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# Experimental and Theoretical Insight into Electrocatalytic Hydrogen Evolution with Nickel Bis(aryldithiolene) Complexes as Catalysts

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Supporting Information

**ABSTRACT:** A series of neutral and monoanionic nickel dithiolene complexes with *p*methoxyphenyl-substituted 1,2-dithiolene ligands have been prepared and characterized with physicochemical methods. Two of the complexes, the monoanion of the symmetric  $[Ni\{S_2C_2(Ph-p-OCH_3)_2\}_2]$  (3<sup>-</sup>) with  $NBu_4^+$  as a counterion and the neutral asymmetric  $[Ni\{S_2C_2(Ph)(Ph-p-OCH_3)\}_2]$  (2), have been structurally characterized by single-crystal X-ray crystallography. All complexes have been employed as protonreducing catalysts in N,N-dimethylformamide with trifluoroacetic acid as the proton source. The complexes are active catalysts with good faradaic yields, reaching 83% for 2 but relatively high overpotential requirements (0.91 and 1.55 V measured at the middle of the catalytic wave for two processes observed depending on the different routes of the mechanism). The similarity of the experimental data regardless of whether the neutral or anionic form of the complexes is used indicates that the neutral form acts as a precatalyst. On the basis of detailed density functional theory calculations, the proposed



mechanism reveals two different main routes after protonation of the dianion of the catalyst in accordance with the experimental data, indicating the role of the concentration of the acid and the influence of the methoxy groups. Protonation at sulfur seems be more favorable than that at the metal, which is in marked contrast with the catalytic mechanism proposed for analogous cobalt dithiolene complexes.

# 1. INTRODUCTION

The need for easily accessible renewable energy<sup>1</sup> has led to growth in the research field of artificial photosynthesis. In this context, water splitting can lead to evolution of hydrogen, which can be used as a cheap, green fuel.<sup>2</sup> Hydrogen could also play an important role in the storage of energy obtained from diluted sources, such as solar and wind, via the conversion of electricity to chemical energy by electrolysis of water. Although the latter is a well-known technology, it has drawbacks, principally because of the use of noble-metal catalysts, such as platinum. A challenging approach for overcoming this issue would be to develop novel, efficient, and stable catalysts that employ abundant, and as a consequence cheap, metals such as iron, cobalt, nickel, and copper. On this basis, researchers have synthesized various complexes of these metals as catalysts of the reductive side of the water-splitting reaction, with reports of cobalt complexes, such as cobaloximes or macrocyclic and polypyridine cobalt complexes, being especially prevalent in the literature.<sup>3-6</sup> Recently, a number of reviews on the activity of related complexes have appeared.<sup>7-9</sup>

In the past decade, many novel complexes that can be used as catalysts for hydrogen production have been designed. Biomimetic approaches, in which chemists take inspiration from catalysts that Nature uses, have been particularly fruitful. In the context of hydrogen production, the most appropriate biomimetic targets are the hydrogenases.<sup>10–13</sup> In the same vein, a ligand that has attractive properties is the dithiolene that is found in the active site of molybdopterin.<sup>14</sup> Metal dithiolenes have long been used in solar energy conversion applications, such as hydrogen evolution<sup>15–17</sup> and in dye-sensitized solar cells.<sup>18,19</sup> The noninnocent nature of the dithiolene ligand framework<sup>20</sup> allows construction of multifunctional complexes because the reversible redox reactions that metal dithiolene complexes undergo can be localized on the metal, leading to reduced metal oxidation states, or on the ligand, depending on

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#### Scheme 1. Oxidation States and Nomenclature for a Dithiolene Ligand



the orbital contribution of each fragment.<sup>21</sup> The redox noninnocent character of dithiolene ligands is mainly based on their ability to reversibly take up or release electrons, yielding enedithiolate and dithioketone forms with distinct electronic structures and chemical properties, respectively (Scheme 1). Which one of these oxidation states is adopted depends on the substituents on the SCCS moiety of the dithiolene ligand and the nature of the metal. The term 1,2dithiolene is a general term that describes the ligand framework and its use does not refer to a specific oxidation state on the metal or ligand. The oxidation state and charge localization in metal dithiolene complexes have been the focus of extensive theoretical work,<sup>21,22</sup> which has provided insight regarding the chemical reactivity of dithiolene complexes<sup>23</sup> in various applications, including hydrogen evolution.

An initial report by Kisch et al.<sup>15</sup> investigated photocatalytic hydrogen evolution with various dithiolene complexes. Several years later, Sellman et al. reported on the mechanism of hydrogen evolution from the stoichiometric reaction of protons with an iron(II) bis(dithiolene) complex.<sup>24</sup> The redox events and hydrogen-evolving activity of  $[M(mnt)_2]^{3-}$  (M = Rh, Co, Ni; mnt<sup>2-</sup> = maleonitrile dithiolate ligand) complexes upon protonation have been reported by Vlček and Vlček,<sup>25</sup> where the authors propose that protonation occurs at the metal centers. Tris(dithiolene) complexes of molybdenum and tungsten were also used as water-splitting catalysts,<sup>14,16,26–28</sup> although they proved to be unstable in the presence of metal ions that destroy the chelating dithiolene ring.<sup>29</sup>

Interest in dithiolene complexes as hydrogen-evolving catalysts has recently reemerged, initially because of the group of Eisenberg and Holland, who reported a series of cobalt benzene-1,2-dithiolate (bdt<sup>2-</sup>) complexes that show promising performance with turnover numbers (TONs) of up to 9000.<sup>30,31</sup> On the basis of experimental data, an ECEC mechanism was proposed for electrocatalytic hydrogen evolution. The mechanism included reduction of the monoanionic complex  $[Co(bdt)_2]^-$  to the dianion, subsequent protonation of the dianion, reduction, and a final protonation step, leading to hydrogen evolution. Theoretical insight into the plausible mechanisms has been proposed by Solis and Hammes-Schiffer.<sup>32</sup> The first protonation was proposed to occur on a sulfur atom, with the second protonation yielding a cobalt(I) hydride. A recent study by Letko et al.<sup>33</sup> reported the preparation and mechanism of electrocatalytic hydrogen evolution using cobalt anisyl complexes that bear different substituents on the benzene rings. Cyclic voltammetry (CV) indicated that reduction to the dianion precedes protonation, as in the aromatic dithiolene (bdt<sup>2-</sup>) complexes studied by McNamara et al.<sup>31</sup> Finally, a recent publication by Eisenberg's group<sup>34</sup> reported on the photocatalytic and electrocatalytic activity of a series of nickel complexes with benzene-1,2dithiolene and related ligands that evolve hydrogen over a wide pH range and in different solvents and exhibit robustness under various experimental conditions.

Motivated by the above results, the knowledge that the electronic properties, and therefore the reactivity, of the dithiolene complexes are influenced by the substituents on the ditholene ligand, and the low cost and abundance of nickel in Nature, we have synthesized and characterized three nickel diphenyl-1,2-dithiolene complexes with varying numbers of methoxy groups on the benzene rings of the ligand framework. Structures are shown in Scheme 2. These complexes were

#### Scheme 2. Structure of the Compounds under Study



tested for their catalytic properties regarding electroreduction of protons to  $H_2$  in *N*,*N*-dimethylformamide (DMF). Because of the electron-donating effect of methoxy groups, fine-tuning of the reduction potentials can be achieved because in this type of complex reduction is mainly localized on the enedithiolate fragment.<sup>35</sup> To the best of our knowledge, this is the first time that a systematic study of the structural and electronic changes that occur during proton reduction has been performed for this class of compounds. Density functional theory (DFT) calculations have also been employed for elucidation of the reactive centers of the complexes and the structural conformations of the intermediates, from which putative reaction mechanisms are proposed.

## 2. EXPERIMENTAL SECTION

**General Considerations.** Reagents and solvents were purchased from Aldrich, Alfa Aesar, Merck, or Fisher and used as received unless otherwise noted. Anisoin and 4-methoxybenzoin were prepared according to Sumrell et al.<sup>36</sup> CDCl<sub>3</sub> was distilled from  $K_2CO_3$  and stored in the dark over 4A molecular sieves.

IR spectra were recorded in KBr pellets with a  $2.0 \text{ cm}^{-1}$  resolution using a Shimadzu IR Affinity-1. Elemental analyses were conducted using a LECO-183 CHNS analyzer. NMR spectra were recorded using a Varian Unity Plus instrument (300 MHz), and spectra were corrected with the residual solvent peak as an internal standard. UV– vis spectra were recorded with Hitachi U-2000 and Varian Cary 3E spectrophotometers in 1.0 cm quartz cuvettes.

**Electrochemistry.** Electrochemical experiments were performed using an AFCBP1 Pine Instrument Company and Bio-Logic SP300 potentiostat. Cyclic voltammograms were recorded in a twocompartment cell with a glassy carbon working electrode, an Ag/ AgCl (KCl 3M) reference electrode, and a platinum wire counter electrode (located in the second compartment). The glassy carbon electrode was polished with diamond paste  $(1 \ \mu m)$  or alumina  $(1 \ \mu m)$ on a polishing cloth before each measurement. The solution was purged with argon or nitrogen gas prior to measurements. At the end of each experiment, sublimed ferrocene was added as an internal standard. Bulk electrolysis was performed in a two-compartment cell with a glassy carbon rod electrode ( $\emptyset$  10 mm, Neyco, Paris, France), an Ag/AgCl reference electrode, and a platinum wire counter electrode (located in the second compartment). The cell was continuously purged with nitrogen (5 mL min<sup>-1</sup>), and the output gas was analyzed at 2 min intervals in a PerkinElmer Clarus 500 gas chromatograph using a previously described setup.<sup>37</sup> All potentials in the text are reported versus  $Fc^{+/0}$  redox couple.

X-ray Structure Determination. Green-black crystals of 2 suitable for X-ray structure determination were grown from the slow evaporation of a dichloromethane-heptane solution of the complex. Red crystals of 3<sup>-</sup> were grown by layering a dichloromethane solution of the complex with *n*-hexane. Data were collected on a SuperNova A Oxford Diffraction diffractometer, equipped with a CCD area detector and a graphite monochromator utilizing Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) for 3 and Cu K $\alpha$  radiation ( $\lambda$  = 1.54184 Å) for 2. Suitable crystals covered with paratone-N oil were mounted on the tip of glass fibers or scooped up in cryoloops at the end of a copper pin and transferred to a goniostat, where they were cooled for data collection. Empirical absorption corrections (multiscan based on symmetry-related measurements) were applied using CrysAlis RED software.<sup>38</sup> The structures were solved by direct methods with SIR92<sup>39</sup> and refined on  $F^2$  using full-matrix least squares with SHELXL97.<sup>40</sup> Software packages used: *CrysAlis CCD* for data collection,<sup>38</sup> *CrysAlis RED* for cell refinement and data reduction,<sup>38</sup> *WINGX* for geometric calculations,<sup>41</sup> and MERCURY for molecular graphics.<sup>42</sup> The non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. Unit cell data and structure refinement details for compounds 2 and 3<sup>-</sup> are listed in Table 1. Full details can be found in the CIF files provided in Supporting Information.

Table 1. Unit Cell Data and Structure Refinement Details for Compounds 2 and  $3^-$ 

	2	3.		
empirical formula	C <sub>30</sub> H <sub>24</sub> NiO <sub>2</sub> S <sub>4</sub>	C48H64NNiO4S4		
fw	603.44	905.95		
cryst syst	triclinic	triclinic		
space group	$P\overline{1}$	$P\overline{1}$		
a (Å)	9.975(5)	9.6860(4)		
b (Å)	10.495(5)	15.9951(11)		
c (Å)	13.500(5)	16.9499(9)		
$\alpha$ (deg)	85.497(5)	106.901(5)		
$\beta$ (deg)	75.295(5)	93.890(4)		
γ (deg)	85.161(5)	107.188(5)		
V (Å <sup>3</sup> )	1359.7(11)	2366.2(2)		
Z	2	2		
$\rho_{\rm calcd}~({\rm g~cm^{-3}})$	1.474	1.272		
radiation, $\lambda$ (Å)	0.71073	1.54184		
$\mu \ (\mathrm{mm}^{-1})$	1.048	2.568		
temperature (K)	100(2)	100(2)		
measd/indep reflns $(R_{int})$	9180/4779 (0.0304)	14960/8430 (0.0311)		
param refined	334	526		
GOF (on $F^2$ )	1.115	1.016		
$\mathrm{R1}^{a}\left[I > 2\sigma(I)\right]$	0.0700	0.0448		
$wR2^{b} [I > 2\sigma(I)]$	0.1921	0.1190		
$(\Delta ho)_{ m max}/(\Delta ho)_{ m min}$ (e Å $^{-3}$ )	1.853 /-0.514	0.769 /-0.364		
${}^{a}\mathrm{R1} = \sum_{v} ( F_{o}  -  F_{c} ) / \sum_{v} [w(F_{o}^{2})^{2}]^{1/2}.$	$\sum( F_{o} ).  {}^{b}wR2 = \{$	$\sum [w(F_{\rm o}^{2} - F_{\rm c}^{2})^{2}]/$		

**DFT Studies.** All quantum-chemical calculations were done with a DFT approach using the B3LYP functional and basis sets of triple- $\zeta$  (TZVP) quality. The ORCA program package (version 2.9.1) was employed for all electronic structure calculations.<sup>43</sup> Two approaches were employed for estimation of the relative energies of different species and the energies of the various reactions. In the first, geometry optimizations were performed for all species in a vacuum using the B3LYP functional and a TZVP basis set. Single-point energy

calculations were then performed on these optimized vacuum structures using the B3LYP functional and an extended TZVP basis set with extra polarization and diffuse functions. These single-point calculations were performed in both vacuum and DMF solvent using the COSMO implicit solvation method that ORCA implements.<sup>44</sup> In addition, normal-mode calculations were performed at the vacuum optimized geometries using the B3LYP functional and original TZVP basis set to obtain the appropriate free-energy contributions to the species energies. The latter were estimated as the sum of the singlepoint vacuum energy, the solvation energy (the difference between the single-point solvent and vacuum energies), and the free-energy contribution from the normal-mode calculations. This approach seems to be similar to that used by many workers, including that described by Konezny and co-workers.<sup>45</sup> In the second approach, performed as a check of the first, potential (rather than free) energies for the reactions were estimated by geometry optimization of all species in DMF solvent using the B3LYP functional and a TZVP basis set, followed by single-point calculations in DMF solvent with the same functional and the larger TZVP basis set.

**Preparation of the Neutral Compounds.** 1–3 were prepared using the benzoin/ $P_4S_{10}$  method of Schrauzer, as modified by Bui et al.,<sup>46</sup> with yields reaching 30%. The analytical data for these complexes are as follows:

Compound 1. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.31–7.41 (m, 20H, aromatic). IR: 1363 (s,  $\bar{\nu}_{C=C}$ ), 1140 (s,  $\bar{\nu}_{C-S}$ ), 882 (s,  $\bar{\nu}_{C-S}$ ) cm<sup>-1</sup>. UV–vis: DMF (860 nm, 29200 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calcd for C<sub>28</sub>H<sub>20</sub>NiS<sub>4</sub>: C, 61.89; H, 3.71; S, 23.60. Found: C, 61.92; H, 3.80; S, 23.44.

Compound 2. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.83 (s, 6H, OMe), 6.81 (d, 4H, p-substituted phenyl ring), 7.39 (m, 14H, aromatic). IR: 1357 (s,  $\overline{\nu}_{C=C}$ ), 1254 (s,  $\overline{\nu}_{C-OMe}$ ), 1144 (s,  $\overline{\nu}_{C-S}$ ), 886 (s,  $\overline{\nu}_{C-S}$ ) cm<sup>-1</sup>. UV–vis: DMF (902 nm, 32100 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calcd for C<sub>30</sub>H<sub>24</sub>NiO<sub>2</sub>S<sub>4</sub>: C, 59.71; H, 4.01; S, 21.25. Found: C, 59.58; H, 4.12; S, 21.17.

Compound 3. <sup>1</sup>H NMR in CDCl<sub>3</sub>:  $\delta$  3.86 (s, 12H, OMe), 6.85 (d, 8H, p-substituted phenyl ring), 7.38 (d, 8H, aromatic). IR: 1350 (s,  $\overline{\nu}_{C=C}$ ), 1249 (s,  $\overline{\nu}_{C-OMe}$ ), 1143 (s,  $\overline{\nu}_{C-S}$ ), 887 (s,  $\overline{\nu}_{C-S}$ ) cm<sup>-1</sup>. UV–vis: DMF (934 nm, 30600 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calcd for C<sub>32</sub>H<sub>28</sub>NiO<sub>4</sub>S<sub>4</sub>: C, 57.93; H, 4.25; S, 19.33. Found: C, 57.81; H, 4.38; S, 19.39.

**Preparation of the Anionic Complexes 1<sup>-</sup>**, **2**<sup>-</sup>, **and 3**<sup>-</sup>. A total of 0.1 mmol of each neutral complex was suspended in a 1:1 mixture of dichloromethane and methanol (30 mL total volume). A total of 1.1 equiv of powdered NaBH<sub>4</sub> was added under stirring, and the greenblack suspension gradually turned into a red-brown effervescent solution. The solution was stirred for 10 min until gas evolution ceased, and then 1 equiv of tetra-*n*-butylammonium bromide was added as a solid. The resulting suspension was stirred for 10 min, filtered using a sintered funnel and washed with copious amounts of warm water, methanol, and ether. The resulting solids were dried under vacuum overnight. Yields were quantitative. The anionic compounds are paramagnetic, and thus no NMR spectra were recorded.

**1**<sup>-</sup>. IR: 1455 (s,  $\bar{\nu}_{C=C}$ ), 1177 (s,  $\bar{\nu}_{C-S}$ ), 867 (s,  $\bar{\nu}_{C-S}$ ) cm<sup>-1</sup>. UV–vis: DMF (938 nm, 13900 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calcd for C<sub>44</sub>H<sub>56</sub>NNiS<sub>4</sub>: C, 67.25; H, 7.18; N, 1.78; S, 16.32. Found: C, 67.18; H, 7.24; N, 1.69; S, 16.41.

**2**<sup>-</sup>. IR: 1453 (s,  $\overline{\nu}_{C=C}$ ), 1239 (s,  $\overline{\nu}_{C-OMe}$ ), 1175 (s,  $\overline{\nu}_{C-S}$ ), 844 (s,  $\overline{\nu}_{C-S}$ ) cm<sup>-1</sup>. UV–vis: DMF (953 nm, 15200 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calcd for C<sub>46</sub>H<sub>60</sub>NNiO<sub>2</sub>S<sub>4</sub>: C, 65.31; H, 7.15; N, 1.66; S, 15.16. Found: C, 65.26; H, 7.07; N, 1.75; S, 15.02.

**3**<sup>-</sup>. IR: 1450 (s,  $\overline{\nu}_{C=C}$ ), 1244 (s,  $\overline{\nu}_{C-OMe}$ ), 1174 (s,  $\overline{\nu}_{C-S}$ ), 874 (s,  $\overline{\nu}_{C-S}$ ) cm<sup>-1</sup>. UV–vis: DMF (967 nm, 10000 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calcd for C<sub>48</sub>H<sub>64</sub>NNiO<sub>4</sub>S<sub>4</sub>: C, 63.63; H, 7.12; N, 1.55; S, 14.16. Found: C, 63.72; H, 7.20; N, 1.63; S, 14.20.

## 3. RESULTS AND DISCUSSION

**Synthesis of the Complexes.** The three nickel dithiolene complexes under study were prepared using literature procedures, more specifically using the benzoin/ $P_4S_{10}$  method, where a benzoin is reacted with an excess of phosphorus(V) sulfide in refluxing dioxane to yield the intermediate

thiophosphoric ester, which reacts with nickel(II) chloride in a dioxane–water mixture. Although more efficient methods to prepare the complexes have been proposed in the literature, such as the use of 1,3-dithiol-2-ones<sup>47,48</sup> or alkylated phosphorus intermediates,<sup>49</sup> the benzoin method has been applied because of its simplicity and the availability of starting benzoins.

The anionic complexes were prepared using sodium borohydride as a mild reducing agent and precipitated with tetra-*n*-butylammonium bromide. Alkylammonium salts with shorter carbon chains (e.g., tetraethylammonium) can be used, but the resulting compounds are less soluble in nonpolar solvents.

**UV–Vis Spectroscopy.** All complexes exhibit absorption spectra similar to those reported earlier for similar nickel bis(dithiolene) complexes.<sup>50</sup> Normalized absorption spectra in DMF for neutral and monoanionic complexes are shown in Figure 1. The spectra for the neutral complexes exhibit two



Figure 1. Normalized absorption spectra for neutral complexes 1-3 and monoanionic complexes  $1^-$ ,  $2^-$ , and  $3^-$  as tetrabutylammonium salts in DMF solution.

major bands around 600 and 900 nm, with the latter being described as  $\pi - \pi^*$  transitions of the dithiolene ligand.<sup>51,52</sup> For 1–3, the prominent band is observed at 860, 902, and 934 nm with molar absorptivity values of 29200, 32100, and 30600 M<sup>-1</sup> cm<sup>-1</sup>, respectively. Increasing methoxy substitution induces a 30–40 nm bathochromic shift in the near-IR band because the increasing electron-donating effect of additional methoxy groups decreases the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap of the complex, as reported for similar compounds.<sup>51,53</sup>

This trend is also observed in the monoanionic complexes, where the near-IR band bathochromic shifts compared to the corresponding neutral complexes and are located at 938, 953, and 967 nm for  $1^-$ ,  $2^-$ , and  $3^-$ , respectively, with molar absorptivity values almost half of those of the neutral complexes, namely, 13900 ( $1^-$ ), 15200 ( $2^-$ ), and 10000 ( $3^-$ )  $M^{-1}$  cm<sup>-1</sup>.

**Vibrational Spectroscopy.** The complexes exhibit IR spectra typical of similar complexes.<sup>54,55</sup> For the neutral complexes 1-3,  $\overline{\nu}_{C-C}$  values are in the region of 1350–1360 cm<sup>-1</sup>, with a decrease in the wavenumber value as the number of methoxy groups increases. In all methoxy-substituted

complexes (2, 3, 2<sup>-</sup>, and 3<sup>-</sup>), a band corresponding to the aryl–OMe vibration is observed around 1250 cm<sup>-1</sup> for the neutral complexes and 1240 cm<sup>-1</sup> for the anionic complexes. This band is absent in the case of unsubstituted compounds 1 and 1<sup>-</sup>. The  $\bar{\nu}_{C-S}$  values are observed in the region of ~880 cm<sup>-1</sup> and follow the opposite trend compared to the  $\bar{\nu}_{C-C}$  values. Examination of the spectra of the anionic complexes leads to the observation that upon reduction the  $\bar{\nu}_{C-C}$  values increase and the  $\bar{\nu}_{C-S}$  values decrease, which is attributed to the fact that in the reduced complexes the ligands possess enedithiolate character (Scheme 1).<sup>55</sup>

**Structural Analysis.** Single crystals suitable for structure determination were isolated for complexes 2 and  $3^-$  (Figures 2 and 3), and selected bond distances are presented in Table 2. Complex  $3^-$  was isolated as tetrabutylammonium salt.



Figure 2. ORTEP diagram at 30% probability level for compound 2.



**Figure 3.** ORTEP diagram at 30% probability level for compound  $3^-$ . The NBu<sub>4</sub><sup>+</sup> counterion is omitted for clarity.

To the best of our knowledge, **2** is the first example of an asymmetric phenyl-substituted bis(dithiolene) complex to be structurally characterized. The neutral form of  $3^-$ , i.e., **3**, was reported earlier by Arumugam et al.<sup>49</sup> The structure of the complexes is representative for the nickel bis(dithiolene) system, with an almost perfectly planar configuration of the NiS<sub>4</sub> core for both complexes. Bond lengths (Ni–S, C–S, and C–C) are comparable to those reported for analogous complexes, with the average Ni–S bonds in the literature<sup>56</sup> being 2.101–2.223 Å, the S–C bonds 1.642–1.777 Å, and the C–C bonds 1.284–1.520 Å.

It is of interest to compare how the addition of methoxy groups affects the bond lengths of complexes 1–3. The Ni–S and C–S bonds remain practically unaffected, but the C1–C2 and C16–C17 bonds vary notably. In complex 1, the C–C bond distance of the dithiolene moiety (C1–C2 and C16–C17) is ~1.388 Å, and the addition of one methoxy group leads to a significant elongation of the same bonds (1.423 and 1.402 Å). However, the addition of one more methoxy group to the remaining phenyl ring leads to intermediate bond lengths

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1-3 and  $3^-$ 

bond <sup>a</sup> /compound	151	2	349	3-
Ni1-S1	2.1209	2.130(2)	2.1222(6)	2.1416(5)
Ni1-S2	2.1227	2.129(2)	2.1217(6)	2.1292(6)
Ni1-S3	2.1209	2.128(2)	2.1341(6)	2.1510(5)
Ni1-S4	2.1227	2.115(2)	2.1182(6)	2.1358(6)
C1-S1	1.716	1.699(6)	1.717(2)	1.744(2)
C2-S2	1.703	1.711(6)	1.703(2)	1.742(2)
C16-S3	1.716	1.707(6)	1.717(2)	1.745(2)
C17-S4	1.703	1.714(7)	1.710(2)	1.743(3)
C1-C2	1.388(3)	1.423(8)	1.394(3)	1.368(3)
C16-C17	1.388(3)	1.402(9)	1.391(3)	1.362(2)
S1-Ni1-S2	90.85	91.17(7)	90.91(2)	90.78(2)
S3-Ni1-S4	90.88	91.14(7)	91.25(2)	90.85(2)

"For the sake of comparison, numbering for 3 is in accordance with 2, i.e., bond in 2/bond in 3: Ni1-S2/Ni1-S2', Ni1-S3/Ni1-S1', Ni-S4/Ni-S2, C2-S2/C2-S2', C16-S3/C1'-S1', C17-S4/C2'-S2, C16-C17/C1'-C2', S1-Ni1-S2/S1-Ni1-S2', and S3-Ni1-S4/S2-Ni1-S1'.

(1.394 and 1.391 Å), so in terms of the C–C<sub>ene</sub> bond length, the trend is 1 < 3 < 2. The noninnocence of the dithiolene ligands in neutral nickel bis(dithiolene) complexes 1-3 involves the coordination of two radical anionic ligands to a nickel(II) ion.<sup>22</sup> The radical anionic nature of the coordinated dithiolene ligand is well depicted by the two extreme resonant forms A and B in Scheme 3, where for simplicity only one of

Scheme 3. Limiting (A and B) and Delocalized (C) Structures for a Nickel Dithiolene Complex



the coordinated ligands is depicted, with one sulfur atom with radical-anion character and the other one engaged in a thioketone function. Form C depicts the delocalized nature of the coordinated ligand as a sum of forms A and B, where the electron density is distributed over the five-atom  $NiS_2C_2$  ring.

When R = R', the negative charge is delocalized in a symmetrical manner over the SCCS core (form C). Actually, this is also supported from the aforementioned trend for the  $C{-}C_{\text{ene}}$  bond length, indicating that the two symmetric complexes 1 and 3 adopt a structure where the charge is evenly distributed over the  $NiS_2C_2$  core (form C, Scheme 3). Moreover, it has been proven by S K-edge X-ray absorption spectroscopy data combined with theoretical calculations that if the contribution of the metal  $d_{xz}$  orbital dials up to 25%, then 0.4 of an electron spin is located in each ligand, with the metal orbital acting as a superexchange pathway between the two partially spin-polarized ligands.<sup>19</sup> When  $R \neq R'$ , as in our case for complex 2 (R = phenyl and R' = 4-methoxyphenyl), one of the first two resonance forms must contribute more to the bonding scheme. While differences in the C-S and Ni-S bond lengths are within experimental error, the C-C bonds provide insight into the electronic structure of 2. As mentioned earlier, 2 exhibits elongated C1–C2 and C16–C17 bonds, an indication that in 2 the C–C bond resembles a single bond. Thus, one of the two first structures (forms A and B) of Scheme 3 better describes the structure of 2. The DFT calculations (vide infra) indicate that protonation occurs at the sulfur atom, which is in proximity to the 4-methoxyphenyl group of 2. On the basis of the fact that the thiolate sulfur atom, which facilitates protonation, we propose that the bonding scheme in catalyst 2 is best described by form B (R = phenyl and R' = 4-methoxyphenyl) of Scheme 3.

A comparison between the neutral and monoanionic complexes 3 and 3<sup>-</sup> at first reveals a shortening of the C1–C2 and C16–C17 bonds with a concomitant elongation of the C–S and Ni–S bonds. This trend has been observed for the  $[Ni(S_2C_2Me_2)_2]^{0/1-/2-}$  series in a detailed study by Lim et al.<sup>57</sup> DFT and vibrational data indicate that the reduction is a ligand-based event and leads to electronic saturation of the ligand, with the dianionic extreme being better described as two dianionic enedithiolate ligands coordinated to a nickel(II) ion. Thus, a shortening of the C–C bonds is anticipated as these bonds acquire a double-bond character, which is further corroborated by the increased wavenumber values observed in the IR spectra for the vibration of C–C bonds. Elongation of the C–S bonds is attributed to the loss of dithioketone character upon reduction.

**Electrochemistry.** The electrochemical behavior of all complexes was investigated with CV in DMF in the presence of  $nBu_4NPF_6$  (0.1 M) as the supporting electrolyte. Examination of either the monoanionic or neutral compounds revealed the same behavior so only the electrochemical characteristics of the neutral compounds are reported here. Two well-defined reversible redox events are observed, corresponding to the one- and two-electron reductions of complexes 1-3, as documented in the literature for compound  $1.5^{8}$  The introduction of methoxy groups on the phenyl rings has an effect on the reduction potential because the methoxy electron-donating groups lead to increased electron density on the sulfur atoms. A trend can be observed where the most difficult complex to reduce is 3 and the easiest to reduce is 1 (Table 3).

Table 3. Reduction Potentials for Complexes 1-3

E vs Fc <sup>+/0</sup>			
neutral/monoanion	monoanion/dianion		
-0.274	-1.260		
-0.319	-1.289		
-0.370	-1.325		
	<i>E</i> vs neutral/monoanion -0.274 -0.319 -0.370		

Reduction potential values are in the range of -0.274 to -0.370 V vs Fc<sup>+/0</sup> for the first reduction to the monoanion (0/ 1– process) and -1.260 to -1.325 V vs Fc<sup>+/0</sup> for the second reduction to the dianion (1–/2– process). Although the behavior is similar to the respective cobalt compound,<sup>33</sup> the reductions of 3 are found at less negative potential values than those of the cobalt analogue complexes. Normalized cyclic voltammograms are shown in Figure 4, and reduction potentials can be found in Table 3.

**Electrocatalytic Proton Reduction.** Trifluoroacetic acid (TFA;  $pK_a = 6.0$  in DMF<sup>59,60</sup>) has been employed as the proton source in hydrogen evolution experiments. The addition of TFA aliquots to solutions of catalyst **1**, **2**, or **3** in DMF triggers the appearance of catalytic waves that grow at



**Figure 4.** Normalized cyclic voltammograms for compounds 1-3 in DMF at a scan rate of 100 mV s<sup>-1</sup> with nBu<sub>4</sub>NPF<sub>6</sub> in DMF under argon at room temperature (glassy carbon working electrode).

potentials significantly more cathodic than the reversible redox potential corresponding to the formation of the dianionic species. For complex 1, two catalytic processes are observed at approximately -1.75 and -1.9 V vs Fc<sup>+/0</sup> (midwave potentials; see Figure 5) measured at the middle of the catalytic waves for



Figure 5. Cyclic voltammogram of 1 in the presence of increasing equivalents of TFA: no acid, red; 1 equiv, green; 3 equiv, light blue; 5 equiv, burgundy; 10 equiv, dark blue (glassy carbon working electrode).

5 mM TFA concentration. Direct reduction of TFA at the glassy carbon electrode occurs at potentials more negative than -2.2 V vs Fc<sup>+/0</sup> (Figure S3). We can therefore conclude that both catalytic waves are mediated by the nickel-based catalysts. For comparison, similar cobalt and nickel dithiolene complexes (with maleonitriledithiolate or 1,2-benzenedithiolate ligands) exhibit only one wave in the presence of organic acids.<sup>30,31,61</sup>

As the acid concentration increases and reaches 10 mM, the process with a half-wave potential of -1.75 V saturates and the process with a half-wave potential of -1.9 V prevails. The equilibrium potential for the reduction of TFA (5 mM) into H<sub>2</sub> in DMF is -0.94 V vs Fc<sup>+/0</sup> and was calculated using the method described in refs 59 and 62 (see the Supporting Information, eq S1). This value allows overpotential require-

ments of 0.81 and 0.96 V to be determined at the midwave potentials for the two above-mentioned processes, respectively. The aforementioned trend is followed by complexes 2 and 3 (Figures S1 and S2) with similar overpotential requirements.

At the same time, there is a concomitant loss of the reversibility of the 1-/2- redox process, indicating that a fast chemical reaction, likely protonation, takes place after reduction to the dianion. This is in accordance with the fact that the sulfur atoms, which act as intramolecular proton relays/protonation sites, are nucleophilic enough for protonation to occur only when the complex is fully reduced.<sup>33,63</sup> The peak potential of the cathodic wave ( $E_p$ ) moves toward more positive potentials with increasing amounts of protons, as expected for such an EC process (eq 1).<sup>64</sup> Plotting  $E_p$  as a function of log [TFA] for catalysts 1–3 results in linear relationships between these two quantities (Figure S4) with slopes of 37.5, 47.6, and 50.5 mV per log unit, respectively. Protonation constant ( $k_{H+}$ ) values of  $1.78 \times 10^5$ ,  $3.51 \times 10^7$ , and  $4.31 \times 10^7$  s<sup>-1</sup> could then be determined using eq 1 for the initial protonation step following the 1-/2- reduction process.

$$E_{\rm p} = E^{\circ} - 0.78 \frac{RT}{F} + \frac{RT \ln 10}{2F} \log \left( \frac{RTk_{\rm H^+}[{\rm TFA}]}{F\nu} \right)$$
(1)

However, the current enhancement observed at the 1-/2- cathodic peak for catalysts 1-3 (53, 41, and 53%, respectively; Figures 5 and S1 and S2) in the presence of 10 mM TFA is larger than the ~11% increase of the peak current expected for an EC process,<sup>66</sup> suggesting that a catalytic process might also occur at this potential value.

The production of hydrogen was confirmed using controlled potential bulk electrolysis in DMF at -1.67 V vs Fc<sup>+/0</sup>, corresponding to the onset potential of the first catalytic wave mentioned above. The concentrations of the catalyst and TFA were 1 and 50 mM, respectively. Bulk electrolysis was performed for 3 h using a glassy carbon rod electrode, and the evolved hydrogen was quantified by gas chromatography. A faradaic yield of 66–83% is observed for all three complexes, with the highest value for the asymmetric complex 2. Complex 2 also performs best with a TON of 25, compared to 15 and 12 for 1 and 3, respectively (Table 4). Bulk electrolysis using a

Table 4. Bulk Electrolysis Results for Complexes 1-3 in DMF in the Presence of 50 mM TFA

compound	TON	faradaic yield <sup>a</sup>
1	15	0.66
2	25	0.83
3	12	0.74
$2^b$	47	0.23

<sup>*a*</sup>Bulk electrolysis was performed at -1.67 V vs Fc<sup>+/0</sup> for a 3 h period with a catalyst concentration of 1 mM. <sup>*b*</sup>The catalyst concentration was 0.1 mM.

mercury pool electrode resulted in less efficiency for all complexes, with a hydrogen sulfide smell evolving after the end of the experiment, which indicates a degree of catalyst degradation.

In order to find out if a catalytic process occurs at the potential corresponding to the formation of the dianion, as enhancement of the peak current implies, bulk electrolysis experiments were also performed at -1.3 V vs Fc<sup>+/0</sup> for complexes 1 and 2. Catalysts 1 and 2 achieved 2 and 1 TONs

corresponding to hydrogen evolution with 57% and 34% faradaic yield, respectively, indicating that this catalytic process is rather reduced but not missing, in accordance with DFT calculations.

Taking into consideration that the hydrogen-evolving systems reported up to now with dithiolene catalysts perform better when the catalyst is in lower concentration (micromolar for photocatalysis and  $10^{-4}$  M for electrocatalysis<sup>30,31,67</sup>), we also employed catalyst 2 with a concentration of 0.1 mM. The TON (determined from gas chromatography measurements) increased to 47 for the same time of bulk electrolysis (glassy carbon electrode, 3 h), with the faradaic yield dropping to 23%. Thus, we propose that higher catalyst concentrations could lead to destructive pathways between two dithiolene catalyst molecules. CV measurements performed on the bulk electrolysis solution at the end of the experiment display features similar to those of Figure S1. Furthermore, the addition of iodine in the bulk electrolysis solution after the end of the experiment resulted in a color change from red to green, indicating oxidation of the red anionic species to the green neutral.

Study of the Decomposition of Catalysts. In order to investigate whether decomposition of the catalyst occurs on the surface of the electrode, an implication of heterogeneous catalysis, rinse test experiments were performed in which, after three distinct experiments detailed below, the working electrode was rinsed with solvent and immersed again in a fresh solution of acid in order to examine whether a catalytic activity remains in the absence of catalyst in solution. First, the glassy carbon working electrode was conditioned through measurement of a single cyclic voltammogram in acidic solutions of catalyst 2. Little current enhancement was observed in CV measurements for the rinsed electrode (Figure 6). Second, a linear sweep voltammogram from -0.5 to -1.7 V



**Figure 6.** Rinse tests for catalyst **2** in the presence of 1 and 10 equiv of TFA: (solid line) in the presence of catalyst; (dashed line) in the absence of catalyst (glassy carbon working electrode).

vs  $Fc^{+/0}$  was measured in the presence of catalyst (Figure S5). This procedure should avoid reoxidation of the deposit (therefore cleaning the electrode surface) during the backward scan. However, a subsequent CV measurement starting from -1.0 V vs  $Fc^{+/0}$  showed no current enhancement (Figure 7, red trace) in the potential region, where catalysis occurs in the presence of catalyst (Figure 7, dotted gray trace). Third, we



**Figure 7.** Rinse tests for catalyst **2** in the presence of 10 equiv of TFA: (gray trace) cyclic voltammogram in the presence of catalyst; (red trace) cyclic voltammogram in the absence of catalyst starting from -1.0 V vs Fc<sup>+/0</sup> after linear sweep voltammetry; (black trace) cyclic voltammogram in the absence of catalyst starting from -1.0 V vs Fc<sup>+/0</sup> after 3 min potential application (glassy carbon working electrode).

used a conditioning procedure previously reported to demonstrate deposition of NiS onto a glassy carbon electrode for a similar  $[Ni(bdt)_2]^-$  complex.<sup>61</sup> The working electrode was poised for 3 min at a constant potential negative to the potential of the 1-/2- process and corresponding to the onset of the catalytic wave  $(-1.65 \text{ V vs Fc}^{+/0})$ . The subsequent recording of the cyclic voltammogram (Figure 7, black trace) indicated that there was little enhancement of the catalytic wave in the absence of catalyst. The same behavior was observed with catalyst 1 (Figure S6). Finally, the linear dependence of  $i_{cat.}$  on the square root of the scan rate (Figure 8) indicated a homogeneous, diffusion-controlled process.<sup>65</sup> All of the above experiments indicate that, under the experimental conditions reported in this work, homogeneous catalysis occurs at the surface of the electrode.

Computational Investigation of the Hydrogen Evolution Mechanism. DFT calculations were employed to



**Figure 8.** Cyclic voltammograms of catalyst **2** in the presence of 10 mM TFA at various scan rates. Inset: linear dependence of  $i_{cat.}$  vs  $v^{1/2}$  ( $R^2 = 0.97$ ; glassy carbon working electrode).

Table 5. Selected Structural Parameters Calculated for Intermediates of the Hydrogen Evolution Mechanism for Catalyst 1

parameter <sup>a</sup>	[1]47	[1]-	<b>[1</b> ] <sup>2-</sup>	[1(SH)] <sup>-</sup>	[1(SH)] <sup>2-</sup>	[1(SH-SH)]	[1(SH-SH)] <sup>-</sup>
Ni1-S1	2.160	2.184	2.222	2.227	2.404	2.230	2.369
Ni1-S2	2.161	2.183	2.213	2.237	2.374	2.200	2.310
Ni1-S3	2.160	2.185	2.219	2.185	2.312	2.205	2.335
Ni1-S4	2.161	2.186	2.219	2.203	2.311	2.236	2.335
C1-S1	1.722	1.757	1.790	1.803	1.804	1.806	1.805
C2-S2	1.721	1.755	1.778	1.770	1.769	1.769	1.765
C16-S3	1.722	1.758	1.783	1.782	1.777	1.771	1.772
C17-S4	1.721	1.755	1.763	1.783	1.787	1.805	1.804
C1-C2	1.392	1.364	1.356	1.351	1.360	1.348	1.359
C16-C17	1.392	1.364	1.353	1.350	1.361	1.349	1.360
S1-H				1.352	1.351	1.353	1.352
S4-H						1.352	1.352
S–Ni–S dihedral angle	0	0	0.8	2.32	20.44	8.87	39.93
					1.04 D 11		

"The numbering scheme is the same as that in Figure 3 assuming protonation at S1 and S4. Bond lengths are given in angstroms and angles in degrees.

investigate the possible reaction pathways for hydrogen evolution by catalysts 1-3 and their monoanions. The electronic structure of all of the stationary points along the reaction path were characterized, and the redox potentials of the electron-transfer steps as well as the energies of the proton-transfer processes were calculated. Although these computed energies can be different from the experimental values, often by as much as 300 mV,<sup>68</sup> the calculations, nevertheless, provide invaluable insight into what is observed experimentally.

The geometries of the neutral complexes and their monoanions were fully optimized in DMF from their experimental single-crystal X-ray structures, as determined herein and in the literature.<sup>51</sup> The calculated geometries in solvent are in good agreement with the experimental ones, with the calculated bond lengths and angles within 0.01 Å and  $2^{\circ}$ , respectively. There is an exception for the Ni–S bond lengths, which are overestimated by as much as 0.04 Å, but this is anticipated with DFT calculations. Calculated structural parameters, namely, bond lengths and S–Ni–S dihedral angles for complex 1, its monoanion, and all of its intermediates, are summarized in Table 5.

The proposed mechanism for the  $2e^{-}/2H^{+}$  reduction/ protonation of 1 leading to evolution of hydrogen is shown in Scheme 4. All of the protonation energies were computed with respect to the CF<sub>3</sub>COOH/CF<sub>3</sub>COO<sup>-</sup> couple, and the standard redox potential,  $E^{\circ}$ , was calculated using the relation  $E^{\circ} = (-\Delta G^{\circ}/nF) - E^{\circ}_{ref}$  where  $\Delta G^{\circ}$  is the free energy of reduction, n is the number of electrons being transferred, F is the Faraday constant, and  $E^{\circ}_{ref}$  is the absolute reduction potential of the ferrocene couple computed at the same level of theory. As Scheme 4 indicates, the mechanism initially involves reduction to the monoanion followed by reduction to the dianion, and the next step is protonation of the latter, which proceeds downhill by 61 kJ mol<sup>-1</sup>. Overall, this scheme agrees with our experimental findings in which hydrogen is produced after formation of the dianion, and it is also identified as the favorable path compared with protonation of the monoanion, yielding [1(SH)], which is computed to be endothermic by as much as 18 kJ mol<sup>-1</sup>. Moreover, protonation of the monoanion at the nickel atom is less favorable to [1(SH)] by 74 kJ mol<sup>-1</sup>.

These calculations indicate that the most favorable protonation site of the dianion of 1 is on any one of the sulfur atoms of the dithiolene ligands rather than the nickel atom. Indeed, the nickel-protonated counterpart  $[1(NiH)]^-$  is less stable by 64 kJ mol<sup>-1</sup> than  $[1(SH)]^-$  (Scheme 4). After the first protonation, two different steps can take place, either a second protonation via a thermoneutral reaction  $(-14 \text{ kJ mol}^{-1})$  (route A) or reduction and then protonation (route B).

Protonation of  $[1(SH)]^-$  (route A) leads only to one intermediate, which is doubly protonated on two sulfur atoms on distinct dithiolene rings, namely, [1(SH-SH)]. Hydrogen evolution from this state to afford complex 1 is slightly exergonic by  $-25 \text{ kJ mol}^{-1}$  (route A<sub>1</sub>, Scheme 4) in accordance with the experimental evidence of catalytic hydrogen evolution at the potential of the 1-/2- process. [1(SH-SH)] is calculated to be more stable than the state where both protons are on sulfur atoms of the same chelate ring by 32 kJ mol<sup>-1</sup>. Subsequent reduction with a potential of -1.3 V vs Fc<sup>+/0</sup> (compared to experimental -1.75 V vs Fc<sup>+/0</sup>) leads to the reduced diprotonated intermediate  $[1(SH-SH)]^{-}$  (route A<sub>2</sub>, Scheme 4). This intermediate can also be reached via the alternative route B because the singly protonated  $[1(SH)]^{-}$  is reduced at -1.9 V vs Fc<sup>+/0</sup> (compared to the -1.9 V vs Fc<sup>+/0</sup> experimentally observed) to produce  $[1(SH)]^{2-}$ . For this reduction process, one has a unique singly protonated singly reduced species but two singly protonated doubly reduced species that are close in energy. The singly reduced species has the proton on a sulfur atom, whereas the two doubly reduced species have protons on either a sulfur atom or the metal. In each case, however, reduction occurs primarily on the sulfur atoms (>1 electron gain in charge) with small compensating changes on the other atoms. For the doubly reduced species with sulfur protonation, the protonated sulfur atom gains an amount of negative charge similar to those of the other three sulfur atoms. By comparison to the sulfur-protonated doubly reduced species, the proton atom gains  $\sim -0.30$  units of charge in the metal-protonated doubly reduced species, indicative of its hydride nature.

Our calculations indicate that  $[1(SH)]^{2-}$  is more stable than  $[1(NiH)]^{2-}$  by only 1 kJ mol<sup>-1</sup>, thereby not excluding the

Scheme 4. Proposed Mechanism for Hydrogen Evolution with Catalyst 1 together with Calculated Protonation Enthalpies and Redox Potentials $^{a}$ 



<sup>a</sup>Experimentally determined electrochemical potentials are also indicated. Potentials are reported vs Fc<sup>+/0</sup>.



Figure 9. Calculated structures for intermediates in the proposed hydrogen evolution mechanism for 1.

possibility of nickel-ion protonation. However, the next stepprotonation of the dianion—yields the species  $[1(SH-SH)]^-$ , in an energetically downhill process of -83 kJ mol-1 with respect to  $[1(SH)]^{2-}$ . This monoanionic species is 19 kJ mol<sup>-1</sup> more stable than the one with two protons on the same sulfur ligand, and no stable species protonated at nickel was observed. Other studies have suggested that a nickel hydride intermediate is formed before hydrogen evolution,<sup>32</sup> but this is probably due to the differences in the electronic properties of the dithiolene ligands that we employ. From this point, evolution of hydrogen proceeds via an exothermic reaction by  $-140 \text{ kJ mol}^{-1}$ , yielding the monoanion of complex 1, which therefore acts as the catalyst for the reduction of H<sup>+</sup>. According to our experimental data (Figure 5), the two routes compete at low ratios of acid to catalyst (1–3 equiv of acid), whereas at higher ratios ( $\geq 10$ equiv), route A saturates and route B appears dominant. The calculated structures for the intermediates along with the catalytic cycle are shown in Figure 9. Holding the potential value at -1.67 V vs Fc<sup>+/0</sup> in the bulk electrolysis experiment makes route A prevail because route B requires significantly more negative potential values.

In route B, formation of the protonated  $[1(NiH)]^{2-}$  species is possible, but no stable species protonated at both sulfur and nickel could be found, as mentioned before. These findings are in contrast to the ones for the related cobalt dithiolene complexes. In fact, extensive studies on cobalt dithiolenes by Letko et al.<sup>33</sup> revealed that a Co-H intermediate species is formed in the hydrogen evolution cycle. More specifically, the monoanionic cobalt species is reduced to the dianion, and protonation occurs at the cobalt ion. Subsequent reduction and protonation leads to a (Co-H)/(S-H) diprotonated species that releases dihydrogen. However, we propose that in nickel aryldithiolene complexes the protonation and redox effects are located mainly on the ligand framework because of the decreased contribution of nickel orbitals: ~25% Ni 3d orbitals for all three oxidation states of the similar  $[Ni(S_2C_2Me_2)_2]$ complexes,<sup>69</sup> as opposed to 62% for cobalt complexes.<sup>33</sup> As observed earlier<sup>57</sup> for the similar compound  $[Ni(S_2C_2Me_2)_2]$ across the 0/1-/2- oxidation states, the redox events take place on the ligands because of the increased contribution of S  $3p_z$  in the  $5b_{2g}$  molecular orbital, even though the nickel contribution increases upon reduction to the dianion. We propose that this is also the case for the nickel dithiolene complexes under study.

Upon protonation after reduction to the dianionic state  $[1]^{2-}$ , only a minor tetrahedral distortion is observed  $(2.32^{\circ})$ 

for intermediate  $[1(SH)]^-$ . Subsequent protonation as discussed before (route A) leads to a more distorted structure  $(8.87^{\circ} \text{ for } [1(\text{SH}-\text{SH})])$ . In route B, the generated  $[1(\text{SH})]^{2-1}$ exhibits a dihedral S-Ni-S angle of 20.44°, whereas the corresponding [1(NiH)]<sup>2-</sup> intermediate (Figure S7) exhibits a calculated S-Ni-S dihedral angle of 75.04°. When the diprotonated and reduced state  $[1(SH-SH)]^-$  is reached, the dihedral angle is calculated to be 39.93°, which is much larger than that in the neutral form. Another important parameter is the H…H distance in the protonated intermediates, which increases from 3.0 Å in [1(SH-SH)] to 4.0 Å in [1(SH-SH)]<sup>-</sup>. Additional studies, including explicit dynamics of the complexes, are therefore required to identify the mechanism for hydrogen evolution from these species. Alternatively, transient cleavage of a Ni-S bond, as observed in some higher energy species in the course of our DFT studies (data not shown), with hydrogen passage via the nickel might be envisaged.

For the symmetric tetramethoxy complex 3, the mechanism proposed is the same as that for 1 with analogous intermediates.

In the case of the asymmetric dithiolene complex 2, the same general mechanism is proposed (Scheme S1). Metal dithiolene complexes with asymmetric dithiolene ligands show fluxional behavior in solution.<sup>70</sup> This prompted us to calculate the intermediates of both the cis and trans isomers. Similar  $\Delta G$  values for reactions involving the protonated intermediates were found for the isomers, but there is a difference in the reduction potential values, with the trans isomer and its protonated forms exhibiting more negative reduction potentials. Overall, these calculated values compare well with our experimental data. In the final step where hydrogen is evolved by this catalyst, the trans-protonated complex releases hydrogen in a more exergonic process (-154 kJ mol<sup>-1</sup>).

This difference suggests that the electron-donating ability of the trans methoxy groups preferentially enriches the sulfur atom that participates in the protonation, and this is proposed to be the sulfur atom proximal to the (4-methoxyphenyl)phenyl group of 2 (Figure 2). However, on the basis of the calculated values, both isomers can be expected to be active catalysts, with the observed activity being a suitable average of the process for both. Moreover, theoretical data indicate that asymmetric substitution of the phenyl groups reflects on the charges of the sulfur atoms, with the atoms S1 and S3 (Figure 2) always being more negative compared to atoms S2 and S4 (actually the slight differences are 0.02, 0.01, and 0.03e for the neutral form, monoanion, and dianion, respectively). This discrepancy between the reduction potential and free-energy values for the trans and cis isomers along with the different structural features that the asymmetric complex exhibits can account for the fact that 2 is a better catalyst than 1 and 3, with the series eventually being 2 > 3 > 1.

## 4. CONCLUSIONS

Experimental and theoretical investigations of a series of methoxy-substituted nickel aryldithiolene complexes provide insight into the hydrogen-evolving mechanism for these complexes. In each case, the sulfur atoms of the doubly reduced catalyst are more nucleophilic than those when the catalyst is in other oxidation states because upon reduction the charge is stored on the ligands, with the nickel retaining a 2+ charge throughout the series neutral/monoanion/dianion. The mechanisms proposed include reduction of the catalyst to the dianion, protonation at the sulfur atom, and subsequent protonation and reduction (route A) or reduction and then protonation (route B), both leading to the abstraction of hydrogen in an exergonic process that regenerates the monoanionic catalyst.

We propose that the presence of methoxy groups in the asymmetric catalyst 2 renders the S1 atom more nucleophilic than S2 because of partial localization of the charge on S1 (thiolate form). Thus, the higher activity of 2 is explained on the grounds of the asymmetric nature of the ligand.

The observation that the complex after protonation and further reduction adopts a highly distorted tetrahedral structure, as witnessed by the calculated dihedral angle changes between S1-Ni1-S2 and S3-Ni1-S4, indicates that the catalysts must undergo a significant geometrical distortion in order for hydrogen to evolve. It is possible that this large change could be responsible for impeding the hydrogen-evolving activity of these compounds. This may be reflected in the reduced activity of the compounds in the hydrogen-evolving reaction. The high overpotential values required for compounds 1-3 to sustain catalysis are a limiting factor for the applicability of these systems in hydrogen-evolving cathodes, but in-depth analysis of the mechanistic aspects involved in the reaction steps can lead to the design and study of more effective catalysts with more rigid structures and reduced charge delocalization over the NiS4 core. The determination of structure-activity relationships within this class of compounds is therefore underway in our group with the aim of developing improved-by-design catalysts.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02000.

Cyclic voltammograms, linear fit of  $E_p$  versus log [TFA], linear sweep voltammetry, rinse tests, DFT-calculated structure, eq S1, proposed mechanism for hydrogen evolution, and bond lengths and angles (PDF)

X-ray crystallographic data in CIF format. CCDC 1440700 (CIF)

X-ray crystallographic data in CIF format. CCDC 1440701 (CIF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

- (1) Cook, T. R.; Dogutan, D. K.; Reece, S. Y.; Surendranath, Y.; Teets, T. S.; Nocera, D. G. Chem. Rev. 2010, 110, 6474.
- (2) Esswein, A. J.; Nocera, D. G. Chem. Rev. 2007, 107, 4022.
- (3) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. Angew. Chem., Int. Ed. 2011, 50, 7238.
- (4) Kawano, K.; Yamauchi, K.; Sakai, K. Chem. Commun. 2014, 50, 9872.
- (5) Eckenhoff, W. T.; McNamara, W. R.; Du, P.; Eisenberg, R. Biochim. Biophys. Acta, Bioenerg. 2013, 1827, 958.
- (6) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. Acc. Chem. Res. 2009, 42, 1995.
- (7) Queyriaux, N.; Jane, R. T.; Massin, J.; Artero, V.; Chavarot-Kerlidou, M. Coord. Chem. Rev. 2015, 304–305, 3.
- (8) Kaeffer, N.; Chavarot-Kerlidou, M.; Artero, V. Acc. Chem. Res. 2015, 48, 1286.
- (9) Zee, D. Z.; Chantarojsiri, T.; Long, J. R.; Chang, C. J. Acc. Chem. Res. 2015, 48, 2027.
- (10) Ginovska-Pangovska, B.; Dutta, A.; Reback, M. L.; Linehan, J. C.; Shaw, W. J. *Acc. Chem. Res.* **2014**, *47*, 2621.
- (11) Begum, A.; Moula, G.; Sarkar, S. *Chem. Eur. J.* 2010, *16*, 12324.
  (12) Simmons, T. R.; Berggren, G.; Bacchi, M.; Fontecave, M.;
- Artero, V. Coord. Chem. Rev. 2014, 270–271, 127.
- (13) Lubitz, W.; Ogata, H.; Rüdiger, O.; Reijerse, E. Chem. Rev. 2014, 114, 4081.
- (14) Gomez-Mingot, M.; Porcher, J.-P.; Todorova, T. K.; Fogeron, T.; Mellot-Draznieks, C.; Li, Y.; Fontecave, M. J. Phys. Chem. B 2015, 119, 13524.
- (15) Henning, R.; Schlamann, W.; Kisch, H. Angew. Chem., Int. Ed. Engl. 1980, 19, 645.
- (16) Katakis, D. F.; Mitsopoulou, C.; Konstantatos, J.; Vrachnou, E.; Falaras, P. J. Photochem. Photobiol., A **1992**, 68, 375.
- (17) Zarkadoulas, A.; Koutsouri, E.; Mitsopoulou, C. A. *Coord. Chem. Rev.* **2012**, *256*, 2424.
- (18) Islam, A.; Sugihara, H.; Hara, K.; Singh, L. P.; Katoh, R.; Yanagida, M.; Takahashi, Y.; Murata, S.; Arakawa, H.; Fujihashi, G. *Inorg. Chem.* **2001**, *40*, 5371.
- (19) Islam, A.; Sugihara, H.; Hara, K.; Singh, L. P.; Katoh, R.; Yanagida, M.; Takahashi, Y.; Murata, S.; Arakawa, H. J. Photochem. Photobiol., A **2001**, 145, 135.
- (20) Eisenberg, R.; Gray, H. B. Inorg. Chem. 2011, 50, 9741.
- (21) Sproules, S.; Wieghardt, K. Coord. Chem. Rev. 2011, 255, 837.
- (22) Queen, M. S.; Towey, B. D.; Murray, K. A.; Veldkamp, B. S.; Byker, H. J.; Szilagyi, R. K. *Coord. Chem. Rev.* **2013**, 257, 564.
- (23) Mitsopoulou, C. A. Coord. Chem. Rev. 2010, 254, 1448.
- (24) Sellmann, D.; Geck, M.; Moll, M. J. Am. Chem. Soc. 1991, 113, 5259.
- (25) Vlček, A., Jr.; Vlček, A. A. Inorg. Chim. Acta 1980, 41, 123.
- (26) Humphry-Baker, R.; Mitsopoulou, C. A.; Katakis, D.; Vrachnou, E. J. Photochem. Photobiol., A **1998**, 114, 137.
- (27) Katakis, D.; Mitsopoulou, C.; Vrachnou, E. J. Photochem. Photobiol., A 1994, 81, 103.
- (28) Lyris, E.; Argyropoulos, D.; Mitsopoulou, C.-A.; Katakis, D.; Vrachnou, E. J. Photochem. Photobiol., A **1997**, 108, 51.
- (29) Mitsopoulou, C.; Lyris, E.; Veltsos, S.; Katakis, D. Inorg. React. Mech. 2001, 3, 99.
- (30) McNamara, W. R.; Han, Z.; Alperin, P. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *J. Am. Chem. Soc.* **2011**, *133*, 15368.
- (31) McNamara, W. R.; Han, Z.; Yin, C.-J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15594.
- (32) Solis, B. H.; Hammes-Schiffer, S. J. Am. Chem. Soc. 2012, 134, 15253.
- (33) Letko, C. S.; Panetier, J. A.; Head-Gordon, M.; Tilley, T. D. J. Am. Chem. Soc. 2014, 136, 9364.
- (34) Das, A.; Han, Z.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. ACS Catal. 2015, 5, 1397.
- (35) Wang, K. Dithiolene Chemistry; John Wiley & Sons, Inc.: New York, 2003; pp 267-314.

- (36) Sumrell, G.; Stevens, J. I.; Goheen, G. E. J. Org. Chem. 1957, 22, 39.
- (37) Cobo, S.; Heidkamp, J.; Jacques, P.-A.; Fize, J.; Fourmond, V.; Guetaz, L.; Jousselme, B.; Ivanova, V.; Dau, H.; Palacin, S.; Fontecave, M.; Artero, V. *Nat. Mater.* **2012**, *11*, 802.
- (38) CrysAlis CCD and CrysAlis RED, version 1.171.32.15; Oxford Diffraction Ltd.: Abingdon, Oxford, England, 2008.
- (39) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. J. Appl. Crystallogr. **1994**, 27, 435.
- (40) Sheldrick, G. M. SHELXL-97, Program for Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.
- (41) Farrugia, L. J. Appl. Crystallogr. 1999, 32, 837.
- (42) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. J. Appl. Crystallogr. **2008**, 41, 466.
- (43) Neese, F. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 73.
- (44) Sinnecker, S.; Rajendran, A.; Klamt, A.; Diedenhofen, M.; Neese, F. J. Phys. Chem. A 2006, 110, 2235.
- (45) Konezny, S. J.; Doherty, M. D.; Luca, O. R.; Crabtree, R. H.; Soloveichik, G. L.; Batista, V. S. J. Phys. Chem. C 2012, 116, 6349.
- (46) Bui, T.-T.; Garreau-de Bonneval, B.; Moineau-Chane Ching, K. I. New J. Chem. 2010, 34, 337.
- (47) Papavassiliou, G. C.; Anyfantis, G. C.; Mousdis, G. A. Crystals 2012, 2, 762.
- (48) Chandrasekaran, P.; Arumugam, K.; Jayarathne, U.; Pérez, L. M.; Mague, J. T.; Donahue, J. P. *Inorg. Chem.* **2009**, *48*, 2103.
- (49) Arumugam, K.; Bollinger, J. E.; Fink, M.; Donahue, J. P. Inorg. Chem. 2007, 46, 3283.
- (50) Kirk, M. L.; McNaughton, R. L.; Helton, M. E. Dithiolene Chemistry; John Wiley & Sons, Inc.: New York, 2003; pp 111–212.
- (51) Miao, Q.; Gao, J.; Wang, Z.; Yu, H.; Luo, Y.; Ma, T. Inorg. Chim. Acta 2011, 376, 619.
- (52) Schrauzer, G. N.; Mayweg, V. P. J. Am. Chem. Soc. 1965, 87, 3585.
- (53) Garreau-de Bonneval, B.; Moineau-Chane Ching, K. I.; Alary, F.; Bui, T.-T.; Valade, L. *Coord. Chem. Rev.* **2010**, 254, 1457.
- (54) Schlaepfer, C. W.; Nakamoto, K. Inorg. Chem. 1975, 14, 1338. (55) Johnson, M. K. Dithiolene Chemistry; John Wiley & Sons, Inc.: New York, 2003; pp 213–266.
- (56) Beswick, C. L.; Schulman, J. M.; Stiefel, E. I. Dithiolene Chemistry; John Wiley & Sons, Inc.: New York, 2003; pp 55-110.
- (57) Lim, B. S.; Fomitchev, D. V.; Holm, R. H. *Inorg. Chem.* **2001**, *40*, 4257.
- (58) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K. Inorg. Chem. 1983, 22, 1208.
- (59) Fourmond, V.; Canaguier, S.; Golly, B.; Field, M. J.; Fontecave, M.; Artero, V. Energy Environ. Sci. 2011, 4, 2417.
- (60) Felton, G. A. N.; Glass, R. S.; Lichtenberger, D. L.; Evans, D. H. Inorg. Chem. **2006**, 45, 9181.
- (61) Fang, M.; Engelhard, M. H.; Zhu, Z.; Helm, M. L.; Roberts, J. A. S. ACS Catal. 2014, 4, 90.
- (62) Fourmond, V.; Jacques, P.-A.; Fontecave, M.; Artero, V. Inorg. Chem. 2010, 49, 10338.
- (63) Makedonas, C.; Mitsopoulou, C. A. Eur. J. Inorg. Chem. 2006, 2006, 590.
- (64) Costentin, C.; Passard, G.; Robert, M.; Saveant, J.-M. *Chem. Sci.* 2013, 4, 819.
- (65) Bard, J. A.; Faulkner, R. L. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, 2001.

(66) Savéant, J.-M. Elements of Molecular and Biomolecular Electrochemistry: An Electrochemical Approach to Electron Transfer Chemistry; John Wiley & Sons: New York, 2006.

(67) Eckenhoff, W. T.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2014**, *53*, 9860.

(68) Marenich, A. V.; Ho, J.; Coote, M. L.; Cramer, C. J.; Truhlar, D. G. Phys. Chem. Chem. Phys. **2014**, *16*, 15068.

(69) Szilagyi, R. K.; Lim, B. S.; Glaser, T.; Holm, R. H.; Hedman, B.;
Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* 2003, *125*, 9158.
(70) Argyropoulos, D.; Mitsopoulou, C.-A.; Katakis, D. Inorg. Chem.
1996, 35, 5549.