0.96863500	-1.02897400
C	-5.57753700	-1.73626200	-0.08237800
C	-6.96289800	-1.87484500	-0.11275900
C	-7.69582500	-1.23351600	-1.10895800
C	-7.03943700	-0.46218000	-2.06544600
C	-5.65226500	-0.34319200	-2.01973100
C	0.01014600	4.05086400	0.11179900
C	0.37901600	5.01652300	-0.83094100
C	0.39879200	6.37582500	-0.52644400
C	0.03277200	6.79979100	0.74908400
C	-0.34425200	5.86418200	1.71014400
C	-0.34860400	4.50976500	1.38496700
C	4.79257900	-1.08488300	-1.02182400
C	5.51668000	-0.52068600	-2.07922900
C	6.89958800	-0.65304800	-2.18058900
C	7.59474400	-1.37663400	-1.21415900
C	6.90406500	-1.95694000	-0.15262100
C	5.52214900	-1.80640800	-0.06861700

(TPFC)Ge(III) radical

E=-5208.26126319

Ge	0.00159800	-1.02234900	-0.65448300
F	-4.89126500	-2.53546700	-2.03284200
F	-7.57481000	-2.80105100	-1.95175200
F	-8.98668700	-1.81961600	0.16809000
F	-7.68321100	-0.57449700	2.21620000
F	-4.99892400	-0.31697800	2.15931700
F	4.94345000	-0.35294700	2.27446800
F	7.62536400	-0.61729200	2.38825500
F	8.97205100	-1.83978000	0.35450300
F	7.60612200	-2.79209400	-1.80828800
F	4.92534300	-2.51955100	-1.94593600
F	0.87425500	3.78581700	-2.37678800
F	0.89966800	6.48479800	-2.46300600
F	0.03938000	7.93246600	-0.31553100
F	-0.84256300	6.65309400	1.92821300
F	-0.85946800	3.95560900	2.03276200
N	-1.40691400	0.25797800	-0.06962100
N	-1.23591100	-2.41477000	0.01237500
N	1.22548800	-2.41690300	0.03054200

N	1.40368100	0.25547700	-0.05329800
C	-1.24626500	1.63383400	-0.10599300
C	-2.54170900	2.24225900	-0.11538400
H	-2.73078600	3.30529000	-0.13579100
C	-3.47216200	1.23908700	-0.08597100
H	-4.54636800	1.35118500	-0.08050400
C	-2.77826000	-0.01355600	-0.05423800
C	-3.36605200	-1.29277600	0.01607300
C	-2.60322500	-2.47095000	0.08217100
C	-2.96337800	-3.83749200	0.31707200
H	-3.97105300	-4.20812500	0.44253500
C	-1.79328300	-4.57455900	0.39750700
H	-1.70337900	-5.63496000	0.58845600
C	-0.71703800	-3.66331300	0.20821500
C	0.70118500	-3.66451000	0.21907700
C	1.77246900	-4.57744400	0.42684900
H	1.67742000	-5.63752500	0.61705400
C	2.94498600	-3.84235900	0.36641000
H	3.94965800	-4.21450000	0.51013700
C	2.59135600	-2.47514300	0.12546300
C	3.35727100	-1.29806500	0.08137900
C	2.77330800	-0.01737000	0.00535600
C	3.46762700	1.23537800	0.02255700
H	4.54061800	1.34708000	0.07308400
C	2.53827300	2.23925600	-0.01850300
H	2.72569400	3.30252200	0.00944300
C	1.24386300	1.63117900	-0.07408900
C	-0.00021700	2.28614000	-0.11989400
C	-4.84939700	-1.41169000	0.05760400
C	-5.55111700	-2.04911300	-0.97361000
C	-6.93620600	-2.19261700	-0.94675000
C	-7.65891000	-1.69002000	0.13279700
C	-6.99178000	-1.05117400	1.17563900
C	-5.60551800	-0.92424800	1.13102500
C	4.83921500	-1.42070500	0.15610200
C	5.57188000	-0.94894900	1.25239000
C	6.95652900	-1.07952900	1.32655800
C	7.64565900	-1.70680300	0.29102300
C	6.94637700	-2.19433800	-0.81062800
C	5.56251400	-2.04722000	-0.86677800
C	0.00598200	3.77724200	-0.16903700
C	0.45052100	4.46636000	-1.30354900
C	0.46949100	5.85781300	-1.36292500
C	0.02884500	6.59861800	-0.26841400

C	-0.42303500	5.94371700	0.87510000
C	-0.42574500	4.55124600	0.91440400

(TPFC)Ge(IV) cation

E=-5208.05403882

Ge	-0.00263300	-1.00813900	-0.01731200
F	4.85408100	-2.58491600	2.04872400
F	7.54703800	-2.81731800	2.01425900
F	8.98097900	-1.79360500	-0.06687500
F	7.70395200	-0.53367500	-2.11933600
F	5.00999700	-0.29810400	-2.09899600
F	-4.96513300	-0.31656600	-2.22764000
F	-7.65887900	-0.54503200	-2.30417600
F	-8.98556400	-1.76521500	-0.25914000
F	-7.60160100	-2.75705500	1.87077500
F	-4.90909800	-2.53182800	1.96104500
F	-0.94297100	3.76428400	2.36985200
F	-0.93483200	6.46812100	2.48622000
F	0.01625900	7.92226000	0.38546100
F	0.96206500	6.65831500	-1.83759100
F	0.95746900	3.95508000	-1.96408700
N	1.38994400	0.23675600	0.03629700
N	1.21846900	-2.42715100	-0.05785800
N	-1.22830300	-2.42224800	-0.07732100
N	-1.39084600	0.24253100	0.01223700
C	1.23675500	1.63227400	0.12217400
C	2.53253900	2.20959900	0.20535400
H	2.72882800	3.26693700	0.29697800
C	3.45642300	1.19908600	0.16396200
H	4.52973500	1.30163300	0.21755700
C	2.77496800	-0.04631000	0.05471600
C	3.36740600	-1.32193100	-0.01421800
C	2.60411000	-2.49030500	-0.07176300
C	2.95041400	-3.87124800	-0.15028000
H	3.95875900	-4.25709900	-0.18302300
C	1.78114000	-4.61445700	-0.18084500
H	1.69910700	-5.69069100	-0.23885900
C	0.69731200	-3.70380100	-0.12488900
C	-0.71125500	-3.70104100	-0.13565100
C	-1.79770500	-4.60730400	-0.20886300
H	-1.71909300	-5.68388600	-0.26515900
C	-2.96428900	-3.85925800	-0.19868700
H	-3.97356100	-4.24083700	-0.24886900
C	-2.61362800	-2.47962900	-0.11680700

C	-3.37299800	-1.30771900	-0.08597700
C	-2.77720200	-0.03380700	-0.01653000
C	-3.45541000	1.21735200	0.03033700
H	-4.52929500	1.32685300	0.03310300
C	-2.52833100	2.22454800	0.07747500
H	-2.72242800	3.28567900	0.11124700
C	-1.23350200	1.63907500	0.07210500
C	0.00278200	2.29286700	0.12861400
C	4.85138200	-1.43209000	-0.02328800
C	5.53694900	-2.07633100	1.01447600
C	6.92344800	-2.20372800	1.01011200
C	7.65829800	-1.67841000	-0.05294700
C	7.00383200	-1.03147500	-1.10168500
C	5.61660900	-0.91777900	-1.07793700
C	-4.85695100	-1.41388100	-0.12903400
C	-5.59659100	-0.91680900	-1.20963900
C	-6.98329000	-1.02698800	-1.26251900
C	-7.66313100	-1.65355200	-0.21755200
C	-6.95388100	-2.16233300	0.87062000
C	-5.56740400	-2.03855900	0.90384200
C	0.00671400	3.78244500	0.19905900
C	-0.47128300	4.46021500	1.32683100
C	-0.47452000	5.85071100	1.39969900
C	0.01345300	6.59579200	0.32568000
C	0.49849500	5.94807200	-0.81094400
C	0.48892500	4.55669800	-0.86315900

TEMPO radical

E=-483.77943688

C	-2.12309700	0.13069900	0.00000000
C	-1.35993800	0.58241900	1.24561700
C	0.07375000	0.01946700	1.33271800
C	0.07375000	0.01946700	-1.33271800
C	-1.35993800	0.58241900	-1.24561700
H	-1.30691600	1.67895900	1.24359700
H	-1.89157000	0.29633200	2.16045900
H	-2.26149700	-0.95713700	0.00000000
H	-3.12824200	0.56740400	0.00000000
H	-1.30691600	1.67895900	-1.24359700
H	-1.89157000	0.29633200	-2.16045900
N	0.76124800	0.15025000	0.00000000
O	2.02664500	-0.04878800	0.00000000
C	0.88342600	0.83949600	2.35038600
H	0.37797300	0.81164100	3.32124700

H	1.89149200	0.43918600	2.46429700
H	0.96204000	1.88304500	2.03132600
C	0.07375000	-1.46456300	1.75904900
H	1.08887800	-1.86581500	1.70580400
H	-0.28017400	-1.55327700	2.79147600
H	-0.57443500	-2.07893900	1.12876400
C	0.88342600	0.83949600	-2.35038600
H	1.89149200	0.43918600	-2.46429700
H	0.37797300	0.81164100	-3.32124700
H	0.96204000	1.88304500	-2.03132600
C	0.07375000	-1.46456300	-1.75904900
H	-0.28017400	-1.55327700	-2.79147600
H	1.08887800	-1.86581500	-1.70580400
H	-0.57443500	-2.07893900	-1.12876400

TEMPO$^-$ anion

E=-483.77765943

C	-1.24714900	1.42931800	-0.43066700
C	-1.27167200	-0.06796200	-0.04686400
C	1.27167600	-0.06802700	-0.04685800
C	1.24723400	1.42928400	-0.43057100
C	0.00003300	2.15551200	0.07840900
H	-1.26540900	1.50232300	-1.52735200
H	-2.16247700	1.91517400	-0.06165800
H	2.16255200	1.91508600	-0.06146400
H	1.26558900	1.50233100	-1.52724900
H	0.00000200	2.18651700	1.17588800
H	0.00005400	3.20376500	-0.25681700
N	-0.00003000	-0.71598100	-0.47081300
O	-0.00013100	-2.08210200	-0.08765700
C	1.61250900	-0.26213200	1.45419900
H	1.31817800	-1.28607700	1.70749500
H	2.68763500	-0.13425100	1.64174500
H	1.08023900	0.43594600	2.10840400
C	2.37949900	-0.75940500	-0.86769000
H	3.36167700	-0.30545000	-0.67117500
H	2.39751200	-1.82023500	-0.61217000
H	2.15351000	-0.67428400	-1.93635000
C	-2.37952700	-0.75938900	-0.86761800
H	-2.39747600	-1.82021000	-0.61203500
H	-3.36170000	-0.30545700	-0.67106900
H	-2.15360600	-0.67431300	-1.93629900
C	-1.61246200	-0.26194400	1.45421000
H	-2.68756200	-0.13389900	1.64179700

H	-1.31824400	-1.28589800	1.70760000
H	-1.08005500	0.43608800	2.10835000

DFT study of reaction of (TPFC)Ge–H with TEMPO.

The calculation was performed with the Gaussian 09 program.[S2] All gas-phase stationary points were optimized using B3LYP[S3] functional with the 3-21G*[S4] basis set for all atoms. Full Hessian matrixes in Gaussian 09 were calculated to verify the nature of all stationary points as either minima or first-order saddle points. The first-order saddle points were further characterized by intrinsic reaction coordinate (IRC)[S5] calculations to confirm that the transition state was correctly connected to the corresponding reactant and product. For more accurate energies, single point calculations were done with the larger basis set in which 6-311G(2d)[S6] was used for Ge atom, 6-311G(d)[S7] was used for N and O atoms and 6-31G(d,p)[S8] was used for all other atoms.

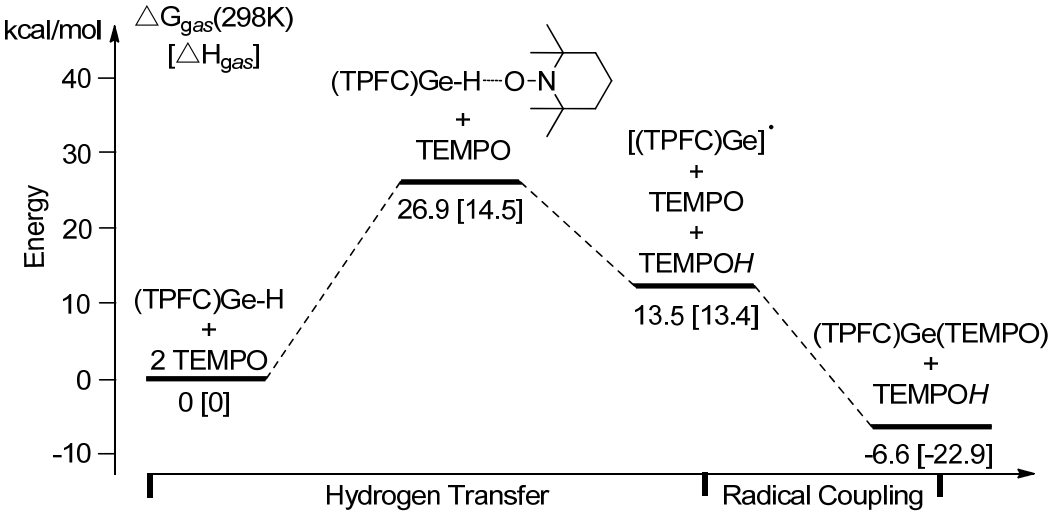


Figure S11. Energy surface of the reaction of (TPFC)Ge–H with TEMPO.

Optimized structures:

(TPFC)Ge–H

E=-5182.03902094

Ge	-0.00846700	-1.00461400	-0.63355700
F	4.90290700	-2.68859300	-1.84952100
F	7.60880700	-3.00824400	-1.61909300
F	8.94197900	-1.92702800	0.52254700
F	7.56674100	-0.51971400	2.43742200
F	4.86379200	-0.18945200	2.21578000
F	-1.07077700	3.95130200	1.90107200
F	-0.99124400	6.68427900	1.80594400
F	0.13792200	7.95084700	-0.35181900
F	1.19564000	6.48394400	-2.41627900
F	1.12800000	3.74981200	-2.32618000
F	-4.94902400	-0.12057100	2.08522600
F	-7.66062200	-0.42125600	2.22714900
F	-8.99201600	-1.83066400	0.28326900

F	-7.60615500	-2.94388100	-1.80796400
F	-4.89160600	-2.65315500	-1.95936800
N	1.21339600	-2.41039200	-0.07826600
N	-1.25581400	-2.39686500	-0.10255800
N	-1.40100300	0.27205200	-0.15716100
N	1.38984700	0.25544700	-0.13479200
C	0.67369000	-3.67140600	0.12950800
C	1.74304600	-4.57107600	0.38929200
H	1.64829000	-5.62400800	0.59504100
C	2.92104000	-3.83235200	0.34936900
H	3.91605000	-4.19974400	0.53430900
C	2.58157200	-2.46513700	0.07592700
C	3.35972700	-1.29763600	0.05532100
C	2.77317400	-0.02881800	-0.01731200
C	3.45931000	1.23168400	0.05733200
H	4.52373300	1.34213700	0.16020800
C	2.53343300	2.23884300	-0.00461500
H	2.72030700	3.29641600	0.05641400
C	1.23191400	1.64389800	-0.11746100
C	0.00516700	2.31604300	-0.16916900
C	-1.23105200	1.66083700	-0.14515700
C	-2.53096300	2.26696400	-0.07850900
H	-2.71504000	3.32551800	-0.04666700
C	-3.46660500	1.26838300	-0.03982000
H	-4.53292200	1.38945800	0.02422700
C	-2.79004900	0.00119600	-0.08112500
C	-3.39205000	-1.26103100	-0.02211300
C	-2.62741900	-2.43717400	0.01956600
C	-2.98772700	-3.80079500	0.28361500
H	-3.99059600	-4.15788300	0.44472900
C	-1.81880900	-4.55212200	0.34973100
H	-1.74019800	-5.60629400	0.55596300
C	-0.73430100	-3.66385200	0.11500200
C	4.83032500	-1.43344700	0.17858400
C	5.54731800	-2.14283000	-0.78240100
C	6.92020600	-2.31285100	-0.67122500
C	7.59567300	-1.76592800	0.41005800
C	6.89975700	-1.05388000	1.37610000
C	5.52583000	-0.89688500	1.25821800
C	0.03020700	3.80019200	-0.20947200
C	-0.49566000	4.56269800	0.82843200
C	-0.46768400	5.94989200	0.78453900
C	0.10323000	6.59138500	-0.30500000
C	0.63792600	5.84850000	-1.34766800

C	0.59462500	4.46227800	-1.29647800
C	-4.86683700	-1.38110900	0.05950200
C	-5.58896000	-0.82873600	1.11352400
C	-6.96743800	-0.97097000	1.19091400
C	-7.64133400	-1.68414700	0.21020700
C	-6.93931600	-2.24716500	-0.84557500
C	-5.56214800	-2.09162600	-0.91664500
H	0.00434900	-1.02919800	-2.18461300

TEMPO

E=-481.09551378

C	-2.12889300	0.14073800	0.00000000
C	-1.37085500	0.61929200	1.25275200
C	0.05652600	0.04020900	1.34330600
C	0.05652600	0.04020900	-1.34330600
C	-1.37085500	0.61929200	-1.25275200
H	-1.30437700	1.71466800	1.22000300
H	-1.90739100	0.34487000	2.16877200
H	-2.22437700	-0.95088400	0.00000000
H	-3.14278500	0.55801200	0.00000000
H	-1.30437700	1.71466800	-1.22000300
H	-1.90739100	0.34487000	-2.16877200
N	0.74167500	0.15214300	0.00000000
O	2.03293500	-0.24856900	0.00000000
C	0.91902600	0.85677400	2.32615600
H	0.53708600	0.74636100	3.34599300
H	1.94600100	0.49288200	2.26542700
H	0.90323600	1.91546300	2.04728600
C	0.05652600	-1.44543600	1.77133200
H	1.07678800	-1.82338400	1.66810400
H	-0.26712100	-1.53517500	2.81361700
H	-0.60890200	-2.04472500	1.14319600
C	0.91902600	0.85677400	-2.32615600
H	1.94600100	0.49288200	-2.26542700
H	0.53708600	0.74636100	-3.34599300
H	0.90323600	1.91546300	-2.04728600
C	0.05652600	-1.44543600	-1.77133200
H	-0.26712100	-1.53517500	-2.81361700
H	1.07678800	-1.82338400	-1.66810400
H	-0.60890200	-2.04472500	-1.14319600

TS

E=-5663.12879395

Ge	0.00625600	-0.43483200	-0.38733300

F	-4.74780700	-2.46063600	0.24919200
F	-7.45847700	-2.75721300	0.12725500
F	-8.96466700	-1.04211300	-1.39849500
F	-7.75182000	0.97821000	-2.80679200
F	-5.04183300	1.29524200	-2.68869000
F	1.15226000	5.09345800	-1.20039900
F	1.10751900	7.63935500	-0.20345200
F	-0.05020500	8.14045200	2.23425300
F	-1.17070700	6.09140000	3.67783600
F	-1.13986400	3.54338600	2.68550500
F	5.13450200	1.25854100	-2.52782300
F	7.84295500	0.91628600	-2.56735400
F	8.99352500	-1.13320900	-1.14922800
F	7.42551500	-2.85186600	0.30895400
F	4.71621500	-2.53005300	0.35366200
N	-1.21730300	-1.52282800	-1.47414400
N	1.24550800	-1.53503800	-1.44391600
N	1.41282900	0.95108700	-0.49068300
N	-1.38511100	0.96256000	-0.52093900
C	-0.68818400	-2.64511400	-2.08727400
C	-1.76803700	-3.42017700	-2.60086800
H	-1.68095800	-4.34733500	-3.14224700
C	-2.94228000	-2.74255700	-2.29297900
H	-3.94269800	-3.03640700	-2.56220200
C	-2.59001400	-1.53620800	-1.59597600
C	-3.36199100	-0.45065100	-1.15690100
C	-2.77078400	0.73029300	-0.68399700
C	-3.45329400	1.94334400	-0.31917900
H	-4.51809300	2.08376100	-0.35905900
C	-2.51889500	2.87482800	0.04760000
H	-2.70112300	3.89297700	0.34317300
C	-1.21869000	2.27456500	-0.07240100
C	0.01539000	2.88337500	0.19135200
C	1.25064900	2.26283800	-0.03610100
C	2.55539200	2.84001900	0.13786500
H	2.74568500	3.84592200	0.46564500
C	3.48735700	1.89656400	-0.20211800
H	4.55514300	2.01850200	-0.19625600
C	2.80009300	0.69880900	-0.60597900
C	3.39173000	-0.48698000	-1.06599100
C	2.62063400	-1.56308100	-1.52968600
C	2.97819100	-2.77309200	-2.21742500
H	3.98210300	-3.07769100	-2.46030000
C	1.80523700	-3.43850200	-2.55549200

H	1.72251900	-4.36505800	-3.09857500
C	0.72067800	-2.65224200	-2.06975500
C	-4.83736700	-0.57653800	-1.22092100
C	-5.47468100	-1.59449500	-0.51375500
C	-6.85136800	-1.75701600	-0.57086200
C	-7.61380900	-0.89062200	-1.34071800
C	-6.99957900	0.13085800	-2.05033000
C	-5.62068900	0.27841500	-1.99046600
C	0.00356200	4.27019200	0.72220500
C	0.56206800	5.32401100	0.00532300
C	0.55203000	6.61805000	0.50741100
C	-0.03306700	6.87295700	1.73916900
C	-0.59974000	5.83668800	2.46694300
C	-0.57450800	4.54549300	1.95871600
C	4.86699700	-0.62784200	-1.08845900
C	5.68153700	0.22828600	-1.82404700
C	7.06016000	0.06746200	-1.84435700
C	7.64310100	-0.96875100	-1.12977800
C	6.84951000	-1.83687700	-0.39423300
C	5.47348600	-1.66097300	-0.37601300
H	-0.02337900	-1.07995000	1.38473300
C	-0.03466600	-5.48379600	3.61383500
C	-1.27962300	-4.94872800	2.88032100
C	-1.36309900	-3.40468000	2.89087200
C	1.28396300	-3.37839800	2.95132400
C	1.23196200	-4.92388000	2.93835600
H	-1.24018300	-5.28280400	1.83557200
H	-2.20044900	-5.34194000	3.32712400
H	-0.06198900	-5.20322900	4.67251300
H	-0.02273000	-6.57961400	3.56842000
H	1.24763400	-5.25858700	1.89322800
H	2.13887200	-5.29857100	3.42758200
N	-0.03324700	-2.87747800	2.41458300
O	-0.04803100	-1.43747400	2.45176000
C	-2.40890900	-2.93641500	1.86011300
H	-3.39500000	-3.33797500	2.10869200
H	-2.46419500	-1.84532200	1.85856500
H	-2.12865000	-3.27441900	0.85870400
C	-1.75619100	-2.85395500	4.28248200
H	-1.63245500	-1.76841800	4.27086600
H	-2.80448700	-3.09751600	4.48752600
H	-1.14125500	-3.27310500	5.08178500
C	2.36562300	-2.89034000	1.96803200
H	2.39894500	-1.79812600	1.96741000

H	3.34730500	-3.27284200	2.26010400
H	2.13773400	-3.23418400	0.95556100
C	1.59923000	-2.81926000	4.35862300
H	2.64134700	-3.04010800	4.61477300
H	1.45202200	-1.73678700	4.33893700
H	0.95497300	-3.25130500	5.12730800

[(TPFC)Ge]$^{\bullet}$

E=-5181.40730458

Ge	-0.00413500	-1.01515500	-0.66613200
F	4.87493400	-2.72781400	-1.82479300
F	7.58535900	-3.03357900	-1.64089700
F	8.95629200	-1.90410100	0.45152300
F	7.61371800	-0.46161600	2.36323300
F	4.90622400	-0.14350600	2.18732700
F	-1.08715300	3.94759900	1.90369600
F	-1.02588900	6.68090000	1.79501400
F	0.10116800	7.94383500	-0.36570700
F	1.17551300	6.47366600	-2.41930300
F	1.12800400	3.73960300	-2.31435800
F	-4.98626700	-0.08857500	2.05378300
F	-7.69983300	-0.38673700	2.14882300
F	-8.99314500	-1.83904100	0.21106400
F	-7.56646600	-2.99881600	-1.82694800
F	-4.85005200	-2.71291900	-1.93047900
N	1.21633200	-2.40515200	-0.00101600
N	-1.24734700	-2.39611200	-0.02480900
N	-1.40390400	0.26759500	-0.11456500
N	1.39540800	0.25633300	-0.09282800
C	0.68227600	-3.66515400	0.19960500
C	1.75948500	-4.57203600	0.42660900
H	1.66753200	-5.62716000	0.62273200
C	2.93583900	-3.83578600	0.36981100
H	3.93414200	-4.20800200	0.52510800
C	2.59090400	-2.46307900	0.11578600
C	3.36440200	-1.29568300	0.07788100
C	2.77897100	-0.02271500	-0.00337800
C	3.46714700	1.23959100	0.03679700
H	4.53338600	1.35390700	0.11402200
C	2.53838100	2.24498700	-0.02282500
H	2.72646600	3.30344000	0.01547800
C	1.23560400	1.64517900	-0.10171200
C	0.00316800	2.30984000	-0.15160300
C	-1.23589800	1.65672300	-0.12906800

C	-2.53757900	2.26354700	-0.09584700
H	-2.72419100	3.32235600	-0.08849800
C	-3.47303000	1.26375500	-0.05902100
H	-4.54059200	1.38493800	-0.01971000
C	-2.79146400	-0.00271800	-0.06612900
C	-3.38818300	-1.27126900	0.00167600
C	-2.62436700	-2.44440800	0.06055900
C	-2.98466900	-3.81472200	0.30564800
H	-3.98879000	-4.18009800	0.43784600
C	-1.81507500	-4.55937200	0.38801900
H	-1.73512500	-5.61535100	0.58481800
C	-0.72669800	-3.66011400	0.18538300
C	4.83774700	-1.42823200	0.17644300
C	5.53808800	-2.15605900	-0.78299500
C	6.91336200	-2.31994300	-0.69490500
C	7.60779600	-1.74882900	0.36154000
C	6.92831200	-1.01907900	1.32611900
C	5.55195300	-0.86789400	1.23151200
C	0.02161700	3.79428900	-0.20233500
C	-0.51355600	4.55783500	0.83008200
C	-0.49424700	5.94489300	0.77919500
C	0.07568200	6.58460100	-0.31201300
C	0.61882100	5.84014700	-1.34921400
C	0.58531100	4.45392500	-1.29088400
C	-4.86459000	-1.39330000	0.05817800
C	-5.60700700	-0.81788500	1.08542900
C	-6.98672000	-0.95899900	1.13888100
C	-7.64146500	-1.69376700	0.16110800
C	-6.91895100	-2.28013500	-0.86774300
C	-5.54063100	-2.12610200	-0.91505800

TEMPO*H*

E=-481.70743872

H	-0.00022600	-2.58139400	-0.80246000
C	0.00007500	2.17739000	0.06400200
C	1.25752500	1.45561700	-0.45977200
C	1.30465900	-0.03316900	-0.03975900
C	-1.30465500	-0.03310000	-0.03975600
C	-1.25744000	1.45569800	-0.45973700
H	1.25582500	1.50243500	-1.55631400
H	2.17143100	1.94361400	-0.09990600
H	0.00009300	2.19795200	1.15940000
H	0.00010500	3.21859700	-0.28104400
H	-1.25577600	1.50254300	-1.55627800

H	-2.17130300	1.94374200	-0.09982800
N	-0.00002100	-0.64879100	-0.49190700
O	-0.00009100	-2.06202200	0.04783700
C	2.39264600	-0.76491900	-0.85714900
H	3.37785500	-0.32736000	-0.66427600
H	2.40459100	-1.81993900	-0.57065100
H	2.16176700	-0.68615100	-1.92418800
C	1.62382000	-0.20428700	1.46338300
H	1.42933500	-1.24210400	1.74236200
H	2.68117100	0.02483900	1.63799600
H	1.02368900	0.45302400	2.09507900
C	-2.39266400	-0.76479600	-0.85716200
H	-2.40455100	-1.81985700	-0.57080400
H	-3.37787200	-0.32728800	-0.66418000
H	-2.16184400	-0.68587800	-1.92420200
C	-1.62383000	-0.20425200	1.46337500
H	-2.68118000	0.02488500	1.63798800
H	-1.42935500	-1.24207800	1.74233300
H	-1.02368600	0.45303600	2.09507800

(TPFC)Ge(TEMPO)

E=-5662.61608297

Ge	-0.05260100	-0.66940100	-0.51357000
F	-4.50317600	-2.37683300	0.90272600
F	-7.19843900	-2.72035300	1.22432700
F	-8.95643800	-1.45266100	-0.45778000
F	-8.02428800	0.17013300	-2.46551100
F	-5.32814900	0.52924900	-2.79438600
F	0.21012000	4.85459900	-2.21202100
F	0.27262200	7.45790300	-1.34385700
F	0.15165600	8.00619900	1.33970600
F	-0.03175500	5.97046400	3.16690700
F	-0.09545600	3.36314100	2.30683600
F	5.17557600	0.33849700	-2.81918800
F	7.87760000	-0.05768700	-2.65801300
F	8.91447300	-1.68366000	-0.70536300
F	7.24792400	-2.92001900	1.09179100
F	4.54342000	-2.54135500	0.93584000
O	-0.36749800	-0.67484700	1.26173500
N	-1.27323000	-1.91409100	-1.34355100
N	1.17456700	-2.01391700	-1.15501400
N	1.37828900	0.61126400	-0.77879900
N	-1.40557400	0.68802800	-0.81894700
N	0.23559200	-1.72547100	2.18750800

C	-0.77158600	-3.15483500	-1.70242400
C	-1.86821900	-3.99240800	-2.04234300
H	-1.80428400	-5.01443100	-2.37624300
C	-3.02829900	-3.24601100	-1.86114400
H	-4.03833800	-3.57189300	-2.04447800
C	-2.64953500	-1.93314900	-1.42380400
C	-3.40377500	-0.79021600	-1.12779600
C	-2.79525800	0.44551000	-0.88662500
C	-3.46071100	1.70400300	-0.67891700
H	-4.52639600	1.84308200	-0.71426500
C	-2.51044700	2.67045700	-0.47839700
H	-2.67390100	3.72170700	-0.31560600
C	-1.21924500	2.04476600	-0.55382000
C	0.02482100	2.65531000	-0.39897800
C	1.24004100	1.98761900	-0.55336700
C	2.55208200	2.56658300	-0.50435600
H	2.75318000	3.61440200	-0.36339900
C	3.46732600	1.56504800	-0.69377000
H	4.53671000	1.66855900	-0.73184000
C	2.76347100	0.32346200	-0.85654500
C	3.33831700	-0.93997900	-1.02674300
C	2.54961100	-2.08091600	-1.22747600
C	2.88539900	-3.40035700	-1.67853700
H	3.88511000	-3.76083900	-1.85198200
C	1.70097700	-4.08966500	-1.91774000
H	1.60383800	-5.09198800	-2.29975500
C	0.63086600	-3.20985000	-1.60461700
C	1.07886900	-0.92880400	3.18445100
C	1.51762000	-1.92051000	4.29246900
H	2.17066600	-2.67437100	3.83422300
H	2.11066300	-1.35934600	5.02444600
C	0.33622400	-2.63826200	4.96197400
H	0.70530200	-3.33768500	5.72232900
H	-0.31614000	-1.91805600	5.46813900
C	-0.43963800	-3.40426600	3.87905300
H	-1.29957700	-3.93507600	4.30529500
H	0.22873000	-4.14934200	3.42811600
C	-0.97238500	-2.48777100	2.74861100
C	0.39723100	0.32448800	3.78054200
H	1.12168400	0.84032100	4.42189200
H	-0.47538300	0.07613900	4.38531100
H	0.09267300	1.00552200	2.98354700
C	2.34540500	-0.47615200	2.43235600
H	2.08171100	0.22637700	1.64310400

H	2.86371000	-1.33176300	1.99301400
H	3.02196600	0.02791100	3.13274300
C	-2.15180400	-1.60381300	3.22856500
H	-2.03497300	-1.26665800	4.26082900
H	-3.08408300	-2.17405000	3.15014800
H	-2.22411300	-0.73827200	2.56849100
C	-1.48520300	-3.39836800	1.61287300
H	-2.08544300	-2.83657900	0.89978500
H	-2.12232500	-4.18130900	2.04124600
H	-0.63627700	-3.86266400	1.10490300
C	-4.86939400	-0.94128700	-0.97644500
C	-5.36179000	-1.74915200	0.04700100
C	-6.72649400	-1.92726500	0.22241000
C	-7.61687000	-1.28395400	-0.62616900
C	-7.14459000	-0.46426900	-1.64098100
C	-5.77660100	-0.29896300	-1.80976200
C	0.05742200	4.07568000	0.03447500
C	0.14918200	5.11662600	-0.87882600
C	0.18184200	6.43656300	-0.44641500
C	0.12057000	6.71487500	0.91155900
C	0.02749800	5.68351300	1.83646100
C	-0.00298500	4.36898700	1.39219100
C	4.80766900	-1.11003600	-0.96014700
C	5.67068100	-0.48829100	-1.85594100
C	7.04390300	-0.67400100	-1.77422500
C	7.56946000	-1.49608300	-0.78791400
C	6.72593600	-2.12275600	0.11862700
C	5.35570300	-1.92532100	0.02791700

Reference

[S1] Fang, H.; Ling, Z.; Brothers, P. J.; Fu, X. *Chem. Commun.* **2011**, *47*, 11677–11679.

[S2] Frisch, M. J.; et al. *Gaussian 09*, revision A. 01; Gaussian, Inc.: Wallingford, CT, 2009.

[S3] (a) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[S4] (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.*, **1980**, *102*, 939; (b) Dobbs, K. D.; Hehre, W. J. *J. Comp. Chem.*, **1986**, ***7,*** 359.

[S5] (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (c) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

[S6] (a) Binning Jr., R. C.; Curtiss, L. A. *J. Comp. Chem.*, **1990**, *11***,** 1206; (b) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning Jr., R. C.; Radom, L. *J. Chem. Phys.*, **1995**, *103*, 6104.

[S7] (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.*, **1980**, *72*, 5639; (b) Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.*, **1980**, *72***,** 650.

[S8] (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654; (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.*, **1971**, *54*, 724; (c) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.*, **1972**, *56*, 2257. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acc.*, **1973**, *28*, 213.