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

Cite this: *Chem. Sci.*, 2014, 5, 916Huayi Fang,^a Zhen Ling,^a Ke Lang,^a Penelope J. Brothers,^b Bas de Bruin^{*c} and Xuefeng Fu^{*a}

The [(TPFC)Ge(TEMPO)] (**1**, TPFC = tris(pentafluorophenyl)corrole, TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl) complex was characterized by X-ray diffraction and spectroscopic studies. EPR studies indicate that the weak Ge–O bond in **1** is photo-cleaved to form a tetra-coordinated germanium(III) radical, [(TPFC)Ge(III)][•]: DFT calculations show that the spin density on the germanium center in [(TPFC)Ge(III)][•] has a significant s character. Under visible-light irradiation, **1** reacts rapidly with ammonia, primary/secondary aliphatic amines and aniline to produce (TPFC)Ge–NR¹R² (R¹R² = HH, HⁱPr, H^tPr, H^tBu, HPh, Et₂, ⁱPr₂) complexes in high yields (65–95%).

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Introduction

Metal catalyzed coupling of ammonia with arenes and the hydroamination of olefins with ammonia have been listed among the top ten challenges for catalysis.¹ Related studies on N–H bond activation can be considered as the foundation for both the development of new catalytic amine transformations for the industrial production of bulk chemicals and for understanding biochemical processes in living cells.² In recent years, the N–H bond activation by transition metal complexes in which the formation of metal amides is the key step has received increasing attention.³ Therefore, detailed insights into this elementary step will shed new light for the development of new catalytic processes.

In order for the N–H bonds of ammonia and amines to be activated by transition metals, the logical first step is the coordination of the lone electron pair of these substrates to the vacant coordination site of the transition metals. This leads to

the facile formation of Werner-type complexes, but subsequently hampers the N–H bond activation. On the other hand, radical reaction pathways offer a promising new tool for N–H bond activation and subsequent functionalization while this possibility has been barely explored.^{3e} Finally, the use of main group elements rather than transition metals seems a viable approach towards N–H bond functionalization reactions as the main group elements with filled d-orbitals have a much weaker affinity for the lone pairs of amines, thus preventing the formation of Werner-type complexes.⁴

Recently, the activation of N–H bonds using low-valent diarylstannylene,⁵ diarylgermylene,^{5a,6} N-heterocyclic silylene⁷ and germylene⁸ species has been reported. Silanone⁹ and a nickel-coordinated N-heterocyclic silylene¹⁰ species are also capable of activating N–H bonds. The activation of N–H bonds by silicon and its low-valent heavier congeners typically proceeds *via* two-electron pathways including direct oxidative addition of the N–H bond to the low-valent metal center and metal-ligand cooperative processes. Although main group element amide complexes have been prepared by other routes, the photo-promoted N–H bond activation by main group element radical species has been rarely encountered, yet offers interesting prospects for the activation of ammonia and amines. From this perspective, we decided to investigate the activation of N–H bonds with germanium radicals. In this paper we report our first results in this new research area, in which we demonstrate the photolysis of [(TPFC)Ge(TEMPO)] **1** (TPFC = tris(pentafluorophenyl)corrole, TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl) to generate a tetra-coordinated germanium(III) complex, [(TPFC)Ge(III)][•]: Under visible-light irradiation, **1** reacts rapidly with the N–H bonds in ammonia and primary/secondary aliphatic amines to form germanium amides in high yields at room temperature. These reactions proceed *via* discrete radical

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† Electronic supplementary information (ESI) available: Details of the UV-Vis spectrum of (TPFC)Ge(TEMPO), the solid state structure of (TPFC)Ge–OH, the CSI-MS spectra and their simulation for (TPFC)Ge–NH₂ and [(TPFC)Ge]₂NH, the simulation of the EPR spectrum of TEMPO at 238 K, the kinetic study of the light promoted reaction of (TPFC)Ge(TEMPO) with *n*-propylamine, and other experimental and computational details. CCDC [945438–945439]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3sc52326h

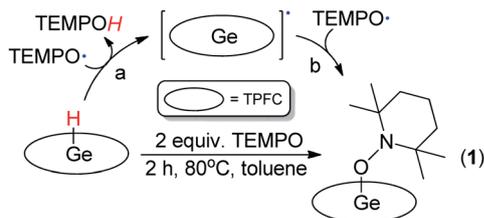
pathways with lower activation barriers than those normally observed for N–H bond activation reactions proceeding *via* two-electron pathways in either main-group or transition metal chemistry.

Results and discussion

Complex [(TPFC)Ge(TEMPO)] (**1**) was prepared by reacting (TPFC)Ge–H¹¹ with two equivalents of TEMPO (Scheme 1). This leads to a hydrogen atom transfer (HAT) from the germanium hydride to the TEMPO radical (Scheme 1, step a), a reaction similar to the previously reported HAT from Ph₃GeH to TEMPO.¹² The resulting germanium radical [(TPFC)Ge]• undergoes a radical coupling with another molecule of TEMPO radical to form **1** (Scheme 1, step b). The formation of 2,2,6,6-tetramethylpiperidin-*N*-ol (TEMPOH) as a side-product of this reaction was observed by ESI-MS and NMR spectroscopy.

The molecular structure of **1**, as determined by X-ray diffraction, shows that its 6-membered piperidinyl ring is locked in a chair form (Fig. 1a). The Ge(1)–O(1) bond length (1.786(3) Å) is nearly identical to those in (TPFC)Ge–OH (1.785(4) Å) (see ESI, Fig. S4†) and (TPFC)Ge–OCH₂CH₃ (1.789(8) Å),¹¹ and a little longer than the Ge–O bond in [(TPC)Ge]₂O (in the range 1.718(11) to 1.773(13) Å).¹³ However, the Ge(IV)–O bond in **1** is slightly shorter than the low-valent Ge(II)–O bond (1.804(2) Å) in ArGe(TEMPO) (Ar = C₆H₃-2,6-(C₆H₃-2,6-*i*-Pr₂)₂)¹⁴ and the Ge(IV)–O bond (averaging 1.825 Å) in a dialkylgermylene bis-TEMPO adduct R₂Ge(TEMPO)₂.¹⁵ The germanium center protrudes slightly (0.50 Å) from the N₄-plane of the corrole ligand, comparable with (TPFC)Ge–OH (0.48 Å) and (TPFC)Ge–OCH₂CH₃ (0.49 Å).¹¹ As a direct result of the presence of the bulky axial TEMPO ligand, the coordination geometry around the germanium center in **1** is distorted away from an idealized square pyramid, leading to a significant decrease in the angle of the Ge–O bond relative to the N₄-plane (Fig. 1b). The N–O bond length (1.477(4) Å) in **1** is nearly identical to those in ArGe(TEMPO) (1.476(2) Å)¹⁴ and the dialkylgermylene bis-TEMPO adduct R₂Ge(TEMPO)₂ (1.482(av) Å),¹⁵ consistent with the presence of a classical N–O single bond, and it is significantly longer than the N–O bonds of stable nitroxide radicals (typically 1.23–1.30 Å and 1.296(3) Å for the TEMPO radical).¹⁶

The formation of the [(TPFC)Ge]• intermediate was observed by monitoring the reaction of (TPFC)Ge–H with the TEMPO radical by EPR spectroscopy. In order to reduce the signal intensity of the TEMPO radical to give a clear measurement of the [(TPFC)Ge]• radical by EPR spectroscopy, a minute amount



Scheme 1 Synthesis of [(TPFC)Ge(TEMPO)] (**1**).

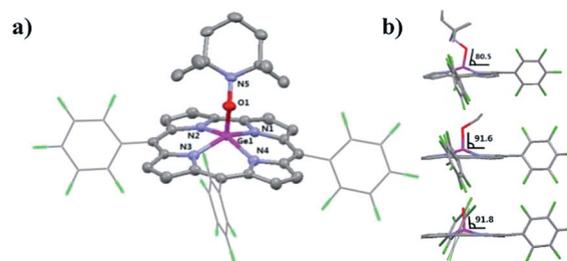


Fig. 1 (a) Thermal ellipsoid plot (50% probability level) of **1** (hydrogen atoms omitted and the three –C₆F₅ group are in wireframe style for clarity); (b) angles (°) between the Ge–O bond and the mean N₄-plane in complex **1** (top), (TPFC)Ge–OCH₂CH₃ (middle)¹¹ and (TPFC)Ge–OH (bottom, this work).

of TEMPO was mixed with (TPFC)Ge–H ([TEMPO]:[(TPFC)Ge–H] = 1 : 3000). The sample was heated at 80 °C and monitored every 10 or 20 minutes by room temperature EPR spectroscopy (Fig. 2a). The EPR spectrometer was equipped with a Mn marker which was used as the reference signal. The intensity of the TEMPO radical signal decayed fast and the weak broad singlet which can be assigned to the [(TPFC)Ge]• radical kept growing and became clearly observable (Fig. 2b).

The [(TPFC)Ge]• radical could also be independently prepared by homolysis of the Ge–H bond of (TPFC)Ge–H by leaving this compound stirring in a toluene solution under

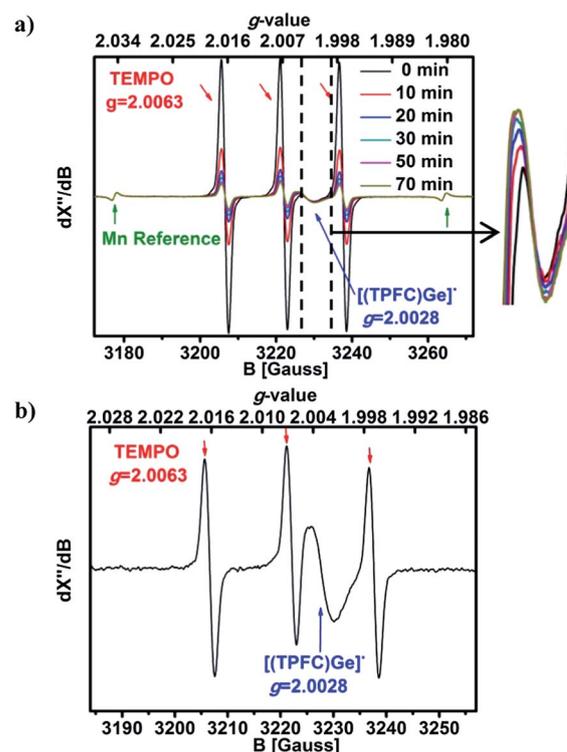


Fig. 2 (a) EPR monitoring of the hydrogen transfer reaction of TEMPO/(TPFC)Ge–H at a ratio of 1/3000; the weak signal assigned to [(TPFC)Ge]• has been expanded on the right, and (b) EPR spectrum of the reaction solution after heating at 80 °C for 70 minutes (3 mg (TPFC) Ge–H in 0.6 mL toluene; microwave frequency: 9.047662 GHz; microwave power: 1 mW).

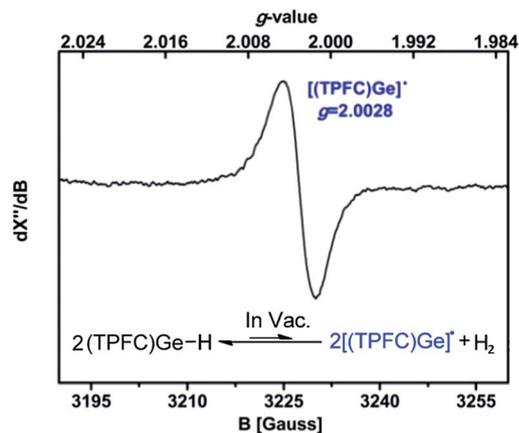


Fig. 3 EPR spectrum of $[(\text{TPFC})\text{Ge}]^\bullet$ formed via the homolysis of Ge-H in vacuum (microwave frequency: 9.047070 GHz; microwave power: 4 mW).

vacuum in a sealed EPR tube for a few days. This sample showed an identical singlet in the EPR spectrum (Fig. 3) to that observed in Fig. 2. The EPR spectra analysis thus revealed that the paramagnetic $[(\text{TPFC})\text{Ge}]^\bullet$ radical has a g -value of 2.0028. Therefore, the weak broad singlet appearing in between the second and third peak of the TEMPO radical signal (Fig. 2) was ascribed to the signal of the $[(\text{TPFC})\text{Ge}]^\bullet$ radical.

In the presence of one equivalent of TEMPOH, about 6% of complex **1** (in d^8 -toluene, 8.8 mmol L^{-1}) undergoes thermal dissociation to form 2,2,6,6-tetramethylpiperidine and (TPFC) Ge-OH within 48 hours at 100 °C, as observed by ^1H NMR spectroscopy, resulting from the cleavage of the N-O bond.

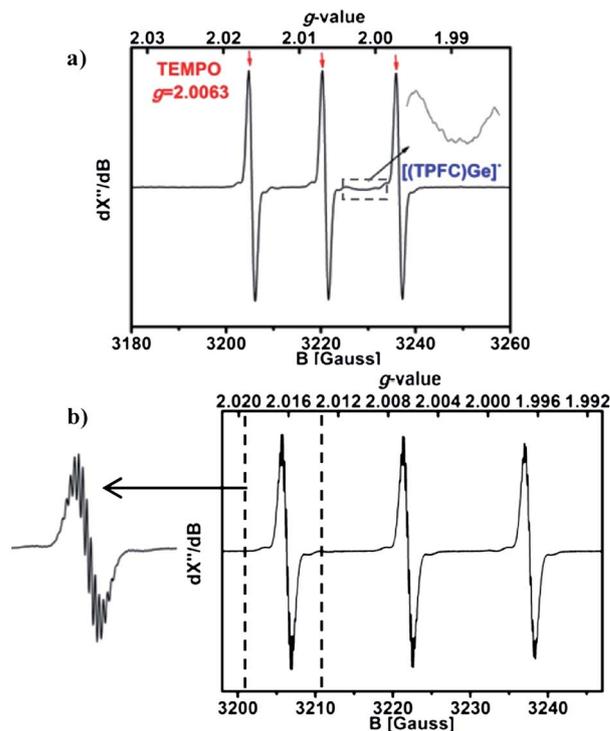


Fig. 4 EPR spectra of **1** in toluene solution (a) at room temperature (microwave frequency 9.044484 GHz; microwave power 1 mW) and (b) at 238 K (microwave frequency 9.049704 GHz; microwave power 0.1 mW).

This reactivity is similar to that previously reported for TEMPO adducts with silicon,¹² iron,¹⁷ uranium¹⁸ and rhenium.¹⁹ However, in the absence of TEMPOH, no

Table 1 The reactions of complex **1** with amines and aniline in the dark and under visible light irradiation

Entry	Amines ^a	In dark			Under irradiation(420–780 nm)			Products
		Temp./°C	Time	Yield ^b /%	Temp./°C	Time	Yield ^b /%	
1	NH_3	R.T.	12 h	>95 ^c	R.T.	15 min	>95 ^d	2
2		40	90 h	50	R.T.	15 min	>95	4
3		40	105 h	40	R.T.	15 min	>95	5
4		80	127 h	Trace	R.T.	15 min	>95	6
5		110	12 h	11	R.T.	6 h	>95	7
6		100	96 h	21	R.T.	45 min	>95	8
7		100	96 h	Trace	R.T.	128 h	65	9

^a 3.5×10^{-3} mmol $(\text{TPFC})\text{Ge}(\text{TEMPO})$ with 10 equivalents of the liquid amine substrates in 0.4 mL d^8 -toluene. ^b Based on the amount of **1** and measured by ^1H NMR spectroscopy. ^c Calcd 3 atm of NH_3 was added. ^d Calcd 1 atm of NH_3 was added.

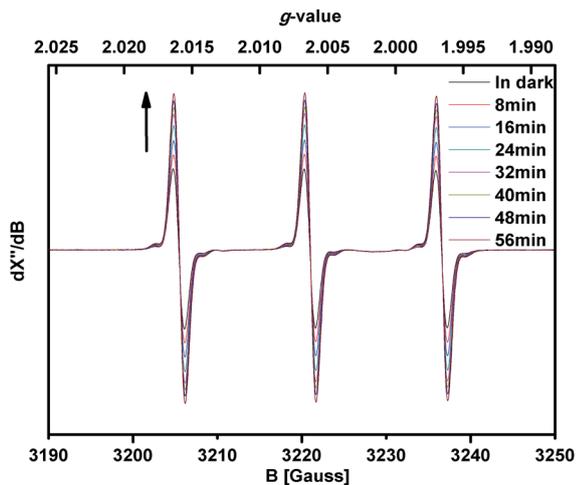
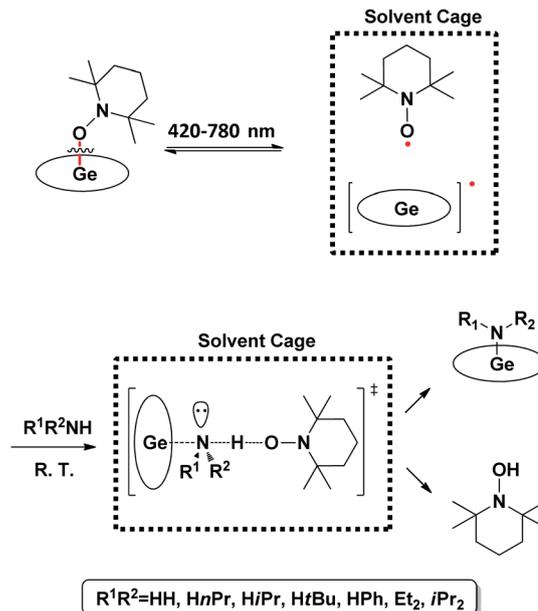
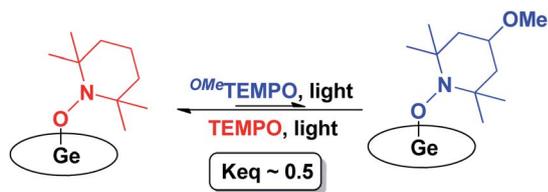


Fig. 5 *In situ* EPR spectrum of **1** in toluene with continuous irradiation of visible light at room temperature (microwave frequency: 9.044484 GHz; microwave power: 1 mW).



Scheme 3 N–H bond activation through a termolecular pathway.



Scheme 2 Visible light promoted axial ligand exchange.

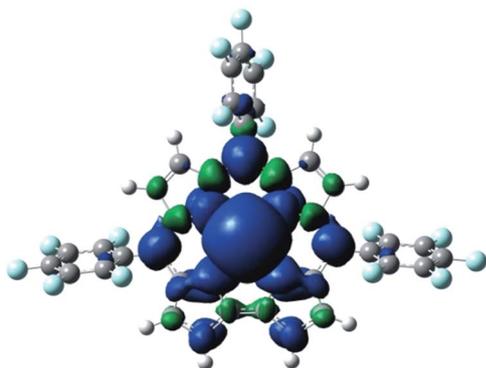


Fig. 6 Spin density of the [(TPFC)Ge][•] radical (isovalue = 0.0004).

observable decomposition of complex **1** was observed under identical conditions, which implies that TEMPOH acts as a hydrogen source for the formation of 2,2,6,6-tetramethylpiperidine and (TPFC)Ge–OH. Furthermore, the activation of the ring methyl C–C bonds of TEMPO²⁰ was not observed at temperatures up to 150 °C.

It is quite interesting that when complex **1** was exposed to excess ammonia (3 atm, in *d*⁸-toluene), it slowly transformed over a period of 12 hours at room temperature in the dark to the germanium amide complex (TPFC)Ge–NH₂ (**2**) and a stoichiometric amount of TEMPOH. Prolonged reaction times resulted

in the observation of a new set of corrole hydrogen resonances in the ¹H NMR spectrum (52% yield), ascribed to the formation of [(TPFC)Ge]₂NH (**3**) according to mass spectrometry ([M]⁺ observed at *m/z* 1747.95, calc. 1747.97, ESI, Fig. S6[†]). The ¹H NMR spectra for **2** and **3** are similar to those observed for (TPC)Ge–OH and [(TPC)Ge]₂O.¹³ The ratio of complex **2** to complex **3** remained constant over 9 days in *d*⁸-toluene at room temperature, allowing the estimation of the equilibrium constant for the interconversion of **2** and **3**, *K*_{eq} = 53.8 ± 1.5 at 298 K. Similar experiments at 40 °C in the dark with two aliphatic amines allowed us to roughly estimate the equilibrium constants for the reactions of **1** with *n*-propylamine (*K*_{eq}(^{*n*}Pr) ≈ 0.2) and *i*-propylamine (*K*_{eq}(^{*i*}Pr) ≈ 0.1). Amines with bulky substituents resulted in much slower reaction rates and poor yields even at elevated reaction temperatures (Table 1).

Remarkably, the photochemical reactions of **1** with ammonia, aliphatic amines and aniline, using a 500 W high-pressure xenon lamp equipped with a 420–780 nm filter, led to much more rapid N–H bond activation reactions to form TEMPOH and the amide products (TPFC)Ge–NR¹R² (R¹R² = HH, H^{*n*}Pr, H^{*i*}Pr, H^{*t*}Bu, HPh, Et₂, ^{*i*}Pr₂) in almost quantitative yields (Table 1).²¹ Steric effects were proved to have no significant influence on the N–H bond activation of primary aliphatic amines (Table 1, entries 2–4). N–H bond activation of the very bulky diisopropylamine required 128 hours to reach 65% yield (Table 1, entry 7). The reaction with aniline also took a longer reaction time, around 6 hours, to reach almost quantitative yields (>95%), which is likely due to the electron-withdrawing property of the phenyl ring which makes the nitrogen atom more electron positive than in the other amine substrates (Table 1, entry 5).

The distorted Ge–O bond in **1** is relatively weak, and photo-induced homolytic splitting of this bond (the reverse of the process shown in Scheme 1, step b) may be responsible for the

observed rapid and smooth N–H bond activation by **1** under visible light irradiation. Moreover, the EPR spectrum of **1** recorded in toluene at room temperature shows a clear hyperfine-split signal characteristic of the TEMPO radical as well as a relatively weak, broad singlet (Fig. 4a). The weak broad singlet appearing in between the second and third peak of the TEMPO signal (Fig. 4a) is identical to the signal of the $[(\text{TPFC})\text{Ge}]^{\cdot}$ radical observed in Fig. 2. The closed-shell complex **1** is diamagnetic, thus the observed EPR signal is most likely a consequence of a small extent of homolysis of the Ge–O bond. The isotropic solution phase EPR spectrum of **1** at 238 K (Fig. 4b) shows a hyperfine splitting pattern which is identical to the EPR spectrum of free TEMPO in a diluted toluene solution recorded under similar conditions (Fig. S7†). It is worth noting that this appears to be the first experimental observation of a resolved hydrogen hyperfine splitting pattern in an EPR spectrum of TEMPO, for which the previously reported proton hyperfine values could apparently only be determined by ^1H NMR methods.²² The EPR proton and nitrogen hyperfine coupling constants determined by spectral simulations are listed in Table S1 (ESI†).

Photolysis of **1** by prolonged exposure to visible light at room temperature led to a clear increase in the intensity of the EPR signal at $g = 2.0063$ ($S = 1/2$) characteristic of the free TEMPO radical (Fig. 5). Although an increased intensity of the $[(\text{TPFC})\text{Ge}]^{\cdot}$ singlet ($S = 1/2$, $g = 2.0028$) was not clearly observable (most likely as a result of either its relatively weak signal intensity or its high chemical reactivity), evidence for its formation was provided by a light-induced axial ligand exchange reaction. Visible-light irradiation of a mixture of $(\text{TPFC})\text{Ge}(\text{TEMPO})$ and $^{\text{OMe}}\text{TEMPO}$ radical ($^{\text{OMe}}\text{TEMPO} = (4\text{-methoxy-}2,2,6,6\text{-tetramethylpiperidin-1-yl})\text{oxyl}$) in d^8 -toluene at room temperature led to the formation of $(\text{TPFC})\text{Ge}(^{\text{OMe}}\text{TEMPO})$ with an equilibrium constant $K_{\text{eq}} \approx 0.5$ resulting from the dissociation of $(\text{TPFC})\text{Ge}(\text{TEMPO})$ and the recoupling of $[(\text{TPFC})\text{Ge}]^{\cdot}$ with the $^{\text{OMe}}\text{TEMPO}$ radical. In comparison, no axial ligand exchange was observed in the dark for weeks under similar reaction conditions.

The $^{\text{OMe}}\text{TEMPO}$ and TEMPO radicals are structurally similar and differ only in the substituent on the *para*-position of the six-membered piperidinyl ring, so that the exchange process should be nearly degenerate ($\Delta G^\circ \approx 0$) and the equilibrium constant should approach one. However, the methoxyl group in the $^{\text{OMe}}\text{TEMPO}$ radical induces the configuration of the N-containing six-membered ring to be closer to a chair form than that of the TEMPO radical, which facilitates the photo-cleavage of the Ge–O bond in $(\text{TPFC})\text{Ge}(^{\text{OMe}}\text{TEMPO})$. Therefore, the equilibrium constant for the reaction shown in Scheme 2 deviates slightly from one.

The photochemical reaction of **1** in the presence of ethylene led exclusively to the formation of $(\text{TPFC})\text{Ge-CH}_2\text{CH}_2\text{-Y}$ ($\text{Y} = (2,2,6,6\text{-tetramethylpiperidin-1-yl})\text{oxyl}$, **10**) in 65% yield. Ethylene effectively inserts into the Ge–O bond of **1**, which further confirmed the formation of the TEMPO and $[(\text{TPFC})\text{Ge}]^{\cdot}$ radicals upon photolysis of **1**. Complex **10** is formed by the radical coupling of ethylene with the $[(\text{TPFC})\text{Ge}]^{\cdot}$ and TEMPO radicals.

Computational studies using DFT methods confirmed that homolysis of the Ge–O bond of complex **1** is thermodynamically feasible. The calculation revealed a rather small BDE of 35.4

kcal mol⁻¹ of the Ge–O bond of **1** in the gas phase (see ESI†). The formation of $[(\text{TPFC})\text{Ge}]^{\cdot}$ and TEMPO radicals is calculated to be endergonic by $\Delta G^\circ_{\text{tot}} = 20.6$ kcal mol⁻¹ ($\Delta G^\circ_{\text{gas}} = 19.6$ kcal mol⁻¹). In comparison, the Ge–O bond heterolysis to produce cationic $[(\text{TPFC})\text{Ge}(\text{iv})]$ and the TEMPO⁻ anion is endergonic to a much larger extent with $\Delta G^\circ_{\text{tot}} = +103.7$ kcal mol⁻¹ ($\Delta G^\circ_{\text{gas}} = +151.8$ kcal mol⁻¹). In the HOMO of **1** (Fig. S9a†), the conjugated π -system of the TPFC ligand is mixed with the N–O π^* orbital. The LUMO of **1** (Fig. S9b†) is essentially a π^* -orbital of the TPFC ligand.

Therefore, the Ge–O bond photo-cleavage most likely occurs *via* its HOMO–LUMO electronic transition, in which the electron density migrates from the π^* -orbital of the N–O bond of the axial TEMPO ligand to the $[(\text{TPFC})\text{Ge}]$ moiety. The calculations further showed that the tetra-coordinated germanium center in $[(\text{TPFC})\text{Ge}]^{\cdot}$ has a domed coordination geometry. 51% of the spin density of $[(\text{TPFC})\text{Ge}]^{\cdot}$ is located on the germanium center, while the rest of the spin density is delocalized over the corrole ligand (Fig. 6).

The SOMO of $[(\text{TPFC})\text{Ge}]^{\cdot}$ (Fig. S10†) together with the corresponding spin density plot show that the spin density on the germanium center has distinct *s* character (*i.e.* a sp^3 hybrid orbital of the germanium center), while the spin density on the center of most of the previously reported stable germanium radical with a formal oxidation state of +3 and a triple-coordinated metal center was in orbitals with mainly *p* character.²³

Combining the aforementioned observations, the N–H bond activation by **1** most likely proceeds *via* a termolecular transition state (Scheme 3) similar to that proposed for methane activation by rhodium porphyrin complexes²⁴ and the activation of NH_3 by a palladium pincer dimer.^{3e} Accordingly, aniline (which has contracted frontier orbitals as a consequence of the electron withdrawing effect of the phenyl ring) and the bulkier secondary aliphatic amines are less reactive. Furthermore, a stepwise radical chain pathway (*i.e.* with radicals escaping the solvent cage) can be excluded by considering the formation of **10** without the generation of $(\text{TPFC})\text{Ge-CH}_2\text{CH}_2\text{-Ge}(\text{TPFC})$ or other byproducts.

Summary and conclusions

Most previously reported N–H bond activation processes involve mononuclear direct two-electron concerted oxidative addition reactions of the N–H bond to a low-valent metal center,^{3b} external base assisted N–H bond cleavage,²⁵ or metal-ligand cooperative effects.^{3d} N–H bond activations through radicaloid pathways provide an alternative route with an expected lower activation energy, but are far more rarely encountered.^{3e} The photochemical N–H bond activation reactions by **1** are strongly suggestive of a radical pathway. The experimental observations including the EPR measurement of **1** under visible light irradiation, the light-promoted axial ligand exchange study, the single insertion of ethylene into the Ge–O bond to form a $\text{Ge-CH}_2\text{-CH}_2\text{-O}^{\text{Tempo}}$ moiety, as well as the DFT calculations provide clear evidence for the formation of the reactive TEMPO/ $[(\text{TPFC})\text{Ge}]^{\cdot}$ radical pair which activates the N–H bond in a concerted way to form $(\text{TPFC})\text{Ge-NR}^1\text{R}^2$ ($\text{R}^1\text{R}^2 = \text{HH}, \text{H}^n\text{Pr}, \text{H}^i\text{Pr}, \text{H}^t\text{Bu}, \text{HPh}, \text{Et}_2, ^i\text{Pr}_2$) products. Further reactivity studies of

the tetra-coordinated germanium radical with other small molecules are in progress. We hope that the findings reported in this paper will stimulate a broader development of the thus far under-investigated area of substrate activation with radical-chemistry and main-group element chemistry.

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