Expanded Ring N-Heterocyclic Carbene Adducts of Group 15 Element Trichlorides: Synthesis and Reduction Studies

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ELECTRONIC SUPPLEMENTARY INFORMATION

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Contents

1. Crystallographic Studies

Table S1. Summary of crystallographic data for **1**, **3-5**, [6-DipCl]Cl **1S** and [(6-Dip)GeCl$_2$] **2S**.

	1	**3**^{a}	**4**·(benzene)	**5**·(benzene)^a	**1S**·(benzene)$_{0.5}$	**2S**·(toluene)^a
empirical formula	$C_{28}H_{40}Cl_3N_2P$	$C_{28}H_{40}Cl_3N_2Sb$	$C_{62}H_{86}Cl_2N_4P_4$	$C_{50}H_{64}N_4$	$C_{31}H_{43}Cl_2N_2$	$C_{35}H_{48}Cl_2GeN_2$
formula weight	541.94	632.72	1082.13	721.05	514.57	640.24
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1$	$P2_1/n$	$C222_1$	$C2/c$	$P2_12_12_1$
T (K)	123(2)	123(2)	100(2)	100(2)	100(2)	123(2)
a (Å)	8.1527(16)	8.7102(5)	18.416(4)	11.656(2)	20.472(4)	9.9126(3)
b (Å)	10.830(2)	15.3670(5)	17.227(3)	14.612(3)	14.638(3)	14.6493(4)
c (Å)	31.317(6)	11.5589(7)	19.145(4)	23.686(5)	21.347(4)	22.7915(6)
α (deg.)	90	90	90	90	90	90
β (deg)	95.02(3)	109.300(7)	92.03(3)	90	115.09(3)	90
γ (deg.)	90	90	90	90	90	90
vol (Å^3)	2754.5(10)	1460.21(13)	6070(2)	4033.9(14)	5793(2)	3309.61(16)
Z	4	2	4	4	8	4
ρ (calcd) (g.cm^{-3})	1.307	1.439	1.184	1.187	1.180	1.285
μ (mm^{-1})	0.411	1.238	0.253	0.069	0.246	1.113
F(000)	1152	648	2320	1568	2216	1352

reflections collected	24625	11963	52324	15178	23208	23126
unique reflections	6635	6677	13132	3948	5092	7587
R_{int}	0.0302	0.0232	0.1044	0.0485	0.0486	0.0245
R1 indices [$I>2\sigma(I)$]	0.0349	0.0230	0.0650	0.0350	0.0910	0.0234
wR2 indices (all data)	0.0913	0.0501	0.1899	0.0866	0.2531	0.0546
Largest peak and hole (e.A^{-3})	0.40, -0.33	0.53, -0.24	0.69, -0.63	0.20, -0.16	1.94, -0.97	0.26, -0.19
CCDC No.	1012343	1012344	1012345	1012346	1012341	1012342

[a] the absolute structure parameters for the crystal structures of **3**, **5** and **2S** are -0.01(1), 0(2) and -0.01(1) respectively.

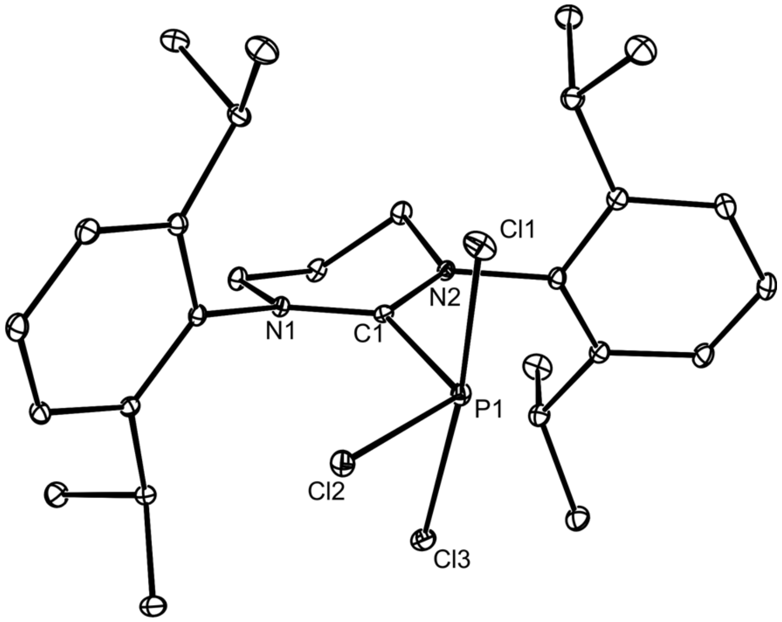


Figure S1. Molecular structure of **1** (25% displacement ellipsoids are shown; hydrogens omitted). See main text for geometrical parameters.

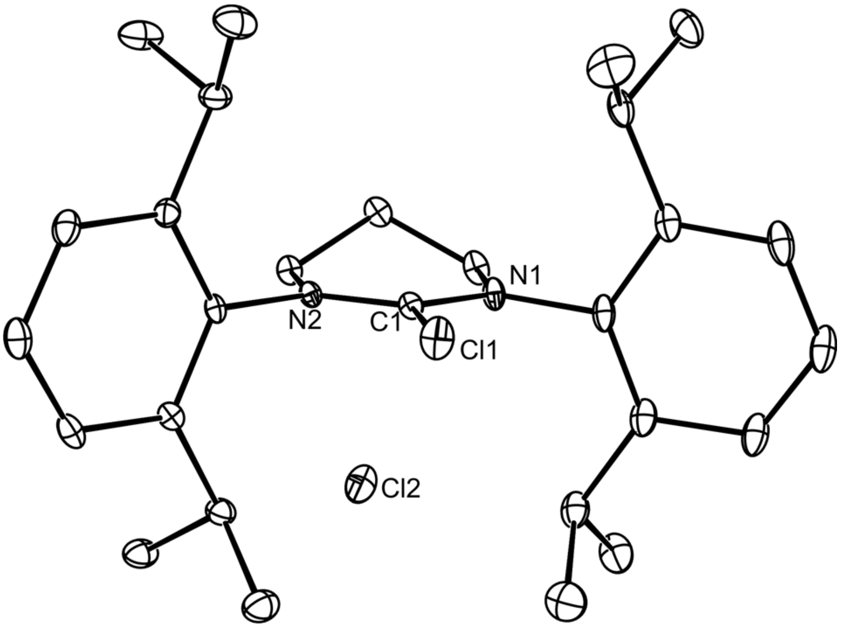


Figure S2. Molecular structure of [6-DipCl]Cl **1S** (25% displacement ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Cl(1)-C(1) 1.719(4), N(2)-C(1) 1.315(5), N(1)-C(1) 1.321(4), N(2)-C(1)-N(1) 124.0(3), N(2)-C(1)-Cl(1) 118.5(3), N(1)-C(1)-Cl(1) 117.5(3).

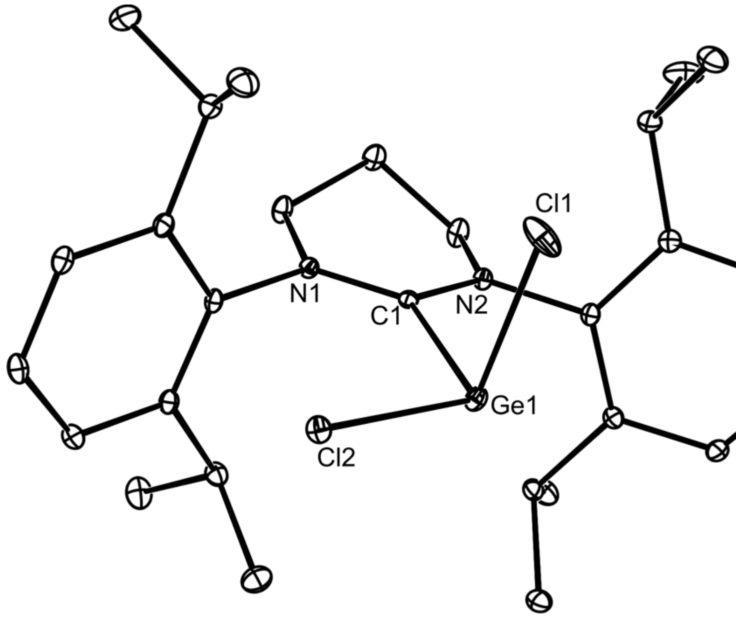


Figure S3. Molecular structure of [(6-Dip)GeCl$_2$] **2S** (25% displacement ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Ge(1)-C(1) 2.1894(16), Ge(1)-Cl(2) 2.2773(4), Ge(1)-Cl(1) 2.2807(5), N(1)-C(1) 1.3396(17), C(1)-N(2) 1.341(2), C(1)-Ge(1)-Cl(2) 103.42(4), C(1)-Ge(1)-Cl(1) 91.62(4), Cl(2)-Ge(1)-Cl(1) 94.595(17), N(1)-C(1)-N(2) 118.36(15).

2. Electrochemical Studies

Experimental Details

Materials. Tetra(*n*-butyl)ammonium hexafluorophosphate ([NBu$^n_4$][PF$_6$]; 98%, Beijing Health Science and Technology Co.) was recrystallized twice from ethanol (96%, Merck Emplura). Ferrocene (Fc; 98%, Ega-Chemie), acetone (≥99.0 %, Merck Emplura), and acetonitrile (≥99.9%, Merck LiChrosolv) were used as supplied. Dichloromethane (≥99.9%, Merck Suprasolv) was distilled over CaH_2 under a N_2 atmosphere prior to use. High-purity N_2 (99.999 %, H_2O < 3 ppm, O_2 < 2 ppm) was used to remove oxygen from the solutions during electrochemical experiments.

Electrochemical instrumentation and procedures. Electrochemical measurements were undertaken using either a BAS Epsilon electrochemical workstation or a custom-made FTACV instrument (Monash University and LaTrobe University, Australia)[1] in three-electrode cells at ambient temperature (290-295 K). All voltammetric studies were performed under a high purity N_2 atmosphere. This was achieved in laboratory based experiments by preliminary de-aeration of the solution with CH_2Cl_2-saturated nitrogen for *ca* 15 min, or by undertaking experiments in a glove-box environment under a N_2 atmosphere.

In voltammetric studies, the working electrodes were glassy carbon (GC; surface area, $A = 0.067$ cm^2) or gold ($A = 0.033$ cm^2) macrodisk electrodes embedded in an isolating inert sheath (BAS) or a carbon fibre microelectrode (diameter, $d = 12$ μm). Oxidative bulk electrolysis experiments were performed under ambient laboratory conditions in a three compartment cell with fine porosity glass frits separating the working and auxiliary electrode chambers from the working electrode compartment using platinum gauze as a working electrode. AgCl-covered silver wire immersed in the dichloromethane solution of **5** containing 0.20 or 0.40 M $[NBu^n{}_4][PF_6]$ was employed as a quasi-reference electrode. To calibrate the potential of the quasi-reference electrode, a small concentration of an Fc internal redox reference standard was introduced into the test solution. Current data are normalised to the electrode surface area.

Further details on the employed experimental procedures can be found elsewhere.[2]

Electrochemical Studies on Dichloromethane Solutions of 5.

Within the potential range of -2.6 to 1.0 V *vs.* $Fc^{0/+}$, d.c. cyclic voltammetric analyses of **5** in dichloromethane solutions containing 0.40 M $[NBu^n{}_4][PF_6]$ as the supporting electrolyte allow detection of a single chemically irreversible oxidation process (Fig. S4).

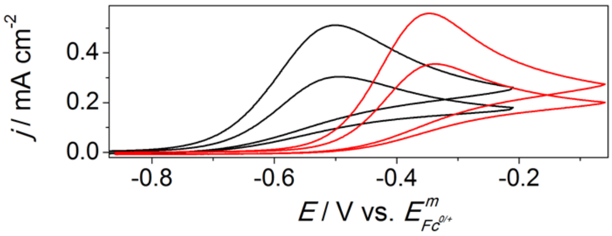


Figure S4. d.c. cyclic voltammograms (v = 0.10 V s^{-1}; two consecutive cycles shown) for oxidation of 1.7 (*black*) and 2.0 mM (*red*) **5** in dry and deoxygenated CH_2Cl_2 (0.40 ([NBu$^n_4$][PF$_6$]) (nitrogen-filled glove-box) at 295 K with GC (*black*) and Au (*red*) electrodes. Potentials are referred to the midpoint potential for the Fc$^{0/+}$ process measured under given voltammetric conditions.

The diffusion controlled nature of the peak current for the d.c. voltammetric oxidation of **5** was established from its close to linear dependence on the square root of the potential sweep rate (v = 0.04-1.0 V s^{-1} range) with a bulk concentration C_0 = 0.6-2.0 mM and an electrode surface area A = 0.033 and 0.067 cm^2 at the Au and GC electrodes, respectively. The diffusion coefficient of **5** in CH_2Cl_2 (0.40 M [NBu$^n_4$][PF$_6$]) at 291 ± 1 K was estimated to be $5.0 \cdot 10^{-6} \pm 0.3 \cdot 10^{-6}$ cm^2 s^{-1} on the basis of the (two electron) limiting oxidation current obtained under near steady-state voltammetric conditions with a carbon fibre microelectrode and the relevant theory[3] and analysis of the chronoamperometric data for the diffusion-controlled oxidation of **5** at the macroelectrodes and use of the Cottrell equation.[3]

Notwithstanding the dominance of diffusion control in the process shown in Fig. S4, the electrode mechanism for the oxidation of **5**, most probably, involves adsorption of the compound itself and/or intermediates since the potential for voltammetric oxidation of **5** exhibits a pronounced dependence on the electrode's chemical identity (Fig. S4) and history (Fig. S5). Repeated cycling of the potential (as shown in Fig. S4) shifts the oxidation of **5** towards more positive potentials with both Au and GC electrodes. The effect is enhanced when the positive potential limit is extended and is more pronounced with an Au rather than GC electrode (Fig. S5). On the contrary, voltammetric reductive pretreatment of the electrode surface provided by sweeping the potential to *ca* -2.6 V *vs.* Fc$^{0/+}$ (exemplified in Fig. S6) reproducibly shifts the oxidation of **5** to more negative potentials.

Another noteworthy feature in the voltammetry of **5** in CH_2Cl_2 (0.40 M $[NBu^n{}_4][PF_6]$) is the detection of an irreversible reduction process at *ca* -2.5 V *vs.* $Fc^{0/+}$ coupled to oxidation of **5** (Fig. S6). This new process also increases with increase in C_0 and is not detected in the absence of **5**.

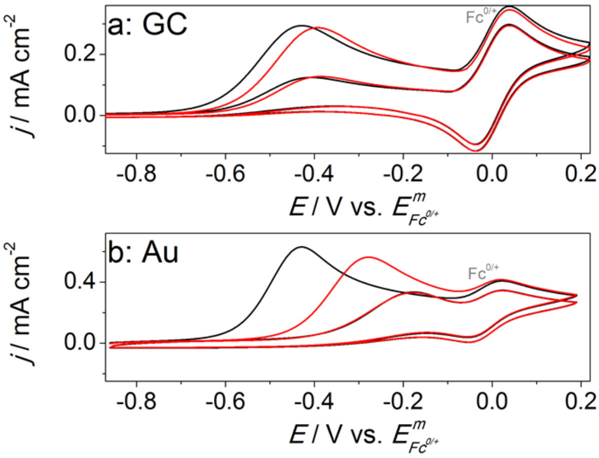


Figure S5. d.c. cyclic voltammograms (v = 0.10 V s^{-1}) for oxidation of (a) 1.0 and (b) 2.0 mM **5** and Fc (internal standard) in deoxygenated CH_2Cl_2 (0.40 $[NBu^n{}_4][PF_6]$) obtained with (a) GC or (b) Au electrodes at 293-295 K. *Black* data were obtained after 'reductive' d.c. voltammetric pretreatment (-1.0 - -2.6 V range, v = 0.10 V s^{-1}). *Red* data were obtained immediately after recording the *black* curve. Five cycles of the potential were recorded, but only first two are shown. Potentials are referred to the midpoint potential for the $Fc^{0/+}$ process.

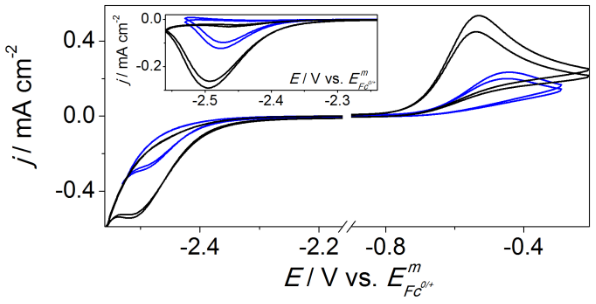


Figure S6. d.c. cyclic voltammetry (v = 0.10 V s^{-1}) for oxidation and subsequent reduction of 1.0 (*blue*) and 2.0 mM (*black*) **5** in dry and deoxygenated CH_2Cl_2 (0.40 $[NBu^n{}_4][PF_6]$) (nitrogen-filled glove-box) with a GC electrode at 295 K. Inset shows background-corrected voltammograms for the reduction process. Potentials are referred to the midpoint potential for the $Fc^{0/+}$ process under given d.c. voltammetric conditions.

The mechanistically sensitive technique of Fourier transformed a.c. voltammetry[1] reveals that at least two electron transfer processes contribute to oxidation of **5** on a freshly polished GC electrode as evidenced by bifurcation of the fundamental harmonic component seen in the positive d.c. potential sweep (Fig. S7). However, bifurcation was not detected in the fundamental harmonics derived from Au electrodes, irrespective of their pre-treatment (Fig. S7), which further emphasises the pronounced dependence of the electrode process on the properties of the electrode surface.

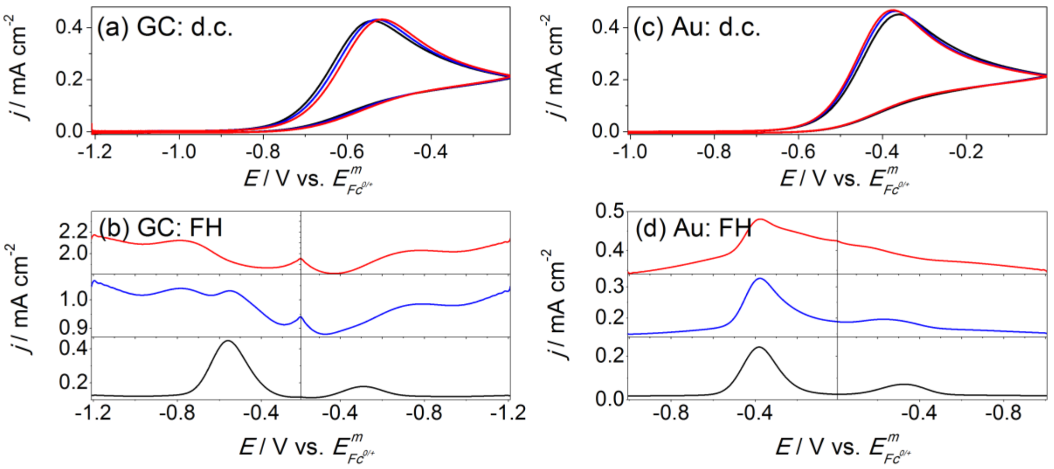
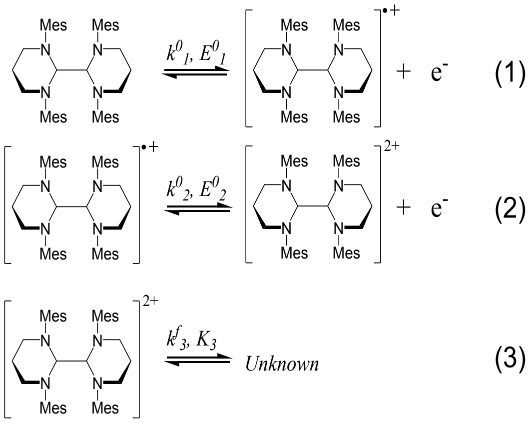


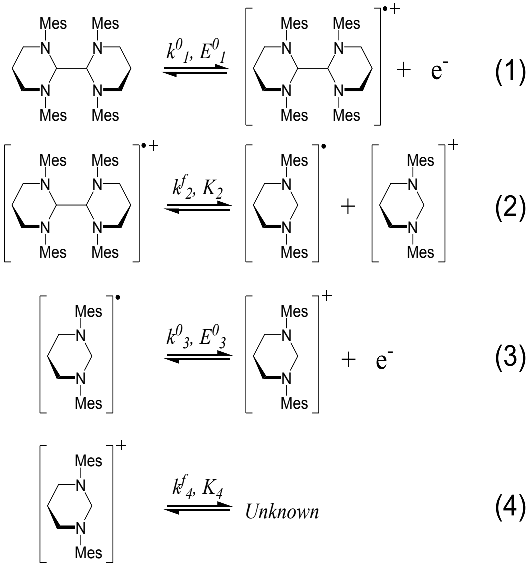
Figure S7. (a, c) Aperiodic d.c. and (b, d) fundamental harmonic components of a.c. cyclic voltammograms (frequency of the periodic component, $f = 9$ (*black*), 89 (*blue*) and 219 Hz (*red*); amplitude of the periodic component, $\Delta E = 0.080$ V; d.c. potential scan rate, $v = 0.075$ V s^{-1}) for oxidation of 2.0 mM **5** in dry and deoxygenated CH_2Cl_2 (0.40 M $[NBu^n{}_4][PF_6]$) (glove-box) with (a, b) GC and (c, d) Au electrodes at 295 K. *Black* data were obtained with freshly polished electrodes. Afterwards, 89 (*blue*) and then 219 Hz (*red*) data were obtained with same electrode. Potentials are referred to the midpoint potential for the $Fc^{0/+}$ process measured under d.c. voltammetric conditions relevant to Fig. S5.

Simulations based on the Butler-Volmer electron transfer model with charge transfer coefficients fixed at 0.50 and use of the DigiElch 7.F software package[4] unequivocally reveal that the d.c. and a.c. voltammetric data for oxidation of **5** cannot be mimicked by a model based on a simultaneous transfer of 2 electrons followed by irreversible chemical transformation of the generated $\mathbf{5}^{2+}$ dication species. In principle, simulations based on two consecutive one electron transfers and various scenarios (see, *e.g.* Schemes S1 and S2) involving chemical transformation of the oxidation products of **5** can acceptably reproduce the d.c. and low frequency (9 Hz) a.c. voltammetric behaviour (Fig. S8).

Scheme S1. Putative mechanism for oxidation of **5** *via* an 'EEC' reaction scheme



Scheme S2. Alternative putative mechanism for oxidation of **5** involving splitting following an initial one electron charge transfer process



However, the value of quantification of the voltammetric data for oxidation of **5** is severely restricted by lack of knowledge of the reversible potential (E^0) values and presence of adsorption. Nevertheless, heuristic simulation-experiment comparisons suggest that the heterogeneous electron transfer rate constant for the first electron transfer step is unlikely to exceed 10^{-2} cm s^{-1} and that E^0 for the first process is more positive than that for the second charge transfer by at least 0.10 V (Fig. S8 and Schemes S1 and S2). In summary, voltammetric oxidation of **5** proceeds *via* a complicated mechanism involving multiple charge transfer and chemical transformation steps as well as adsorption.

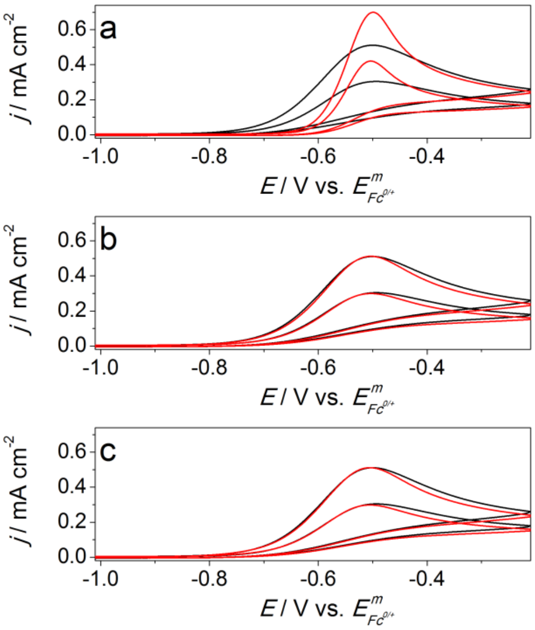


Figure S8. d.c. cyclic voltammograms (v = 0.10 V s^{-1}; two consecutive cycles) for oxidation of 1.7 mM **5** in dry and deoxygenated CH_2Cl_2 (0.40 [NBu^n_4][PF_6]) (N_2-filled glove-box) at 295 K with a GC electrode (*black*) and simulated data (*red*). Simulations are based on a Butler-Volmer model with all α = 0.50; two-dimensional diffusion model; diffusion coefficients, D(**5**) = D(**5**$^{+\bullet}$) = D(**5**$^{2+}$) = 5.0·10^{-6} cm^2 s^{-1}, D([$Mes_2N_2C_4H_7$]$^\bullet$) = D([$Mes_2N_2C_4H_7$]$^+$) = 1.0·10^{-5} cm^2 s^{-1}; electrode surface area, A = 0.067 cm^2; double-layer capacitance, C_{DL} = 40 μF cm^{-2}; uncompensated resistance, R_u = 260 Ω. Mechanism used in simulations is

(a) based on a simultaneous two electron oxidation of **5** (E^0 = -0.70 V; k^0 = 1.0·10^{-5} cm s^{-1}) to produce the dication **5**$^{2+}$, which is irreversibly converted to the electrochemically inactive product *via* the first order chemical reaction (equilibrium constant, K = 1.0·10^5; forward rate constant, k^f = 1.0·10^2 s^{-1});

(b) shown in Scheme S1; the relevant parameters are: E^0_1 = -0.73 V, E^0_3 = -1.0 V, k^0_1 = k^0_2 = 1.0·10^{-4} cm s^{-1}, k^f_3 = 1.0·10^3 s^{-1}, K_3 = 1.0·10^5;

(c) shown in Scheme S2; the relevant parameters are: E^0_1 = -0.65 V, E^0_2 = -0.80 V, k^0_1 = 5.0·10^{-4} cm s^{-1}, k^0_3 = 1.0·10^{-1} cm s^{-1}, k^f_2 = 1.0·10^5 s^{-1}, K_2 = 1.0·10^5, k^f_4 = 1.0·10^1 s^{-1}, K_4 = 1.0·10^5.

3. References

(1) A. M. Bond, N. W. Duffy, S.-X. Guo, J. Zhang, D. Elton, *Anal. Chem.*, 2005, **77**, 186A-195A.

(2) A. N. Simonov, P. Kemppinen, C. Pozo-Gonzalo, J. F. Boas, A. Bilic, A. D. Scully, A. Attia, A. Nafady, E. A. Mashkina, K. N. Winzenberg, S. E. Watkins, A. M. Bond, *J. Phys. Chem. B*, 2014, **118**, 6839−6849.

(3) A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications.* 2nd Edition; John Wiley & Sons, Inc.: New York, USA, 2001.

(4) http://www.elchsoft.com.