To Invert or Not To Invert – Reasons for the Occurrence of Normal and Inverted Formal Potentials in Molecular Multi-Electron Transfer Systems

Bernd Speiser

Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18,

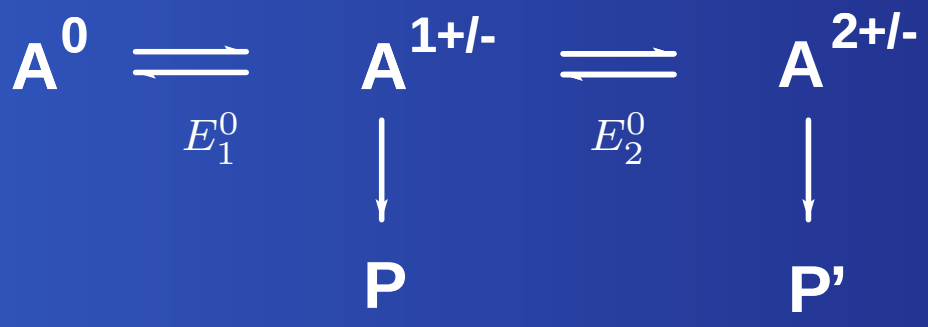
D–72076 Tübingen, Germany

bernd.speiser@uni-tuebingen.de

Multi-Electron Transfers: Examples

- basic research:
  - thermodynamics and kinetics
  - mechanisms
- natural processes:
  - redox enzymes
  - photosynthesis
  - nitrogen fixation (nitrogenase and model systems)
- technical applications:
  - catalysis
  - fuel cells

Two-Electron Transfers and Dis/Comproportionation



disproportionation/comproportionation:

$$K_{\mathrm{disp}} = \frac{[\mathrm{A}^{0}][\mathrm{A}^{2+/-}]}{[\mathrm{A}^{1+/-}]^{2}} = \exp[-\frac{F}{RT}|\Delta E^{0}|]$$

$$|\Delta E^{0}| = \begin{cases} E_2^0 - E_1^0 & \text{for oxidation} \\ -(E_2^0 - E_1^0) & \text{for reduction} \end{cases}$$

Normal and Inverted Potential Ordering

- expected potential difference between two successive electron transfers: several volts
- solvation effects $\longrightarrow$ several 100 mV
- 2nd electron transfer more difficult: **normal** potential ordering
- $\longrightarrow$ equilibrium on side of $A^{1+/-}$
- $\longrightarrow$ $A^{1+/-}$ stable against disproportionation

Normal and Inverted Potential Ordering

- expected potential difference between two successive electron transfers: several volts
- solvation effects $\longrightarrow$ several 100 mV
- 2nd electron transfer more difficult: **normal** potential ordering
- $\longrightarrow$ equilibrium on side of $A^{1+/-}$
- $\longrightarrow$ $A^{1+/-}$ stable against disproportionation

- $\longrightarrow$ 2nd electron transfer more easy: **inverted** potential ordering (Evans)
- $\longrightarrow$ equilibrium on side of A^{0} and $A^{2+/-}$
- $\longrightarrow$ $A^{1+/-}$ unstable against disproportionation
- structural changes during electron transfer?

Normal and Inverted Potential Ordering

- expected potential difference between two successive electron transfers: several volts
- solvation effects $\longrightarrow$ several 100 mV
- 2nd electron transfer more difficult: **normal** potential ordering
- $\longrightarrow$ equilibrium on side of $A^{1+/-}$
- $\longrightarrow$ $A^{1+/-}$ stable against disproportionation

- $\longrightarrow$ 2nd electron transfer more easy: **inverted** potential ordering (Evans)
- $\longrightarrow$ equilibrium on side of A^{0} and $A^{2+/-}$
- $\longrightarrow$ $A^{1+/-}$ unstable against disproportionation
- structural changes during electron transfer?

"a many-facetted mechanism" (Heinze)
cyclic voltammetry as analytical technique

Multi-Electron Transfer: Examples and Some Systematics

- examples from
  - organic (sterically hindered anilines, hexaaminobenzenes, hexathiobenzenes, meso-ionic dithiocarboxylates)
  - organometallic (Ru(arene) complexes, fc-substituted silsesquioxanes)
  - inorganic (boron subhalides)

  chemistry
- electrons are transferred to
  - single redox center ($= 1$ electroactive group)
  - complex redox center

    (> 1 electroactive groups) $\left\{ \begin{array}{l} \text{fully delocalized} \\ \text{conjugated with some separation} \end{array} \right.$
  - multiple redox centers (> 1 electroactive groups)

Multi-Electron Transfer: Examples and Some Systematics

- examples from
  - organic (sterically hindered anilines, hexaaminobenzenes, hexathiobenzenes, meso-ionic dithiocarboxylates)
  - organometallic (Ru(arene) complexes, fc-substituted silsesquioxanes)
  - inorganic (boron subhalides)

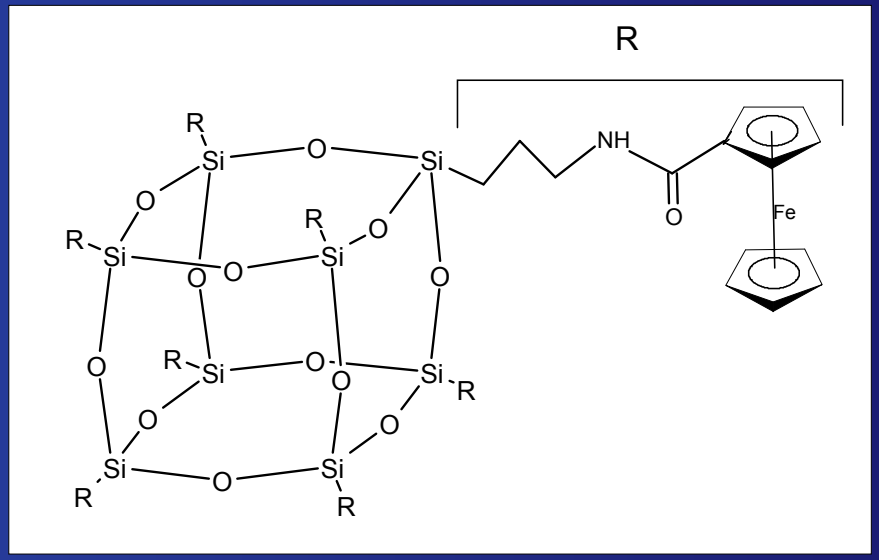
  chemistry
- electrons are transferred to
  - single redox center ($= 1$ electroactive group)
  - complex redox center

    (> 1 electroactive groups) { fully delocalized / conjugated with some separation }
  - multiple redox centers (> 1 electroactive groups)

"interaction"

An Octa-Ferrocenyl Silsesquioxane — Structure

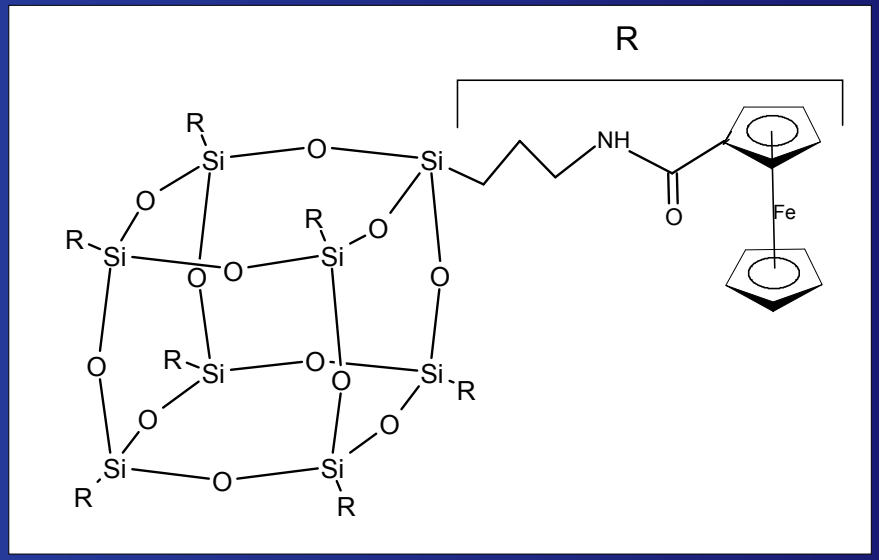
- cage compound
- cube as core structural element
- redox-active centers bound by Si-C linker



synthesis: D. Ruiz Abad and H.A. Mayer

An Octa-Ferrocenyl Silsesquioxane — Structure

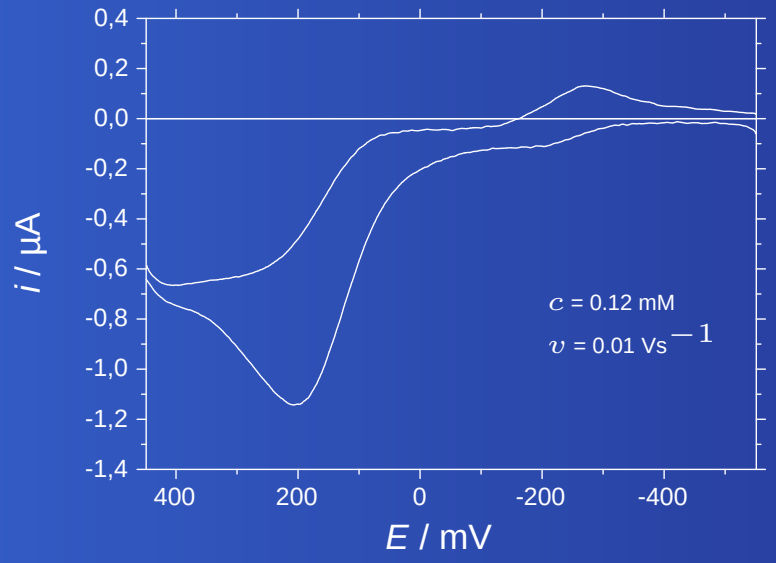
- cage compound
- cube as core structural element
- redox-active centers bound by Si-C linker

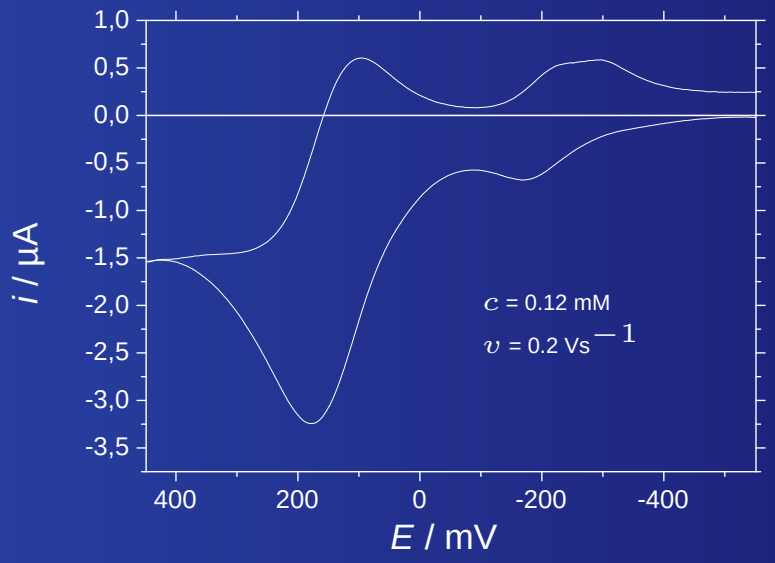


synthesis: D. Ruiz Abad and H.A. Mayer

model compound for redox-actively modified silica nanoparticles

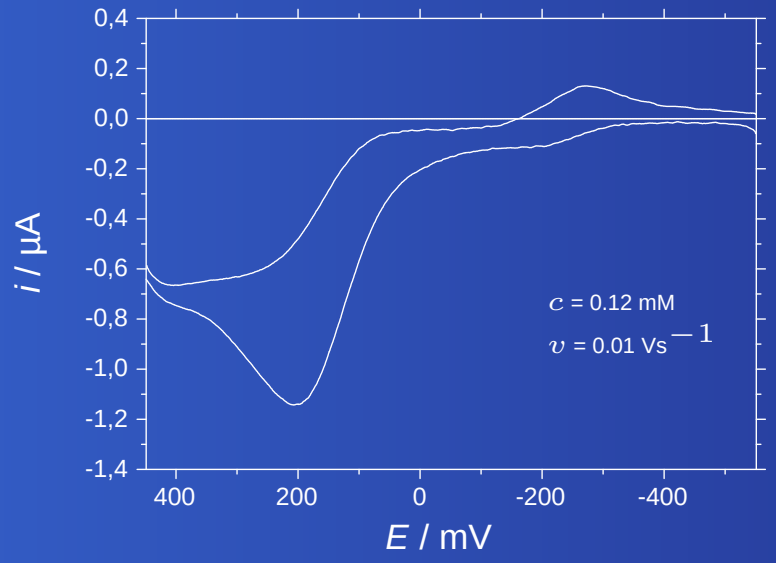
An Octa-Ferrocenyl Silsesquioxane — Cyclic Voltammetry

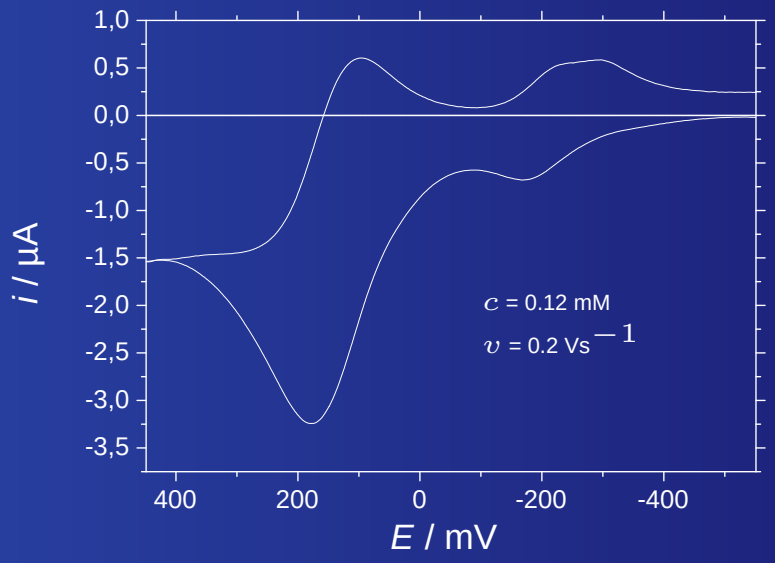




DMSO/0.1 M NBu_4PF_6; Pt electrode

An Octa-Ferrocenyl Silsesquioxane — Cyclic Voltammetry

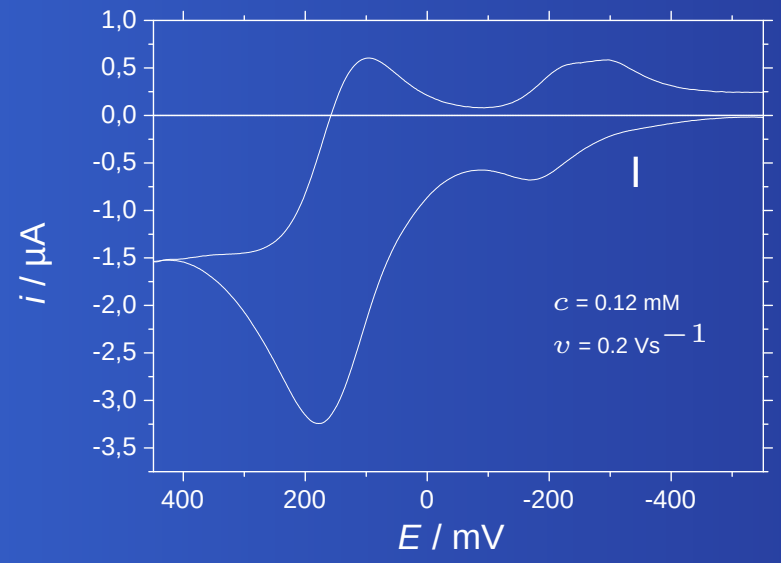




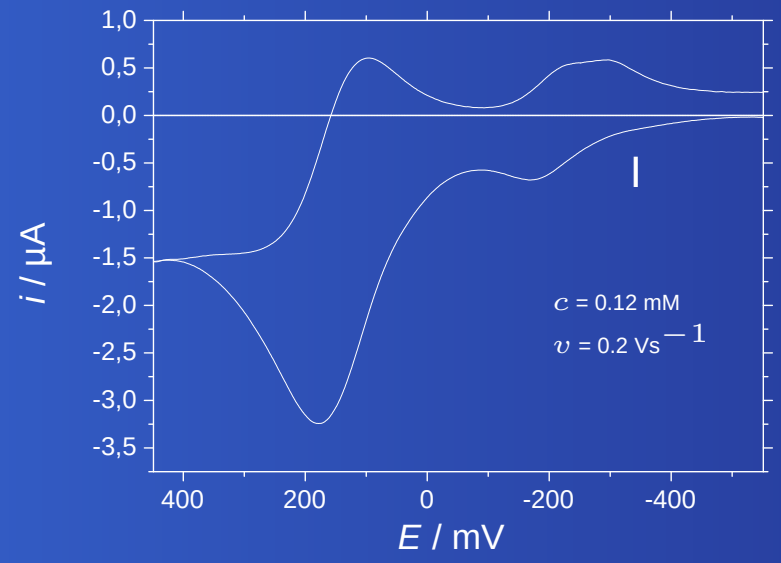
- two redox signals
- follow-up reaction at small υ

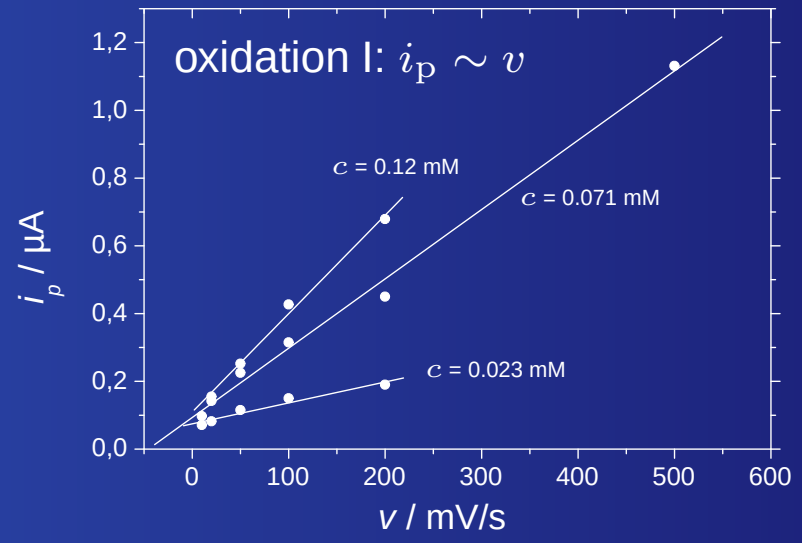
DMSO/0.1 M NBu_4PF_6; Pt electrode

An Octa-Ferrocenyl Silsesquioxane — Cyclic Voltammetry, Analysis



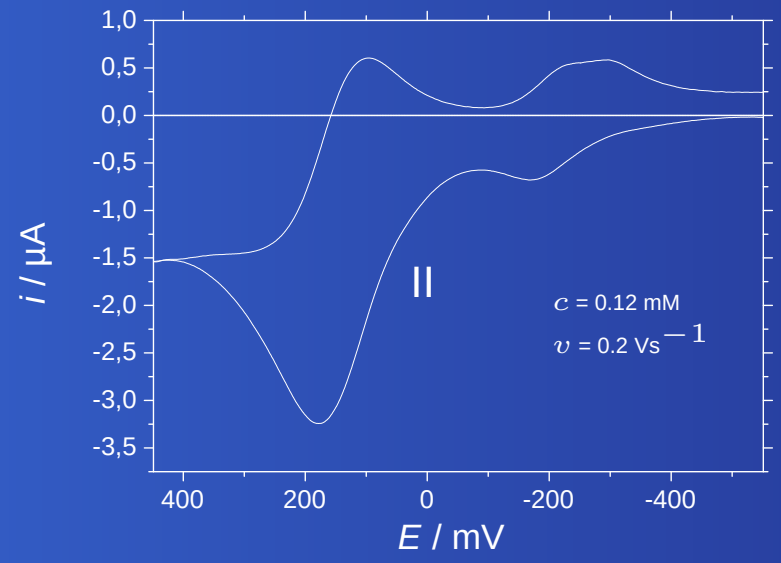
An Octa-Ferrocenyl Silsesquioxane — Cyclic Voltammetry, Analysis





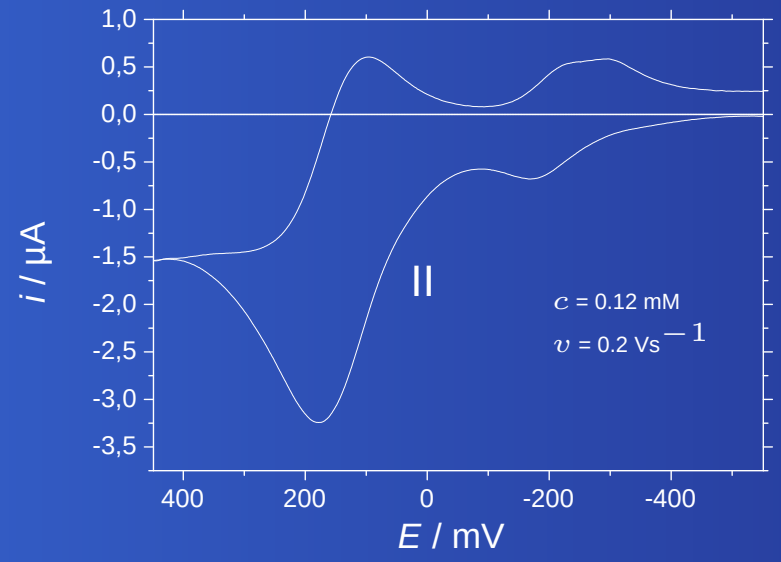
- oxidation I: adsorbed species

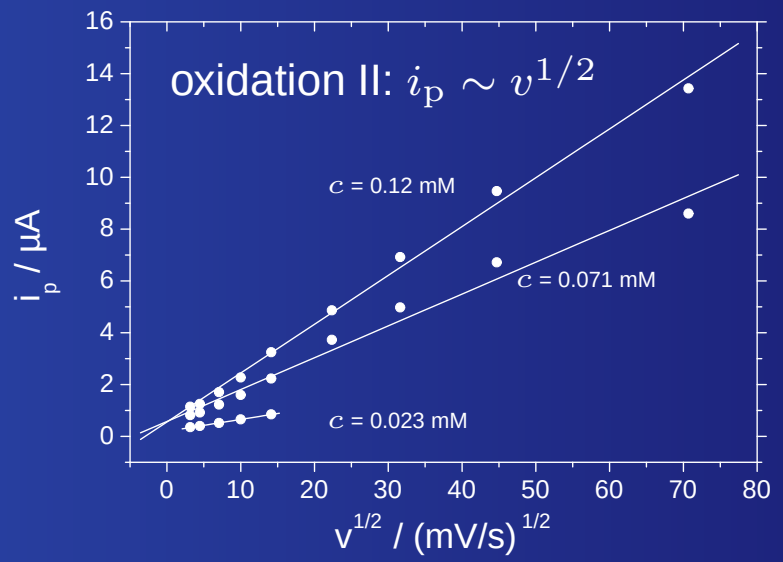
An Octa-Ferrocenyl Silsesquioxane — Cyclic Voltammetry, Analysis



- oxidation I: adsorbed species

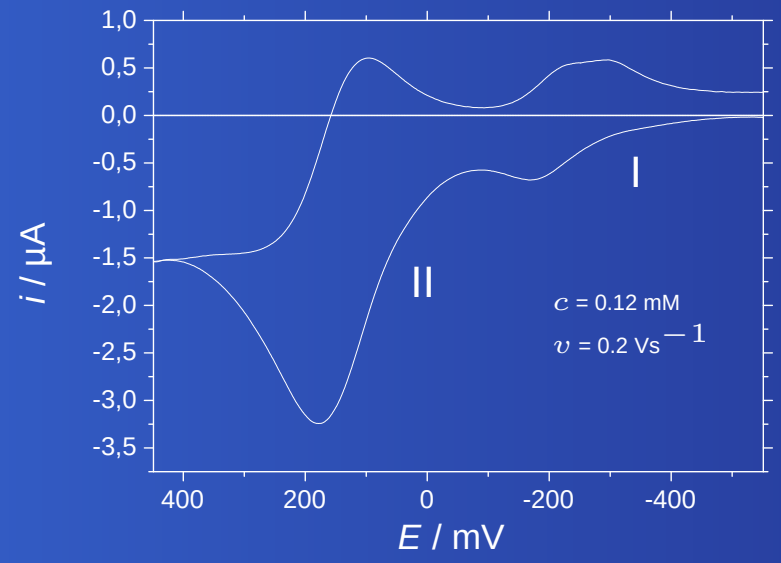
An Octa-Ferrocenyl Silsesquioxane — Cyclic Voltammetry, Analysis





- oxidation I: adsorbed species
- oxidation II: diffusing species

An Octa-Ferrocenyl Silsesquioxane — Cyclic Voltammetry, Analysis



- oxidation I: adsorbed species
- oxidation II: diffusing species

oxidation II –

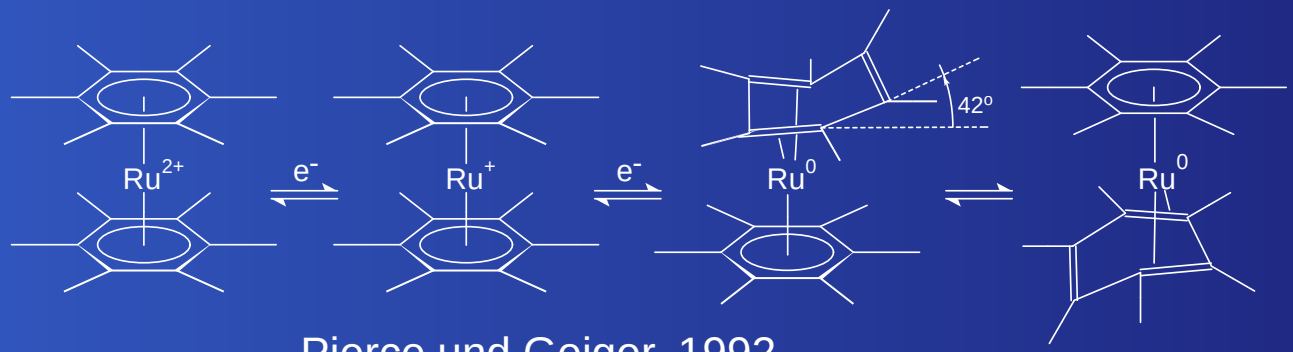
signal shape and ΔE_{p}: 1 e^-
resulting D is much too large
assumption: $n = 8$, similar E^0

$\longrightarrow D \approx 1.1 \times 10^{-7}$ cm^2s^{-1} scales with molecular weight as compared to Fc

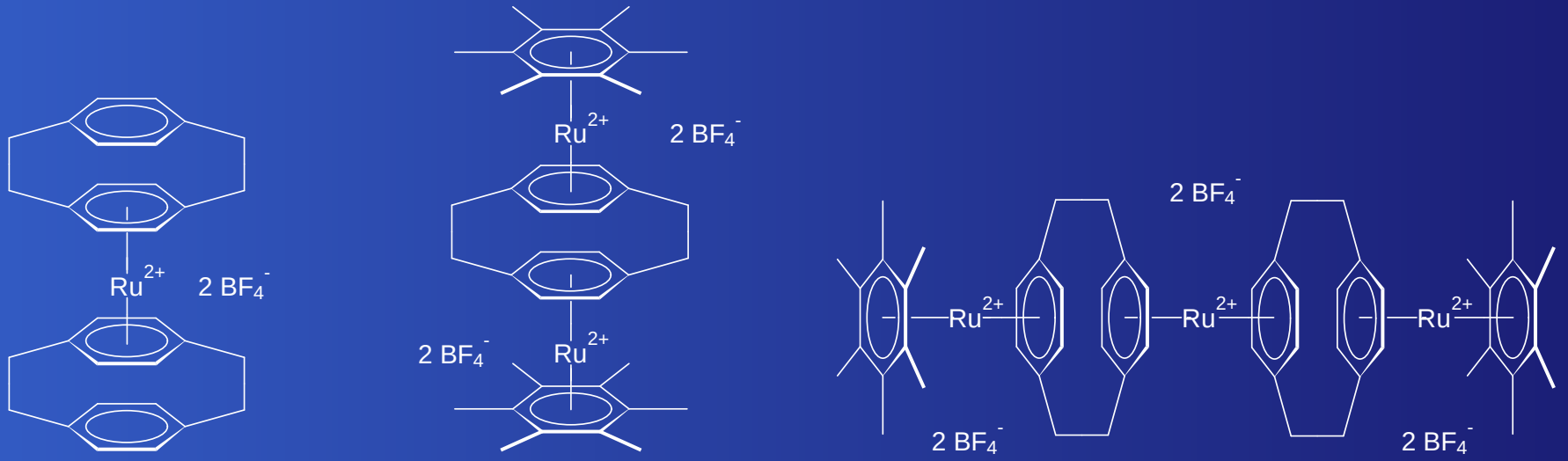
An Octa-Ferrocenyl Silsesquioxane — Multi-Electron Transfer

- eight electrons transferred independently
- equal (or at least very similar) formal potential
- example of separated, non-interacting redox centers

Ruthenium Complexes with Arene Ligands

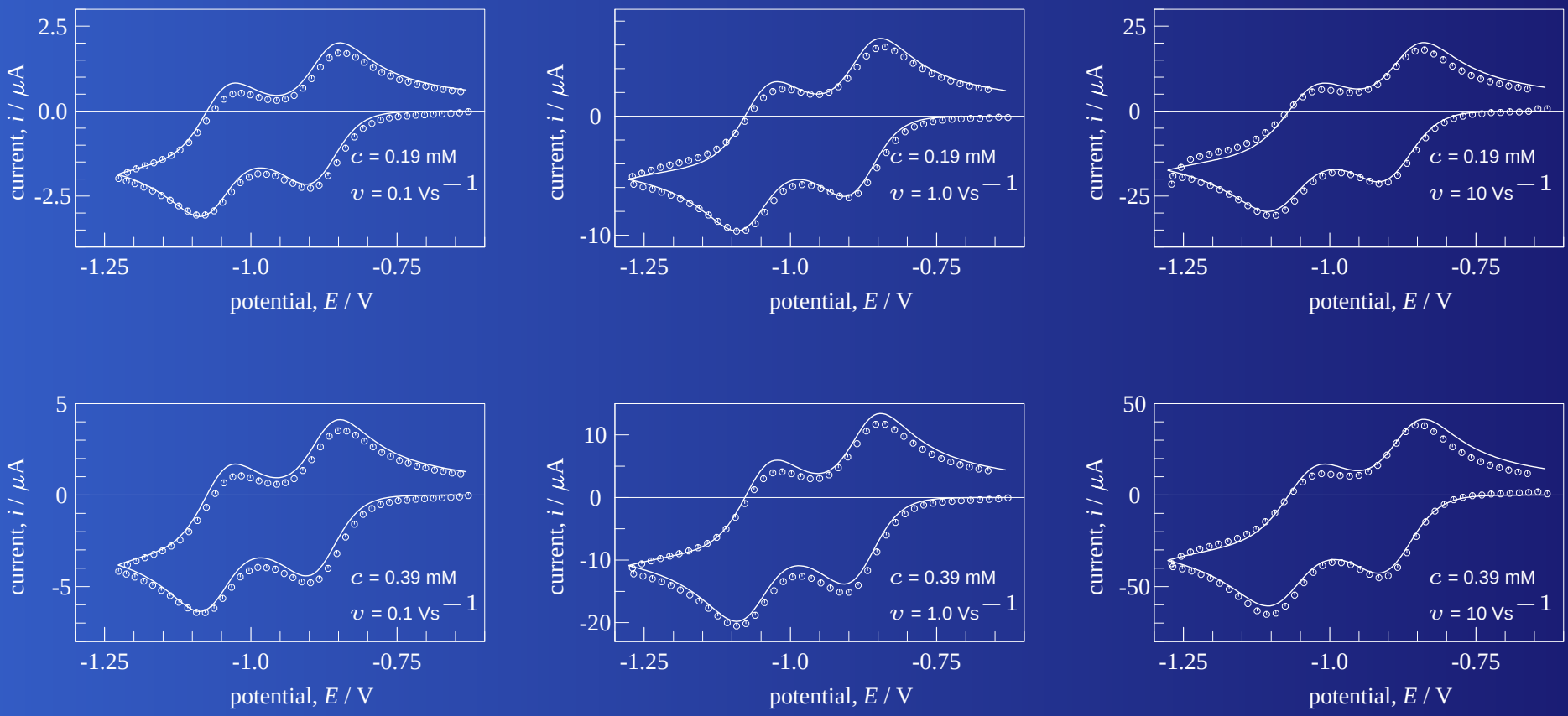


Pierce und Geiger, 1992



Boekelheide et al., 1982 – 1986

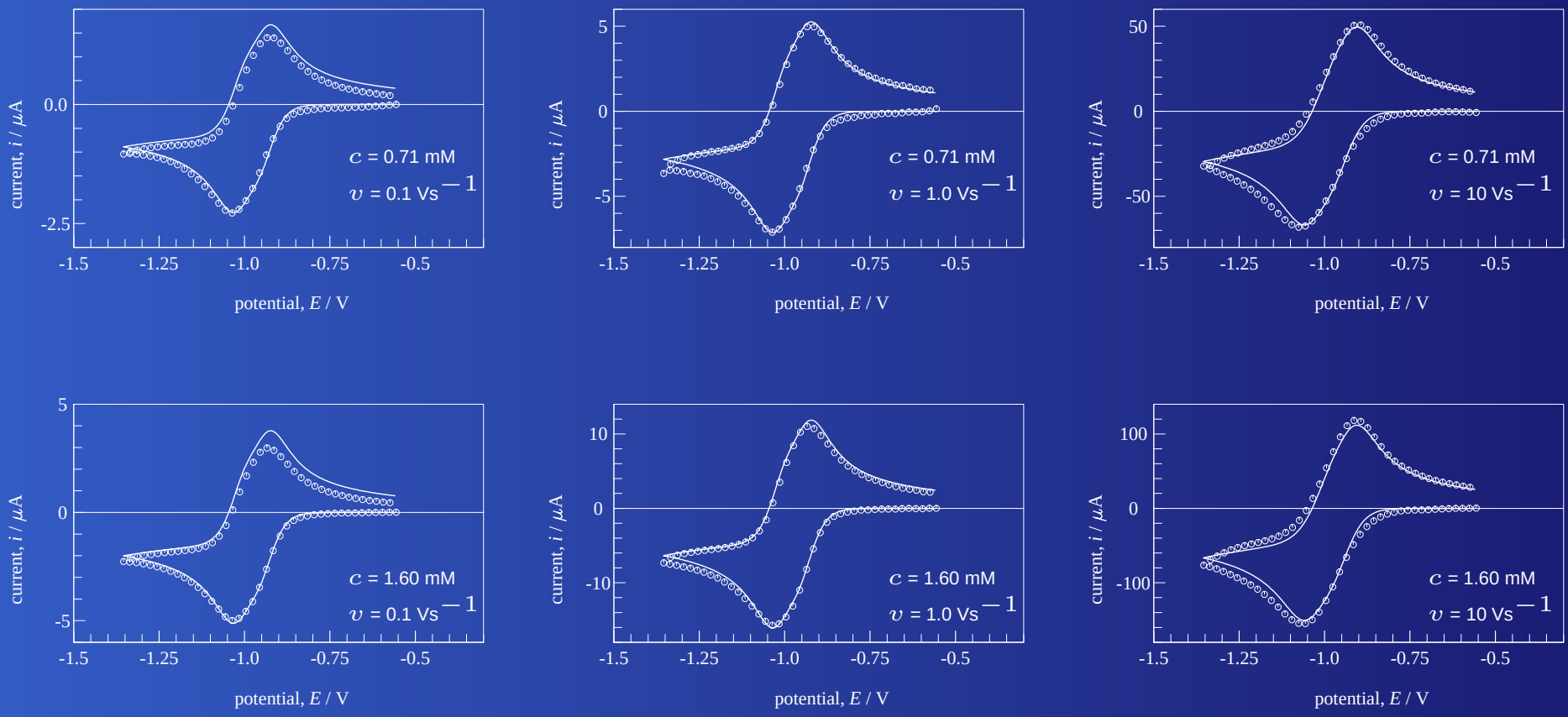
Cyclic Voltammetry of Bis([2$_2$]paracyclophane)Ru(II) in CH_2Cl_2



CH_2Cl_2/0.1 M NBu_4PF_6; GC electrode; circles: experiment, line: simulation

$E_1^0 = -0.875$ V, $E_2^0 = -1.060$ V, $k_{s1} = 0.077$ cm/s, $k_{s2} = 0.041$ cm/s

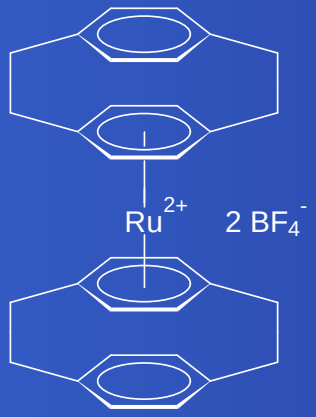
Cyclic Voltammetry of Bis([2_2]paracyclophane)Ru(II) in PC



propylene carbonate/0.1 M NBu_4PF_6; GC electrode

$E_1^0 = -0.938$ V, $E_2^0 = -1.015$ V, $k_{s1} = 0.018$ cm/s, $k_{s2} = 0.012$ cm/s

Cyclic Voltammetry of Bis([2_2]paracyclophane)Ru(II) – Comparison

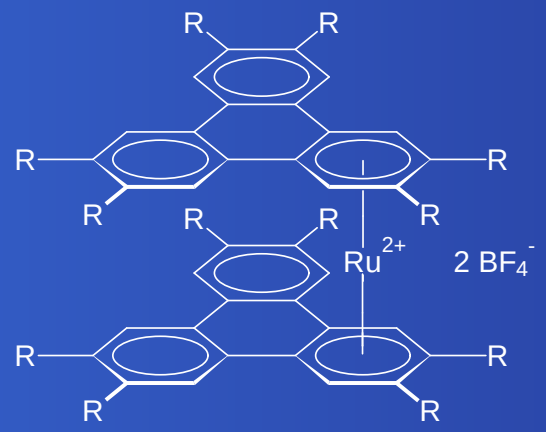


	propylene carbonate	dichloromethan
$E_1^0 =$	-0.938 V	-0.875 V
$E_2^0 =$	-1.015 V	-1.060 V
$k_{s1} =$	0.018 cm s^{-1}	0.077 cm s^{-1}
$k_{s2} =$	0.012 cm s^{-1}	0.041 cm s^{-1}

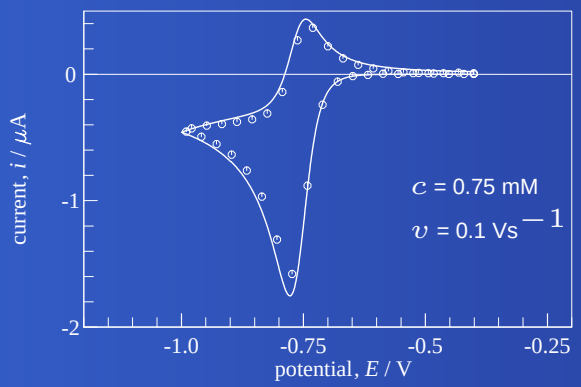
- “normal” potential ordering
- $|\Delta E^0|$ in CH_2Cl_2 larger than in PC $\longrightarrow$ peak splitting
- 1st electron transfer faster than 2nd
- electron transfer in CH_2Cl_2 four times faster than in PC $\longrightarrow$ effect of τ_L (Marcus theory)

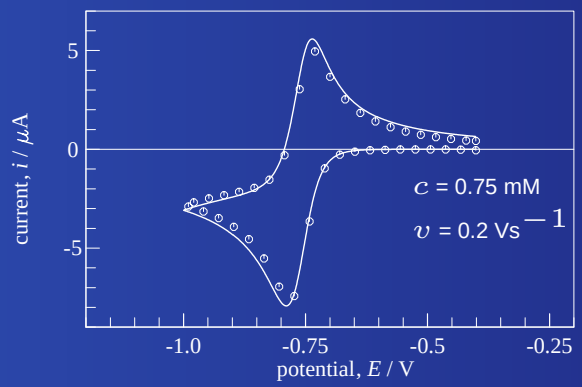
solvent effect on kinetics and thermodynamics of electron transfers

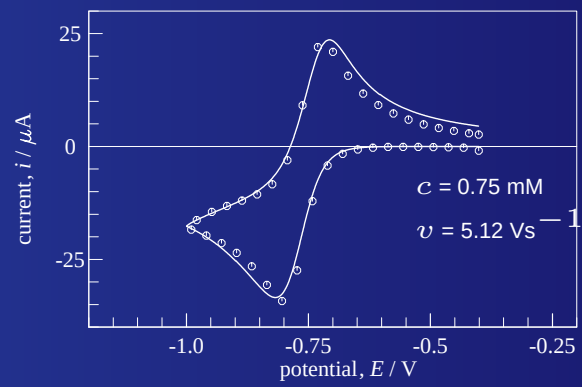
Bis(η^6-triphenylene)Ru(II)

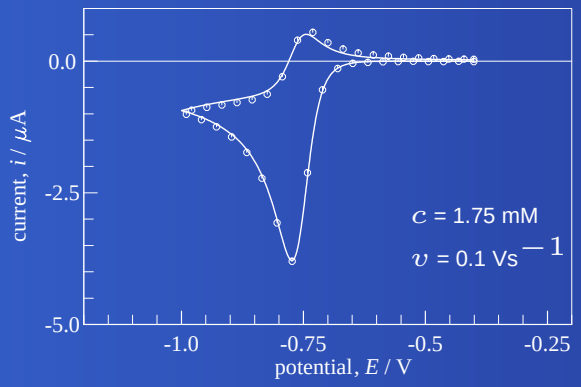


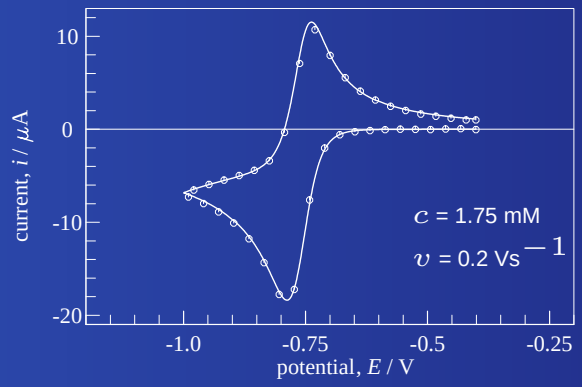
Cyclic Voltammetry of Bis(η^6-triphenylene)Ru(II) in PC

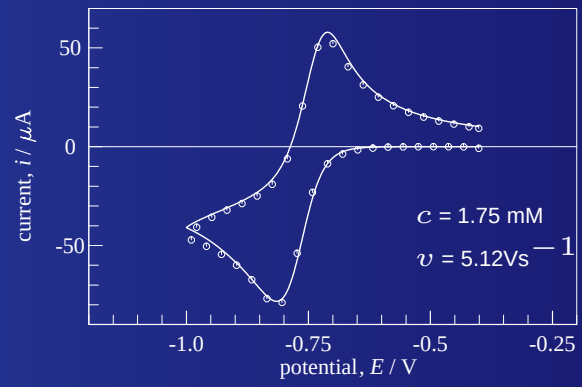






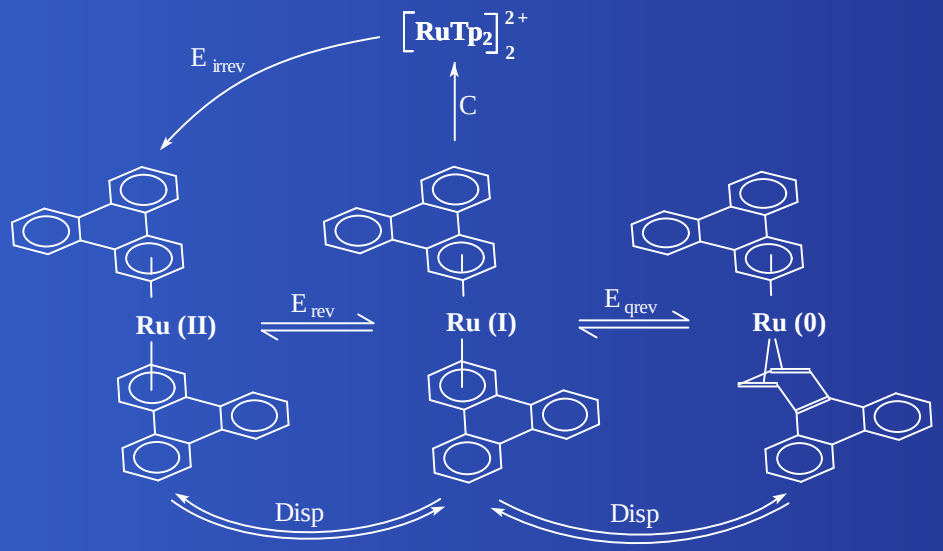






propylene carbonate/0.1 M NBu_4PF_6; GC electrode

Reduction Mechanism of Bis(η^6-triphenylene)Ru(II) in PC



$k_\mathrm{s}(\mathrm{II/I}) = 0.019$ cm s^{-1}
$\alpha(\mathrm{II/I}) = 0.5$
$k_\mathrm{s}(\mathrm{I/0}) = 0.002$ cm s^{-1}
$\alpha(\mathrm{I/0}) = 0.5$
$E^0(\mathrm{II/I}) = -0.775$ V
$E^0(\mathrm{I/0}) = -0.754$ V
$K_\mathrm{disp} = 2.195$
$k_{\mathrm{f,disp}} = 2.26 \times 10^6$ M^{-1}s^{-1}
$k_\mathrm{C} = 840$ M^{-1}s^{-1}

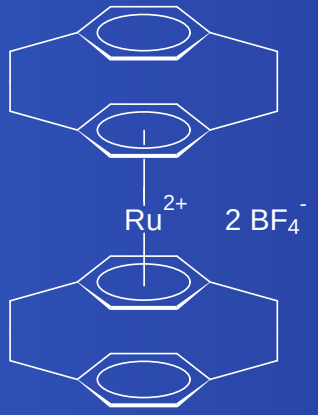
potential inversion by $\approx$ 20 mV

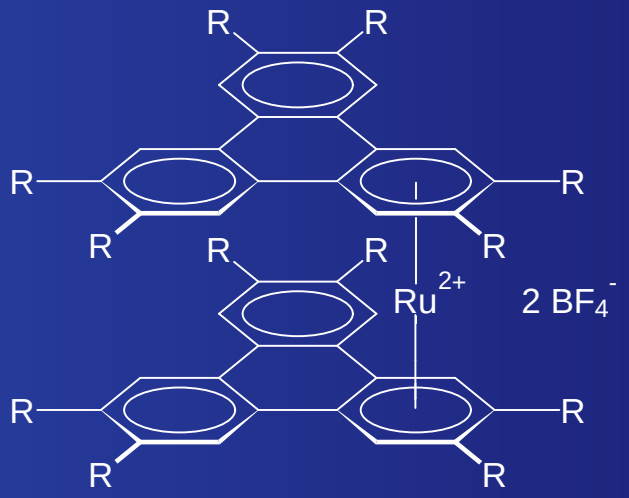
2nd electron transfer very slow

Two-Electron Reduction of Ru-Complexes in Comparison

differences:

- “inverted” potential ordering for triphenylene complex
- 2nd electron transfer slower for triphenylene complex by factor 10

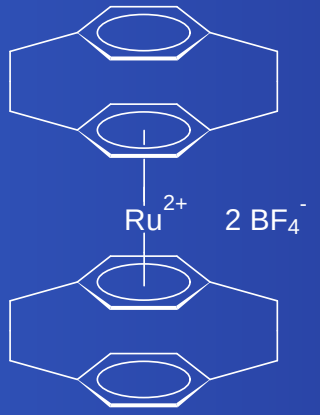


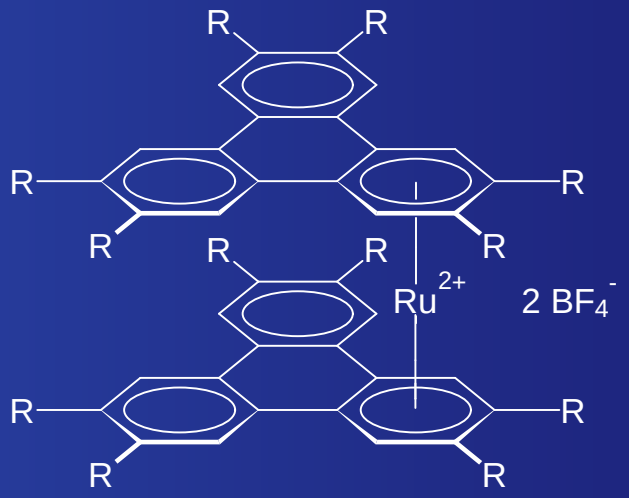


Two-Electron Reduction of Ru-Complexes in Comparison

differences:

- “inverted” potential ordering for triphenylene complex
- 2nd electron transfer slower for triphenylene complex by factor 10



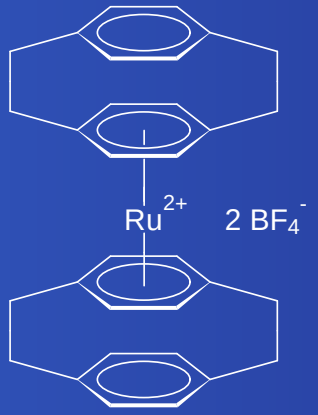


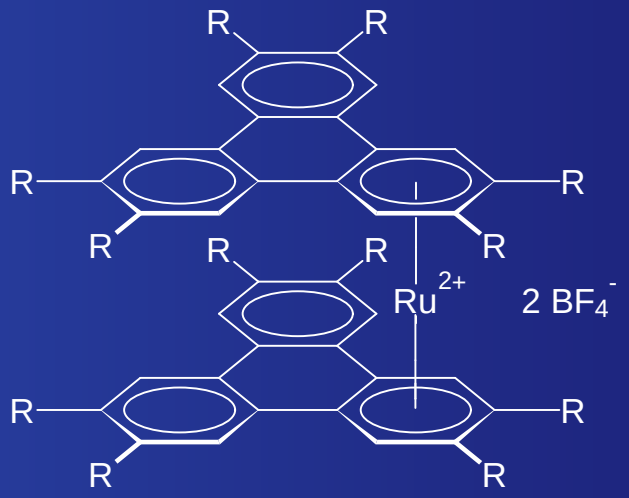
change of hapticity $\eta^6 \longrightarrow \eta^4$

Two-Electron Reduction of Ru-Complexes in Comparison

differences:

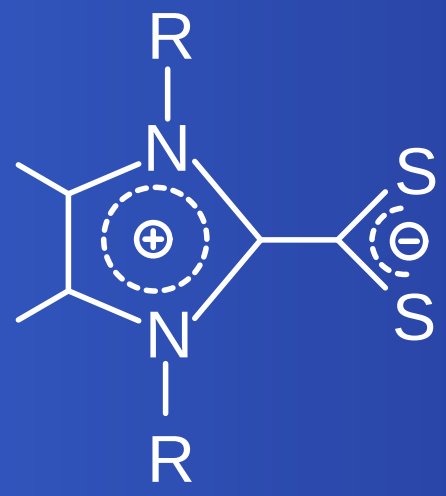
- “inverted” potential ordering for triphenylene complex
- 2nd electron transfer slower for triphenylene complex by factor 10





structural distortion of aromatic rings in triphenylene complex more difficult

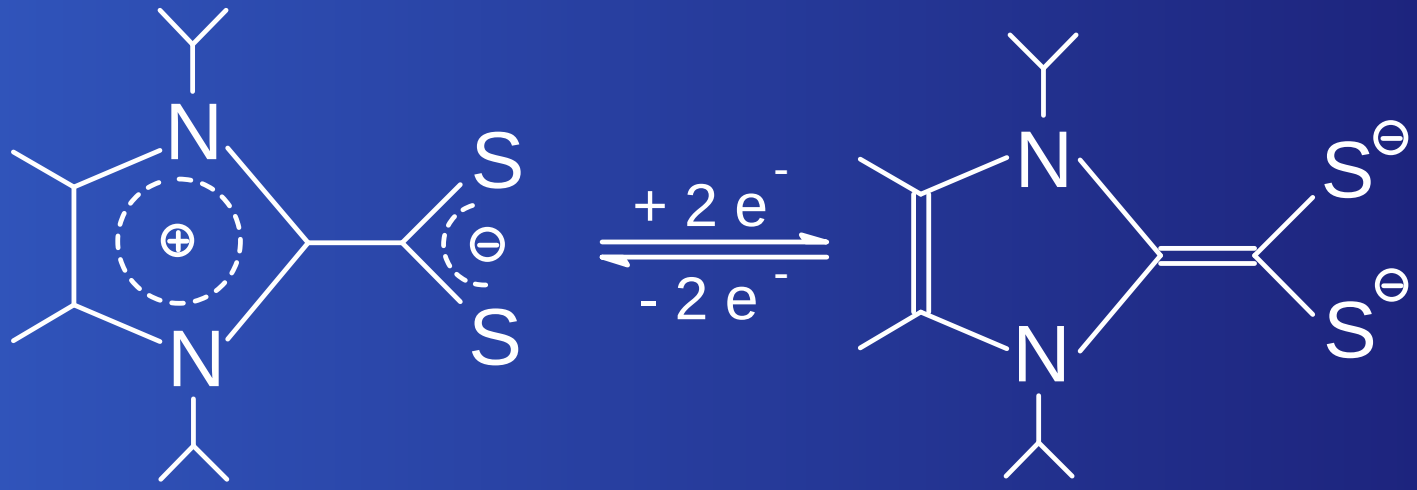
Imidazolium-2-dithiocarboxylates: Synthesis



R = CH_3
R = C_2H_5
R = i-C_3H_7

synthesis from carbene and CS_2: N. Kuhn et al., Z. Naturf. *49b*, 1473 – 1480 (1994)

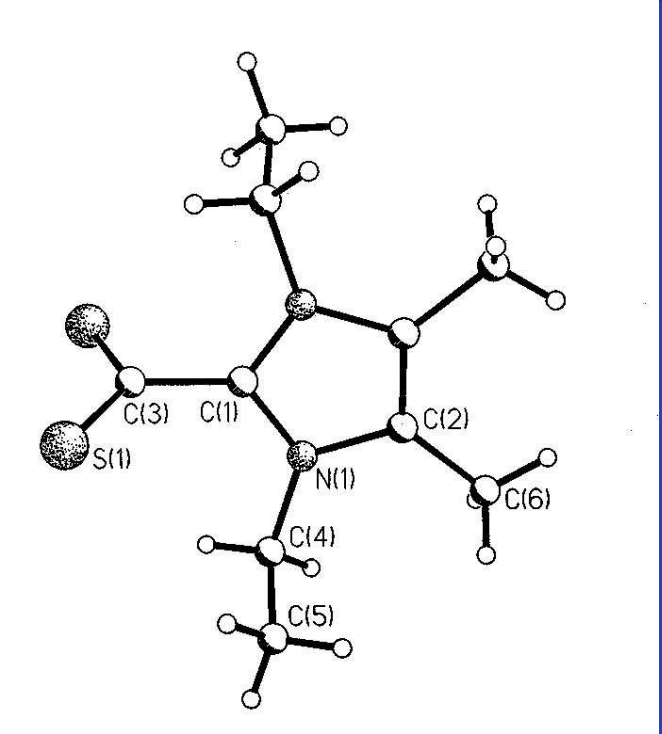
Imidazolium-2-dithiocarboxylates: Chemical Reduction



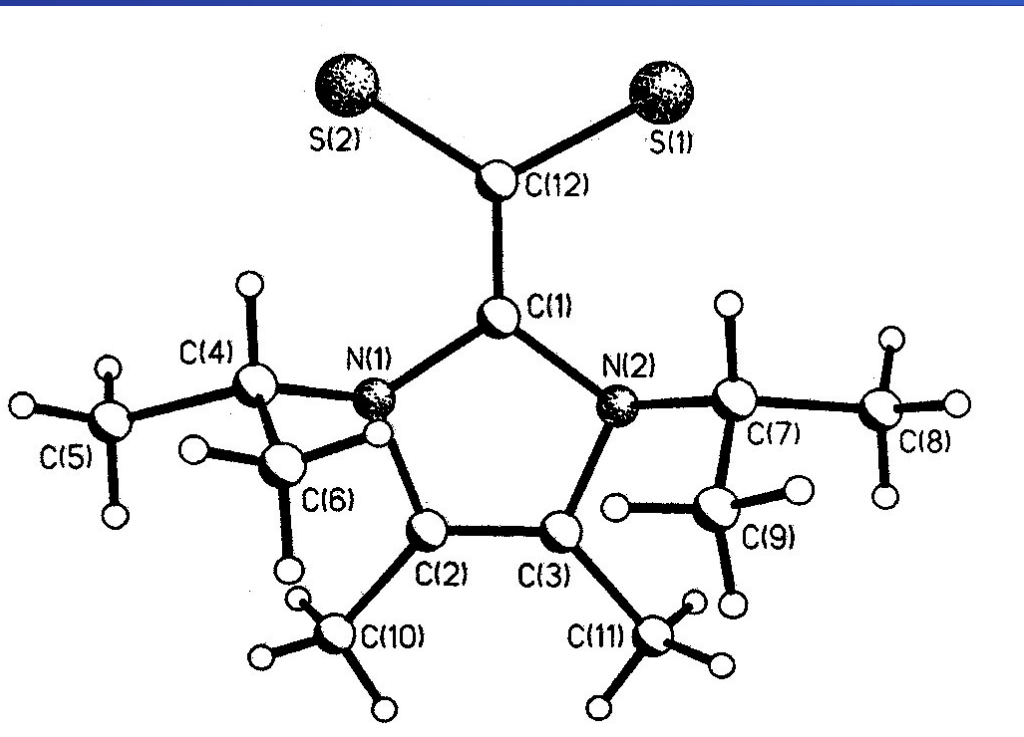
reducing agent potassium:

N. Kuhn et al., J. Chem. Soc. Chem. Commun. *1997*, 627 – 628

Imidazolium-2-dithiocarboxylates: Structures



neutral molecule: N. Kuhn et al., J. Chem. Soc. Chem. Commun. *1997*, 627 – 628

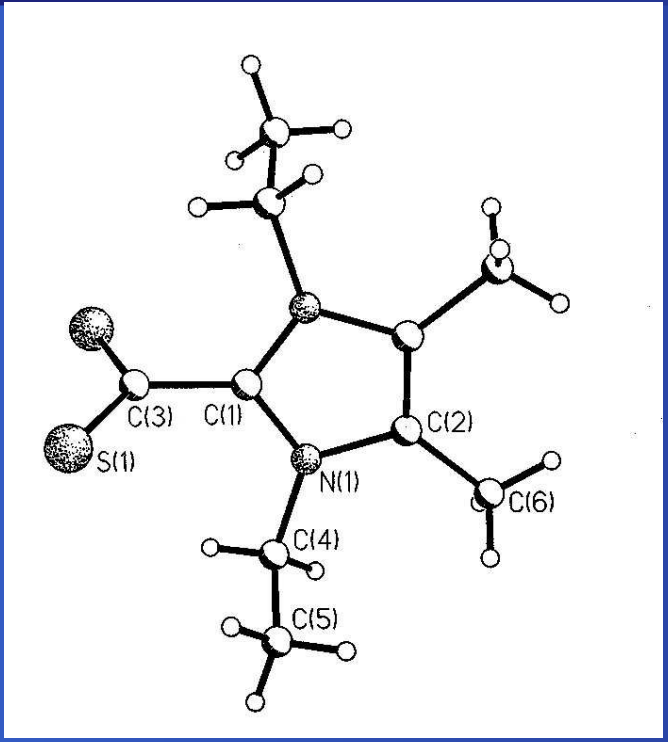


dianion: N. Kuhn et al., Z. Naturf. *49b*, 1473 – 1480 (1994)

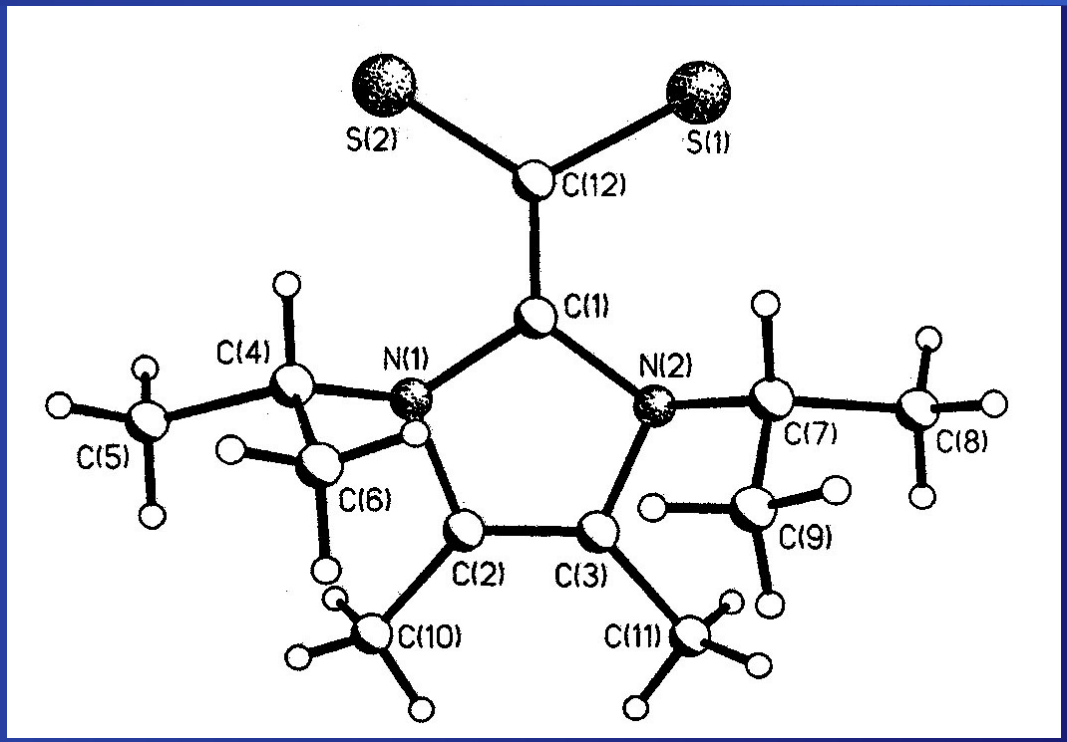
orthogonal

planar

Imidazolium-2-dithiocarboxylates: Structures



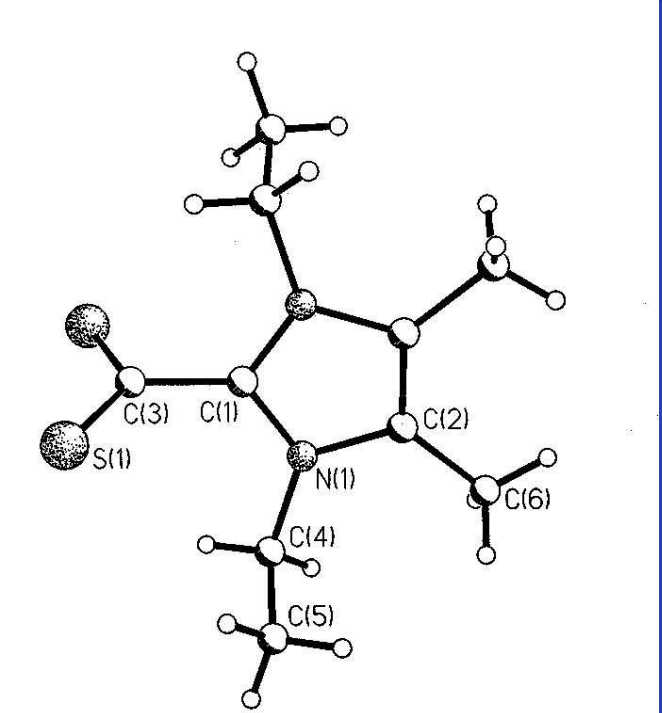
neutral molecule: N. Kuhn et al., J. Chem. Soc. Chem. Commun. *1997*, 627 – 628



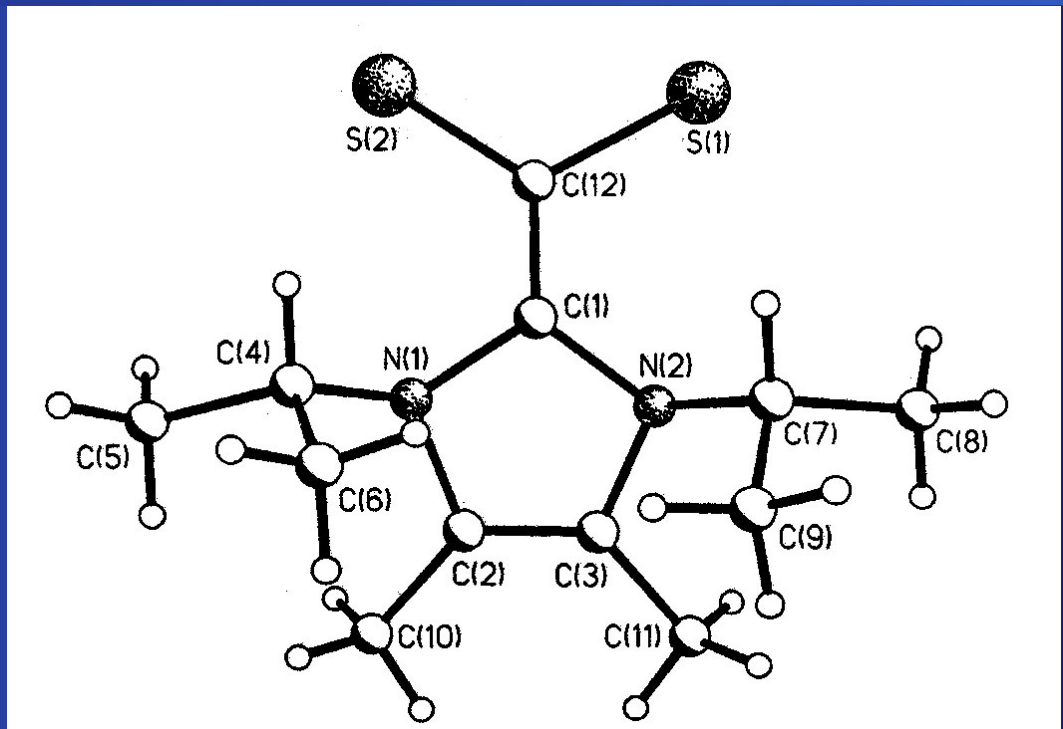
dianion: N. Kuhn et al., Z. Naturf. *49b*, 1473 – 1480 (1994)

electrochemical reduction?

Imidazolium-2-dithiocarboxylates: Structures



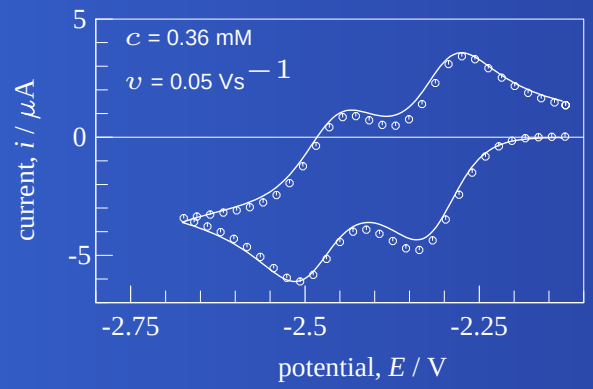
neutral molecule: N. Kuhn et al., J. Chem. Soc. Chem. Commun. *1997*, 627 – 628

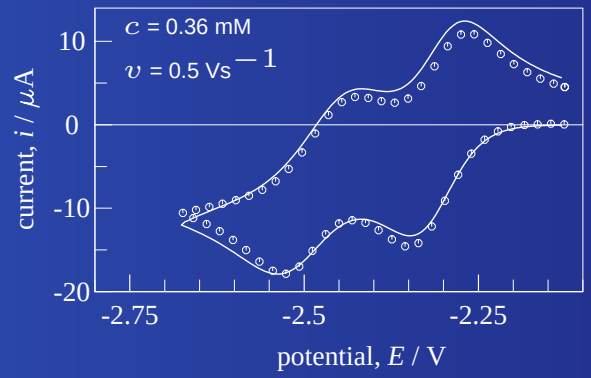


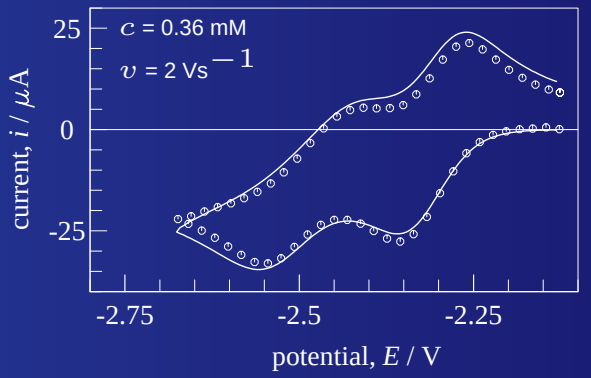
dianion: N. Kuhn et al., Z. Naturf. *49b*, 1473 – 1480 (1994)

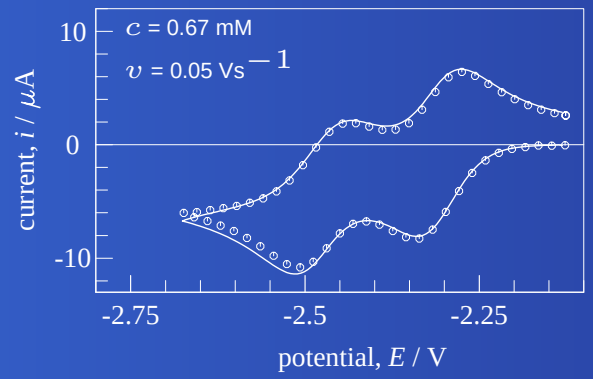
cyclic voltammetry as analytical technique

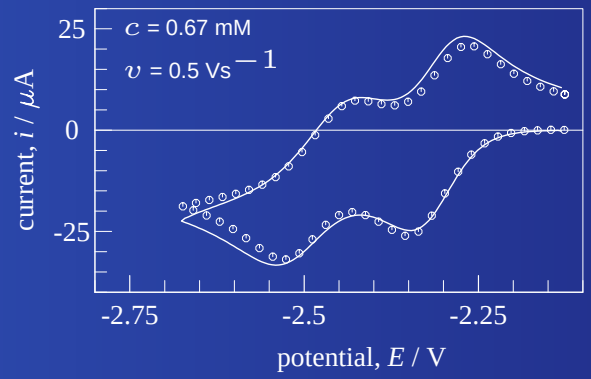
Cyclic Voltammetry of 1,3-Dimethyldithiocarboxylate

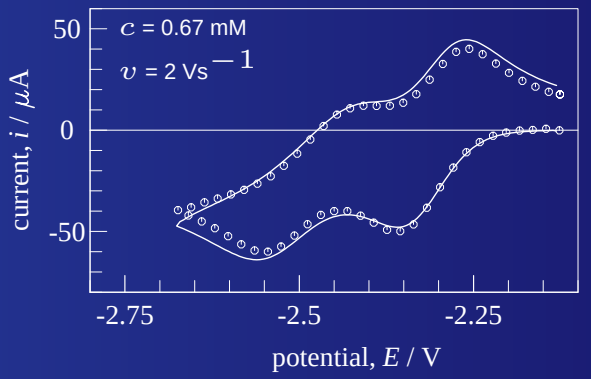






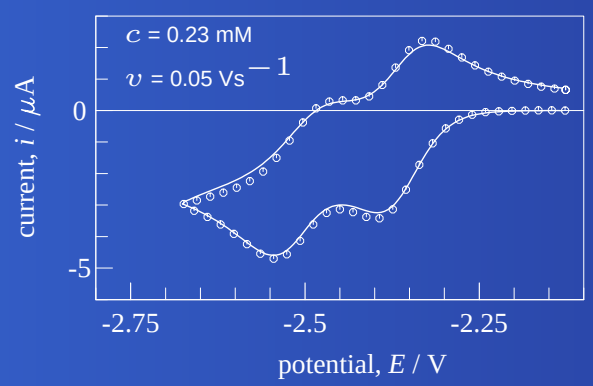


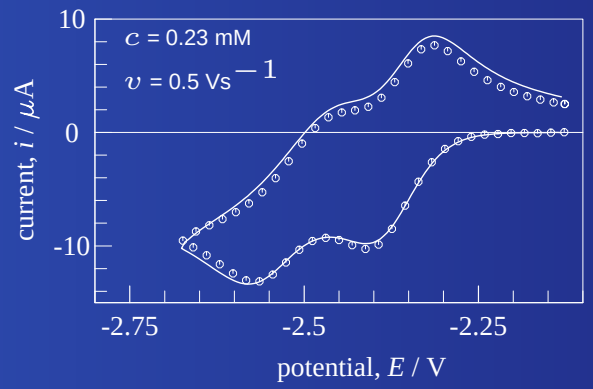


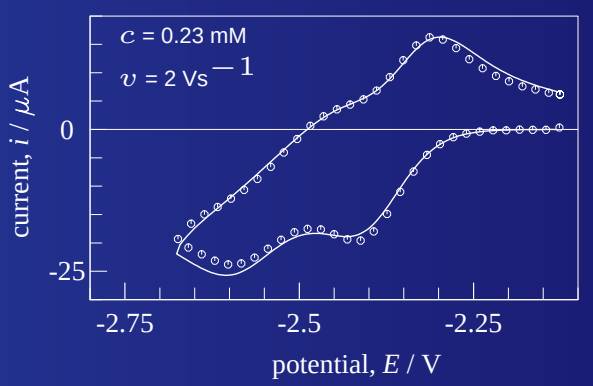


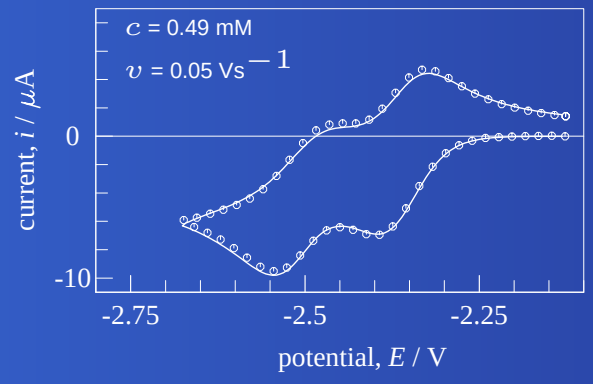
THF/0.2 M NBu_4PF_6; GC electrode

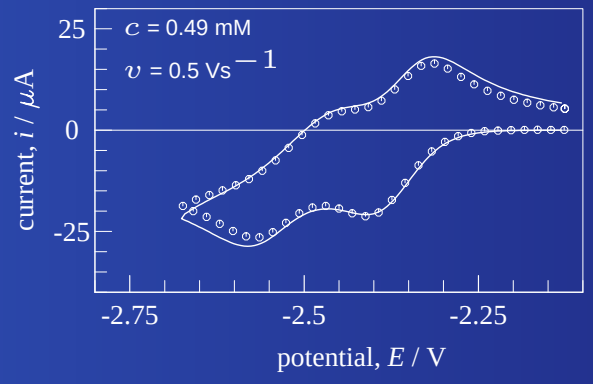
Cyclic Voltammetry of 1,3-Diethyldithiocarboxylate

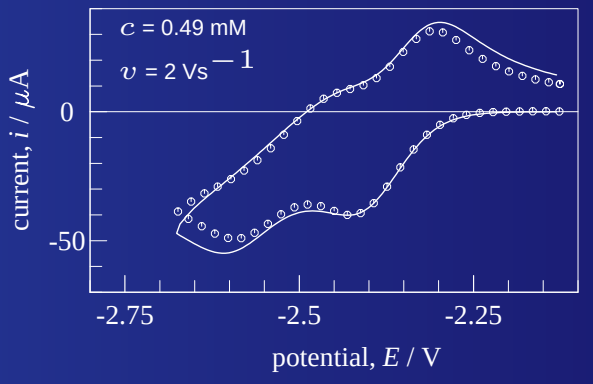






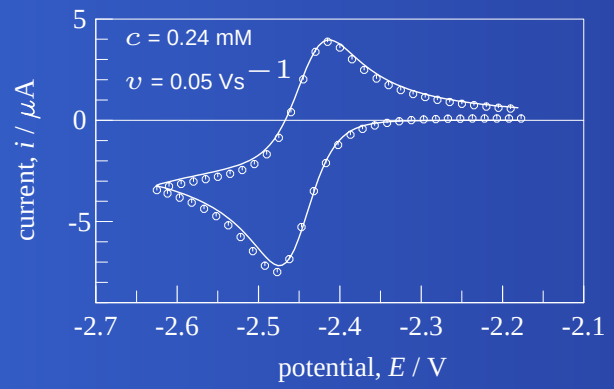


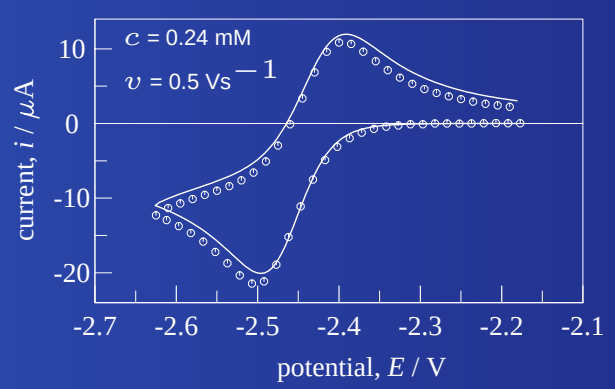


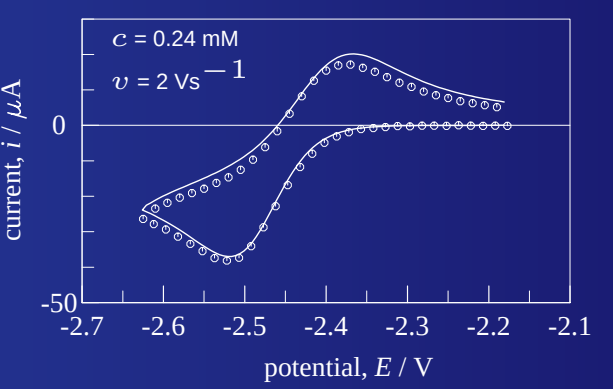


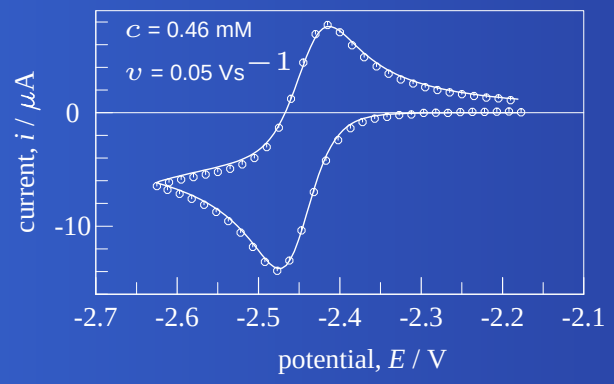
THF/0.2 M NBu_4PF_6; GC electrode

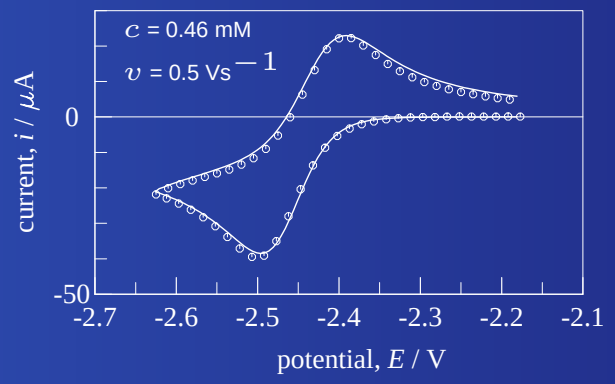
Cyclic Voltammetry of 1,3-Diisopropyldithiocarboxylate

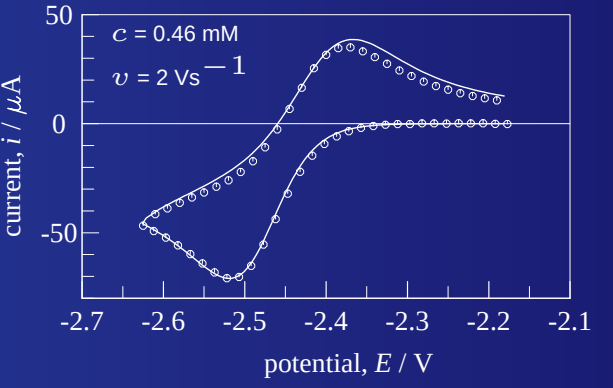






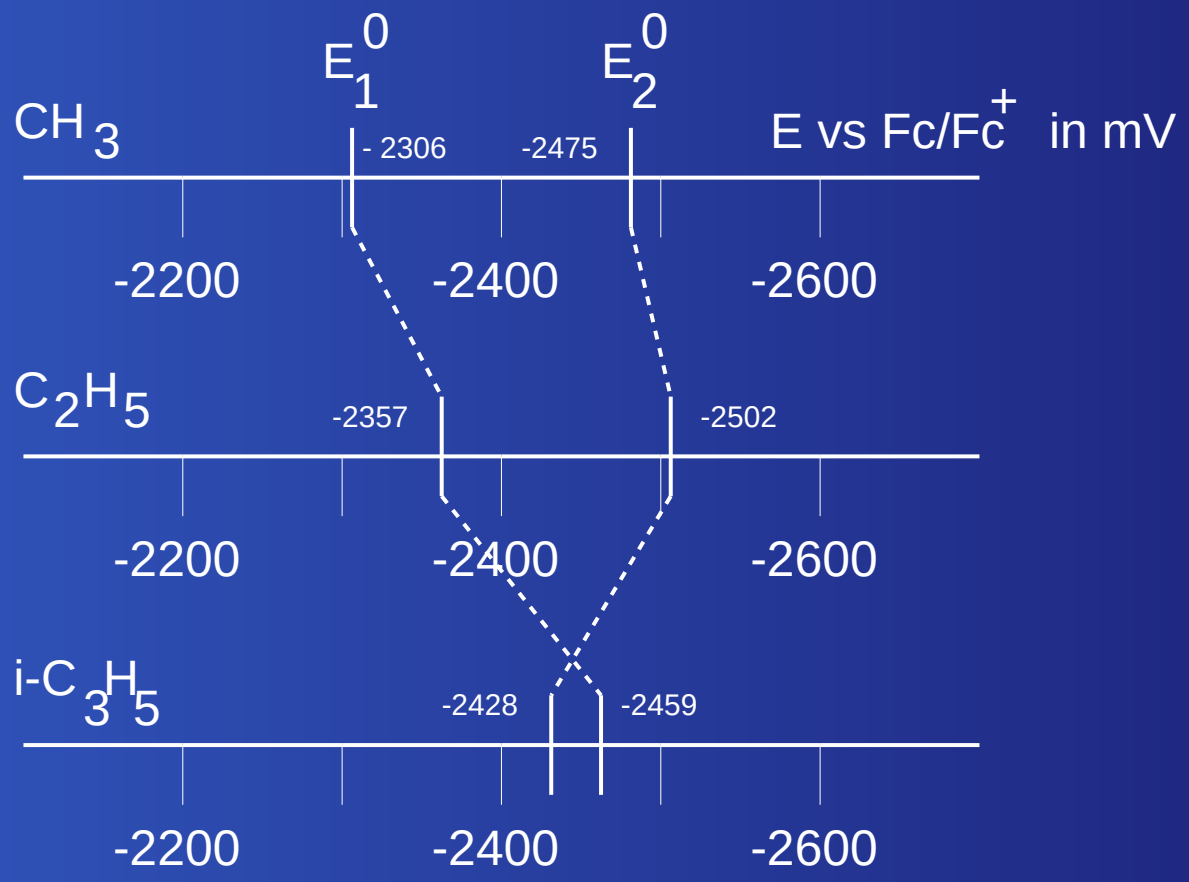




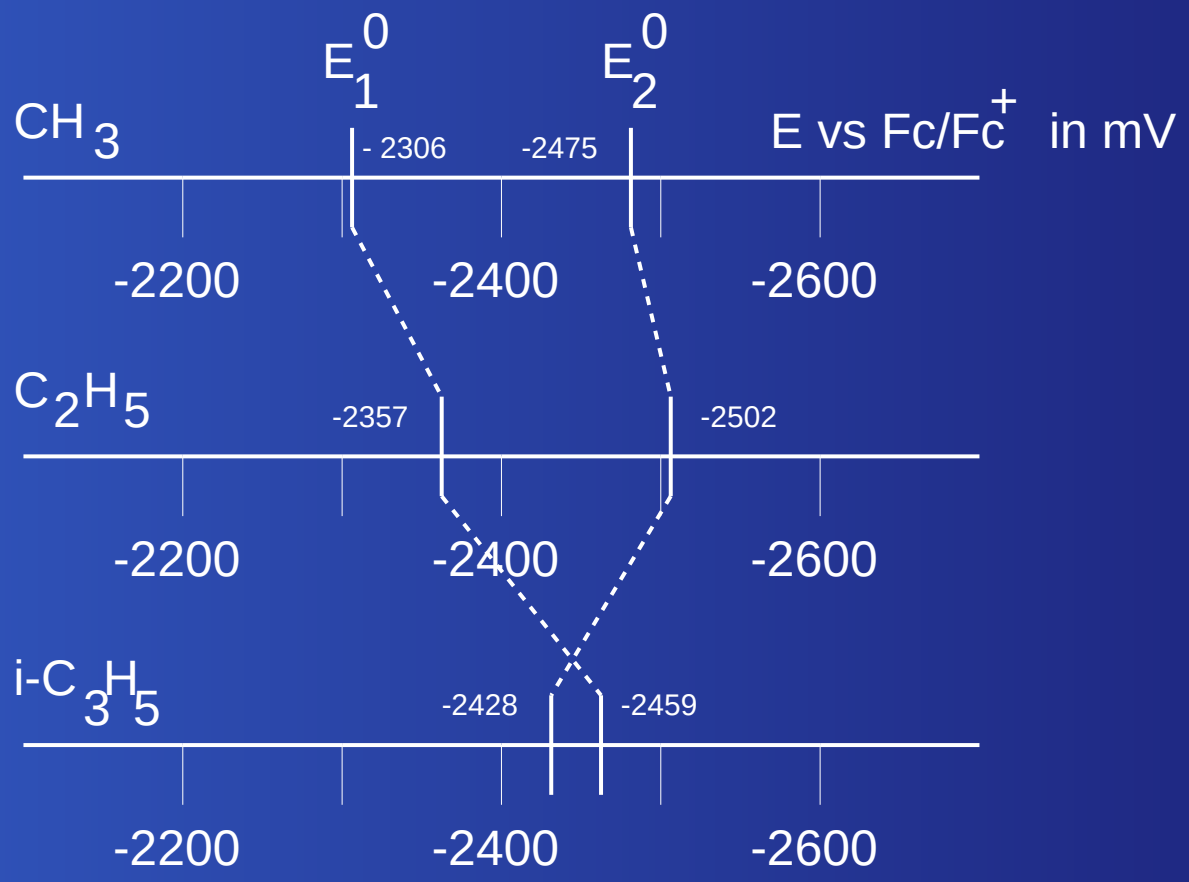


THF/0.2 M NBu_4PF_6; GC electrode

Imidazolium-2-dithiocarboxylates: Redox Potentials



Imidazolium-2-dithiocarboxylates: Redox Potentials



potential inversion for isopropyl derivative

Imidazolium-2-dithiocarboxylates: Kinetic Constants

R	k_{s1}/cm s^{-1}	k_{s2}/cm s^{-1}	k_{comp}/M^{-1}s^{-1}	D/ cm^2 s^{-1}	k_f/ s^{-1}
CH_3	0.029	0.009	2.7×10^5	1.0×10^{-5}	0.07
C_2H_5	0.019	0.0075	1.45×10^5	1.4×10^{-5}	0.25
i-C_3H_7	0.027	0.011	—	1.2×10^{-5}	0.045

Imidazolium-2-dithiocarboxylates: Kinetic Constants

R	k_{s1}/cm s^{-1}	k_{s2}/cm s^{-1}	k_{comp}/M^{-1}s^{-1}	D/ cm^2 s^{-1}	k_f/ s^{-1}
CH_3	0.029	0.009	2.7×10^5	1.0×10^{-5}	0.07
C_2H_5	0.019	0.0075	1.45×10^5	1.4×10^{-5}	0.25
i-C_3H_7	0.027	0.011	—	1.2×10^{-5}	0.045

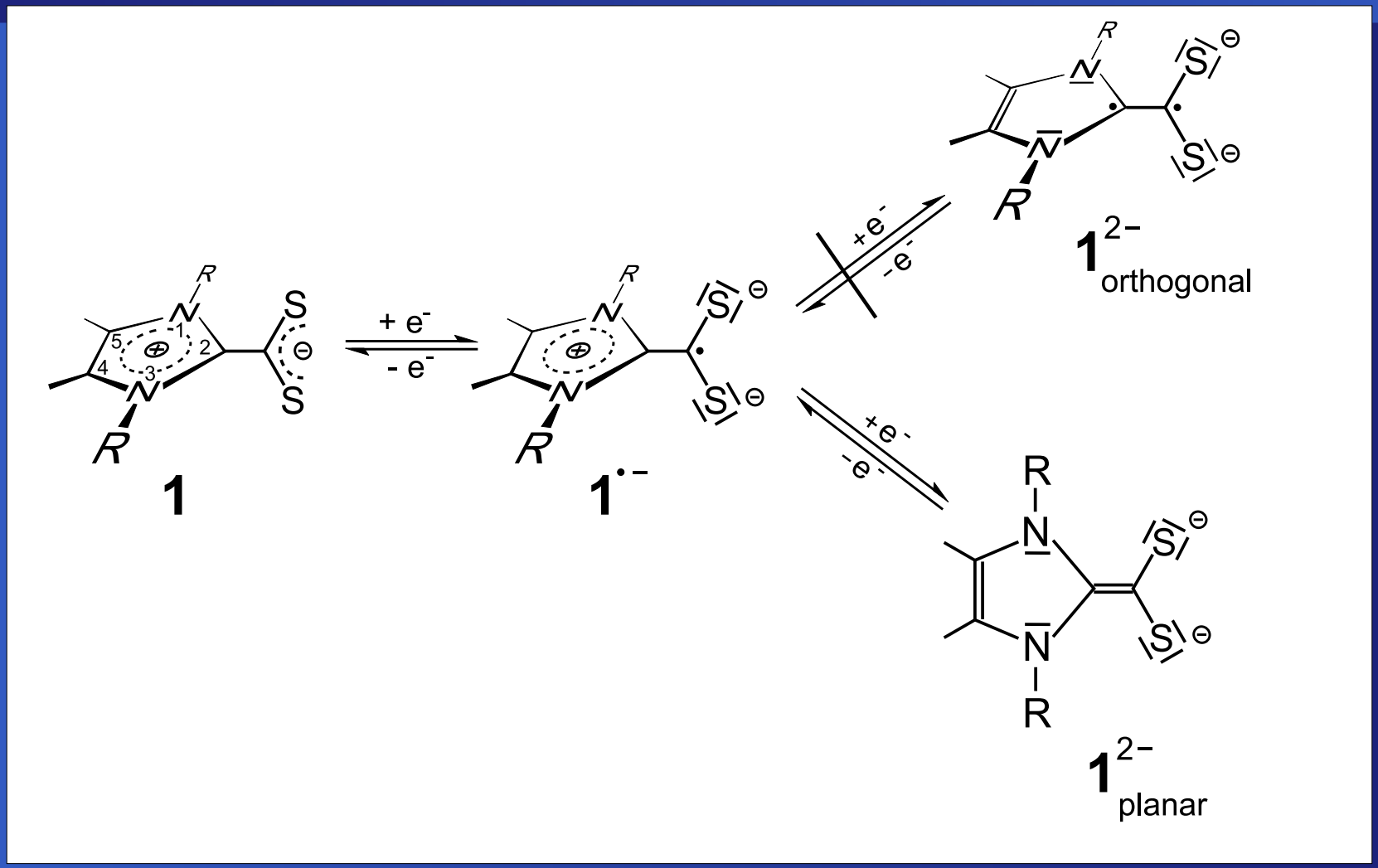
2nd electron transfer slower

Imidazolium-2-dithiocarboxylates: Kinetic Constants

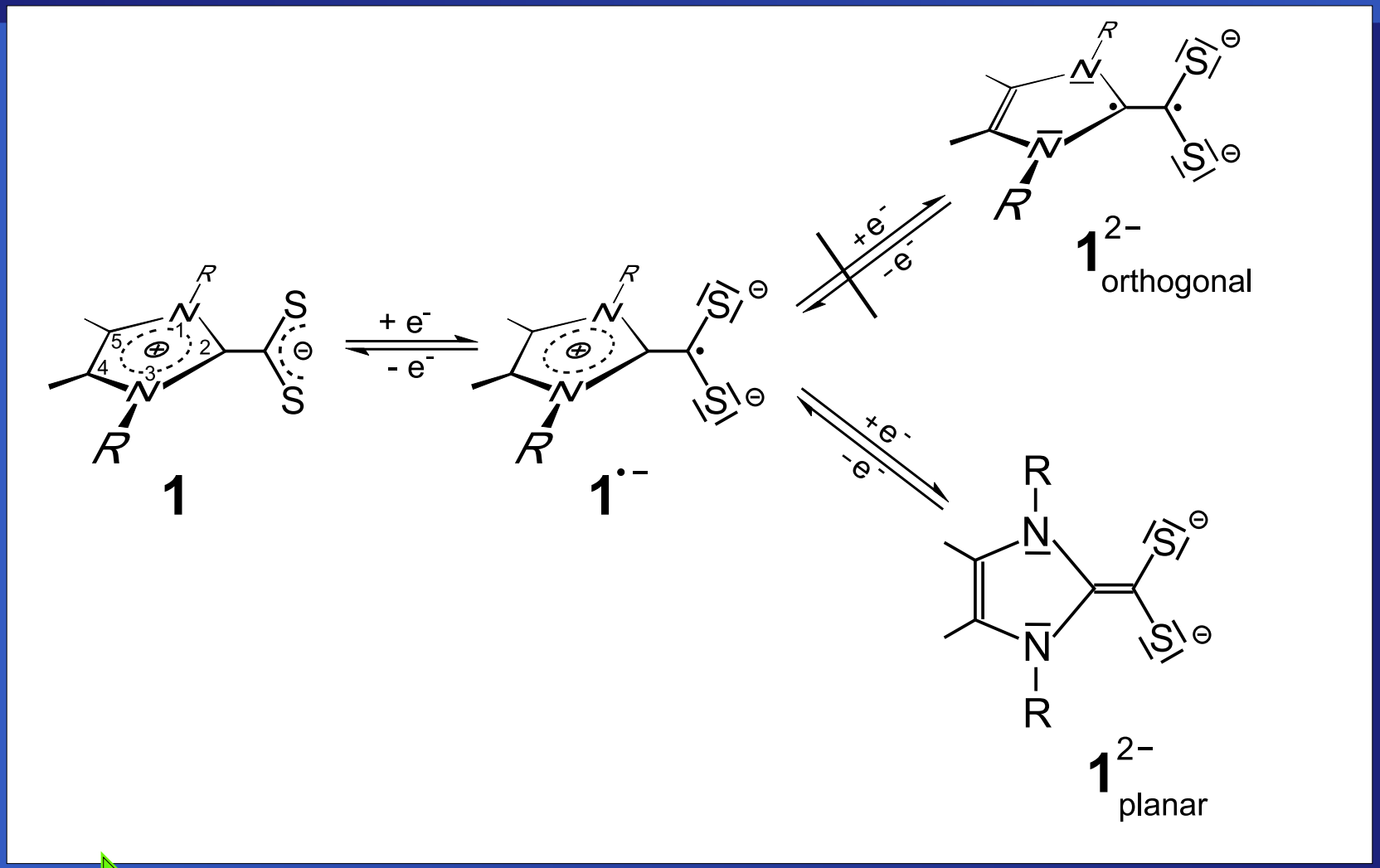
R	k_{s1}/cm s^{-1}	k_{s2}/cm s^{-1}	k_{comp}/M^{-1}s^{-1}	D/ cm^2 s^{-1}	k_f/ s^{-1}
CH_3	0.029	0.009	2.7×10^5	1.0×10^{-5}	0.07
C_2H_5	0.019	0.0075	1.45×10^5	1.4×10^{-5}	0.25
i-C_3H_7	0.027	0.011	—	1.2×10^{-5}	0.045

based on Marcus theory: structural change in 2nd step

Imidazolium-2-dithiocarboxylates: Structural Reorganisation

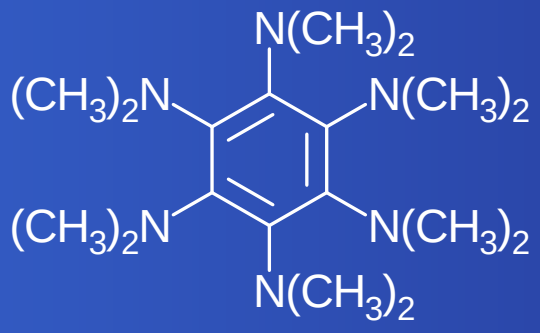


Imidazolium-2-dithiocarboxylates: Structural Reorganisation

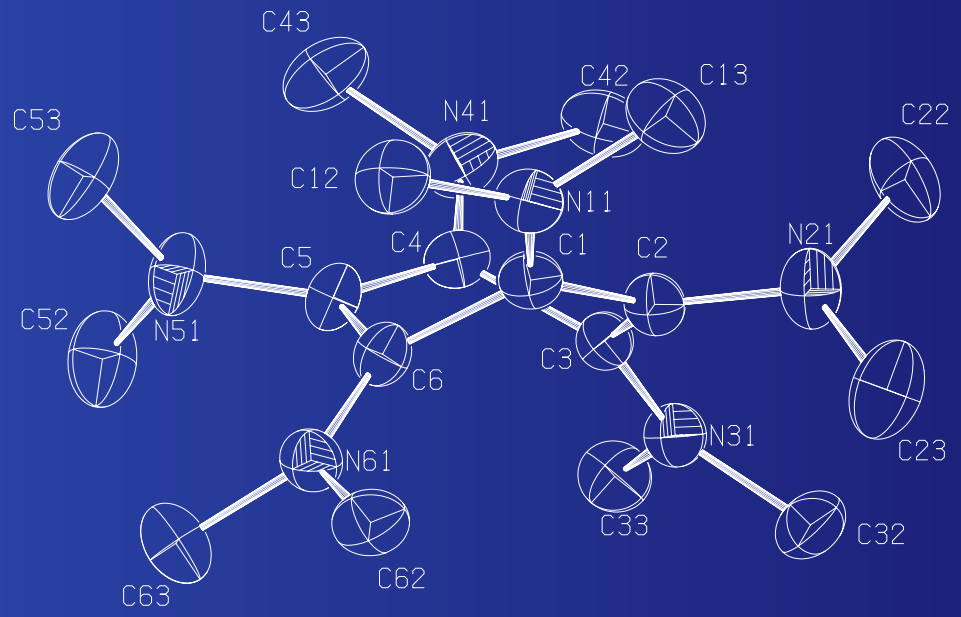


substituents R hinder planarization

Hexakis(dimethylamino)benzene and its Dication: Structures

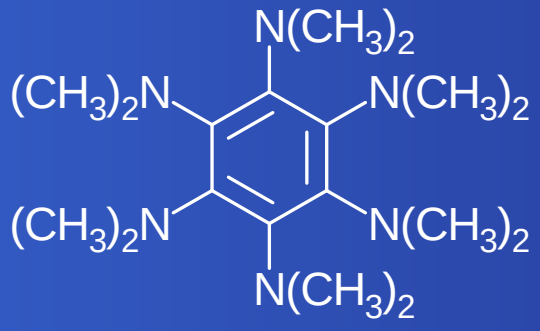


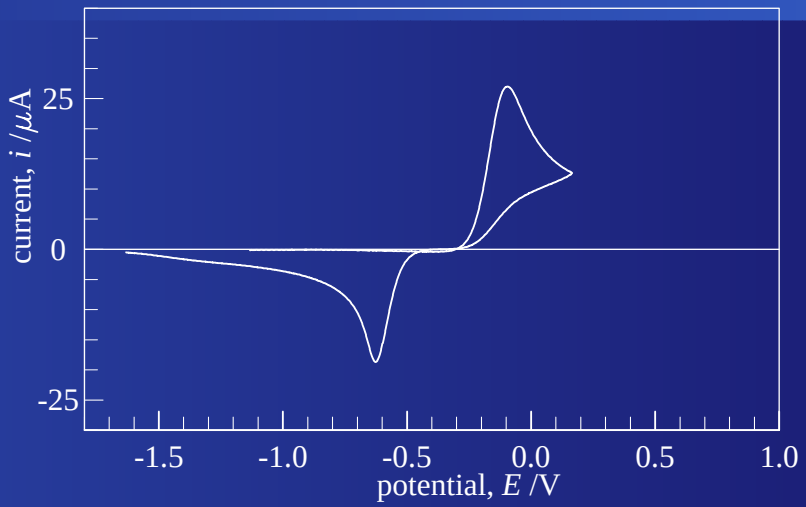
Hückel-aromatic compound; planar

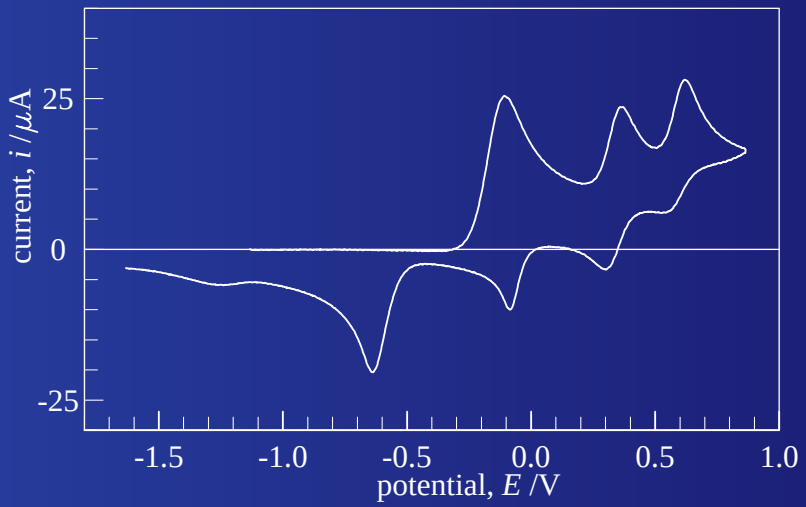


two polymethine-units; twist

Hexakis(dimethylamino)benzene: Cyclic Voltammetry

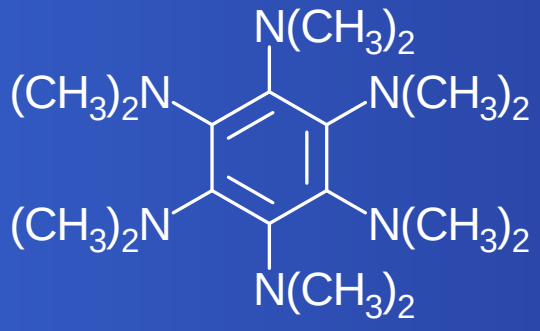


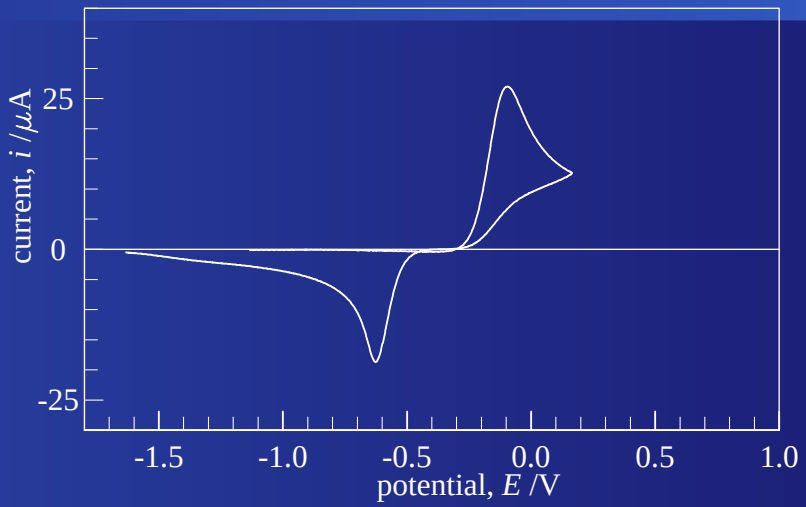


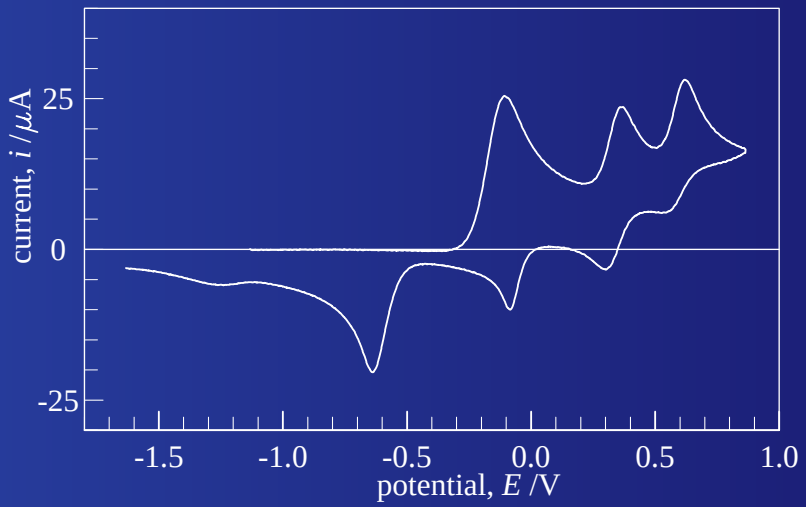


CH_3CN/CH_2Cl_2 1:1, 0.1 M NBu_4PF_6; Pt electrode; $v = 1.0$ Vs^{-1}, $c = 0.24$ mM

Hexakis(dimethylamino)benzene: Cyclic Voltammetry





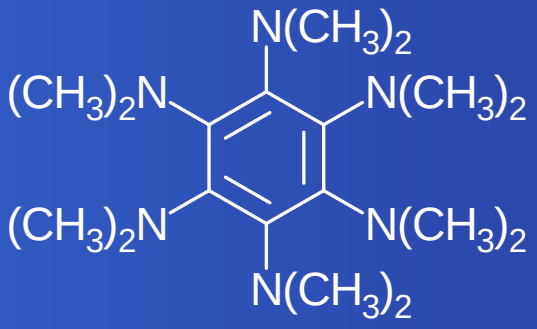


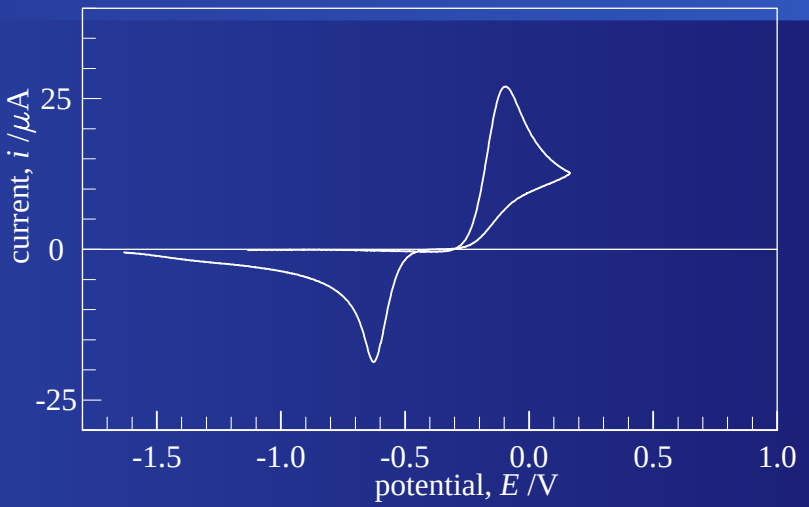
extreme potential inversion

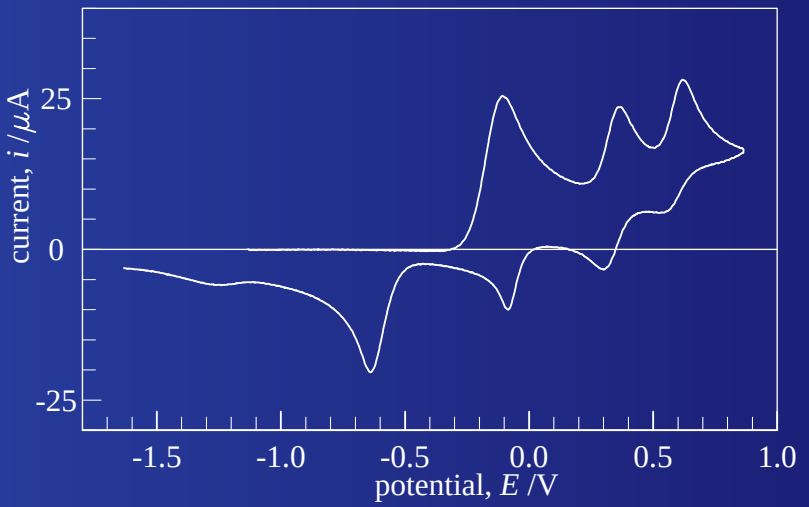
for two-electron oxidation

CH_3CN/CH_2Cl_2 1:1, 0.1 M NBu_4PF_6; Pt electrode; $v = 1.0$ Vs^{-1}, $c = 0.24$ mM

Hexakis(dimethylamino)benzene: Cyclic Voltammetry





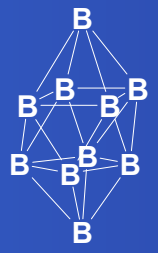
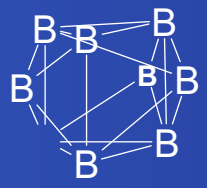
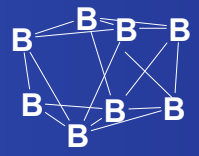
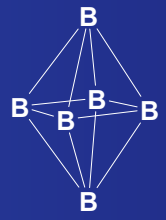
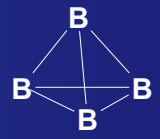


change from aromatic

to bis(polymethine) structure

CH_3CN/CH_2Cl_2 1:1, 0.1 M NBu_4PF_6; Pt electrode; $v = 1.0$ Vs^{-1}, $c = 0.24$ mM

Boron Subhalides: Cluster Structures

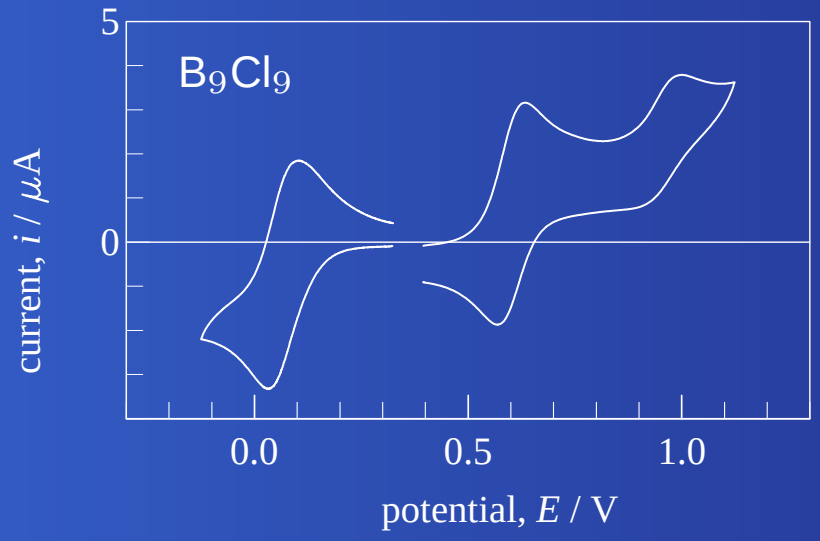
$\ldots \quad B_{10}X_{10} \quad B_9X_9 \quad B_8X_8 \quad \ldots \quad B_6X_6 \quad \ldots \quad B_4X_4$

X = Cl, Br, I

dianions: closo structure according to Wade's rules

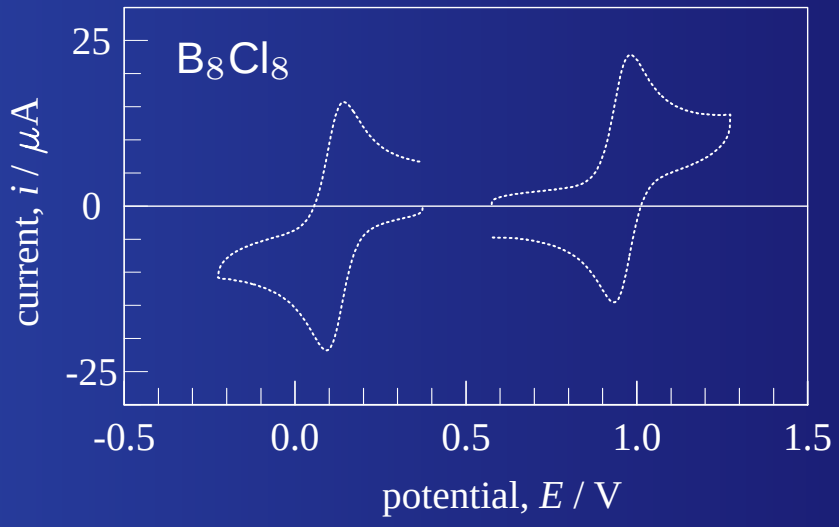
neutral molecules: hypercloso cluster with electron deficit

Boron Subhalides: Cyclic Voltammetry of $B_8X_8^{\bullet -}$ and $B_9X_9^{\bullet -}$



$v = 0.1$ V/s

$c = 0.29$ mM

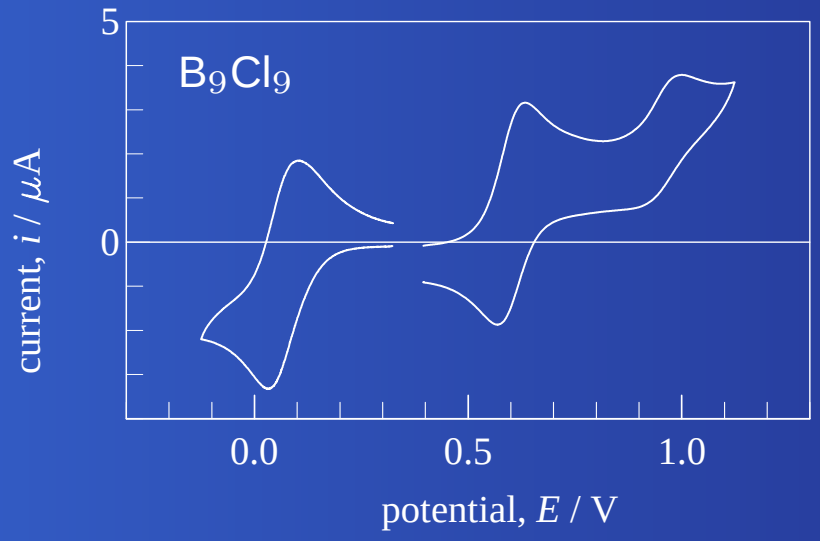


$v = 0.2$ V/s

$c \approx 2$ mM

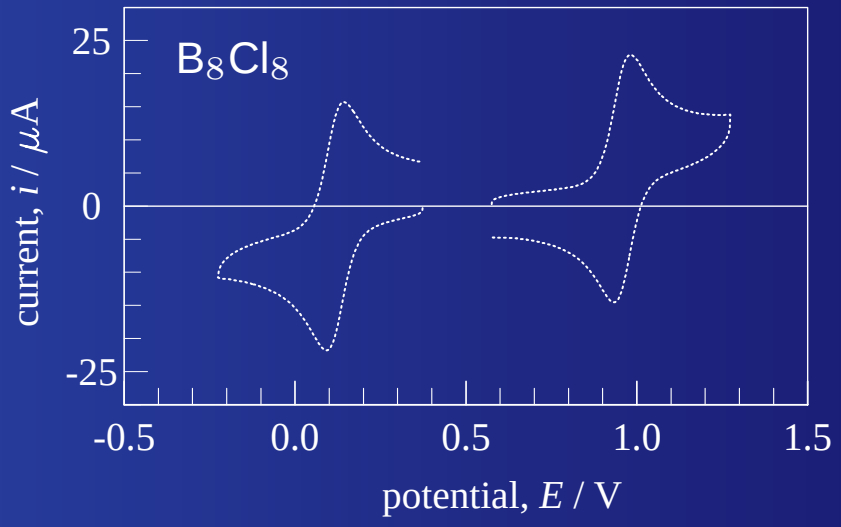
CH_2Cl_2/0.1 M NBu_4PF_6; Pt electrode

Boron Subhalides: Cyclic Voltammetry of $B_8X_8^{\bullet -}$ and $B_9X_9^{\bullet -}$



$v = 0.1$ V/s

$c = 0.29$ mM



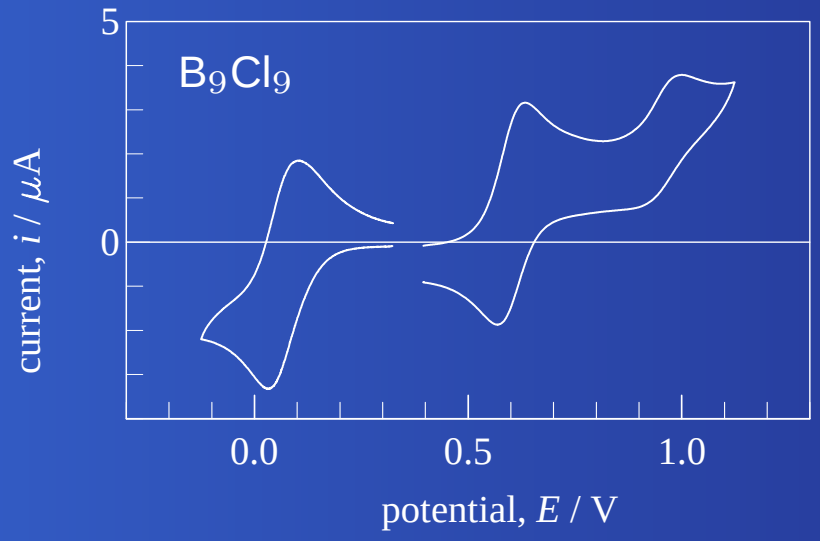
$v = 0.2$ V/s

$c \approx 2$ mM

CH_2Cl_2/0.1 M NBu_4PF_6; Pt electrode

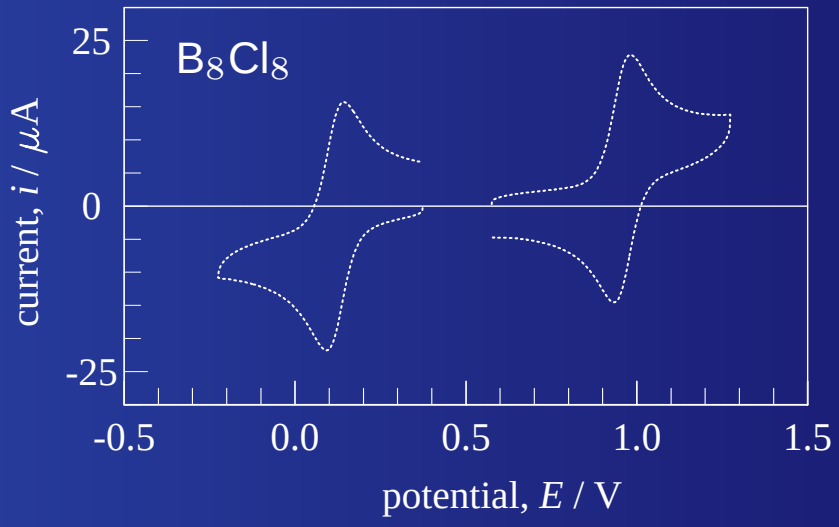
normal potential ordering; no dramatic structural changes

Boron Subhalides: Cyclic Voltammetry of $B_8X_8^{\bullet -}$ and $B_9X_9^{\bullet -}$



$v = 0.1$ V/s

$c = 0.29$ mM



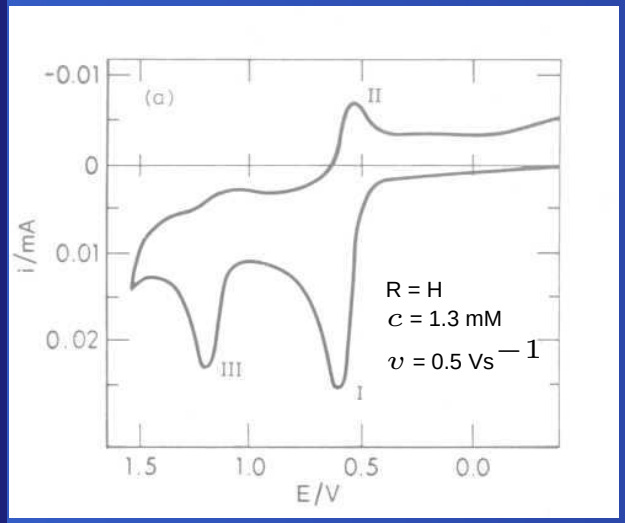
$v = 0.2$ V/s

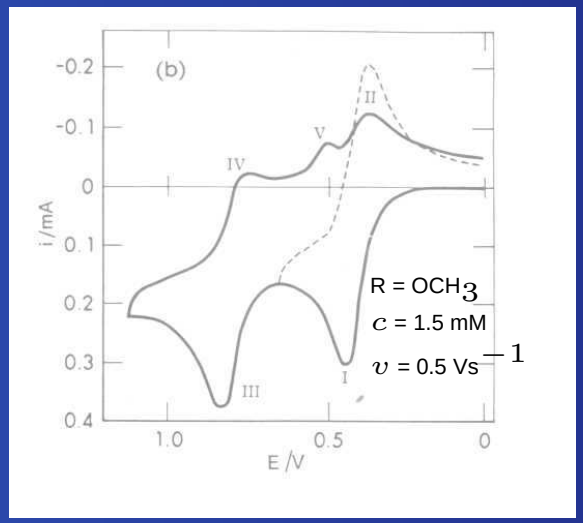
$c \approx 2$ mM

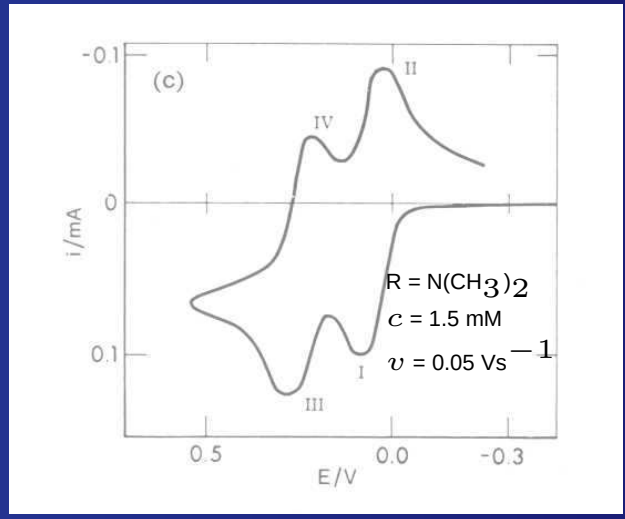
CH_2Cl_2/0.1 M NBu_4PF_6; Pt electrode

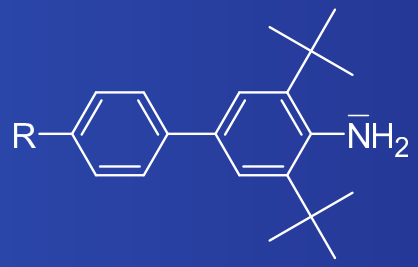
π-back bonding compensates electron deficit in hypercloso clusters

Sterically Hindered Biphenylamines: Structure and Cyclic Voltammograms





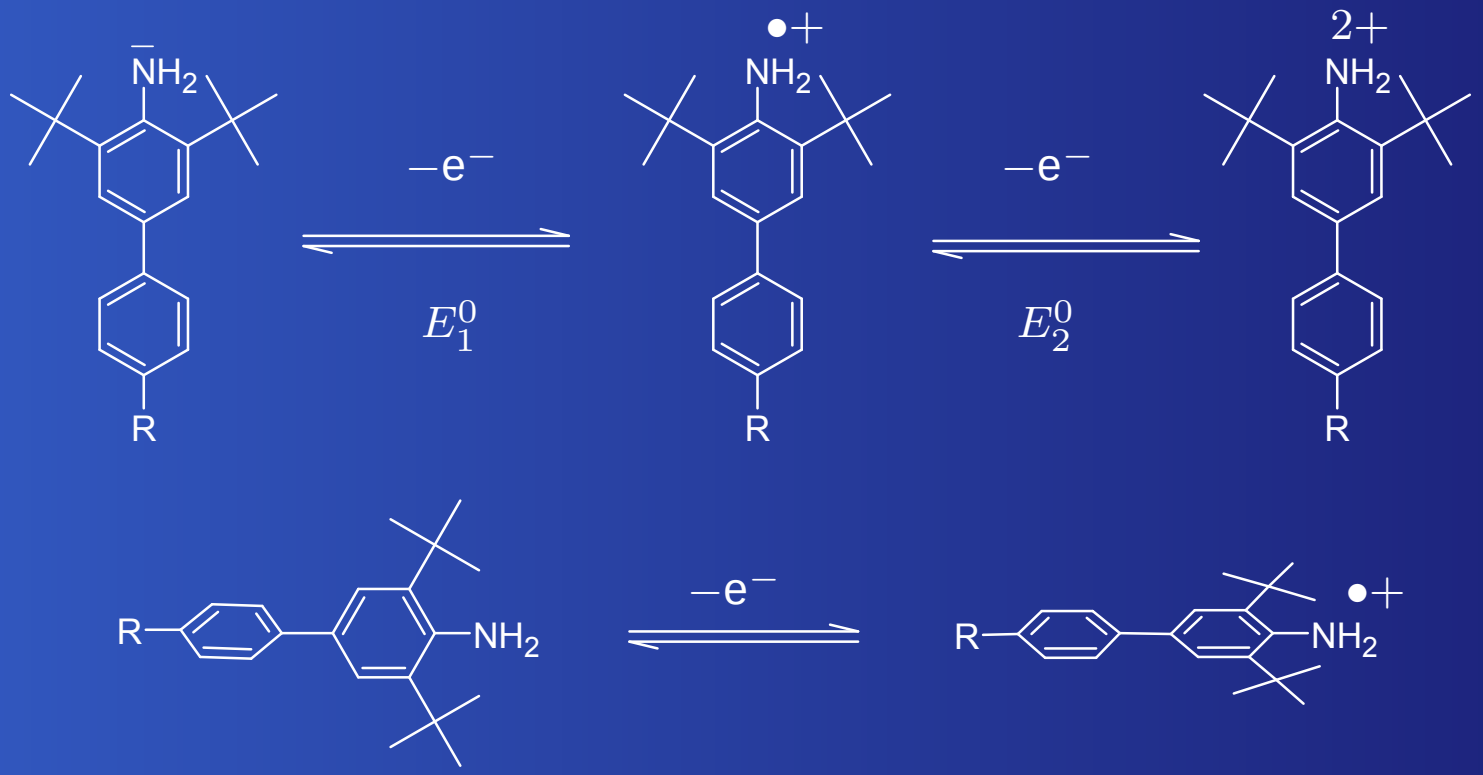




B. Speiser, A. Rieker, and S. Pons, J. Electroanal. Chem. 147, 205 – 222 (1983).

CH_3CN/0.1 M NEt_4ClO_4; Pt electrode; potentials vs. Ag/Ag^+ (0.01 M in CH_3CN)

Sterically Hindered Biphenylamines: Two-Electron Oxidation Mechanism



Hammett correlation with σ^+ substituent constants

stabilization of radical cation by planarization – normal potential ordering

Conclusions: Multi-Electron Transfers

- mechanistic variations — side/follow-up reactions
  - each case to be analyzed carefully
  - ensemble of voltammograms
  - simulation, parameter fitting
  - thermodynamics and kinetics
- various examples for normal **and** inverted potential ordering
  - structural change
  - solvation, ion pairing

Conclusions: Multi-Electron Transfers

- mechanistic variations — side/follow-up reactions
  - each case to be analyzed carefully
  - ensemble of voltammograms
  - simulation, parameter fitting
  - thermodynamics and kinetics
- various examples for normal **and** inverted potential ordering
  - structural change
  - solvation, ion pairing

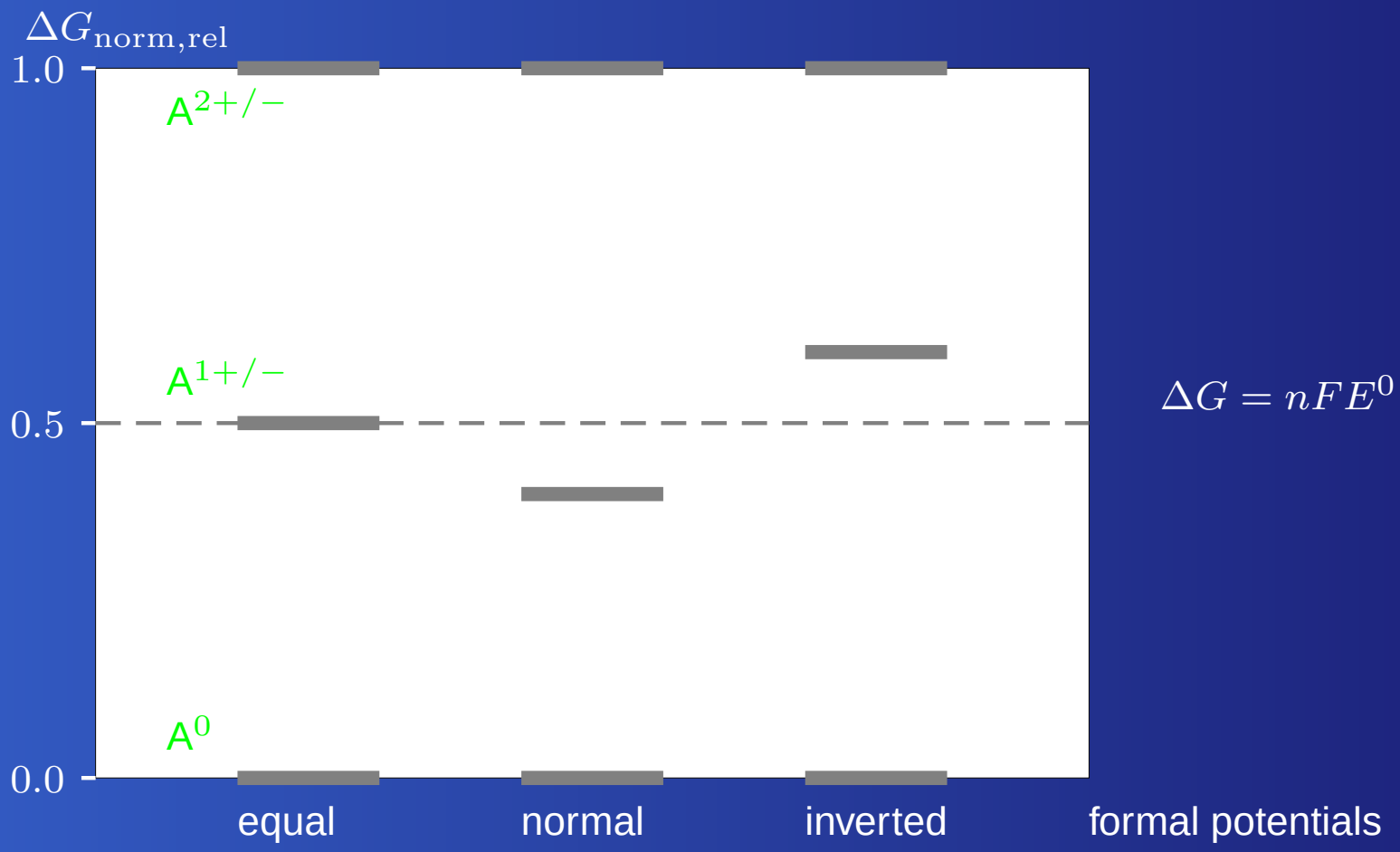
⇒ however: not fully systematic

Conclusions: Multi-Electron Transfers

- mechanistic variations — side/follow-up reactions
  - each case to be analyzed carefully
  - ensemble of voltammograms
  - simulation, parameter fitting
  - thermodynamics and kinetics
- various examples for normal **and** inverted potential ordering
  - structural change
  - solvation, ion pairing

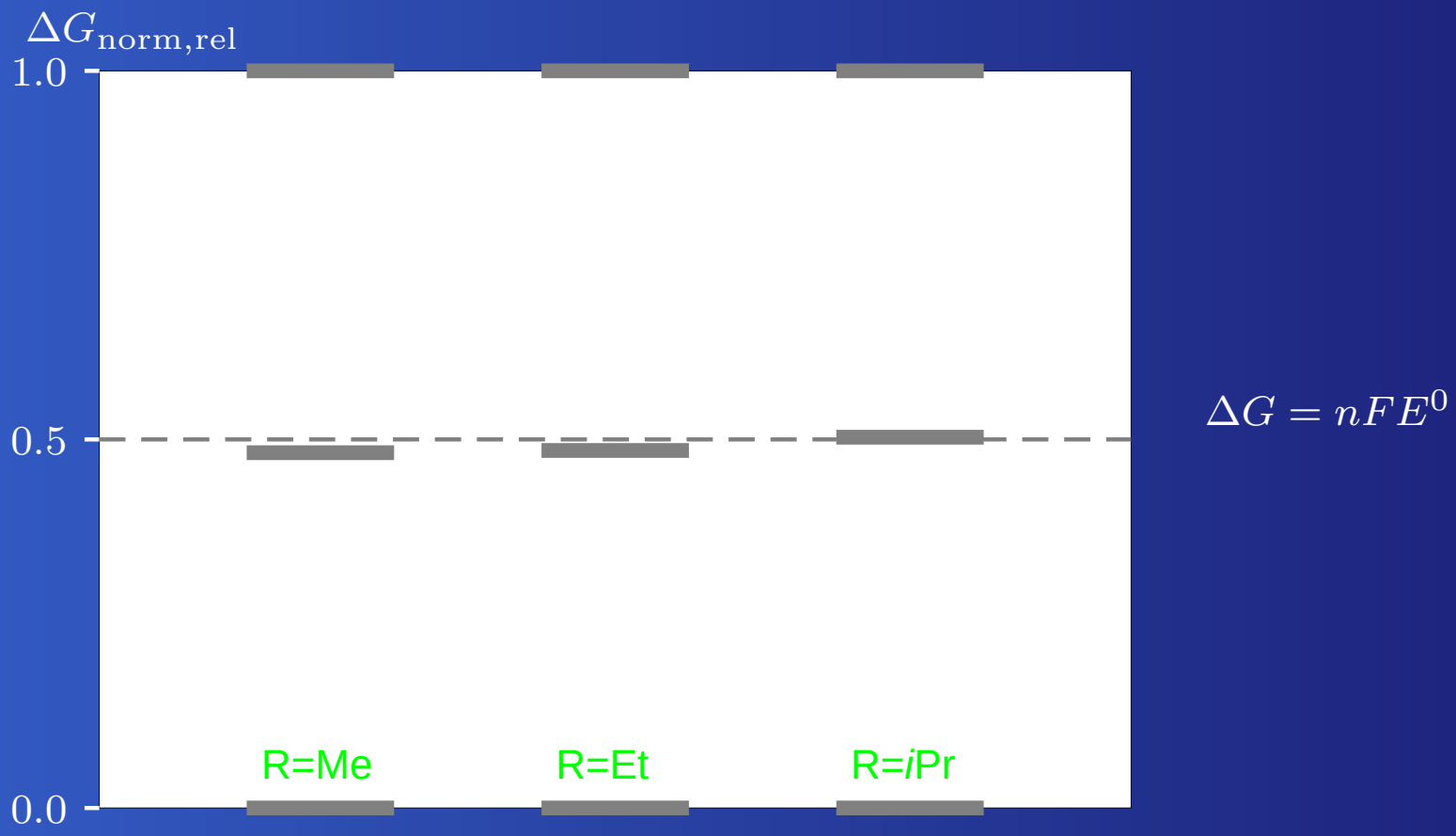
⇒ two reaction steps, three species

Conclusion: Normal vs. Inverted Potential Ordering



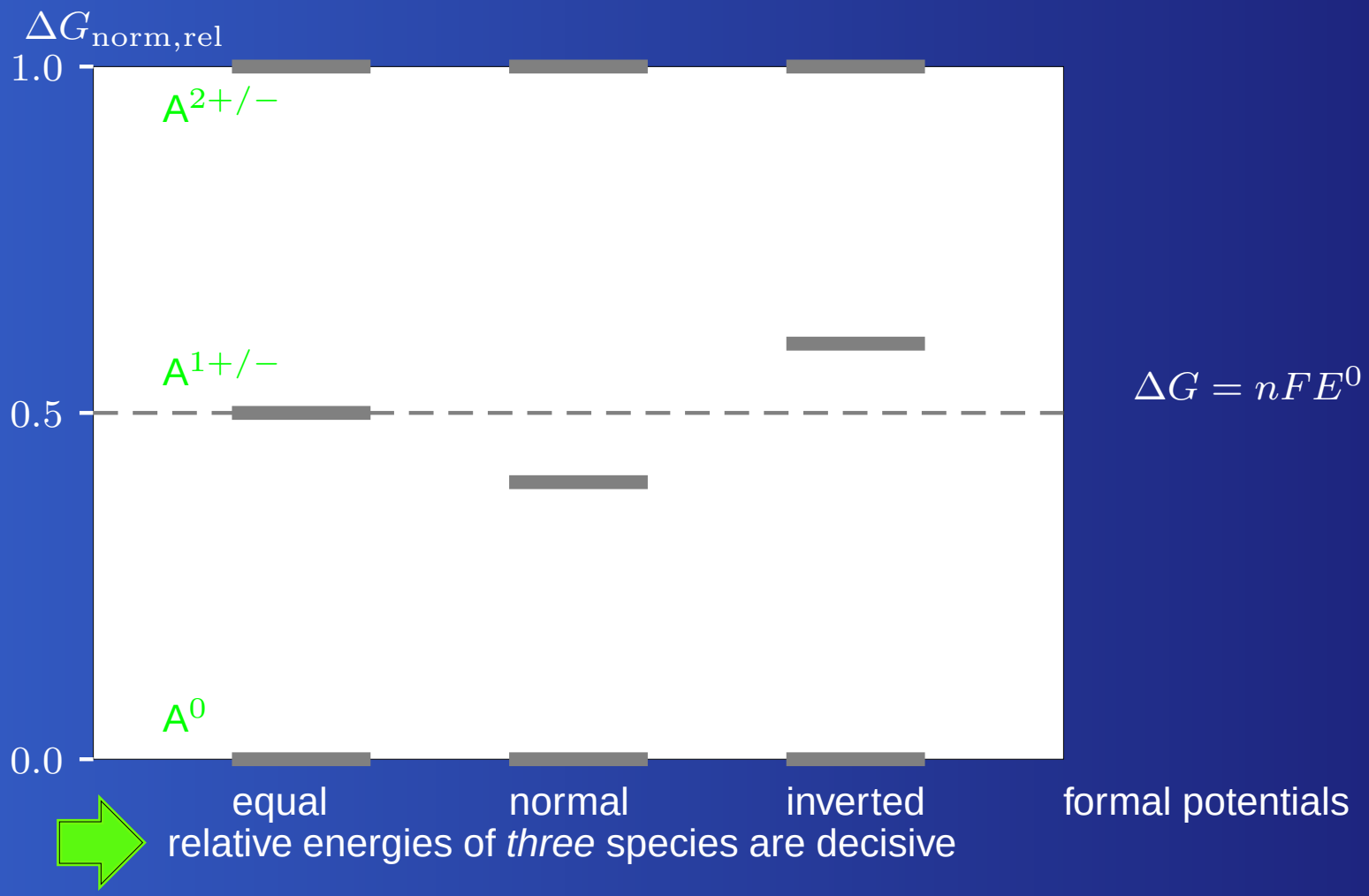
normalized relative energies of species in general two-electron transfer system

Conclusion: Normal vs. Inverted Potential Ordering



normalized relative energies of species in dithiocarboxylate system

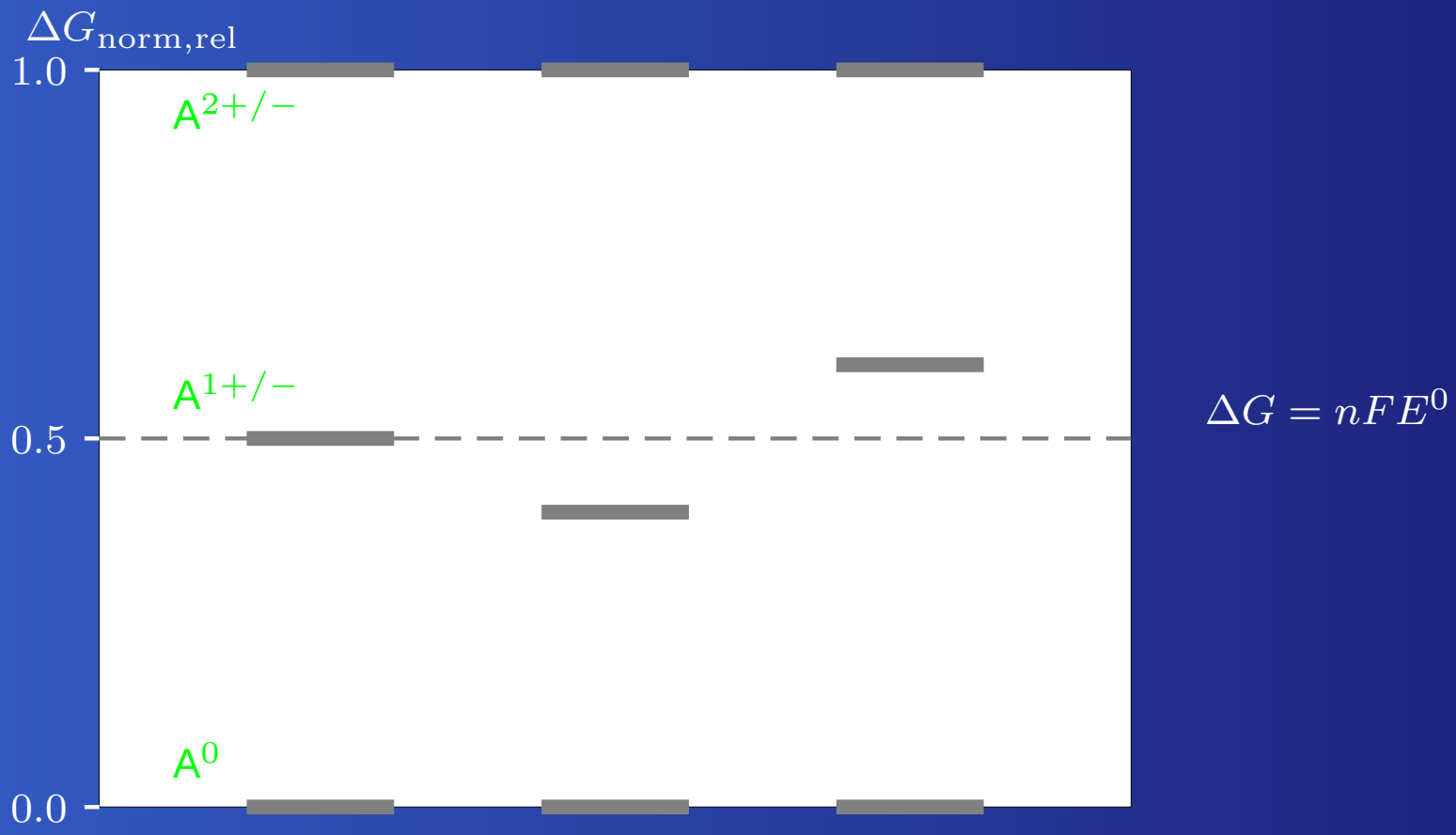
Conclusion: Normal vs. Inverted Potential Ordering



relative energies of *three* species are decisive

normalized relative energies of species in general two-electron transfer system

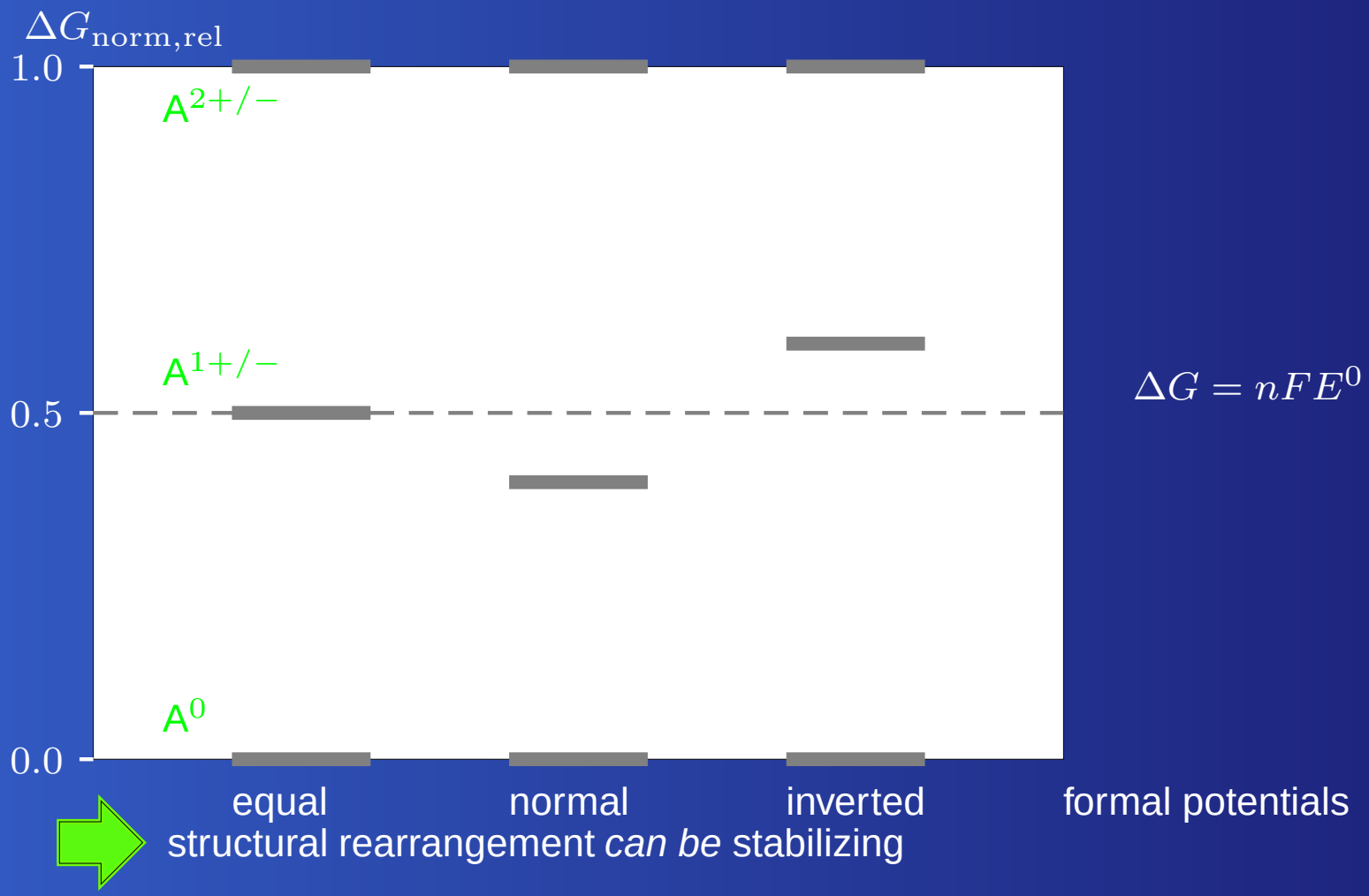
Conclusion: Normal vs. Inverted Potential Ordering



stabilization of $A^{2+/-}$ or destabilization of $A^{1+/-}$ leads to potential inversion

normalized relative energies of species in general two-electron transfer system

Conclusion: Normal vs. Inverted Potential Ordering



normalized relative energies of species in general two-electron transfer system

Conclusion: The Message

The Message:
two is not enough . . .

all redox states must be considered!

Acknowledgements: Co-workers and Cooperation Partners

- Fc-silsesquioxanes: Thomas Reißig, David Ruiz Abad, Hermann Mayer
- Ru(arene) complexes: Bernhard Gollas, Stefan Dümmling
- Dithiocarboxylates: Stefan Dümmling, Gerd Weyers, N. Kuhn
- Hexaminobenzenes: Marc Würde, Cäcilie Maichle-Mössmer, Jens J. Wolff
- Boron Subhalides: Carsten Tittel, Tina Wizemann, Wolfgang Einholz
- Biphenylamines: Peter Hertl, Anton Rieker