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

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The [(TPFC)Ge(TEMPO)] (1, TPFC = tris(pentafluorophenyl)corrole, TEMPO = (2,2,6,6tetramethylpiperidin-1-yl)oxyl) complex was characterized by X-ray diffraction and spectroscopic studies. EPR studies indicated that the weak Ge–O bond in 1 was photo-cleaved to form a tetra-coordinated germanium (III) radical, [(TPFC)Ge(III)]'. The DFT calculation showed that the spin density on the ger-¹⁰ manium center in [(TPFC)Ge(III)]' had significant s character. Under visible-light irradiation, 1 reacted

rapidly with ammonia, primary/secondary aliphatic amines and aniline to produce (TPFC)Ge–NR¹R² (R¹R² = HⁿPr, HⁱPr, HⁱBu, HPh, Et₂, ^{*i*}Pr₂) complexes in high yields (65% - 95%).

Introduction

Metal catalyzed coupling of ammonia with arenes and the hy-¹⁵ droamination 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 stone for both developing new catalytic amine transformations for the industrial production of bulk chemicals and for understanding biochemical

²⁰ processes in living cells.² In recent years, N–H bond activation by transition metal complexes is receiving increasing attention³ in which the formation of metal amides is the key step. Therefore, detailed insights into this elementary step will shed new light on 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 facile formation of Werner-type complexes, but subsequently hampers
- ³⁰ 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
- ³⁵ 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 dia-⁴⁰ rylstannylene,⁵ diarylgermylene,^{5a,6} *N*-heterocyclic silylene⁷ and germylene⁸ species has been reported. Silanone⁹ and a nickelcoordinated 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-

⁴⁵ 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, photo-promoted N-H bond activation by main group element radical species has only been rarely 50 encountered, yet offers interesting prospects to activate 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 = TEMPO (2,2,6,6-55 tris(pentafluorophenyl)-corrole, tetramethylpiperidin-1-yl)oxyl) to generate a tetra-coordinated germanium (III) complex, [(TPFC)Ge(III)]• (TPFC = tris(pentafluorophenyl)corrole. Under visible-light irradiation, 1 reacted rapidly with N-H bonds in ammonia, primary/secondary 60 aliphatic amines to form germanium amides in high yields at room temperature. These reactions proceed via discrete radical pathways with lower activation barriers than those normally observed for N-H bond activation reactions proceeding via twoelectron pathways in either main-group or transition metal chem-65 istry.

Results and discussion

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Complex [(TPFC)Ge(TEMPO)] (1) was prepared by reacting (TPFC)Ge-H¹¹ with two equivalents of TEMPO (Scheme 1).



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

This leads to 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 Ph_3GeH to TEM- PO.¹² The resulting germanium radical [(TPFC)Ge][•] underwent 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 (TEMPO*H*) as a side-product of this s reaction was observed by ESI-MS and NMR spectroscopy.

The molecular structure of 1, as determined by X-ray diffraction, showed that its 6-membered piperidinyl ring is locked in a chair form (Figure 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 ¹⁰ ESI, Figure S4) and (TPFC)Ge–OCH₂CH₃ (1.789(8) Å),¹¹ and is 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 = $C_6H_3-2, 6-(C_6H_3-2, 6-iPr_2)_2$)¹⁴ and the 15 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 20 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 (Figure 1b). The N-O bond length (1.477(4) Å) in 1 is nearly identical to those in 25 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 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



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Figure 1. a) Thermal ellipsoid plot (50% probability level) of **1** (hydrogen atoms omitted for clarity); b) Angles (⁰) 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).

- ³⁵ The formation of the [(TPFC)Ge]' intermediate was observed by monitoring the reaction of (TPFC)Ge–H with TEMPO radical by EPR spectroscopy. In order to reduce the signal intensity of TEMPO radical to give a clear observation of the [(TPFC)Ge]' radical by EPR spectroscopy, a minute amount of TEMPO was
- ⁴⁰ 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 (Figure 2a). The EPR spectrometer was equipped with a Mn marker which was used as the reference signal. The intensity of the TEMPO radical
- ⁴⁵ signal decayed fast and the weak broad singlet which can be assigned to the [(TPFC)Ge]' radical kept growing and became clearly observable (Figure 2b).

The [(TPFC)Ge]' radical could also be independently prepared by homolysis of the Ge–H bond of (TPFC)Ge–H by leaving this 50 compound stirring in toluene solution under vacuum in a sealed EPR tube for a few days. This sample showed an identical singlet in the EPR spectrum (Figure 3) to that observed in Figure 2. The EPR spectra analysis thus revealed that the paramagnetic [(TPFC)Ge][•] radical has a *g*-value of 2.0028. Therefore, the weak ⁵⁵ broad singlet appearing in between the second and third peak of the TEMPO radical signal (Figure 2) was ascribed to the signal of [(TPFC)Ge][•] radical.



Figure 2. a) EPR monitoring of the hydrogen transfer reaction with ⁶⁰ TEMPO'/(TPFC)Ge–H ratio of 1/3000; weak signal assigned to [(TPFC)Ge]' expanded to 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).



Figure 3. EPR spectrum of [(TPFC)Ge]' formed via the homolysis of Ge-H in vacuum (microwave frequency: 9.047070 GHz; microwave power: 4 mW).

In the presence of one equivalent of TEMPOH, about 6% of ⁷⁰ complex 1 (in d^8 -toluene, 8.8 mmol L⁻¹) underwent thermal dissociation to form 2,2,6,6,-tetramethylpiperidine and (TPFC)Ge–OH within 48 hours at 100 °C, observed by ¹H NMR spectrosco-

py, resulting from cleavage of the N–O bond. This reactivity is similar to that previously reported for TEMPO adducts of silicon,¹² iron,¹⁷ uranium¹⁸ and rhenium.¹⁹ However, in the absence of TEMPOH no observable decomposition of complex **1** was ⁵ observed under identical conditions, which implies that TEM-

- POH acts as a hydrogen source for the formation of 2,2,6,6,tetramethylpiperidine and (TPFC)Ge–OH. Furthermore, activation of the ring-methyl C–C bond 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 d⁸-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. More prolonged reaction times ¹⁵ 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, Figure S6). The ¹H NMR spectra for 2 and 3 are similar to those observed for
- ²⁰ (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 an estimation of the equilibrium constant $K_{eq} = 53.8 \pm 1.5$ at 298 K for the interconversion of **2** and **3**. Similar experiments at 40 °C in the dark with two aliphatic
- ²⁵ amine showed us to roughly estimate the equilibrium constants for the reactions of 1 with *n*-propylamine ($K_{eq}(nPr) \approx 0.2$) and *i*propylamine ($K_{eq}(iPr) \approx 0.1$). Amines with bulky substituents showed much slower reaction rates and poor yields even at elevated reaction temperatures (Table 1).
- ³⁰ Remarkably, 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 = HPr, H*i*Pr, H*t*Bu, HPh,
- ³⁵ 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
- ⁴⁰ 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 other amine substrates (Table 1, entry 5).
- ⁴⁵ The distorted Ge–O bond in **1** is relatively weak, and photoinduced 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
- ⁵⁰ toluene at room temperature showed a clear hyperfine-split signal characteristic of the TEMPO radical as well as a relatively weak, broad singlet (Figure 4a). The weak broad singlet appearing in between the second and third peak of the TEMPO signal (Figure 4a) was identical to the signal of [(TPFC)Ge]^{*} radical observed in
- ⁵⁵ Figure 2. The closed-shell complex **1** is diamagnetic, thus the observed EPR signal was 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 (Figure 4b) showed a hyper-fine splitting pattern which was identical to the EPR spectrum of
- 60 free TEMPO in dilute toluene solution recorded under similar

conditions (Figure 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 ⁶⁵ 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).



Figure 4. a) EPR spectrum of **1** in toluene solution at room temperature 70 (microwave frequency 9.044484 GHz; microwave power 1 mW) and b) at 238 K (microwave frequency 9.049704 GHz; microwave power 0.1 mW).

Photolysis of 1 by prolonged exposure to visible light at room temperature led to a clear increase in intensity of the EPR signal at g = 2.0063 ($S = \frac{1}{2}$) characteristic of the free TEMPO radical ⁷⁵ (Figure 5).



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

Table 1.	. The	reactions	of co	omplex 1	with	amines a	ınd	aniline	in th	ie dark	c and	l under	visible	light	irradiation	•
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$(TPFC)Ge(TEMPO) + R^1R^2NH \xrightarrow{d^8-toluene} (TPFC)Ge-NR^1R^2 + TEMPOH$										
.	л : а		In dark		Under irrad	D 1 (
Entry	Amines	Temp./ºC	ſemp./ºC Time		Temp./ºC	Time	Yield/% ^b	Products		
1	NH ₃	R.T	12 h	>95 ^c	R.T.	15 min	>95 ^d	2		
2	∕∕VH ₂	40	90 h	50	R.T.	15 min	>95	4		
3	NH ₂	40	105 h	40	R.T.	15 min	>95	5		
4	MH ₂	80	127 h	trace	R.T.	15 min	>95	6		
5	NH ₂	110	12 h	11	R.T.	6 h	>95	7		
6	∧ _N ∧ H	100	96 h	21	R.T.	45 min	>95	8		
7	\downarrow_{N}	100	96 h	trace	R.T.	128 h	65	9		

^{*a*} 3.5×10^{-3} mmol (TPFC)Ge(TEMPO) with 10 equivalent of liquid amine substrates in 0.4 mL d⁸-toluene. ^{*b*} Based on the amount of 1 and was measured by ¹H NMR spectra. ^{*c*} Calcd. 3 atm of NH₃ was added. ^{*d*} Calcd. 1 atm of NH₃ was added.

Although an increased intensity of the [(TPFC)Ge]' singlet (*S* $_{5} = \frac{1}{2}$, g = 2.0028) was not clearly observable (most likely 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 (TPFC)Ge(TEMPO) and ^{OMe}TEMPO radical ¹⁰ (^{OMe}TEMPO = (4-methoxy-2,2,6,6-tetramethylpiperidin-1-yl)oxyl) in d^{8} -toluene at room temperature led to formation of (TPFC)Ge(^{OMe}TEMPO) with an equilibrium constant $K_{eq} \approx 0.5$ resulting from the dissociation of (TPFC)Ge(TEMPO) and recoupling of [(TPFC)Ge]' with the ^{OMe}TEMPO radical. In compar-15 ison, no axial ligand exchange was observed in the dark for weeks under similar reaction conditions.



Scheme 2. Visible light promoted axial ligand exchange.

The ^{*OMe*}TEMPO and TEMPO radicals are structurally similar ²⁰ and differ only in the substituent on the para-position of the sixmembered 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 ^{*OMe*}TEM-PO radical induces the configuration of *N*-containing six-²⁵ membered ring to be closer to a chair form than that of TEMPO radical, which facilitates the photo-cleavage of the Ge–O bond in (TPFC)Ge(^{OMe}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 ³⁰ led to exclusively formation of (TPFC)Ge-CH₂CH₂-Y (Y = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, **10**) in 65% yield. Ethylene effectively inserts into the Ge–O bond of **1**, which further confirmed the formation of the TEMPO and [(TPFC)Ge]' radicals upon photolysis of **1**. Complex **10** is formed by radical coupling ³⁵ of ethylene with the [(TPFC)Ge]' 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). For-⁴⁰ mation of [(TPFC)Ge]' and TEMPO radical is calculated to be endergonic by $\Delta G^{o}_{tol} = 20.6$ kcal mol⁻¹ ($\Delta G^{o}_{gas} = 19.6$ kcal mol⁻¹). In comparison, Ge–O bond heterolysis to produce cationic [(TPFC)Ge(IV)] and the TEMPO⁻ anion is endergonic to a much larger amount as $\Delta G^{o}_{tol} = +103.7$ kcal mol⁻¹ ($\Delta G^{o}_{gas} = +151.8$ kcal ⁴⁵ mol⁻¹). In the HOMO of **1** (Figure S9a), the conjugated π -system of the TPFC ligand is mixed with the N–O π^* orbital. The LUMO of **1** (Figure S9b) is essentially a π^* -orbital of the TPFC ligand.

Therefore, Ge–O bond photo-cleavage most likely occurs via its HOMO-LUMO electronic transition, in which the electron ⁵⁰ density migrates from the π^* -orbital of the N–O bond of the axial TEMPO ligand to the [(TPFC)Ge] moiety. The calculations further showed that the tetra-coordinated germanium center in [(TPFC)Ge]' had a domed coordination geometry. 51% of the spin density of [(TPFC)Ge]' is located on the germanium center, while the rest of the spin density is delocalized over the corrole ligand (Figure 6).



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

The SOMO of [(TPFC)Ge]' (Figure S10) together with the corresponding spin density plot showed 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 10 formal oxidation state of +3 and a triple-coordianted metal center

was in orbitals with mainly p character.²³



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

Combining the aforementioned observations, N-H bond acti-15 vation by 1 most likely proceeds via a termolecular transition state (Scheme 3) similar to that proposed for methane activation by rhodium porphyrin complexes 24 and the activation of NH₃ by a palladium pincer dimer.^{3e} Accordingly, aniline (which has more contracted frontier orbitals as a consequence of the electron with-20 drawing 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 (TPFC)Ge-CH2CH2-Ge(TPFC) or other byproducts.

25 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 30 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 35 including the EPR measurement of 1 under visible light irradiation. light-promoted axial ligand exchange, single insertion of ethylene into the Ge-O bond to form a Ge-CH2-CH2-O^{Tempo} moiety, as well as DFT calculations providing clear evidence for the formation of a reactive TEMPO'/[(TPFC)Ge]' radical pair 40 which activates the N-H bond in a concerted way to form $(TPFC)Ge-NR^{1}R^{2}$ $(R^{1}R^{2} = HPr, HPr, HtBu, HPh, Et_{2}, iPr_{2})$ products. Further reactivity studies of the tetra-coordinated germanium radical with other small molecules were in progress. We hope that the findings reported in this paper will stimulate a broader 45 development of the thus far under-investigated area of substrate activation with radical-chemistry and main-group element chemistry.

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Notes and references

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* Electronic Supplementary Information (ESI) available: Details of UV-Vis spectrum of (TPFC)Ge(TEMPO), solid state structure of (TPFC)Ge-

- 65 OH, CSI-MS spectra and its simulation of (TPFC)Ge-NH2 and [(TPFC)Ge]₂NH, simulation of EPR spectrum of TEMPO at 238K, kinetic study of the light promoted reaction of (TPFC)Ge(TEMPO) with *n*-propylamine, and other experiment and computational details. CCDC reference numbers 945438-945439. See DOI: 10.1039/b000000x/
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