

# Towards biologically inspired fuel-cell electrocatalysts: electrochemistry of a diiron hydrogenase mimic

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**W**e have a long-standing interest in the electrochemical characterization of synthetic analogues of hydrogenase biocatalysts, with the ultimate goal of parlaying the information towards the modification of the surfaces of inexpensive electrodes by the immobilization of homogeneous catalysts for H<sub>2</sub> production and/or uptake. The initial stage of the study is focused on the synthesis of suitably ligated base metals or metal complexes with hydrogenase-like functional activity followed by the assessment of their electrochemical activities. In this regard, N-heterocyclic carbene (NHC) ligands have taken on remarkable roles, because of their unique steric and electronic properties, in organometallic chemistry and homogeneous catalysis. They are now also exploited as candidates in synthetic analogues of bioorganometallic enzymes as in the [FeFe]-hydrogenase active site. In the present paper, we contrast the electrochemical behaviors of the complex (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>IMes] with the saturated analogue, SIMes (SIMes =

1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) in the (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>(SIMes)] complex, and with the protonated imidazolium salts that are precursors of the NHC ligands, H-NHC<sup>+</sup>Cl<sup>-</sup>. Our goal was to further confirm and gain insight into the nature of the 2-electron process of (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>IMes] as well as to establish the extent to which the NHC ligands are involved with respect to the overall electron uptake by the complexes.

## KEYWORDS

Di-Iron Complexes as Hydrogenase Mimics Enzyme-based Proton Reduction Catalysts Biologically-Modified Electrode Surfaces Bioinspired Electrocatalysts Electrochemistry of Di-iron Hydrogenase Mimic

## INTRODUCTION

With their unique steric and electronic properties, N-heterocyclic carbene (NHC) ligands have developed remarkable roles in organometallic chemistry and homogeneous catalysis. It is thus not unexpected that they are also exploited as candidates in synthetic analogues of bioorganometallic enzymes as in the [FeFe]-hydrogenase active site (Herrmann 2002, Fontecilla-Camps et al. 2007, Herrmann et al. 1999, Capon et al. 2005, Liu and Darensbourg 2007, Thomas et al. 2007, Morvan et al. 2007, Duan et al. 2007, Jiang et al. 2007, Thomas et al. 2008). In fact, one of the major challenges of isolating a mixed-valent diiron complex with “rotated” geometry and bridging CO that matches

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that of the 2Fe2S subsite in [FeFe]-hydrogenase was met by incorporating the IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and PMe<sub>3</sub> ligands into the (μ-pdt)[Fe(CO)<sub>3</sub>]<sub>2</sub> parent precursor (Scheme 1) (Herrmann 1999). Further studies led to assignment of oxidation states in the one-electron oxidized, mixed-valent product. A series of NHC ligands was used in attempts to nail down the electronic-*vs.*-steric influences that provided the rotated structure with a bridging CO ligand (Thomas et al. 2008).

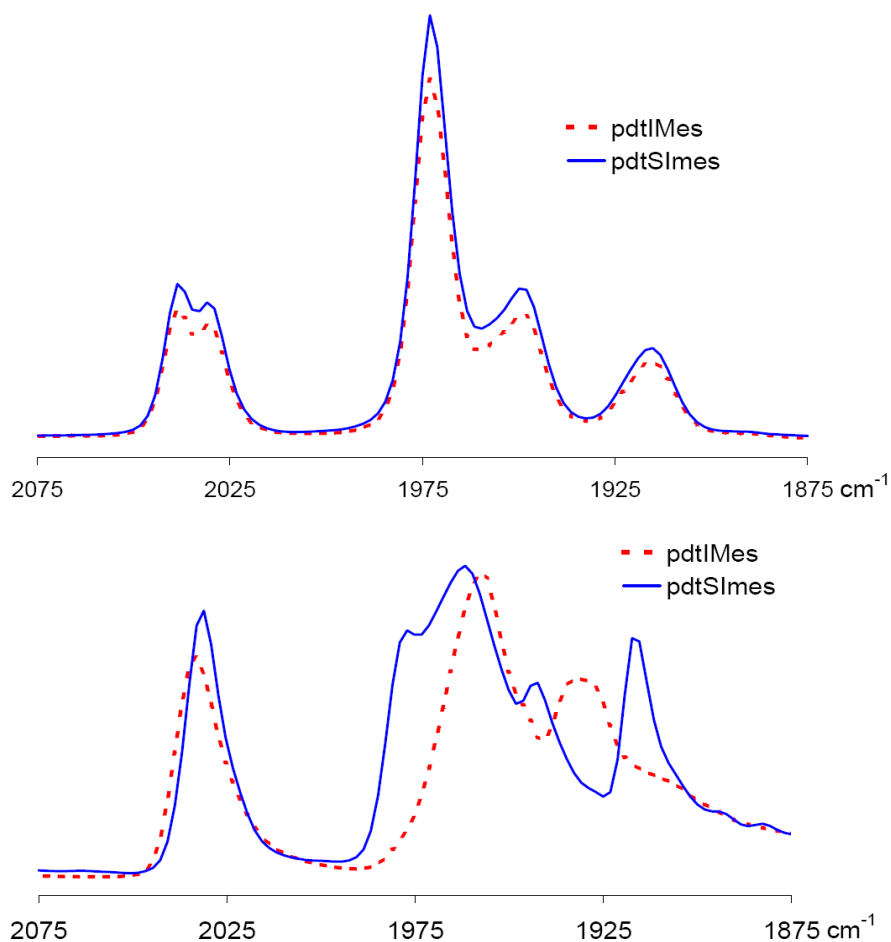
The synthesis of (μ-pdt)[Fe(CO)<sub>2</sub>IMes][Fe(CO)<sub>2</sub>PMe<sub>3</sub>] shown in Scheme 1, proceeds via stepwise substitution of carbonyls, necessarily placing the NHC first on the diiron unit. This mono-substituted diiron complex was earlier demonstrated to be an electrocatalyst for H<sub>2</sub> production at its single reduction process which occurs at -2.17 V (referenced against the Fc/Fc<sup>+</sup> redox couple) (Herrmann 2002). This reduction was determined by bulk electrolysis to be a 2-electron process for which DFT computations suggested simultaneous electron uptake into a σ\* orbital of the Fe-Fe bond and into the π\* manifold of the NHC ligand. The electron transfer into both positions was kinetically favored as a triplet state involving Fe-(σ\*)<sup>1</sup>-Fe-L(π\*)<sup>1</sup>, or triplet Fe<sup>0</sup>-Fe<sup>1</sup>(IMes<sup>-1</sup>), required minimal structural rearrangement as compared to Fe-(σ\*)<sup>2</sup>-Fe-L(π\*)<sup>0</sup> or, alternatively, singlet Fe<sup>0</sup>-Fe<sup>0</sup>(IMes).

Subsequent studies in this rapidly developing field of electrocatalysis of H<sub>2</sub> production by base-metal molecular catalysts related to the [FeFe]-hydrogenase active site have uncovered a rich landscape of chemical consequences that might occur upon one- and two-electron reduction of (μ-SRS)[Fe(CO)<sub>3</sub>]<sub>2</sub> compounds. These include, for example plausible arguments for electron processes that result in one Fe(CO)<sub>3</sub> rotation yielding a { (μ-SRS)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>3</sub>]<sub>rotated</sub> }<sup>-</sup> structure (for R = edt or SCH<sub>2</sub>CH<sub>2</sub>S) that accepts a second electron more easily than did the neutral structure accept the first. The second electron reduction is stabilized by conversion of one Fe-S<sub>bridge</sub> bond into an Fe-S<sub>terminal</sub> as shown in Scheme 1.

Substantiating the Fe-S<sub>br</sub> cleavage reaction for the (μ-pdt)[Fe(CO)<sub>3</sub>]<sub>2</sub> (pdt or S(CH<sub>2</sub>)<sub>3</sub>S) single-electron reduced species, Heinekey, et al., isolated and structurally characterized a tetrairon derivative, shown to have an -S(CH<sub>2</sub>)<sub>3</sub>S- ligand that spanned two Fe<sub>2</sub>(CO)<sub>x</sub> moieties. To our

knowledge, this is the only reduced diiron carbonyl species that has been structurally characterized. Thus the fluxionality, well established for the (μ-SRS)[Fe(CO)<sub>3</sub>]<sub>2</sub> compounds, the response of the Fe-SR bond to reduction, and the electrochemically active, non-innocent ligands may be involved in the electrochemical events of these “deceptively simple” molecules that serve as solution electrocatalysts for proton reduction.

Below we contrast the electrochemical behaviors of the complex (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>IMes] with the saturated analogue, SIMes (SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) in the (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>(SIMes)] complex and with the protonated imidazolium salts which are precursors of the NHC ligands, H-NHC<sup>+</sup>Cl<sup>-</sup>. Our goal was to further confirm and gain insight into the nature of the 2-electron process of (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>IMes], as well as to establish the extent to which the NHC ligands are involved (innocently or otherwise) with respect to the overall

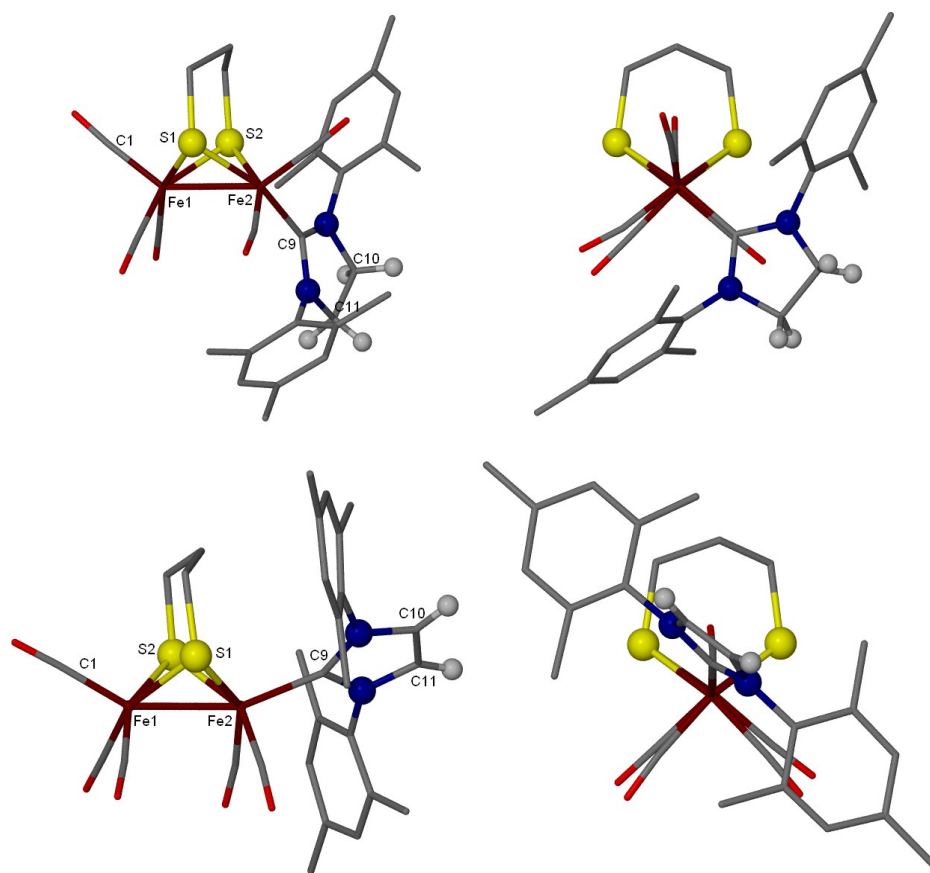


**Figure 1.** Top: toluene solution IR spectra of pdt-IMes (solid line) and pdt-SIMes (dashed line). Bottom: solid state IR spectra of pdt-IMes (solid line) and pdt-SIMes (dashed line).

electron uptake by the complexes.

## MATERIALS AND METHODS

All reactions and operations were conducted on a double-manifold Schlenk vacuum line under an atmosphere of N<sub>2</sub> or Ar. Hexane, THF, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN were first degassed with N<sub>2</sub> for 30 minutes and then purified by an MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. Hexane and CH<sub>2</sub>Cl<sub>2</sub> were freshly collected from the solvent system and used in experiments. THF and CH<sub>3</sub>CN were further purified as following: THF was purified by distillation under N<sub>2</sub> from sodium/benzophenone; CH<sub>3</sub>CN was first stirred with CaH<sub>2</sub> at 22 °C for 5 hrs and then distilled. The collected THF and CH<sub>3</sub>CN were stored over molecular sieves under Ar for experimental uses.



**Figure 2.** The molecular structures of pdt-SIMes (upper), and pdt-IMes (lower), as ball and stick drawings in a side view parallel with the Fe-Fe vector (left-side structures) and a corresponding perpendicular view (right-side structures). Salient metric parameters of pdt-SIMes (values for pdt-IMes in italics): Fe(1)-Fe(2): 2.5627(6) Å; Fe(2)-C(9): 1.989(3); Fe(1)-C(1): 1.784(4); Fe(1)-S(1): 2.2587(10); Fe(2)-S(1): 2.2776(10); S(1)-Fe(2)-C(9): 162.62(8)°; S(2)-Fe(2)-C(11): 90.08(8); Fe(1)-S(1)-Fe(2): 68.80(3); Fe(1)-S(2)-Fe(2): 69.83(3).

The known complexes,  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3]_2$  and  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3][\text{Fe}(\text{CO})_2\text{IMes}]$  (pdt = 1,3-propanedithiolate) were prepared according to literatures (Tye et al. 2005, Lyon et al. 2001). Other materials were of reagent grade and were directly used as purchased from Sigma-Aldrich or TCI Chemical Companies.

<sup>1</sup>H-NMR spectra were measured on a Unity+ 300 MHz superconducting NMR instrument. Solution and solid ATR infrared spectra were measured on a Bruker Tensor 27 FTIR spectrometer using 0.1 mm NaCl sealed cells.

## Electrochemistry

Cyclic voltammograms (CV) were recorded on a BAS-100W electrochemical analyzer (BioAnalytical Systems, West Lafayette, IN) using a three-electrode configuration. The working electrode was a glassy carbon disk (area = 0.071 cm<sup>2</sup>) (BAS, MF-2012), the reference electrode was Ag/AgNO<sub>3</sub> (0.01 M Ag<sup>+</sup> / 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub>) prepared by anodizing a silver wire in an CH<sub>3</sub>CN solution of 0.01 M AgNO<sub>3</sub> / 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub>, and the counter electrode was a coiled platinum wire. The electrochemical cell was a 15-mL glass container (BAS, MR-1208). The three-electrode configuration had a total resistance of 0.6 kΩ. The glassy carbon working electrode was successively polished with 15, 3, and 1 μm diamond paste, and then sonicated in Milli-Q Plus water (Millipore Systems, Houston TX) for 10 min. Deaeration of all solutions was accomplished by bubbling Ar gas through the solution for 5 min and a blanket of Ar was maintained over the solution during the electrochemical measurements. All experiments were performed on CH<sub>3</sub>CN solutions containing 2.0 mM in analyte and 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> at room temperature. All potentials were reported relative to the Cp<sub>2</sub>Fe<sup>+</sup>/Cp<sub>2</sub>Fe (Fc<sup>+</sup>/Fc) internal reference. All CV's presented herein were carried out at a scan rate (ν) of 200 mV/s.

Controlled-potential coulometry was performed for the determination of the number of electrons transferred per molecule. For this purpose, a 40-mL sample of 1.0 mM in analyte and 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> was prepared in CH<sub>3</sub>CN and placed in the bulk electrolysis cell (BAS, MF-1056) under an Ar gas atmosphere. The working electrode utilized for the

bulk electrolysis cell was a reticulated vitreous carbon (RVC) electrode (BAS, MF-2077).

### Synthesis of $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3][\text{Fe}(\text{CO})_3\text{SIMes}]$

A mixture of  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3]_2$  (1.000 g, 2.6 mmol) and solid 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (0.887 g, 2.6 mmol) was dissolved in 50 ml THF. After stirring for 10 min., to the mixture solution was slowly added 12 mmol of KOtBu in 20 ml THF. The reaction solution was stirred at RT for ca. 0.5 h to reach the completion as indicated by IR monitor. The reaction solution was filtered through Celite to remove solid residues. After removal of THF under vacuum, the crude product was extracted with 50 ml ether and filtered through Celite again. Then the extract was frozen at  $-20\text{ }^\circ\text{C}$  in 3 days to give analytical pure product as dark brown solids (1.183 g, 65%). Crystals suitable for X-ray diffraction were grown via layering a concentrated  $\text{CH}_2\text{Cl}_2$  solution with hexane at  $-20\text{ }^\circ\text{C}$ . IR (toluene,  $\text{cm}^{-1}$ ): 2039(m), 2031(m), 1973(s), 1948(m), 1915(w).  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ ):  $\delta$  = 7.01 (s, 4H, Mes), 4.11 (s, 4H, im), 2.44 (s, 12H, Mes), 2.29 (s, 6H, Mes), 1.82 (m, 2H, pdt), 1.59 (m, 4H, pdt). Anal. Calcd. (Found) for  $\text{C}_{29}\text{H}_{32}\text{Fe}_2\text{N}_2\text{O}_5\text{S}_2$ : C, 52.43 (52.25); H, 4.85 (4.91); N, 4.22 (4.32).

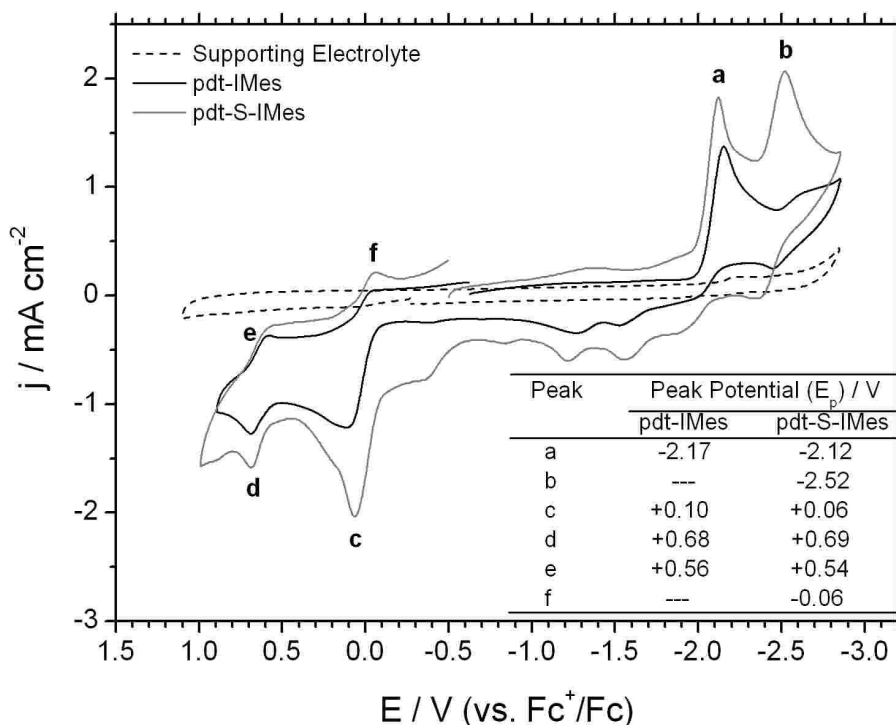
### X-ray Structure Determinations

For all reported structures a Bausch and Lomb 10X microscope was used to identify suitable crystals of the same habit. Each crystal was coated in paratone, affixed to a Nylon loop and placed under streaming nitrogen (110K) in a Bruker SMART 1000 CCD diffractometer (See details in .cif files). The space groups were determined on the basis of systematic absences and intensity statistics. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ . Anisotropic displacement parameters were determined for all nonhydrogen atoms. Hydrogen atoms were placed at idealized positions and refined with fixed isotropic displacement parameters. The following is a list of programs used: data collection and cell refinement, SMART WNT/2000 Version 5.632 or FRAMBO Version 4.1.05 (GADDS); data reductions, SAINTPLUS Version 6.63; absorption correction, SADABS; structural solutions, SHELXS-97; structural refinement, SHELXL-97; graphics and publication materials, X-Seed Version 1.5.

## RESULTS AND DISCUSSION

### Synthesis and IR spectroscopy.

The complex,  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3][\text{Fe}(\text{CO})_3\text{SIMes}]$  (abbreviated as **pdt-SIMes**, SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was synthesized in a one-pot reaction as described earlier (Thomas et al. 2008). As shown in Figure 1 (top), the  $\nu(\text{CO})$  IR spectrum of **pdt-SIMes** in toluene exhibits five bands at 2039(m), 2031(m), 1973(s), 1948(m) and 1915(w). The frequency and pattern of this solution IR spectrum of **pdt-SIMes** is almost identical to that of  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3][\text{Fe}(\text{CO})_3\text{IMes}]$  (abbreviated as **pdt-IMes**, the dashed red line in Figure 1, top). This observation suggests that both complexes adopt a similar structural conformation in solution. In contrast, and consistent with their different molecular structures found by x-ray diffraction, *vide infra*, the solid state IR spectra of **pdt-SIMes** (five bands at 2031 (s), 1977 (s, sh), 1962 (s), 1942 (s, sh) and 1917 (s)  $\text{cm}^{-1}$ ) and **pdt-IMes** (2033 (s), 1958 (s), 1929 (s) and 1906 (s, sh)  $\text{cm}^{-1}$ ) (measured by ATR-FTIR as powders from pulverized crystals) are quite different with the latter providing a better match to its solution state spectrum. Several NHC complexes,  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3][\text{Fe}(\text{CO})_2(\text{NHC})]$



**Figure 3.** Cyclic voltammograms of **pdt-IMes** (black line) and **pdt-S-IMes** (grey line) complexes (2.0 mM) in 0.1 M  $n\text{-Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ . The dash line represents the CV of the supporting electrolyte. Experimental conditions: potential sweep rate =  $200\text{ mV s}^{-1}$ , glassy carbon electrode.



prepared by ourselves and others have found the NHC ligands to typically adopt apical positions. Thus it can be inferred that in solution, **pdT-SIMes** adopts the same structural conformation as **pdT-IMes**, i.e. in both, the NHC ligand lies at the apical position, while the more complex pattern of the solid state IR spectrum of

**pdT-SIMes** reflects a mixture of isomeric forms.

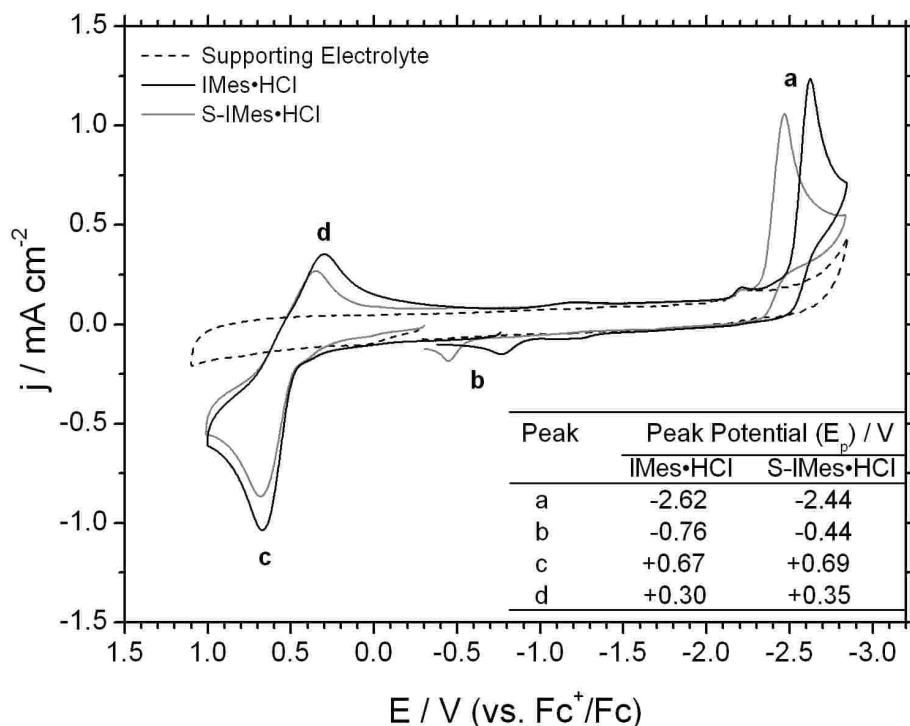
### Molecular Structure of **pdT-SIMes**.

The solid state structure of **pdT-SIMes** was analyzed by single crystal X-ray diffraction. The structure and selected structural parameters are given in Figure 2 along with stick drawings of the **pdT-IMes** structure for comparison. The X-ray study revealed a core  $\text{Fe}_2\text{S}_2$  framework as is typical of this class of dithiolate-bridged diiron complexes. The Fe-Fe distance is 2.562 Å, similar to that (2.525 Å) of **pdT-IMes**. In contrast to the apical position of the IMes ligand in **pdT-IMes** the SIMes ligand is positioned at the basal site on the Fe(2) atom in **pdT-SIMes**. The C-C bond distances of the five-membered rings also provide differences of note. In **pdT-SIMes** the C-C distance is 1.526 Å, consistent with a typical single C-C bond, while in **pdT-IMes**, the value of 1.288 Å fits the expectation of a C=C double bond. The Fe- $\text{C}_{\text{NHC}}$  bond length of **pdT-SIMes** is 1.989 Å, statistically not different from that of **pdT-IMes**, 2.013 Å.

Figure 2 also compares the orientation of the imidazole ring and pendant mesitylene groups. In the apical position of the **pdT-IMes** complex the plane of the NHC roughly bisects the S-Fe-C angles of the  $\text{Fe}(\text{CO})_2(\text{S})_2$  basal "plane" of the square pyramid, while the large Mes rings flank the two sides of the Fe-Fe bond vector. In the basal position of the **pdT-SIMes** structure, the NHC plane largely aligns with the Fe(2)-S(1) bond vector that is trans to the carbene donor C(9).

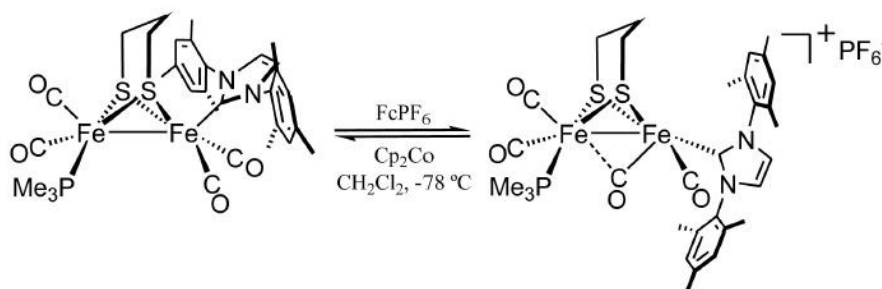
### Electrochemical studies.

Figure 3 shows the cyclic voltammograms (CVs) of **pdT-IMes** (black line) and **pdT-SIMes** (grey line) under the same experimental conditions. The electrochemistry of **pdT-IMes** has been previously described (Tye et al. 2005, Thomas et al. 2008). In brief, the peak at -2.17 V (vs.  $\text{Fc}^+/\text{Fc}$ ) (peak **a** in Figure 3) has been ascribed to a two-electron-reduction event by bulk electrolysis (BE). DFT calculations indicate that the first electron is transferred to the  $\text{Fe}(\text{CO})_3$



**Figure 4.** Cyclic voltammograms of the IMes•HCl (black line) and SIMes•HCl (grey line) salts (2.0 mM) in 0.1 M  $n\text{-Bu}_4\text{NBF}_4 / \text{CH}_3\text{CN}$ . The broken line represents the CV of the supporting electrolyte. Experimental conditions:  $\nu = 200 \text{ mV s}^{-1}$ , glassy carbon electrode.

### Scheme 1.



moiety to yield the intermediate  $\text{Fe}^0\text{Fe}^{\text{I}}(\text{IMes}^0)$ ; whereas the second electron is transferred to the IMes ligand to produce  $\text{Fe}^0\text{Fe}^{\text{I}}(\text{IMes}^{-1})$ . Diiron complexes that undergo two consecutive one electron-transfer events have been described (Capon et al. 2007, Capon et al. 2008).

To further investigate the nature of this event, the CV of **pdt-SIMes** was acquired under the same experimental conditions (grey line in Figure 3). In the case of **pdt-SIMes**, peak **a** was shifted 50 mV less negative than that for **pdt-IMes** species indicating that the electron transfer in the saturated ligand is more facile. Continuing in the cathodic direction, the main difference between the CV's of the two complexes was the presence of a new peak at -2.52 V (peak **b**). Bulk electrolysis indicated that the redox events at peak **a** and peak **b** are both one-electron reductions. Because of the structural similarity between the two complexes, it seems reasonable to conclude that in the case of **pdt-SIMes** complex, peak **a** corresponds to the one-electron transfer at the iron center; whereas, peak **b** is related with the electron transfer at the saturated imidazolium ligand. These two events appear overlapped in the case of **pdt-IMes** at -2.17 V yielding a two-electron transfer. The only structural difference between the two diiron complexes resides in the imidazolium ligand.

When reversing the potential in the anodic direction, the next main observed feature was peak **c**, which corresponds to the oxidation of the iron center from  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  to  $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ . The difference in peak potentials between the two complexes was 40 mV being the peak for **pdt-SIMes** more negative. The event related with **pdt-IMes** is irreversible; whereas, that for the saturated analogue is quasi-irreversible showing the reduction event at -0.06 V (peak **f**). The peak potential for features **d** and **e** was virtually the same for the two complexes. The nature of these two events has not been described before in the literature and it will be explained later in this paper.

To corroborate the initial conjecture that peak **b** is related with the electron transfer in the imidazolium ligand, CVs of the two imidazolium salts were run under the same experimental conditions. Figure 4 shows the CVs of the IMes•HCl (black line) and SIMes•HCl (grey line) in  $\text{CH}_3\text{CN}$ . Four well-defined peaks were observed. In the case of the IMes•HCl salt, the more prominent event appears at -2.62 V (peak **a**). Bulk electrolysis results (Table 1) indicate that this peak is related with a one-electron reduction process, as it has been

reported before (Gorodetsky et al. 2004), and corresponds to the irreversible reduction of the imidazolium ion  $[\text{IMes}\cdot\text{H}]^+$  to the radical species. When the potential scan is reversed, a small peak is observed at -0.76 V (peak **b**), which has been previously assigned to the oxidation of new chemical species that are generated from the reduction of the  $[\text{IMes}\cdot\text{H}]^+$  ion at -2.62 V [5]. The nature of peaks **c** (+0.67 V) and **d** (+0.30 V) has not been reported before in the literature. Since the only two species in solution besides the supporting electrolyte are the  $[\text{IMes}\cdot\text{H}]^+$  and  $\text{Cl}^-$  ions, it was hypothesized that these two peaks might be related with the  $\text{Cl}^-$  ion since no other electrochemical events has been reported for the imidazolium species at this potential region. To test this assumption, *n*-Bu<sub>4</sub>NCl was utilized as a source of  $\text{Cl}^-$  ions. The CV (not shown) showed two events at exactly the same potential of those observed in the case of the IMes•HCl salt (black line, Figure 4); therefore, it is clear that peaks **c** and **d** are related with the presence of  $\text{Cl}^-$  ions in solution.

The general shape of the CV for SIMes•HCl (grey line, Figure 5) matches that for IMes•HCl; however, upon close inspection of the peak potentials, two main differences were encountered: (i) the reduction of the  $[\text{SIMes}\cdot\text{H}]^+$  ion (peak **a**) occurs 180 mV more positive than that for the  $[\text{IMes}\cdot\text{H}]^+$  ion. Bulk electrolysis indicated this event corresponds to a one-

**Table 1.** Summary of the electrochemical measurements associated with the cathodic peaks in Figures 3 and 4.

Analyte	Peak Potential $E_p$ /V (vs. Fc/Fc <sup>+</sup> )	Number of Electrons (n) by Bulk Electrolysis
pdt-IMes	-2.17	2.2
pdt-SIMes	-2.12	1.3
	-2.52	0.9
IMes	-2.62	1.1
SIMes	-2.44	1.2

electron reduction as well. (ii) Peak **b** is also shifted 320 mV more positive than that for IMes•HCl. On the other hand, the peak potential for events **c** and **d** was invariable between the CVs of the two imidazolium salts enforcing the idea that these peaks are related with the counter ion. A summary of peak potentials and bulk electrolysis results is showed in Table 1.

When comparing the features in Figures 3 and 4 the following conclusions can be drawn. Comparison of the CVs of **pdt-SIMes** and the SIMes•HCl salt indicates that peak **b** in Figure 3 is related with the electron transfer in the imidazolium ligand. Therefore, peak **a** represents the reduction of the iron center from Fe<sup>I</sup>Fe<sup>I</sup> to Fe<sup>0</sup>Fe<sup>I</sup>. In the case of CV of **pdt-IMes** (solid line, Figure 3) peak **a** is associated with a two-electron reduction. When comparing this CV with that of the IMes•HCl salt is clear that the event related with the electron transfer in the imidazolium ligand (peak at -2.62 V) has shifted towards more positive potentials and has overlapped the peak related with the electron transfer in the Fe center. The saturation of the imidazole ring in the ligand allows the separation of the two events that appear overlapped in the case of the pdt-IMes complex (peak **a**).

## CONCLUSIONS

In summary, the electrochemical studies of mono-NHC carbene substituted diiron complexes (**pdt-IMes** and **pdt-SIMes**) as well as corresponding NHC•HCl salts elucidate overall two electron reduction of the diiron complexes are ascribed to Fe and NHC ligand based one electron reductions. In the case of pdt-IMes, Fe and NHC ligand based one electron reductions are coincidentally overlapped while the two reduction processes are distinct in the **pdt-SIMes** complex. As chloride salts, NHC•HCl, are also redox active. These results are consistent with our previous experimental and theoretical investigations of the redox properties of pdt-IMes. Additionally, this study provides an evidence of that the oxidation event of NHC•HCl salts is in the nature of counter-ion, Cl<sup>-</sup>.

## ACKNOWLEDGMENTS

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## CONFLICT OF INTEREST STATEMENT

No conflict of interest exists among the authors and their affiliated institutions whether in the implementation of the

research described above or in the preparation and submission of the present manuscript.

## CONTRIBUTIONS OF INDIVIDUAL AUTHORS

The research described in this manuscript is a result of a collaborative effort between the bioorganometallic synthesis laboratory of Professor M. Y. Darensbourg and the electrochemical surface science laboratory of Professor M. P. Soriaga. Dr. T. Liu, Dr. C. M. Thomas and Mr. B. Savoie worked in the Darensbourg laboratory; Dr. J. Sanabria-Chinchilla was a member of the Soriaga research group.

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