

# Catalytic reduction of 1-iodooctane by nickel(I) salen electrogenerated at carbon cathodes in dimethylformamide: Effects of added proton donors and a mechanism involving both metal- and ligand-centered one-electron reduction of nickel(II) salen

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## Abstract

In dimethylformamide containing tetramethylammonium tetrafluoroborate, 1-iodooctane is reduced catalytically by nickel(I) salen electrogenerated at a glassy carbon cathode. Cyclic voltammograms for the nickel(II) salen–1-iodooctane system recorded in the absence as well as in the presence of a proton or deuterium donor (1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), phenol, or D<sub>2</sub>O) exhibit enhanced cathodic peaks and diminished anodic peaks for the nickel(II) salen–nickel(I) salen couple, along with a new cathodic peak attributed to reduction of a nickel(II) salen species for which an imino bond of the ligand is octylated. Without a proton donor, controlled-potential catalytic reduction of 1-iodooctane by nickel(I) salen affords hexadecane, octane, and 1-octene. For electrolyses performed in the presence of either HFIP or phenol, the yields of hexadecane and octane are decreased and increased, respectively, whereas that of 1-octene remains unchanged. Bulk electrolyses done in the presence of D<sub>2</sub>O give a product distribution similar to that obtained when no proton donor is added; none of the octane is deuterated, indicating that octyl radicals (not octyl carbanions) are precursors for the formation of octane. Theoretical calculations involving density functional theory have been employed to establish that nickel(II) salen can undergo either a metal- or ligand-centered one-electron reduction. A mechanistic scheme is proposed that invokes both metal- and ligand-centered reduction of nickel(II) salen to explain the effects of proton donors on the catalytic reduction of alkyl halides as well as the pathway for alkylation of the imino bonds of the ligand.

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## 1. Introduction

Catalytic reduction of alkyl halides by electrogenerated nickel(I) species has long been a focus of research conducted in our laboratory and elsewhere [1–61]. Pletcher and co-

workers launched this field in 1978 with two publications dealing, respectively, with mechanistic aspects of the catalytic reduction of several alkyl halides [1] and with the addition of catalytically formed alkyl radicals to olefins [2]; three papers concerning related topics appeared soon thereafter [3–5]. Subsequent investigations of processes catalyzed by nickel(I) tetraazamacrocyclic complexes were carried out by Bakac, Espenson, and Ram [6–10,14,15], and

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Stolzenberg and co-workers probed nickel(I) hydroporphyrin-catalyzed reductions of alkyl halides [11–13,17,20]. A number of interesting reductive cyclizations of halogenated compounds promoted by electrogenerated nickel(I) species have been reported by Ozaki and co-workers [16,19,22,23,25–28] and by Duñach et al. [24,29–31,33,35,37–40]. Additional papers have appeared from the laboratories of Helvenston and Castro [18], Fry and Fry [21], Esteves and co-workers [32], and Gennaro and Isse [34,36]. Recently, it has been shown that a reduced form of nickel(II) salen, with electron density on the imino bonds of the ligand, can promote the electroreductive cyclization of the methyl ester of (*E*)-8-oxo-oct-2-enoic acid [41].

Our interest in this subject began with an examination [42] of the catalytic reduction of 6-bromo- and 6-iodo-1-phenyl-1-hexyne by electrogenerated [[2,2'-[1,2-ethanediy]bis(nitrilomethylidene)]bis[phenolato]]-*N,N',O,O'*nickelate(I)—more simply termed nickel(I) salen—for which 1-phenyl-1-hexyn-6-yl radicals that undergo intramolecular cyclization were proposed to be the key intermediates. Here, and in succeeding sections of this paper, we refer to the reduced form of nickel(II) salen simply as nickel(I) salen, without regard as to whether the catalytically active species should be viewed as arising from a metal- or a ligand-centered one-electron process—the distinction between these two forms of reduced nickel(II) salen will become apparent later in this report. In a study of the nickel(I) salen-mediated reduction of  $\alpha,\omega$ -dihaloalkanes [44], it was determined that alkyl radicals undergo both coupling and disproportionation, as well as hydrogen-atom abstraction from the solvent, to form the observed products. Polymer-bound nickel(I) salen has been shown to catalyze the reductions of several alkyl halides [43,45], whereas solution-phase nickel(I) salen induces the reductive coupling of ethylene halohydrins [46], the reduction of cyclohexanecarbonyl chloride [47], the addition of alkyl radicals to activated olefins [48], the electroreductive intramolecular cyclizations of 6-bromo-1-hexene [50] and haloalkynes [61], the catalytic reduction of 1-bromooctane at a mercury cathode [52], and the catalytic acetoxylation of 1,6-dihaloalkanes in the presence of acetic acid [57]. Other investigations have entailed the use of electrogenerated nickel(I) salen in an ionic liquid [51] as well as the stoichiometric reaction between an alkyl halide and nickel(I) salen (in the presence of dioxygen, water, and light) to afford an aldehyde [54,56] or ketone [60]. In addition, some electrogenerated tetraazamacrocyclic complexes have been employed for the catalytic reduction of ethylene halohydrins [49] and bromo esters of propargylic and allylic ethers [53,58]. Finally, electrogenerated [2,2'-((2,2'-bipyridine)-6,6'-diyl)bis[phenolato]]-*N,N',O,O'*nickelate(I) is a catalyst for the reductive cleavage of 1-iodooctane [55], and nickel(II) salen has been discovered recently [59] to undergo alkylation of the ligand imino bonds during the catalytic reduction of a primary alkyl halide.

In the present work, we have employed cyclic voltammetry and controlled-potential electrolysis to investigate the effect of two proton donors (1,1,1,3,3,3-hexafluoro-2-pro-

panol and phenol) of virtually identical acid strength on the product distributions derived from the catalytic reduction of 1-iodooctane by nickel(I) salen electrogenerated at glassy carbon cathodes in dimethylformamide containing tetramethylammonium tetrafluoroborate. In addition, we have performed experiments involving the use of deuterium oxide, which serves as a trap for carbanions, to prove whether the nickel(I) salen-catalyzed reduction of 1-iodooctane involves alkyl radicals or carbanions as intermediates. As a part of this study, we have carried out the first theoretical calculations, based on the use of density functional theory, to establish that the one-electron reduction of nickel(II) salen can reasonably be considered as either a metal- or a ligand-centered process. Finally, recognizing that the electroreduction of nickel(II) salen can be metal- or ligand-centered has led us to a new view of the mechanism of the nickel(I) salen-catalyzed reduction of alkyl halides, which serves to explain (a) the effects of proton donors on the distribution of products and (b) the fact that, during the catalytic process, the imino bonds of the salen ligand become alkylated.

## 2. Experimental

### 2.1. Reagents

Burdick and Jackson “distilled in glass” dimethylformamide (DMF) was employed without further purification as the solvent for all electrochemical experiments. Tetramethylammonium tetrafluoroborate (TMABF<sub>4</sub>), purchased from Aldrich Chemical Company, was dried and stored in a vacuum oven at 80 °C before being employed as supporting electrolyte. All experiments were performed under an atmosphere of UHP-grade argon (Air Products) that was passed through a gas filter (Alltech Associates) consisting of a one-to-one mixture of Drierite and 5-Å molecular sieves. Each of the following chemicals was used as received from Aldrich Chemical Company: [[2,2'-[1,2-ethanediy]bis(nitrilomethylidene)]bis[phenolato]]-*N,N',O,O'*nickel(II) (hereafter referred to as nickel(II) salen, 98%), octane (99+%), 1-octene (98%), dodecane (99+%), tetradecane (99+%), hexadecane (99+%), 1-iodooctane (98%), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 99+%), and phenol (99+%). Deuterium oxide (99.9 atom% D) was purchased from Cambridge Isotope Laboratories, Inc.

### 2.2. Instrumentation, electrodes, and cells

Instrumentation employed for cyclic voltammetry and controlled-potential electrolyses is described elsewhere [62,63]. For cyclic voltammetry, we constructed a planar, circular working electrode with an area of 0.077 cm<sup>2</sup> by press-fitting a 3-mm-diameter glassy carbon rod (Grade GC-20, Tokai Electrode Manufacturing Company, Tokyo, Japan) into a Teflon shroud. Reticulated vitreous carbon discs, approximately 2.4 cm in diameter, 0.4 cm in thickness, and with an approximate geometric area of

200 cm<sup>2</sup>, were employed as working electrodes for all controlled-potential electrolyses. Procedures for preparing, cleaning, and handling these electrodes are cited in the literature [64]. Electrochemical cells for cyclic voltammetry and controlled-potential electrolysis have also been described previously [43,65]. All potentials are quoted with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of  $-0.76$  V vs. the aqueous saturated calomel electrode (SCE) at 25 °C [66,67].

### 2.3. Separation, identification, and quantitation of electrolysis products

Electrolysis products were separated, identified, and quantitated with the aid of a Hewlett–Packard 5890 Series II gas chromatograph equipped with a 30-m capillary column (0.25 mm i.d., 0.25- $\mu$ m film thickness, J&W Scientific) having a stationary phase of DB-5 (5% phenylpolysiloxane and 95% methylpolysiloxane). Methods for the quantitation of electrolysis products by means of gas chromatography have been described in an earlier publication [68]; a Hewlett–Packard 3392A integrator was used to determine peak areas, and dodecane and tetradecane were used as internal standards. All product yields mentioned in this paper represent the absolute amount of 1-iodooctane incorporated into each species and are accurate to  $\pm 3\%$  absolute. In addition, gas chromatography–mass spectrometry (Hewlett–Packard 6890N gas chromatograph, equipped with a 30 m  $\times$  0.25 mm i.d. Agilent HP-5ms capillary column and coupled to a Hewlett–Packard model 5973 inert mass-selective detector) was employed to confirm the identities of all products by comparison of their retention times and mass spectra with those of commercially available authentic samples.

## 3. Results and discussion

### 3.1. Cyclic voltammetry

Fig. 1 displays cyclic voltammograms recorded with a glassy carbon electrode at a scan rate of 100 mV s<sup>-1</sup> for DMF solutions containing 0.10 M TMABF<sub>4</sub> as a supporting electrolyte. Curve A shows a cyclic voltammogram for the reversible nickel(II) salen–nickel(I) salen couple, with the cathodic ( $E_{pc}$ ) and anodic ( $E_{pa}$ ) peak potentials being  $-0.93$  and  $-0.85$  V, respectively. Under the same conditions, reduction of 1-iodooctane by itself gives rise to a single irreversible peak at  $-1.38$  V corresponding to the two-electron reductive cleavage of the carbon–iodine bond.

When nickel(II) salen and 1-iodooctane are combined, as depicted in curve B, the cathodic current corresponding to electrogeneration of nickel(I) salen ( $-0.92$  V) increases, and the anodic current due to oxidation of nickel(I) salen disappears; both features are characteristic of the catalytic

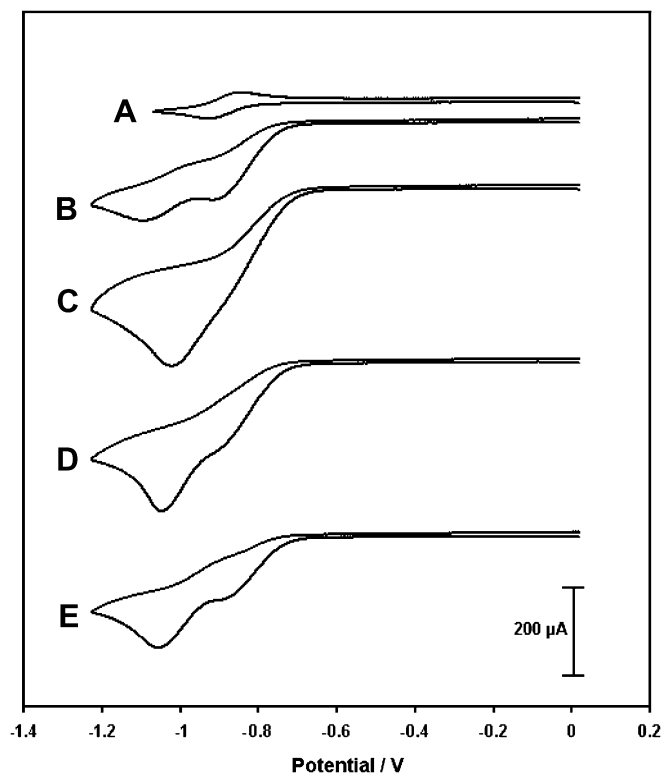


Fig. 1. Cyclic voltammograms recorded with a glassy carbon disk electrode (area = 0.077 cm<sup>2</sup>) in DMF containing 0.10 M TMABF<sub>4</sub> at a scan rate of 100 mV s<sup>-1</sup>: (A) 2.0 mM nickel(II) salen; (B) 2.0 mM nickel(II) salen and 20 mM 1-iodooctane; (C) 2.0 mM nickel(II) salen, 20 mM 1-iodooctane, and 50 mM HFIP; (D) 2.0 mM nickel(II) salen, 20 mM 1-iodooctane, and 50 mM phenol; and (E) 2.0 mM nickel(II) salen, 20 mM 1-iodooctane, and 1.0 M D<sub>2</sub>O. For curve A the scan goes from 0 to  $-1.08$  to 0 V, and for curves B–E the scans go from 0 to  $-1.23$  to 0 V.

reduction of 1-iodooctane. Such behavior has been documented for the catalytic reduction of a wide variety of halogenated organic compounds in non-aqueous media [69]. Furthermore, a new cathodic peak at  $-1.09$  V is seen in curve B; in recent research [59], we have acquired persuasive evidence that this phenomenon is associated with reduction of alkylated nickel(II) salen species arising from addition of octyl radicals across an imino (C=N) bond of the salen ligand. Indeed in some separate experiments [70], we have very recently examined the cyclic voltammetric behavior of nickel(II) salen modified with a methyl group on the carbon atom of each imino bond of the ligand. At a glassy carbon electrode in DMF–0.10 M TMABF<sub>4</sub>, this complex exhibits reversible redox behavior with  $E_{pc} = -1.02$  V and  $E_{pa} = -0.95$  V (values 90–100 mV more negative than those for nickel(II) salen itself); note that the cathodic peak potential for this dimethylated nickel(II) salen species correlates well with the voltammetric phenomena that have earlier [59] been attributed to the reduction of alkylated nickel(II) salen. Another cause of the second cathodic peak at  $-1.09$  V might be the reduction of an octylnickel(III) salen complex arising from oxidative addition of electrogenerated nickel(I) salen to 1-iodooctane. Such a species would be analogous to the

organocobalt(III) salen complexes that, with the aid of HPLC-ESI-MS experiments, we have identified as intermediates for the cobalt(I) salen-catalyzed reductions of ethyl chloroacetate [63], 2,6-bis(chloromethyl)pyridine [71], and  $\alpha,\alpha'$ -dibromo-*m*-xylene [72]. So far, however, our attempts to detect an octylnickel(III) salen intermediate by means of the same experimental procedure have been inconclusive, even though (as mentioned above) we have seen the octylated nickel(II) salen species [59] formed by addition of octyl radicals to the imino (C=N) bonds of the ligand.

Curves C–E of Fig. 1 reveal the effects of added proton donors on cyclic voltammograms for the nickel(II) salen–1-iodooctane system. In the presence of 50 mM HFIP (curve C), a prominent cathodic peak at  $-1.03$  V is observed with a barely perceptible shoulder ( $-0.89$  V) on the rising portion of that peak. When 50 mM phenol is introduced into the nickel(II) salen–1-iodooctane system (curve D), a pair of well-defined irreversible peaks appears at  $-0.92$  and  $-1.05$  V. Finally, the addition of 1.0 M  $D_2O$  to the nickel(II) salen–1-iodooctane system (curve E) produces a cyclic voltammogram that, except for the magnitudes of the peak currents, closely resembles curve D. For the cyclic voltammograms recorded in the presence of the three different proton or deuteron donors, we propose that the

two peaks can be attributed, respectively, to the nickel(I) salen-catalyzed reduction of 1-iodooctane and to the reduction of the alkylated nickel(II) salen species.

Recent research [57,60] in our laboratory has shown that electrogenerated nickel(I) salen can catalytically reduce the proton resulting from ionization (dissociation) of a proton donor. Accordingly, we have made in this investigation a particularly pertinent discovery concerning the cyclic voltammetric behavior of nickel(II) salen in the presence of HFIP or phenol. These two proton donors possess nearly identical *thermodynamic* acidities in DMF ( $pK_a$  for phenol = 18.9 and  $pK_a$  for HFIP = 18.8 [73,74]). However, in DMF containing 0.10 M TMABF<sub>4</sub>, cyclic voltammograms recorded at  $100\text{ mV s}^{-1}$  reveal that nickel(I) salen is a more effective catalyst for the reduction of HFIP than for the reduction of phenol. Curve A of Fig. 2 shows the normal cyclic voltammetric response for the nickel(II) salen–nickel(I) salen couple by itself. Curve B is a cyclic voltammogram for nickel(II) salen in the presence of 100 mM phenol; there is some enhancement in the cathodic current as well as a decrease in the anodic peak current, but there is virtually no shift in the cathodic and anodic peak potentials. On the other hand, when nickel(II) salen is reduced in the presence of 100 mM HFIP (curve C), the

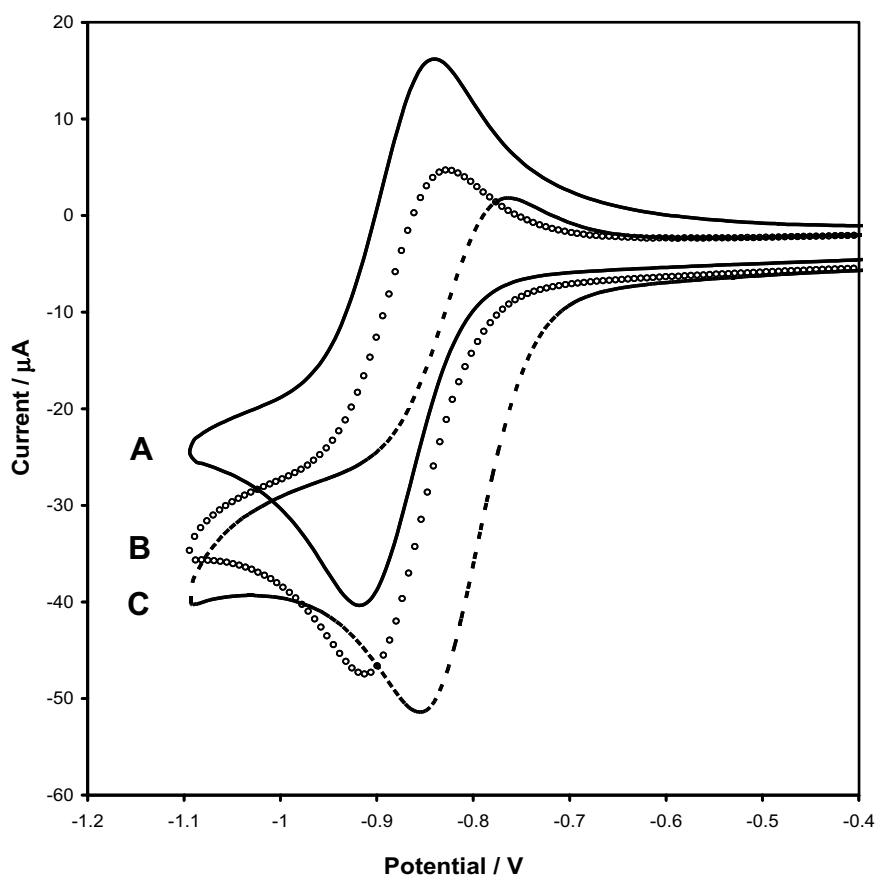


Fig. 2. Cyclic voltammograms recorded with a glassy carbon disk electrode (area =  $0.077\text{ cm}^2$ ) in DMF containing 0.10 M TMABF<sub>4</sub> at a scan rate of  $100\text{ mV s}^{-1}$ : (A) 2.0 mM nickel(II) salen; (B) 2.0 mM nickel(II) salen and 100 mM phenol; and (C) 2.0 mM nickel(II) salen and 100 mM HFIP. Scans go from  $-0.4$  to  $-1.1$  to  $-0.4$  V.

increase in the cathodic peak current and the accompanying diminution of the anodic peak current are more noticeable than those obtained when phenol is added as a proton donor; moreover, the peak potentials for the nickel(II) salen–HFIP system shift noticeably toward more positive values. On the basis of these observations, we conclude that the *kinetic* acidity of phenol is significantly less than that of HFIP, a finding which helps to explain the results of bulk electrolyses discussed below.

A paper by Fry and Reed [75], who investigated the reduction of some norbornyl dihalides at a mercury cathode in DMF containing tetraethylammonium bromide, offers additional insight concerning the origin of differences observed in the cyclic voltammetric behavior of nickel(II) salen in the presence of either phenol or HFIP. As demonstrated by these workers, phenol is less abundant in the double-layer region (where interaction with electrogenerated nickel(I) salen should occur) than in the bulk of the solution. Conversely, if HFIP is present at a higher concentration in the double-layer region than in the bulk of the solution (due to differences in the polarities of phenol and HFIP molecules), the latter proton donor might be expected to react more efficiently with nickel(I) salen than does phenol.

Another interesting aspect of cyclic voltammograms for the nickel(II) salen–1-iodooctane system is whether the

cathodic peak attributed to reduction of an alkylated nickel(II) salen species (Fig. 1, curve B) can also be associated with simultaneous catalytic reduction of the alkyl iodide. To address this matter more specifically, we recorded the family of cyclic voltammograms displayed in Fig. 3. Curve A pertains to the reversible reduction of 2.0 mM nickel(II) salen alone, whereas curves B–E portray cyclic voltammograms for the reduction of 2.0 mM nickel(II) salen in the presence of 2.0, 5.0, 10.0, and 20.0 mM 1-iodooctane. Although one would expect more of the alkylated nickel(II) salen to be formed for higher initial substrate concentrations, we observe for curves B–E an unusually large enhancement in the height of the second cathodic peak, leading us to conclude that catalytic reduction of 1-iodooctane by an alkylated nickel(I) salen species does take place. Support for this latter assertion has been obtained from separate studies of the catalytic reduction of various alkyl halides by the aforementioned dimethylated analogue of nickel(I) salen [70]; results of this investigation will be described in a subsequent report.

### 3.2. Controlled-potential electrolyses

Controlled-potential catalytic reductions of 1-iodooctane with electrogenerated nickel(I) salen were performed

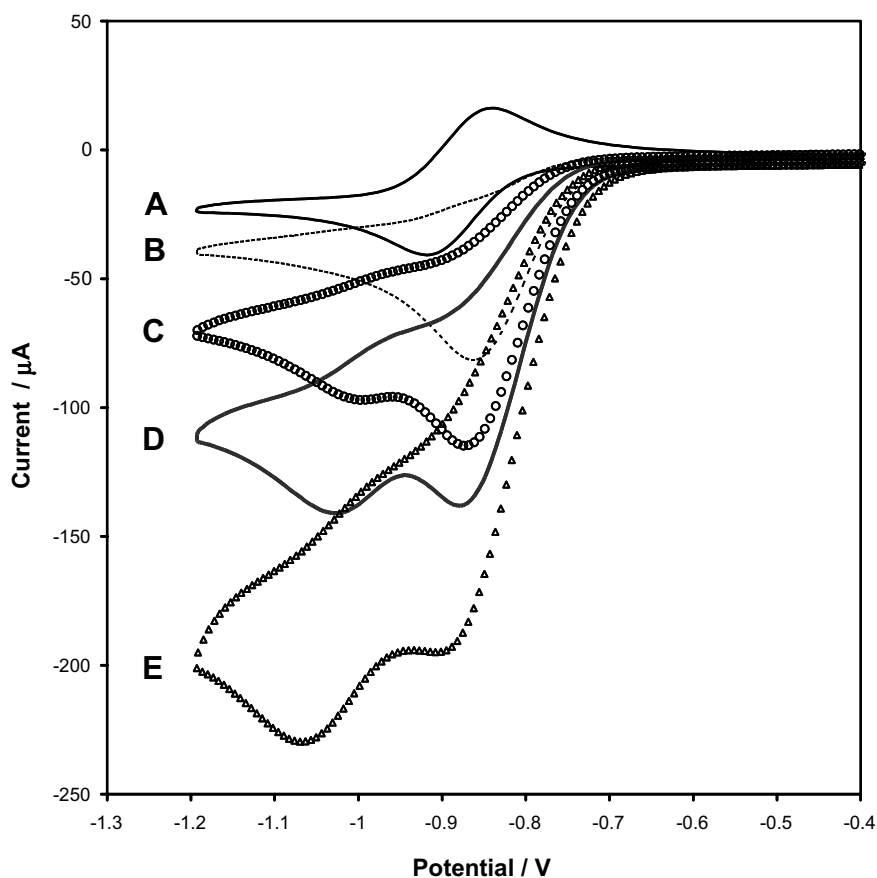


Fig. 3. Cyclic voltammograms recorded with a glassy carbon disk electrode (area = 0.077 cm<sup>2</sup>) in DMF containing 0.10 M TMABF<sub>4</sub> at a scan rate of 100 mV s<sup>-1</sup>: (A) 2.0 mM nickel(II) salen; (B) 2.0 mM nickel(II) salen and 2.0 mM 1-iodooctane; (C) 2.0 mM nickel(II) salen and 5.0 mM 1-iodooctane; (D) 2.0 mM nickel(II) salen and 10.0 mM 1-iodooctane; and (E) 2.0 mM nickel(II) salen and 20.0 mM 1-iodooctane. Scans go from -0.4 to -1.2 to -0.4 V.



Table 1

Coulometric data and product distributions for catalytic reduction of 20 mM 1-iodooctane by 2.0 mM nickel(I) salen electrogenerated at reticulated vitreous carbon cathodes held at  $-1.00$  V in DMF containing 0.10 M TMABF<sub>4</sub>

Entry	<i>n</i>	Added reagent	Product distribution (%)			Total
			1	2	3	
1	0.97	None	88	7	1	96
2 <sup>a</sup>	0.95	None	89	10	TR <sup>b</sup>	99
3	NA <sup>c</sup>	HFIP <sup>d</sup>	53	46	2	101
4	NA <sup>c</sup>	HFIP <sup>e</sup>	42	60	1	103
5	0.96	Phenol <sup>f</sup>	71	32	2	105
6	0.95	D <sub>2</sub> O <sup>g</sup>	93	9	1	103

1 = hexadecane; 2 = octane; 3 = 1-octene.

<sup>a</sup> 5.0 mM 1-iodooctane and 5.0 mM nickel(II) salen.

<sup>b</sup> Traces of 1-octene (<1%) were detected.

<sup>c</sup> Coulometric *n* values were artificially high due to simultaneous catalytic reduction of the proton donor.

<sup>d</sup> 1,1,1,3,3,3-Hexafluoro-2-propanol, 50 mM.

<sup>e</sup> 1,1,1,3,3,3-Hexafluoro-2-propanol, 250 mM.

<sup>f</sup> Concentration of phenol was 50 mM.

<sup>g</sup> Concentration of D<sub>2</sub>O was 1.0 M.

in DMF containing 0.10 M TMABF<sub>4</sub> at reticulated vitreous carbon electrodes held at  $-1.00$  V. Table 1 is a compilation of product distributions and coulometric *n* values for these experiments, with each entry representing the average of at least three separate trials; the *n* values are reported in terms of the number of electrons involved in the reductive cleavage of the carbon–iodine bond. Individual product yields are usually reproducible to  $\pm 3\%$  absolute. It should be noted that we have carried out other bulk electrolyses at potentials ranging from  $-0.95$  to  $-1.10$  V, without observing any significant differences in either the *n* values or product distributions.

Entry 1 presents the results of electrolyses of solutions containing 2 mM nickel(II) salen and 20 mM 1-iodooctane. An *n* value of 0.97 indicates that one electron is transferred per molecule of substrate; the products are hexadecane (88%), octane (7%), and 1-octene (1%). Entry 2 reveals that virtually identical results are obtained for electrolyses involving equimolar amounts of nickel(II) salen and 1-iodooctane. These product distributions are remarkably similar to those observed in a previous study [44] of the nickel(I) salen-catalyzed reductions of a family of  $\alpha$ -bromo- $\omega$ -chloro- and  $\alpha$ -chloro- $\omega$ -iodoalkanes, for which 1-chloroalk- $\omega$ -yl radicals are intermediates. Such product distributions—particularly the ratio of hexadecane (radical-coupling product) to 1-octene (radical-disproportionation product) listed for entries 1 and 2—are in accord with data compiled by Gibian and Corley [76], who reported that coupling-disproportionation ratios ( $k_c/k_d$ ) for primary alkyl radicals in a variety of organic media are approximately 7–8.

Introduction of a reasonably potent proton donor (HFIP or phenol) has a profound effect on product distributions obtained from the 1-iodooctane–nickel(II) salen system. In comparison with entries 1 and 2, the presence of 50 mM HFIP (entry 3) causes the yield of hexadecane (53%) to be lower and the amount of octane (46%) to increase dramatically, whereas the quantity of 1-octene

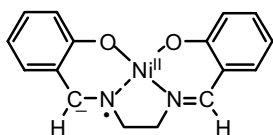
remains essentially unchanged. Entry 4 shows the effect of raising the concentration of HFIP to 250 mM; octane becomes the major product (60%), the yield of 1-octene is still unchanged, and the amount of hexadecane is diminished to 42%. It should be recalled here that HFIP is catalytically reduced by electrogenerated nickel(I) salen, thus rendering the coulometric *n* value meaningless. These trends in the distribution of products arising from the use of HFIP as a proton donor mimic the results obtained in an earlier investigation of the catalytic reduction of alkyl halides by electrogenerated nickel(I) salen [59].

Entry 5 reveals that phenol, though very similar to HFIP in *thermodynamic* acid strength, does not cause such substantial decreases in the yield of hexadecane nor such large increases in the amount of octane as does HFIP. Moreover, useful coulometric *n* values for the catalytic reduction of 1-iodooctane can be obtained in the presence of phenol, due to the sluggishness of the nickel(I) salen–phenol side reaction. Finally, when a relatively high concentration (1.0 M) of D<sub>2</sub>O is introduced into the system (entry 6), there is virtually no change in the product distribution in comparison with entries 1 and 2. We employed a high concentration of D<sub>2</sub>O to ensure, to the fullest extent possible, that any carbanions would be trapped as identifiable deuterium-labeled products. For experiments involving the addition of phenol and D<sub>2</sub>O, the *n* value is essentially 1, which is consistent with the formation of octyl radicals as intermediates in the nickel(I) salen-catalyzed reduction of 1-iodooctane. Furthermore, although D<sub>2</sub>O must possess an acidity comparable to that of H<sub>2</sub>O ( $pK_a = 31.7$  in DMF [73,74]), which makes it an exceedingly poor proton (deuteron) donor in comparison with either HFIP or phenol, the use of D<sub>2</sub>O provides an excellent signature for the intermediacy of alkyl carbanions. Alkanes, which appear prominently among the products derived from direct electrochemical reduction of alkyl halides at carbon cathodes in the presence of 200–1000 mM D<sub>2</sub>O [62,77–80], are usually monodeuterated to

the extent of 40–50%. In the present investigation, however, none of the catalytically produced octane listed as a product in entry 6 of Table 1 contained deuterium, a finding that rules out octyl carbanions as a source of the alkane.

### 3.3. Metal-centered versus ligand-centered one-electron reduction of nickel(II) salen

For almost all of the publications cited in the introduction of this paper, the electrogeneration of nickel(I) salen from nickel(II) salen has been regarded exclusively as a metal-centered process. This conclusion has been buttressed by the results of several low-temperature studies by means of EPR spectroscopy [5,55,81]. However, recent work [41,59] has provided compelling evidence that a ligand-based reduction, involving the imino (C=N) bonds of nickel salen, can occur to form the following species:



In a study of the electroreductive intramolecular cyclization of (*E*)-8-oxo-oct-2-enoic acid methyl ester to *trans*-(2-hydroxycyclohexyl)acetic acid methyl ester, a process catalyzed by a reduced form of nickel(II) salen, Miranda et al. [41] proposed that the above species plays a key role by acting both as a base and as a docking site where an inner-sphere electron transfer to the substrate can occur. In our laboratory we have found, with the aid of GC-MS, HPLC-MS, and <sup>1</sup>H NMR experiments, that catalytic reduction of 1-iodooctane by electrogenerated nickel(I) salen leads to the formation of significant amounts of post-electrolysis nickel salen complexes with octyl moieties added to the original imino bonds [59], results that point strongly to the intermediacy of the above species. Accordingly, we set out to probe the energy levels in nickel(II) salen to assess the relative importance of its nickel- and ligand-centered reductions as a way to gain further insight into the catalytic behavior of the reduced form of nickel(II) salen.

To understand the electronic structure of nickel salen species, including its reduced form(s), we have performed theoretical studies using density functional theory with the standard B3LYP functional (Becke's three-parameter exchange functional [82], together with the correlation functional of Lee et al. [83]). We utilized the 6-31+G\* basis set [84,85] containing a set of polarization functions (f for Ni, d for C, N, and O) as well as a set of diffuse functions (spd for Ni, sp for C, N, and O) to optimize the geometries of neutral nickel(II) salen and the two forms of nickel(I) salen. Single-point calculations were then carried out with a larger 6-311+G(2df) basis set [86–88] (roughly triple-zeta + diffuse functions + 2f,1g on Ni, and 2d,1f on C, N,

and O) to obtain more reliable relative energies. Finally, solvation effects were included by a continuum solvation model (integral equation formalism, polarizable continuum model, IEF-PCM [89,90]) based on the use of 36.7 as the dielectric constant for DMF. All calculations were carried out with the aid of the Gaussian suite of electronic structure programs [91].

First, we will discuss the neutral nickel(II) salen compound. It has an optimized structure of C<sub>2</sub> symmetry with a near-square-planar arrangement around nickel, as expected from simple predictions about nickel(II) bonding. In fact, the only significant non-planar distortions occur for the two methylene groups, causing one of the hydrogens of each –CH<sub>2</sub>– group to be almost perpendicular to the plane of the molecule. We have also analyzed the unoccupied molecular orbitals available for the formation of a nickel(I) salen species. Two low-energy possibilities exist for the reduced form of nickel(II) salen; the lowest unoccupied molecular orbital (LUMO) has b symmetry and is almost completely (>90%) a metal-centered antibonding d orbital (Fig. 4a), whereas the next orbital (LUMO + 1) has a symmetry, is ligand-based, and is distributed across the rings with the largest amplitude on the imino carbons (Fig. 4b). These two unoccupied levels differ in energy by only 2–3 kcal mol<sup>-1</sup>, suggesting that both electronic states are accessible for electrogeneration of a nickel(I) salen species.

Full optimizations of the reduced forms of nickel(II) salen yield structures that are consistent with occupation of the orbitals mentioned above. For the nickel(I) salen species, the ground state is <sup>2</sup>B, and both Ni–N and Ni–O bond distances increase significantly (by 0.10–0.15 Å) rela-

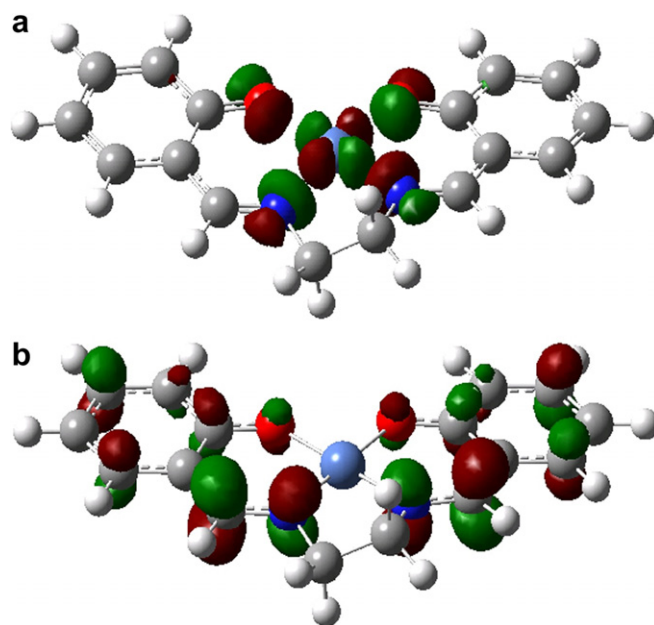


Fig. 4. Plots of the two lowest unoccupied molecular orbitals of nickel(II) salen: (a) LUMO and (b) LUMO + 1. See text for further discussion.

tive to neutral nickel(II) salen, which is consistent with occupation of the antibonding d orbital shown in Fig. 4a. Scrutiny of the spin-densities obtained from a Mulliken population analysis reveals that the one-electron reduction of nickel(II) salen occurs mostly on the nickel center, in accordance with the traditional picture for the nickel(I) salen species. On the other hand, the excited state is  $^2A$ , and it is located  $12 \text{ kcal mol}^{-1}$  higher in energy than the  $^2B$  state. Nickel–oxygen and nickel–nitrogen bond distances are similar to those found for the neutral nickel(II) salen compound, as expected from the nature of the orbital shown in Fig. 4b; bond lengths involving the ligand increase slightly, the largest effect being an increase of approximately  $0.03 \text{ \AA}$  in the lengths of the two imino bonds.

A vibrational analysis of the two electronic states shows that, whereas the  $^2B$  is a minimum, the  $^2A$  has an imaginary frequency indicating a distortion away from  $C_2$  symmetry. Careful study of the potential-energy surface shows that, as the structure distorts from  $C_2$  to  $C_1$  symmetry, the allowed mixing of the a and b orbitals results in an accompanying transfer of spin density from the ligand to the metal. Eventually, the species ends up back in the same  $^2B$  structure with  $C_2$  symmetry. Single-point calculations on the two states evaluated with the larger 6-311+G(2df) basis set or with the inclusion of solvation effects for the IEF-PCM model do not change the relative energies or the spin-density distributions in the two states.

Thus, our results suggest an interesting interplay between the metal- and ligand-centered electronic states. Although these states are close enough within the  $C_2$  symmetry of the molecular framework to contribute to the available electronic states in chemical reactions, the smooth transfer of spin density from the ligand to the metal on distortion provides another channel for the interplay between the two electronic states. These findings imply that the chemistry occurring in such systems may well depend on the nature of the reactants and is consistent with conclusions from recent experiments [41,59] which suggest ligand-based reactivities in many cases.

### 3.4. Mechanistic picture for the catalytic reduction of an alkyl halide

Scheme 1 presents a set of mechanistic steps that can account for the effects of proton donors on the catalytic reduction of an alkyl monohalide (1-iodooctane), that take into consideration the possibility of both metal- and ligand-centered one-electron reduction of nickel(II) salen, that provide pathways for alkylation of the imino bonds of nickel(II) salen during these processes, and that show how the hydrocarbon products are formed.

As depicted in Reaction (1), we propose that one-electron reduction of nickel(II) salen (**1**) can produce either a metal-reduced species (**2**) or a ligand-reduced species (**3**). Upon being formed, **2** as well as **3** can transfer an electron

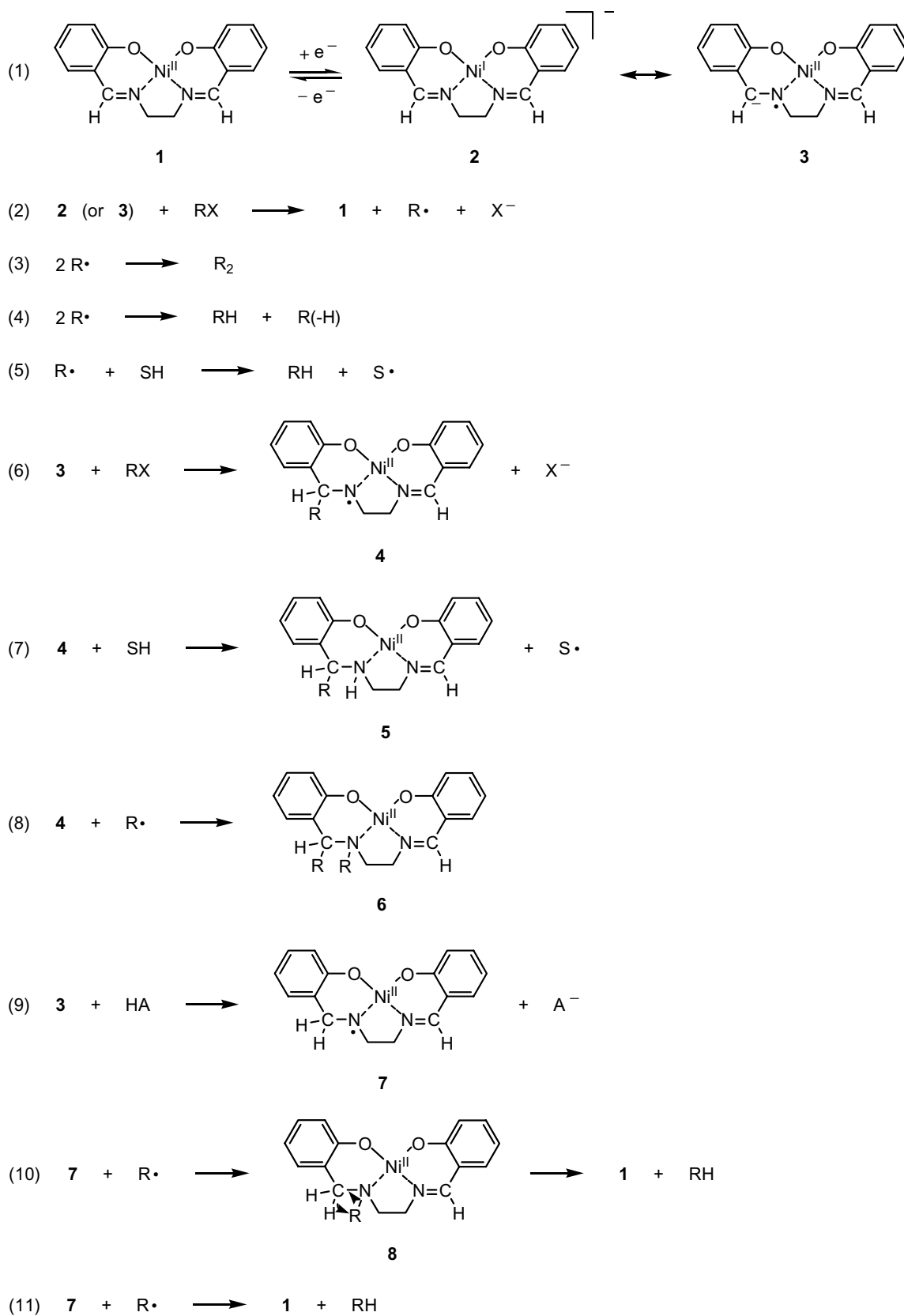
catalytically to an alkyl halide (RX) to give an alkyl radical ( $R^\cdot$ ) and a halide ion ( $X^-$ ) with regeneration of **1** (Reaction (2)). Reactions (3) and (4) show the classic coupling and disproportionation of primary alkyl radicals, whereas in Reaction (5) an alkyl radical ( $R^\cdot$ ) abstracts a hydrogen atom from the solvent (SH) to afford an alkane (RH). Coulometric  $n$  values and product distributions seen in entries 1 and 2 of Table 1 are consistent with the first five steps of Scheme 1 which involve catalytically formed alkyl radicals only. When a large excess of  $D_2O$  (a deuteron donor) is present during the nickel(I) salen-catalyzed reduction of 1-iodooctane (Table 1, entry 6), none of the octane formed is found to be deuterated, which is further evidence that octyl radicals (but not octyl carbanions) are involved as intermediates in the catalytic reduction of the iodoalkane.

Another important process is suggested to be nucleophilic attack of **3** on RX to afford an intermediate (**4**), for which the original imino bond of nickel(II) salen is alkylated (Reaction (6)). Intermediate **4** can engage in two processes—one being abstraction of a hydrogen atom from the solvent to give a monoalkylated nickel(II) salen, **5** (Reaction (7)), and the other being coupling between **4** and  $R^\cdot$  to yield a dialkylated nickel(II) salen, **6** (Reaction (8)); species such as **5** and **6** were characterized and identified in a previous investigation [59]. We suggest that electrochemical reduction of the monoalkylated nickel(II) salen species (**5**) is responsible for the second cathodic peak discussed earlier for Fig. 1. In addition, it is likely that species **3** is protonated by the medium (or by a deliberately added proton donor, e.g., HFIP or phenol) to form a neutral radical **7** (Reaction (9)). When the concentrations of HFIP and phenol are identical (Table 1, entries 3 and 5), the product distributions differ significantly, despite the fact that the thermodynamic acid strengths ( $pK_a$  values) of the two proton donors are virtually identical. On the basis of the results seen in Fig. 2, we believe that the differences observed with HFIP and phenol might be linked to the proposition that the radical-anion (**3**) generated by the one-electron reduction of an imino ( $C=N$ ) bond of nickel(II) salen [41,59] undergoes differential protonation in the presence of these proton donors because their kinetic acidities are not the same. Finally, **7** can undergo coupling with  $R^\cdot$  to give **8**, which could rearrange (with expulsion of RH) to regenerate **1** (Reaction (10)) or, as shown in Reaction (11), **7** could transfer a hydrogen atom to  $R^\cdot$  to yield **1** and RH. These last two reactions provide novel pathways for the production of octane (RH) in yields that are higher—and, thus, amounts of hexadecane,  $R_2$ , that are lower—than those obtained in the absence of any proton donor (Table 1, entries 1 and 2).

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Scheme 1.

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