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Complexes of germanium chlorides (R_nGeCl_{4-n}, n=0-3; R=Me, Ph) with redox active *N*-heteroaromatic ligands: an electrochemical study

Abstract: Methyl and phenyl germanium chlorides (R_nGeCl_{4-n}, n=1, 2, 3), just like $GeCl_4$, form complexes with electroactive bidentate (2,2′-bipyridine) and monodentate (imidazole, pyrimidine and 2,6-dichloro-pyridine) ligands, $R_nGeCl_{4-n}\cdot L_x$ (x=1 or 2 for bi- and monodentate Ls, respectively), which were studied by cyclic voltammetry and electron paramagnetic resonance (EPR) spectroscopy supported by density functional theory (DFT) calculations. Dative interactions of lone pair of N of these heteroaromatic ligands towards Ge lower the reduction potential E_p of such complexes by about 1 V compared to own reduction potential E_o of L. Electron transfer to these complexes is reversible, resulting in corresponding anion radicals. Elimination of Cl^- anion from these species leads to L-coordinated radicals whose one-electron reduction is also reversible. Real-time, time-dependent EPR spectroelectrochemistry of electrogenerated anion radicals of complexes with 2,2′-bipyridine (bipy) has shown that spin in these species is delocalized on the bipy moiety; nitrogen *hfc* constants suggest that two N atoms are non-equivalent and occupy different positions in the Ge environment. These findings are supported by DFT calculations.

Keywords: bipyridine; cyclic voltammetry; DFT; electrochemical reduction; EPR; germanium chlorides; non-innocent ligands.

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Introduction

A great variety of complexes of metals with bipyridine are known, and their chemistry has been widely explored (Pilipenko et al., 1972; Constable, 1989; Happ et al., 2012). Similar complexes of 2,2′-bipyridine (bipy) with silicon halides have been prepared, e.g., with Ph_3SiX (X=Br, I) (Corey and West, 1963); with $RSiCl_3$ (Kummer et al., 1990); with perhalodisilanes Si_2X_6 (X=F, Cl, Br), mixed methylhalodisilanes ($Si_2Me_nX_{6-n}$, X=Cl, I; n=2, 3) and Si_3Cl_8 (Kummer et al., 1979); with substituted iodides $XYSiI_2$ (X, Y=Cl, I, Me, H, Ph) (Kummer et al., 1977); and with $Cl_3Si\text{-}OSiCl_3$ (Kummer et al., 1987). By reaction of Si_2Cl_6 with bipy in tetrahydrofuran, a silylene complex, $(bipy)_2\cdot SiCl_2$ and $bipy\cdot SiCl_4$, can be obtained (Kummer et al., 1969). All these examples come either from monoiodo- and monobromo- or from polyhalo- and polychlorosilanes. As was pointed in Corey and West (1963), such adducts were not formed with monochlorosilanes. Compared to silicon, Ge has a more pronounced metallic character and superior Allred-Rochow electronegativity (1.74 and 2.02 for Si and Ge, respectively; Cotton and Wilkinson, 1972); in general, Ge has greater propensity to form complexes with donor ligands (Schulz and Klapötke, 1995). A number of structural reports are available on the complexes of $GeCl_4$ with various N-donor ligands like NH_3, NMe_3 and bipy (Lebedev and Tronev, 1960; Tanaka et al., 1967; Kupche et al., 1988; Sevast'yanova et al., 1988; Willey et al., 2001). Although electron-withdrawing substituents stabilize such systems, and the stability of hexacoordinate complexes (with equal substitution pattern) increases going down the 14 group elements (Baukov and Tandura, 2002), bipyridine complexes not only of R_2SiCl_2 but also of R_2GeCl_2 are unknown (Schulz and Klapötke, 1995). In fact, with a hard N-ligand such as NBu_3, Me_2GeCl_2 was reported to form a 1:2 complex; however, neither Me_2GeCl_2 nor Ph_2GeCl_2 forms complexes with softer bipy (Poller, 1965; Schulz and Klapötke, 1995).

Besides X-ray diffractometry (Willey et al., 2001) and spectrophotometry (Lebedev et al., 1960), calorimetric titration (Poller, 1965), tensiometry (Sevast'yanova et al., 1988) and ^{73}Ge NMR (Kupche et al., 1988) were used for studying $bipy\cdot GeCl_4$ complexes. These complexes have never received electrochemical consideration. However, provided that bipyridine is electrochemically active, its redox response could provide valuable information on the bonding and electronic interactions in such systems. Moreover, the use of electroactive ligands could shed light on the very fact of formation of coordination compounds

with less than three Cl atoms on Ge and of hypercoordinated intermediates in nucleophile-assisted reactions of halogermanes.

Recently, the concept of non-innocent ligands – i.e., those whose redox interactions with the central metal make its oxidation state not well defined – has received considerable attention (De Bruin et al., 2000; Kaim and Schwederski, 2010). Electrochemically active ligands present a special topic as electron transfer, which modifies the ground state distribution of electron density in such systems, might induce different types of ligating interactions. To the best of our knowledge, only three papers have reported on the synthesis and electrochemical study of the complexes of Si(IV) with redox-active ligands: with 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine (also, of Sn and Pb derivatives) (Piskunov et al., 2010), with tripodal hexadentate 1,1,1-tris(1′-oxophenalenyl-9′-*N*-methyl)ethane (Samanta et al., 2005) and with ferrocenecarboxylato ligands (Silver et al., 1998). No such works on germanium complexes have been published as yet.

In light of the above mentioned, the aim of the present work was to study the formation of complexes of germanium chlorides with electroactive ligands in order to provide an insight into the intramolecular coordinating interactions, electronic structure and reactivity of such systems, which could contribute to the understanding of the reactivity of germanium derivatives in processes involving its coordination expansion.

Results and discussion

Cyclic voltammetry

As was previously shown by polarography and cyclic voltammetry, germanium chlorides R_nGeCl_{4-n} (n=0–4) undergo electrochemical reduction at potentials more negative than -2 V vs. saturated calomel electrode (SCE) (Boczkowski and Bottei, 1973; Corriu et al., 1980a,b; Petrosyan et al., 1988), the reduction process being irreversible and involving the Ge-Cl bond cleavage. Own reduction of bipyridines and, in particular, of bipy is also a well-known process (Tokel-Takvoryan et al., 1973; Roffia et al., 1993) that results, upon one-electron uptake, in relatively stable anion radicals. The voltammogram of reduction of bipy at a glassy carbon (GC) disk electrode in CH_3CN/0.1 M Bu_4NPF_6 is shown in Figure 1A. After the addition of tetrachlorogermane to the solution of bipy, a new redox system (Figure 1B) emerges whose well-shaped

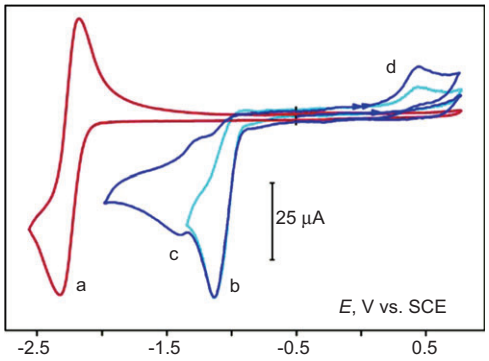


Figure 1 Voltammetry at a GC electrode in CH_3CN/0.1 M Bu_4NPF_6. (a) 2,2′-Bipyridine (C=4×10^{-3} mol/L). (b–d) 2,2′-Bipyridine after the addition of $GeCl_4$. The arrows show the first cycle starting from *E*=-0.5 V towards more positive potentials and the beginning (anodic branch) of the second scan. *v*=0.5 V/s. T=22°C.

reduction signal appears at potentials more than 1 V less negative than those of the reduction of bipy and of $GeCl_4$. The new redox system with a reduction peak potential $E_p\cong$ -1.18 V is supposed to correspond to the reduction of the bipy·$GeCl_4$ complex formed in the solution.

Indeed, separately prepared by the method described in Kupche et al. (1988) and reduced at a GC electrode under similar conditions, bipy·$GeCl_4$ has shown the same voltammogram as the above solution of bipy upon addition of an equivalent amount (1:1 molar ratio) of $GeCl_4$ (Figure 1).

As was reported for the couple $GeCl_4$-bipy·$GeCl_4$ (Kupche et al., 1988), the coordination of bipy with Ge is accompanied by a strong upfield shift of the ^{73}Ge NMR signal (-344.6 ppm), meaning a strong shielding of Ge because of the electronic interaction with the donor bipy ligand. In electrogenerated anion radicals [bipy·$GeCl_4$]$^{\cdot-}$, such interactions must be even stronger, but the short lifetime of these species at room temperature does not allow studying them by ^{73}Ge NMR. However, the dramatic anodic shift of the reduction potential E_p of bipy in the presence of $GeCl_4$ corroborates well this trend. The difference $\Delta E=E_p$(bipy)-E_p(bipy·$GeCl_4$) characterizing the formation of this complex is very large, corresponding in terms of free energy to ΔG=97.4 kJ/mol. Considering the complexation of germanium chlorides with neural (K_1) and reduced bipy (K_2) on the one hand and reduction of bipy (E_{bipy}^{o}) and of the corresponding bipy complex ($E_{bipyR_3GeCl}^{o}$) on the other hand, the ratio of complex formation constants K_2/K_1 can be determined from this value via the square scheme linking these species: ΔG_{comp}=-RTln(K_1)=-FE_{bipy}^{o} -RTln(K_2)+F$E_{bipyR_3GeCl}^{o}$. For $GeCl_4$, it gives the ratio of complexation constants $K_2\cong K_1\times2.3\times10^{17}$. However, it should be noted that the attack of bipy$^{\cdot-}$ on chlorogermane is not

realized directly and the only complex formation occurs between neutral bipy and germanium chloride; this reaction becomes evident upon electron transfer which shifts the equilibrium (with ΔG_{comp}), constantly consuming the neutral bipy·R_3GeCl complex. Thus electron transfer provides a large supplementary driving force to this process; without this additional energy, i.e., before electron transfer, the complexes are not stable enough to be isolated in solid state.

In contrast, this phenomenon can be seen as a facilitation of the reduction of bipy by a virtual electron-withdrawing substituent. From $E_{1/2}$-ρσ correlations in the related reaction series of substituted bipyridines (Elliott et al., 1982; Hino et al., 1992), the complexation with $GeCl_4$ has an equivalent electronic effect on bipy as that of the p-$(CF_3)_3CSO_2$ group or of two p-Me_2S^+ groups (Hansch et al., 1991).

The first electron transfer is followed by a second reversible step (Figure 1C). In addition, a small oxidation peak (D) at E_p=0.32 V, absent before reduction in (B), appears on the backward branch of the voltammogram. Truncated scan with the cathodic vertex before the second reduction step (Figure 1C) shows that the species accounting for this oxidation peak directly results from a one-electron reduction (B) of bipy·$GeCl_4$. The peak current i_p of (D) is practically the same as that of the second redox system (C).

Remarkably, not only $GeCl_4$ and $MeGeCl_3$ (Figure 2) but also dichloro- and even monochlorogermanes (Figure 3) have formed similar redox systems as well in the presence of bipy (Table 1). Although it was reported that Me_2GeCl_2 and Ph_2GeCl_2 do not form complexes with bipy (Poller, 1965; Schultz and Klapötke, 1995) and, to the best of our knowledge, no bipy complexes with monochlorogermanes are known, the reduction potentials of these systems are quite close to that of the $GeCl_4$·bipy complex (Table 1). This fact means that the energy of coordination in these systems is comparable, even for Ph_3GeCl and Me_2GeCl_2. Similar complexes were formed with other redox-active *N*-heteroaromatic ligands (Table 1) such as imidazole, pyrimidine and 2,6-dichloropyridine (DCP). In these cases, 1:2 complexes were formed as was shown by voltammetric titration.

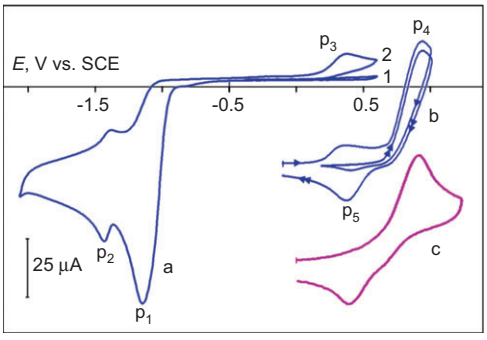


Figure 2 Reduction of bipy·$MeGeCl_3$ at a GC electrode in CH_3CN/0.1 M Bu_4NPF_6.
(a) bipy·$MeGeCl_3$ (C=5.6×10^{-3} mol/L), starting from E=-0.5 V towards anodic direction; (1) first and (2) second anodic branches. (b) Same solution, two anodic scans after the reduction at E_p^1. (c) For comparison, oxidation of Cl^- (LiCl, C=2×10^{-3} mol/L) is shown. ν=0.5 V/s. T=22°C.

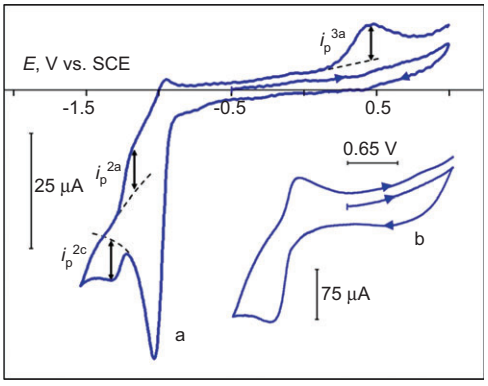


Figure 3 Electroreduction of bipy·Ph_3GeCl (C=3×10^{-3} mol/L) at a GC microdisk electrode in CH_3CN/0.1 M Bu_4NPF_6.
(a) Potential programming with two vertex potentials: -0.5→1.0→-1.6→1.0 V (ν=1 V/s). (b) Same solution, scan rate ν=10 V/s. T=22°C.

The peak currents i_p^1 of the reduction of these complexes are linear with concentration and the ratio $i_p^1/\nu^{1/2}$ remains constant for the scan rates ν=0.01–10 V/s, attesting that the total rate of the process at E_p^1 is limited by diffusion, without any kinetic limitations from preceding or follow-up reactions. With the combined data of voltammetry and chronoamperometry at the same electrode (Malachesky, 1969), the number of electrons transferred at E_p^1 was found to be n≅1 for all complexes. Similar results were obtained by comparing i_p^1 with the one-electron oxidation peak current of ferrocene. For the systems not showing any anodic counterpart of reduction (i.e., situated far from E_o), the peak potential of the first step cathodically shifted on average by 30–35 mV when the scan rate was increased by a factor of 10 (Table 1), a feature characteristic for reversible electron transfer processes followed by a fast first-order chemical reaction of the anion radicals (Hammerich, 2001).

The anodic counterpart of the second reduction peak p_2 of bipy·$MeGeCl_3$ (which itself has Nernstian half-width, E_p-$E_{p/2}$=58 mV) is somewhat large, supposedly because of structural reorganization of the species concerned. Further in the anodic scan, a small peak p_3 appears (Figure 2) whose peak current does not exceed

	L[a]	$-E_p^{1c}$, V	$-E_p^{1a}$, V	$-E^o$, V	$E_p-E_{p/2}$, mV	$\Delta E_p/\Delta\lg(v)$, mV	n	$-E_p^{2}$, V	$-E_o^{2}$, V
Ph_3GeCl	Bipy	0.96	0.90	0.93	82	[c]	1.0	1.43	1.40
	Imidazole[b]	1.62	1.41	1.51	75	[c]	1.1	1.85	
	Pyrimidine[b]	1.17			63	36			
Me_2GeCl_2	Bipy	1.11	1.03	1.07	55	[c]	1.1	1.44	1.38
$MeGeCl_3$	Bipy	1.18	0.98	1.08	60	32	0.9	1.46	1.43
	Imidazole[b]	1.80			75	34			
$GeCl_4$	Bipy	1.16	0.95[d]	1.10[d]	62	31	1.0	1.40	1.35
	DCP[b]	1.72			85	38			

Table 1 Characteristics of the electrochemical reduction of the complexes of chlorogermanes with electroactive heteroaromatic N-donor ligands (CH_3CN/0.1 M Bu_4NPF_6, v=1 V/s, T=20°C).
[a]Bipy=2,2′-bipyridine, DCP=2,6-dichloro-pyridine.
[b]1:2 complex formed.
[c]Non-linear dependence with $\Delta E_p/\Delta\lg(v)$=9–16 mV due to the proximity to E_o and residual ohmic drops.
[d]At v=5 V/s.

that of p_2 at any scan rate. The product formed at this step reacts with Cl_2 produced at p_4 as the reduction peak of the Cl_2/Cl^- couple practically disappears when this product is generated in the cathodic half-cycle (Figure 2B). Once this product is consumed in the reaction layer, the reverse peak p_5 of the Cl_2/Cl^- system reappears.

As is well seen in the case of bipy·Ph_3GeCl, both the cathodic and anodic peaks of the second reduction system ($i_p^{2c}/i_p^{2a}\cong1$; Figure 3) and the small anodic peak i_p^{3a} at E_p=0.45 V have equal currents at moderate scan rates, v=0.2–1 V/s. When increasing the scan rate, the main reduction peak of bipy·Ph_3GeCl becomes practically reversible (Figure 3B), whereas these three peaks do not appear anymore. There follows that the species corresponding to the second and third redox systems arise from first-order decomposition of the anion radicals of bipy complexes of germanium chlorides.

The nature of these species was elucidated by electron paramagnetic resonance (EPR) spectroscopy. With the use of spin trap technique (see below), second reduction peaks with $E_p^c\cong$-1.42 V and $\Delta E_p^{c\text{-}a}\cong$60 mV were assigned to the reversible couples $R_3Ge^{\cdot}/R_3Ge^-$ still associated with bipy. Standard redox potentials of bipy·[$R_3Ge^{\cdot}/R_3Ge^-$] systems have close values, $E_o\cong$-1.40±0.05 V vs. SCE, which is ca. 0.8 V more negative compared to the only reported value of $E_{1/2}(Ph_3Ge^{\cdot}/Ph_3Ge^-)$=-0.61 V determined by photomodulated voltammetry (Holm et al., 2005). In an earlier study on the oxidation of Ph_3Ge^- (as Ph_3GeLi in HMPA/LiCl), an even lower value was proposed, E_p=-0.29 V vs. SCE (Mochida et al., 1988). In the presence of bipy, a remarkable cathodic shift with respect to these values might be expected, provoked by an electron-donating ligand which provides an extra electron density to the Ge-centered radical, thus decreasing its electron affinity and electrophilicity. Although the experimental conditions in Holm et al. (2005) are not similar, one can have the idea about the energy of bipy→$Ph_3Ge^{\cdot}$ dative interaction. Thus, assuming $E_{1/2}\cong E_o$, the energy of this interaction makes up ≈76 kJ/mol.

From the fact that $i_p^2<<i_p^1$, it appears that the bipy·[Ph_3Ge]$^{\cdot}$ complex is less stable than its parent anion radical; in addition, no new paramagnetic species were detected by EPR upon decomposition of [bipy·Ph_3GeCl]$^{\cdot}$. The EPR data from the only report (Sakurai et al., 1975) on free $Ph_3Ge^{\cdot}$ radical in solution (243 K, solvent not specified) most probably describe some secondary organic radicals with C-centered spin (in solid-state $Ph_3Ge^{\cdot}$, spin is Ge-centered; Geoffroy et al., 1976). Thus the reactivity of $Ph_3Ge^{\cdot}$ in solution, even at 243 K, seems to be too high to allow its direct EPR detection.

Concerning the mechanism of formation of [R_nGeCl_{4-n}]·L complexes (L=bipy, 2×imidazole, 2×pyrimidine, 2×DCP), one can see that they are formed indeed *before* electron transfer and not via the reaction of the corresponding heteroaromatic anion radical with a chlorogermane (post electron transfer process). This follows from the fact that the observed reduction E_p^1 is way more positive compared to E_o(L). In fact, in the case of a post electron transfer mechanism, the maximum value of the kinetic shift of E_p vs. E_o(L) provoked by a fast follow-up reaction of electrogenerated anion radicals (even occurring at the diffusion limited rate) cannot exceed 300 mV [in fact, (2.3RT/2F)×lg(10^9)≅0.27 V; Hammerich, 2001], while in reality it is about 1 V (Table 1).

The origin of the anodic peak at E_p≈0.3 V, present in all voltammograms (Figures 1–3), is not very clear. Oxidation of digermanes (which might have been formed from dimerization of $Ph_3Ge^{\cdot}$) at this potential is improbable because the reported E_p^{ox} of $Ph_3GeGePh_3$ (1.958 V vs. Ag/AgCl; Amadoruge et al., 2010), of $Ph_3GeGeMe_3$ (1.16 V

vs. Fc^+/Fc, i.e., ≥1.46 V vs. SCE; Okano and Mochida, 1991) and of hexaalkyldigermanes (1.7 and 1.48 V vs. SCE for Me and Et, respectively; Mochida et al., 1985) is all too high. Another system which might account for this peak is the oxidation of Ph_3GeH formed either via H-atom abstraction by radical $Ph_3Ge^{\cdot}$ or by protonation of Ph_3Ge^- (although this last possibility must certainly be ruled out because the second reduction step is reversible for all complexes; cf. Figures 1–3). No works on electrooxidation of Ph_3GeH have been reported which could support this hypothesis, but some similarities might be found in the oxidation of GeH and GeH_2 hydrides on (100)- and (111)-oriented Ge surfaces in 1 M $HClO_4$ which occurs at -0.1 V (Maroun et al., 2003) and ~0 V vs. SCE (Maroun et al., 1998), respectively. A very easy oxidation of homologous Ph_3SnH (E_p=-0.3 and -0.4 V; Booth and Fleet, 1970; Mazzocchin et al., 1976) was also reported, although confronted with a much higher value of +0.8 V in a more recent study (Tanaka et al., 1996). In contrast, from the analysis of voltammetry of these complexes, the oxidation peak at 0.3 V might be ascribed to a bipy-coordinated [R_3Ge^+/R_3Ge^-] system. Although no data are available so far on the redox potential of this couple, the E_p of non-coordinated $Ph_3Ge^+/Ph_3Ge^{\cdot}$ system might possibly have an intermediate value between the $E_{1/2}^{ox}$ of $Ph_3Si^{\cdot}$ and that of $Ph_3Sn^{\cdot}$ (-0.41 and +0.2 vs. SCE, respectively; Holm et al., 2005). A positive shift of apparent oxidation potential up to E_p^3=0.3 V (0.25–0.45 V for other complexes) might originate from a distortion of the geometry around Ge when instead of three Ph groups in the expectedly pyramidal Ph_3Ge^- there are five Ph-like ligands (three Ph and two pyridyl groups) around a pentacoordinate Ge atom.

It cannot be completed without mentioning that, at millimolar concentrations, partial hydrolysis of chlorogermanes occurs resulting in HCl whose reaction with bipyridine provides protonated bipy·HCl. As was shown by the voltammetry of specially prepared bipy·HCl, the reduction potential of this salt is slightly less cathodic than the E_p of bipy·$GeCl_4$, so it appears as a pre-peak or a shoulder on the reduction peak of the latter (Figure 1, also Figures 2 and 3). The reduction of bipyridinium hydrochloric salt is reversible (n=1), leading to a neutral radical (formally radical anion) which can be seen under the conditions of EPR spectroelectrochemistry (Figure 4).

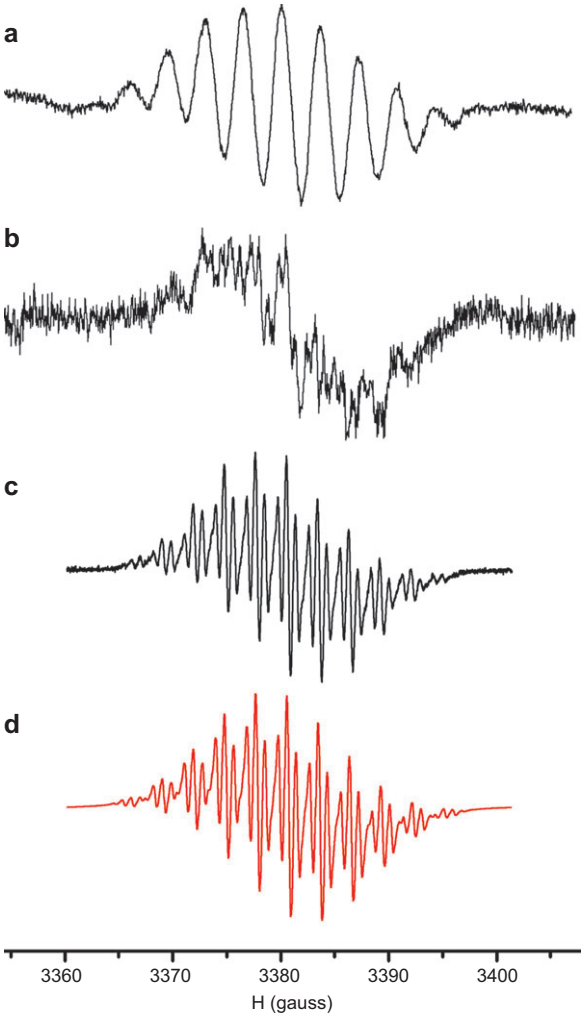


Figure 4 EPR spectra from the electrochemical reduction of Ph_3GeCl in the presence of bipy in CH_3CN/0.1 M Bu_4NPF_6 at a Pt microspiral electrode.
T=254 K. (a) Applied potential E=-0.75 V. (b) Working electrode potential shifted to E=-1.0 V. (c) Resulting spectrum of [bipy·Ph_3GeCl]$^{\cdot}$ (E=-1.25 V). (d) Simulated spectrum of [bipy·Ph_3GeCl]$^{\cdot}$ using the parameters in the text.

EPR Spectroelectrochemistry

As mentioned above, the reduction of bipyridinium hydrochloride corresponds to a reversible one-electron uptake resulting in a neutral radical. Because the reduction potential E_p(bipy·HCl) is less negative than E_p(bipy·Ph_3GeCl), the formation of this radical is unavoidable when trying to reduce germanium chloride complexes. However, by virtue of higher E_p, the bipy·HCl complex can be totally consumed in a pre-electrolysis at the potentials of the foothill of its reduction peak. The working potential could then be shifted to the cathodic direction to reach the reduction potentials of the Ge-bipyridyl complex.

Thus the first signal of the paramagnetic species, appearing upon progressive (with 50-mV increments) cathodic polarization of bipy·Ph_3GeCl in an EPR spectroelectrochemical cell, arises from the radicals of protonated bipy, [bipy·H]$^{\cdot}$ (Figure 4, upper panel). This spectrum has

a Δ=34 G end-to-end width and shows a large characteristic H *hfc* constant (a_H=3.78 G) from an N-linked proton. The line width of this spectrum is broadened by proton exchange. A short *in situ* electrolysis at *E*=-0.75 V allows to reduce bipyridinium hydrochloride and to eliminate the traces of HCl in the space around the working electrode. When these species were totally consumed, the second paramagnetic species could be generated in the solution at a more negative potential, *E*=-1.25 V (Figure 4). The spectrum of this new species is narrower, Δ=28 G; it is centered at g=2.0038 and has a characteristic pattern of bipy-related radicals; it was assigned to the anion radical arising from the one-electron reduction of the bipy·Ph_3GeCl complex. Reconstruction of this spectrum allowed to make the following assignments: two N atoms, non-equivalent in their interaction with the magnetic field, with *hfc* constants $a_{N(ax)}$=2.507 G, $a_{N(eq)}$=1.787 G; two bipy protons at 5,5′-positions with high spin coupling a_H=4.841 G and a_H=4.815 G; two 3,3′-protons with a_H=2.396 and G a_H=2.365 G; and four *o*- and *p*-protons to N with an average *hfc* constant a_H=0.689 G (2H×0.79 G+1H×0.68 G+1H×0.522 G). The non-equivalence of two nitrogen atoms in the anion radical [bipy·Ph_3GeCl]$^{\cdot}$ results from the different positions they occupy in the Ge environment; this result is in good agreement with their orientation and Fermi contact terms (FCT) from DFT calculations. Including ^{73}Ge satellites in the simulation of the spectrum (r=0.998 without ^{73}Ge) did not improve the quality of fitting, which is also consistent with zero FCT on Ge (Table 2).

The fate of [bipy·Ph_3GeCl]$^{\cdot}$ anion radicals was checked by spin-trapping technique when the solution of bipy·Ph_3GeCl was electrolyzed at *E*=-1.0 V (before the second reduction step of this complex) in the presence of a spin trap, α-phenyl-*N*-*tert*-butyl nitrone (PBN). EPR spectroscopy then confirmed the formation of a spin adduct (g=2.0069, a_N=14.72 G and a_H=5.84 G) which was not formed in test experiments without bipy or without Ph_3GeCl. PBN does not form spin adducts with delocalized species like bipy$^{\cdot}$; hence the radical addends trapped under these conditions were identified as $Ph_3Ge^{\cdot}$ radicals. The *hfc* constants of this adduct are close to those reported for trapping of $Ph_3Ge^{\cdot}$ with PBN in benzene (a_N=14.66 G and a_H=6.27 G) (Haire et al., 1988). Thus the formation of $Ph_3Ge^{\cdot}$ in the process following electron transfer at E_p(bipy·Ph_3GeCl) and the concomitant appearance of free Cl^- anion in the solution (Figure 2) agree well with the first-order cleavage of the Ge-Cl bond induced by electroactive ligand.

The kinetics of disappearance of the electrogenerated anion radical [bipy·Ph_3GeCl]$^{\cdot}$ has been studied then by temperature-dependent EPR spectroelectrochemistry in a CH_3CN/0.1 M Bu_4NPF_6 solution (Figure 5). The rate-limiting monomolecular reaction rate constant was found to be k=6.54×10^{-2} s^{-1} at T=224 K. First-order rate constants, plotted as the function of 1/T, provided the Arrhenius parameters of this process: $\Delta H^{\neq}$=29.05 kJ/mol and $\Delta S^{\neq}$=-135 J/(K mol). A large negative value of activation entropy $\Delta S^{\neq}$ for a monomolecular reaction seems strange at first sight. Meanwhile, it can be rationalized by the fact that the elimination of Cl^- is induced by the negative charge from bipy (see Figure 7 in the next section) coordinated to Ge. The whole situation is therefore similar to an E2 bimolecular elimination mechanism when relatively small activation enthalpy $\Delta H^{\neq}$ is accompanied by high negative entropy $\Delta S^{\neq}$. At room temperature, the rate constant of decay of

	l(Ge-Cl)	*l*(Ge-N^1)	*l*(Ge-N^2)	∠C-Ge-Cl	Σ(∠C-Ge-C)	NBO charges, (FCT)[a]			
						Cl	Ge	N^1	N^2
N	2.307	4.126	4.453	105.55 105.45 103.92	340.7	1.623	1.441	1.627	1.627
AR	3.366	2.072	2.690	75.487 75.334 77.870	-341.9	-0.874 (-0.00001)	1.978 (0.00000)	-0.726 (0.00562)	-0.559 (0.00083)
R	–	1.998	2.347	–	-321.4	–	1.981 (0.00000)	-0.759 (0.00000)	-0.621 (0.00000)
A	–	1.956	2.157	–	-307.4[b]	–	1.503	1.536	1.566
C	–	2.100	2.522		-332.9[b]	–	1.988	1.590	1.614

Table 2 Selected geometrical parameters and natural bond orbital (NBO) charges for neutral bipy·Me_3GeCl (N), anion radical [bipy·Me_3GeCl]$^{\cdot\cdot}$ (AR), radical [bipy·Me_3Ge]$^{\cdot}$ (R) and anion [bipy·Me_3Ge]$^-$ (A) and cation [bipy·Me_3Ge]$^+$ by DFT B3LYP/Lanl2DZ calculations (bond lengths in angstrom, angles in degrees).

[a]Fermi contact terms (FCT) for AR and R in megahertz.

[b]Geometry different from that of neutral, AR and R forms: instead of N^1, the N^2 atom is now in the apical position. The sum of ∠$C_{eq}{}^1$-Ge-$C_{eq}{}^2$+∠N^1-Ge-$C_{eq}{}^1$+∠N^1-Ge-$C_{eq}{}^2$ is 366.5° for (A) and 346.4° for (C).

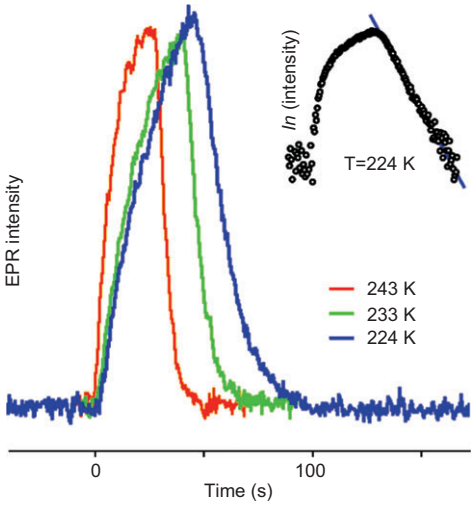


Figure 5 Evolution of the intensity of the central line of the EPR spectrum of [bipy·Ph_3GeCl]$^{\cdot}$ with time at different temperatures. Cell polarization (E=-1.3 V) was applied at t=0 s; the maximum on the curve corresponds to the point when the potential is switched off. In the inset, first-order logarithmic decay at 224 K is shown. Pt microdisk electrode, CH_3CN/0.1 M Bu_4NPF_6.

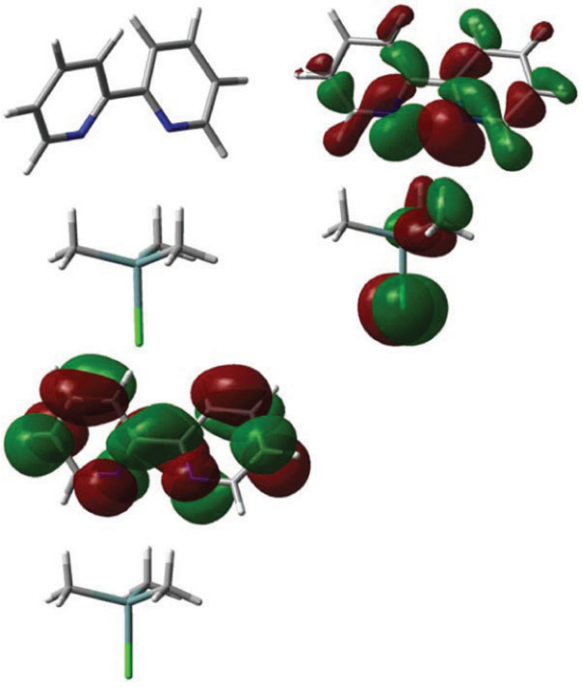


Figure 6 Geometry (left), HOMO (right) and LUMO (bottom) of the neutral bipy·Me_3GeCl complex from DFT B3LYP/Lanl2DZ calculations.

the anion radicals amounts to k=2.7 s^{-1}, which agrees with the data of cyclic voltammetry on the stability of [bipy·Ph_3GeCl]$^{\cdot}$.

DFT calculations

For a better insight into the electronic interactions and structural changes upon the formation and reduction of complexes of bipy with monochlorogermanes, a model complex bipy·Me_3GeCl was considered. Because Me derivatives are less prone to the formation of such complexes compared to Ph-substituted analogues (C_{sp3}- vs. C_{sp2}-hybridized attaching atoms), the features found for bipy·Me_3GeCl must hold, and even to a greater extent, for a Ph-substituted derivative. In addition, a remarkably smaller number of atoms in 3Me vs. 3Ph substitution allowed an important reduction of the calculation time. The geometries of bipy·Me_3GeCl, of its anion radical and of related species were optimized at the DFT B3LYP/Lanl2DZ level with ECP full double zeta basis, which was found to reproduce well long-term and delocalizing electronic interactions in metallatrane-like structures (Soualmi et al., 2008, 2010; Lutter et al., 2012). The optimized structures were subject to harmonic frequency analysis to check the absence of imaginary vibrations, after which NBO analysis (Glendening et al., 2003) was performed at the same level of theory.

As is depicted in Figure 6, the two molecules – bipy and Me_3GeCl – seem to maintain practically undistorted individual geometry before the electron uptake. In Me_3GeCl, the ∠C-Ge-Cl (≈105°) and ∠C-Ge-C (≈113°) angles are close to those of tetrahedral geometry. Two pyridyl rings in bipy are twisted by an angle of 39.59° still keeping their non-eclipsed orientation. The distance between donor and acceptor sites of two molecules (Table 2) is by 15–20% superior to the sum of the van der Waals' radii of the concerned atoms, 2.11 Å (Ge)+1.55 Å (N) (Mantina et al., 2009). With this, the mutual orientation of two compounds is such that lone pairs from both N atoms of bipy can participate in coordination with electron-deficient Ge (HOMO, Figure 6), even though the N···Ge contact in a neutral complex is too long to induce pronounced hexacoordination of Ge. This interaction holds the complex together before electron transfer. As expected, the site of electron uptake is the LUMO of bipy moiety without any admixture of higher lying vacant orbitals of the chlorogermane (LUMO, Figure 6). An interesting point is that in the geometry corresponding to a global minimum of this system, the NBO charges on Cl and the two N atoms are practically equal (Table 2).

Injection of one electron into the LUMO of the above system induces remarkable changes in its geometry (Figure 7). Electron delocalization over two pyridyl moieties makes them practically planar, with the dihedral angle $\angle N^1\text{-}C^2\text{-}C^{2\prime}\text{-}N^2$=1.18°. The N^1-Ge distance becomes shorter than and the N^2-Ge comparable with that in germatranes (Soualmi et al., 2010). N^1-Ge distance is now only 10–15%

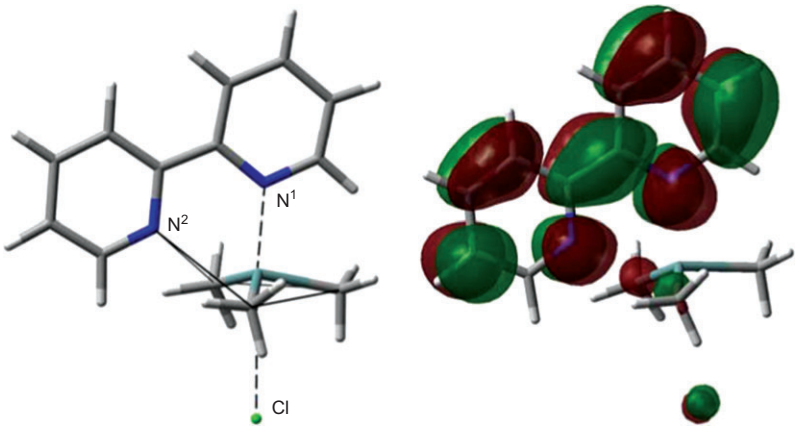


Figure 7 Geometry and SOMO of the anion radical [bipy·Me_3GeCl]$^{\cdot}$ from DFT B3LYP/Lanl2DZ calculations.

longer than a normal N-Ge bond length (Mackay, 1995). The length of the Ge-C bond opposite to the equatorial pyridyl fragment is superior to the other two Ge-C bonds (1.99 vs. 1.96 Å), and all three are longer than the Ge-C bond in neutral Me_3GeCl, in accordance with the electron-donating effect from N^2. The ∠C-Ge-C angles in the anion radial are not equal because of N^2-bipy moiety entering into the cleft between two Me groups (Figure 7) with the angle ∠C-Ge-C=132.73° against 104.62° and 104.59° for the other two. The sum of ∠C-Ge-C angles amounts to 342°, showing a substantial deviation of Ge atom from the plane formed by three C atoms, with inversion of configuration with respect to Cl atom (cf. Figures 6 and 7). On the other side, including an N^2 coordinating atom into the equatorial surrounding of Ge, i.e., considering now a distorted square base bipyramid, gives the sum of angles between four equatorial substituents as 368°, which is closer to 360° (for a non-distorted equatorial plane). Although the axis of N^1-Ge-Cl is not perfectly straight, ∠N^1-Ge-Cl=176.71°, and one of the equatorial quadrilaterals lying out of plane (Table 2), on the whole it corresponds to a distorted tetragonal bipyramid configuration.

Fermi contact terms from DFT calculations are consistent with the *hfc* constants in the EPR spectra of such complexes: spin in their reduced forms is localized over bipy ligand without any transfer to Ge atom. In the anion radical, the Cl atom seems almost apart of the Me_3Ge moiety, *l*(Ge-Cl)=3.36 Å vs. 2.3 Å in neutral complex (cf. 2.15 Å in Me_3GeCl; Mackay, 1995). Interestingly, despite the large Ge-Cl distance, some spin density (FCT≅10 Hz) is present in the Cl atom (Figure 7, Table 2), suggesting that a 3c-4e type bonding might be partly realized in such anion radical providing some stability to these species, in contrast to [bipy·Me_3Ge]$^{\cdot}$ radical; this observation is in line with the results of cyclic voltammetry.

Interestingly, electron withdrawal from [bipy·Me_3Ge]$^{\cdot}$ results in switching the positions of two N atoms relative to Ge: nitrogen atom N^1, originally at the apical position (Figure 7), shifts to the equatorial position, whereas N^2 atom takes the apical position instead (Figure 9). The sum of angles between the trilaterals at Ge (∠C_{eq}^1-Ge-C_{eq}^2+∠N^1-Ge-C_{eq}^1+∠N^1-Ge-C_{eq}^2) is now 366.5° and the angle ∠N^2-Ge-C_{ap}=173°, so that the Ge configuration in [bipy·Me_3Ge]$^{\cdot}$ becomes very close to trigonal bipyramid when Ge uses its three sp^2 orbitals ($4s^{0.38}4p^{0.61}$ natural electron configuration) for equatorial bonding and one pd hybrid for axial bonding. It might appear surprising that there is not a large difference in structures between radical, anion and

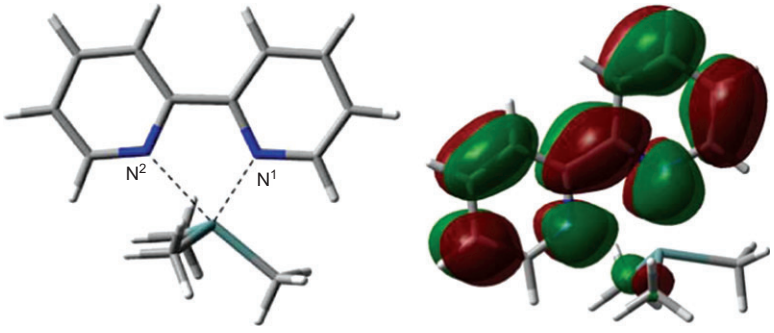


Figure 8 Geometry and spin-carrying SOMO of the radical [bipy·Me_3Ge]$^{\cdot}$ from DFT B3LYP/Lanl2DZ calculations.

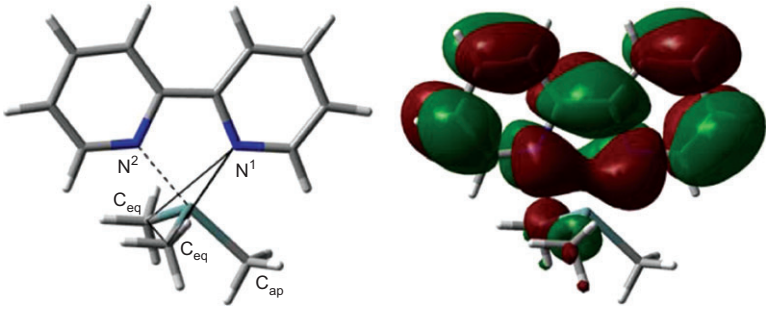


Figure 9 Geometry (apical nitrogen switched from N^1 to N^2) and HOMO of the anion [bipy·Me_3Ge]$^-$ from DFT B3LYP/Lanl2DZ calculations.

cation forms, especially for the last two, bearing opposite charges. It becomes clearer in light of the fact that Ge in all three structures keeps its 10-e configuration (6e from $3\times\sigma_{(Ge\text{-}C)}$+4e from $2\times n_{(N)}$), whereas electron transfers (A-e⇆R⇆C+e) occur at the orthogonal π-system of bipy (Figures 7–9) and therefore have little effect on Ge configuration.

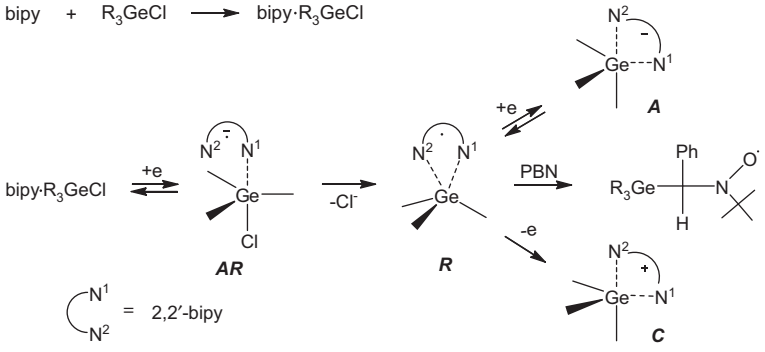
Conclusion

The results of cyclic voltammetry along with the data from EPR spectroelectrochemistry and DFT calculations allow to demonstrate that germanium chlorides, even those with a single Cl atom, do form coordination complexes with *N*-heteroaromatic ligands in solutions. Although they cannot be isolated in solid form, solution electron transfer to such complexes strongly displaces the equilibrium of their formation providing an additional driving force to this process. These complexes undergo reversible one-electron reduction much easier than the corresponding imino compounds themselves. The loss of Cl^- anion by the extracoordinated anion radical intermediates leads to a coordinated radical which, in turn, can be converted into bipy-coordinated anion or cation via one-electron transfers. EPR and DFT calculations converge in that the unpaired electron density in these odd-electron intermediates is entirely localized on the ligand, without any visible electron transfer to the Ge atom. The whole situation can be schematized as shown below (Scheme 1).

The reduction process enables chemical and configurational transformations in a way that, upon one-electron uptake, the N^1 atom of bipy first acts as a "germophilic" reagent, inducing penta- and then hexacoordination on Ge which results in elimination of Cl^-; now, a second nitrogen intervenes as an apicophile stabilizing the radical with inverted pentacoordinate configuration. Despite the coordination with bipy, the electrogenerated ionic and radical species A, C and R are very reactive, rapidly evolving to final products; the above feature therefore might open the possibility to control the reactivity and stereochemical outcome of the ensuing reactions of such species. Further study in this direction is underway.

Experimental section

Voltammetric measurements were carried out with a PAR 2273 (Oak Ridge, TN, USA) scanning potentiostat. An EG&G Model 362 potentiostat (Oak Ridge, TN, USA) was used for EPR spectroelectrochemical experiments. Glassy carbon (GC) working disk electrodes of 3 mm in diameter were used. Because of surface passivation, they were carefully polished and ultrasonically rinsed in acetone before each run. The counter electrode



Scheme 1 Formation and primary electrochemical reactions of complexes of bipyridine with germanium chlorides.

was a GC rod placed in a compartment separated with a sintered glass diaphragm; a polypyrrole electrode was used as the reference, separated from the analyte by an electrolytic bridge filled with CH_3CN/0.1 M Bu_4NPF_6. In some cases, the potentials were additionally corrected using Fc^+/Fc reversible couple (E_0=0.158 V vs. SCE) as an internal standard. The incorporated IR-compensation facility of PAR 2273 was used for correcting the ohmic drops in the solution. All experiments were performed under an inert atmosphere, either in a glovebox or using the Schlenk technique.

EPR spectroelectrochemical experiments were carried out using an X-band Bruker EMX spectrometer (Bruker, Switzerland) operating at 9.46 GHz frequency coupled to a standard rectangular cavity. The spectroelectrochemical cell was a three-electrode version of that described in Zeitouny et al. (2009). 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was used for calibrating g factors.

Germanium chlorides (ABCR) were used as received. 2,2′-Bipyridine (Aldrich, Lyon, France) was freshly sublimed before use. Analytical grade CH_3CN (sds) was distilled under Ar atmosphere from CaH_2 and additionally dried over microwave vacuum activated 4-Å molecular sieves. Before the measurements, electrochemical-grade Bu_4NPF_6 (Fluka, Lyon, France) was dried overnight in vacuum at 80°C.

WINEPR (Bruker, 1990) and SimFonia (Bruker, 1994) provided by Bruker (Switzerland) were used for processing and simulating the EPR spectra. Structure optimization, frequency and NBO analysis were performed via DFT B3LYP/LANL2DZ//HF/6-311G calculations using GAUSSIAN 03 software (Frisch et al., 2003).

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