Reaction of Electrogenerated Ligand-Reduced Nickel Salen with Benzyl Bromide, 1-Bromomethylnaphthalene, and α-Bromodiphenylmethane: A Study of Steric Effects

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Cyclic voltammetry (CV) and controlled-potential electrolysis (CPE) were employed to examine the reactions of electrogenerated ligand-reduced nickel(II) salen with benzyl bromide, 1-bromomethylnaphthalene, and α-bromodiphenylmethane. Cyclic voltammograms for nickel(II) salen in the presence of benzyl bromide or 1-bromomethylnaphthalene exhibit characteristic features for the catalytic reduction of substrates involving radical intermediates. Bulk electrolyses of benzyl bromide and 1-bromomethylnaphthalene at carbon cathodes catalyzed by nickel(II) salen were also carried out at selected potentials to afford various products. These results were compared with similar reaction involving 1-bromooctane as the substrate. Further comparison of the CVs for nickel(II) salen before and after reactions with the four different organic halides reveals that the steric effect could play an important role in the corresponding nucleophilic attack of the substrates by ligand-reduced catalyst (a radical−anion), which follows the sequence of 1-bromooctane > benzyl bromide > 1-bromomethylnaphthalene > α-bromodiphenylmethane in terms of reaction efficiency. Moreover, theoretical calculations using density functional theory were carried out to establish a proposed mechanism for the electrochemical reactions on the basis of previous and current studies.

Nickel(II) salen catalysts have been extensively used for electrochemical reduction of various organic halides.[1−16] In recent years, the corresponding catalytic reaction has been carefully examined to establish detailed mechanistic steps.[17−20] Generally, nickel(II) salen (**1**) would undergo a one-electron reversible reduction to generate either the metal-reduced nickel(I) salen (**2**) or the ligand-reduced radical−anion (**3**, Scheme 1), which can subsequently transfer an electron to the organic halide substrate to produce a radical and a halide ion. Afterward, the substrate radicals can undergo different follow up reactions such as coupling,[7,8] disproportionation,[7] intramolecular cyclization,[5,10] abstraction of hydrogen atom from solvent, etc to afford a series of compounds. However, the S_N2 nucleophilic substitution could also take place between organic halides and species **3** as a side reaction, causing mono- or dialkylation of nickel(II) salen molecules at the ligand imino bonds (C=N) during the catalytic process.[17,19] Consequently, significant amount of substrate materials could be lost[10] and the nickel(II) salen catalysts would be ultimately deactivated.[9,21]

Peters and his colleagues revealed that both monoalkylated and dialkylated nickel salens, which were identified by HPLC−ESI−MS and NMR, could be formed in this electrochemical catalysis.[19] Moreover, they synthesized three dialkylated analogues of nickel(II) salen by placing an alkyl group on the carbon atom of each imino bond of the ligand. The performance of these catalysts for reduction of 1-iodooctane was greatly improved as the side reaction mentioned above became insignificant owing to the steric hindrance.[22] Computational studies were also carried out to justify the reaction mechanism.[20,22]

In an effort to further understand the importance of steric effects in the S_N2 reaction between electrogenerated ligand-reduced nickel(II) salen and organic halides, we have investigated the corresponding catalytic process by using benzyl bromide, 1-bromomethylnaphthalene, and α-bromodiphenylmethane as the substrates. We would expect that the aforementioned nucleophilic substitution to be trivial when the organic halide substrate becomes more bulky. Cyclic voltammetry (CV) and controlled-potential electrolysis (CPE) were employed in this study to explore and justify our proposition. The results were compared with analogous catalytic reaction involving 1-bromooctane, which can undergo significant S_N2 reaction with electrogenerated

ligand-reduced nickel(II) salen.[19,23] Theoretical calculations for the nucleophilic reactions were also carried out and the mechanistic features were discussed based upon the present and previous findings.

Experimental

Reagents.— Each of the following chemicals was purchased and used as received: 1-bromooctane (Alfa Aesar, 98+%), benzyl bromide (Alfa Aesar, 99%), 1-bromomethylnaphthalene (AK Scientific, 98+%), α-bromodiphenylmethane (AK Scientific, 97%), toluene (Alfa Aesar, 99%), bibenzyl (Alfa Aesar, 98+%), benzyl ether (Alfa Aesar, 98%), benzyl alcohol (Alfa Aesar, 99%), 1-methylnaphthalene (Alfa Aesar, 96%), 1,2-bis(1-naphthyl)ethane (Alfa Aesar, 97%), 1-naphthalenemethanol (Alfa Aesar, 98+%), [[2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]bis[phenolato]]-*N*,*N*′,*O*,*O*′]nickel(II) (nickel(II) salen or Ni(II)L, Aldrich, 98%), *n*-dodecane (Alfa Aesar, 99%), *n*-tridecane (Alfa Aesar, 99%), tetramethylammonium hydroxide (TMAOH, Alfa Aesar, 98%), acetonitrile (Fisher, 99.5%), and anhydrous diethyl ether (J.T. Baker, 99.9%). Tetramethylammonium tetrafluoroborate (TMABF₄, Aldrich, 97%), used as the supporting electrolyte, was stored in a vacuum oven at 60 °C prior to use. Anhydrous dimethylformamide (DMF, Burdick & Jackson, 99.9%) was
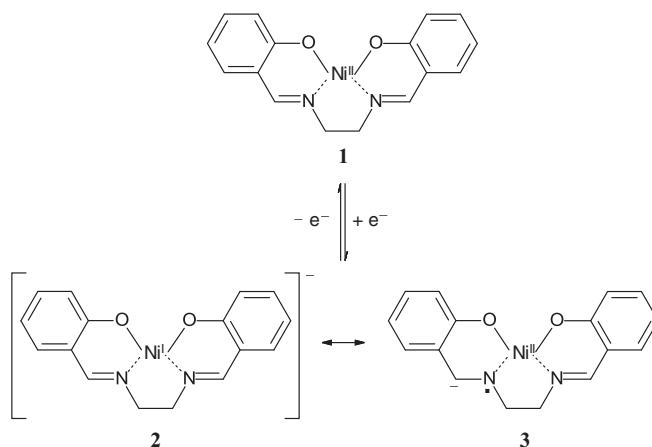
Scheme 1.

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employed as solvent for electrochemical experiments. All deaeration procedures were carried out with Airgas zero-grade argon.

Bis(1-naphthylmethyl) ether was synthesized by mixing 1-bromomethylnaphthalene with TMAOH in a molar ratio of 2:1 in acetonitrile. The pure product was obtained by silica gel column chromatograph after three hours of refluxing. Its identity was confirmed with the aid of ^{1}H NMR (CDCl$_3$): δ 8.10 (d, 2H), 7.85 (dd, 4H), 7.55 (d, 2H), 7.51−7.43 (m, 6H), and 5.07 (s, 4H). Two isomers of bibenzyl were characterized by gas chromatography–mass spectrometry (GC–MS, 70 eV): (a) for 1-methyl-2-(phenylmethyl)benzene, *m/z* 182, M$^+$ (75%); 167, [M − CH$_3$]$^+$ (100%); 152, [M − 2CH$_3$]$^+$ (15%); 104, [M − C$_6$H$_6$]$^+$ (27%); 91, [M − C$_6$H$_4$CH$_3$]$^+$ (29%); 77, C$_6$H$_5^+$ (10%); (b) for 1-methyl-4-(phenylmethyl)benzene, *m/z* 182, M$^+$ (65%); 167, [M − CH$_3$]$^+$ (100%); 152, [M − 2CH$_3$]$^+$ (12%); 105, [M − C$_6$H$_5$]$^+$ (6%); 91, [M − C$_6$H$_4$CH$_3$]$^+$ (11%); 77, C$_6$H$_5^+$ (7%).

Cells, electrodes, and instrumentation.— Cells for CV[23] and CPE[24] have been described previously. For CV experiments, a 3-mm-diameter glassy carbon working electrode (Part No. CHI104, CH Instruments) was used and a platinum wire was employed as the auxiliary electrode. Customized 2.4 cm diameter × 0.4 cm thick reticulated vitreous carbon disks (Duocel RVC 100 PPI, Energy Research and Generation) were used as working cathodes for CPE; these disks were cleaned and handled according to established procedures.[25] The reference electrode consists of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride[26,27] and it has a potential of −0.76 V vs. SCE at 25°C. Potentials are quoted with respect to SCE in this paper. All CV and CPE experiments were carried out with a CH Instruments model 620B electrochemical analyzer.

Separation, identification, and quantitation of products.— Electrolysis products were characterized with the aid of an Agilent Technologies model 6890N gas chromatograph (GC) equipped with a flame ionization detector (FID) and a model 5973N mass-selective detector (MSD). The analytes were separated on Agilent Technologies 30 m × 0.25 mm capillary columns (HP-1 for FID and HP-5MS for MSD) with a stationary phase of either 1% or 5% crosslinked phenylmethylsiloxane. Their identities were confirmed by comparing gas chromatographic retention times as well as mass spectra of suspected products with those of authentic compounds (or the NIST Mass Spectral Library). Quantitation of the products was accomplished by means of GC using an internal standard method, which has been outlined elsewhere.[28] A known amount of *n*-dodecane or *n*-tridecane was added as an electroinactive internal standard to each solution prior to electrolysis. Samples for gas chromatographic analysis were taken from the diethyl ether extracts of the electrolyzed solutions and washed with brine. The GC response factors were determined experimentally with respect to *n*-dodecane or *n*-tridecane for all electrolysis products and yields reported in this paper represent the absolute percentage of starting material incorporated into a particular species.

Results and Discussion

Cyclic voltammetry.— Fig. 1I depicts the CVs for reduction of nickel(II) salen in the presence of four different concentrations of benzyl bromide (as well as for reduction of nickel(II) salen or benzyl bromide by itself) recorded at a scan rate of 100 mV s^{-1} with a glassy carbon electrode in DMF containing 0.050 M TMABF$_4$. Curve A, is a cyclic voltammogram for a 2.0 mM solution of nickel(II) salen, showing a reversible redox couple at E_{pc} of −1.69 V and E_{pa} of −1.61 V. Meanwhile, the irreversible direct reduction of benzyl bromide was found to have a peak potential of −1.77 V (Curve F). When 2.0 mM of nickel(II) salen and 1.0 mM of benzyl bromide were combined, as presented by Curve B, two characteristics of a catalytic process were observed: (a) a small increase in the cathodic peak current and an accompanying positive shift (approximately 140 mV) in the cathodic peak potential (as a new wave) for reduction of nickel(II) salen, and (b) a decrease in the anodic peak current for reoxidation of nickel(I)
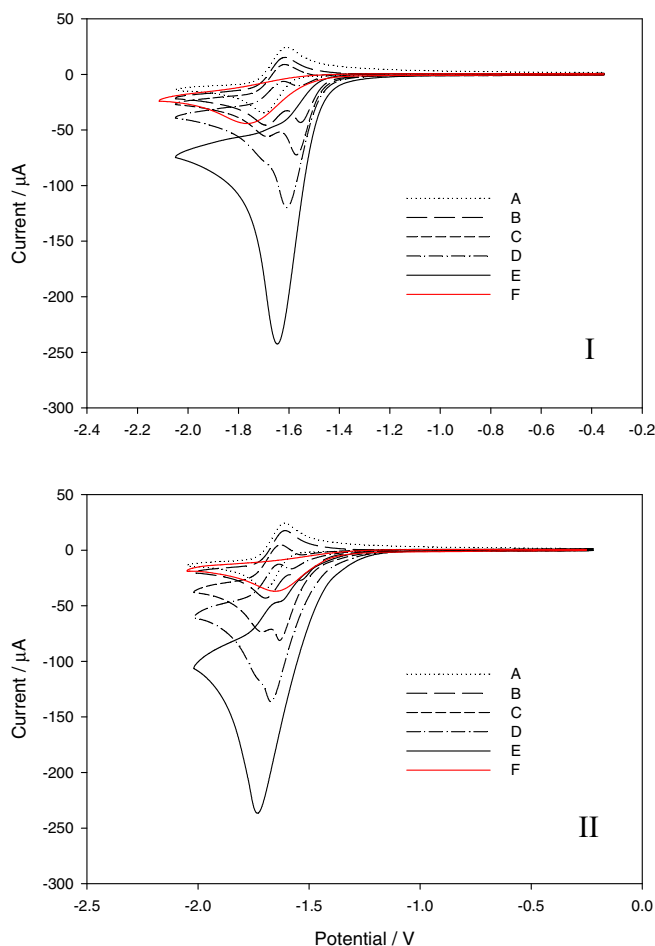

Figure 1. Cyclic voltammograms recorded with a glassy carbon electrode (3-mm-diameter) at 100 mV s^{-1} in DMF containing 0.050 M TMABF$_4$ for 2.0 mM of nickel(II) salen in the presence of (A) 0, (B) 1.0, (C) 2.0, (D) 4.0, and (E) 8.0 mM of substrate; (F) 2.0 mM of substrate (I = benzyl bromide; II = 1-bromomethylnaphthalene).

salen. A second cathodic wave for the direct reduction of nicke(II) salen at −1.69 V was still observed, arising from the formation of nickel(I) salen which was unable to locate a benzyl bromide molecule close to the electrode surface due to depletion of the substrate. Peak current for the new cathodic wave increases with the concentration of benzyl bromide and it eventually merges (with that for the direct reduction of nicke(II) salen) into one large peak (Curves C−E), which is similar to those shown in previous studies of the nickel(I) salen-catalyzed reduction of 1-bromooctane.[19,23]

Fig. 1II depicts CVs recorded under the same experimental conditions except in the presence of 1-bromomethylnaphthalene instead of benzyl bromide. Although the direct reduction of 1-bromomethylnaphthalene takes place at a slightly more positive potential (E_{pc} = −1.65 V) than that of nickel(II) salen, CV features analogous to those discussed for Fig. 1I are apparent. Results indicate that the catalytic reduction of 1-bromomethylnaphthalene by electrogenerated nickel(I) salen is still prominent.

Controlled-potential electrolyses.— To ensure the catalytic process would take place, CPEs were carried out at potentials carefully selected according to the corresponding CVs for reduction of nickel(II) salen in the presence of benzyl bromide and 1-bromomethylnaphthalene (−1.60 V and −1.55 V, respectively). Direct reductions of the substrates at much more negative potentials, which give carbanion intermediates, were also examined for comparison. Compiled in Tables I and II are coulometric results

Table I. Coulometric data and product distributions for CPE of benzyl bromide at reticulated vitreous carbon cathodes in DMF containing 0.050 M TMABF$_4$ under various experimental conditions.

| Substrate (mM) | Ni(II) Salen (mM) | E (V) | n | Product Distribution (%) | | | | | | |
				4	**5**	**6**	**7**	**8**	**9**	Total
10	0	−2.05	1.07	61	4	ND[a]	ND	38	ND	93
10	2	−1.60	1.07	53	18	2	3	9	5	90
20	2	−1.60	1.05	48	19	1	2	18	6	94

4 = toluene; **5** = bibenzyl; **6** = 1-methyl-2-(phenylmethyl)benzene; **7** = 1-methyl-4-(phenylmethyl)benzene; **8** = benzyl ether; **9** = benzyl alcohol.
[a]ND = not detected.

and product yields for the reductions of benzyl bromide and 1-bromomethylnaphthalene, respectively, at reticulated vitreous carbon cathodes in DMF containing 0.050 M TMABF$_4$. Each tabulated entry is the average of at least three identical experiments.

CPEs of 10 mM solutions of benzyl bromide at −2.05 V generate toluene, bibenzyl, and benzyl ether as the major products with a coulometric n value of 1.07. The electrogenerated benzyl anions (via two-electron reduction at this potential) could be involved in various chemical reactions, such as S$_N$2 attack of the substrate to form bibenzyl and benzyl ether, causing the n value to decrease from 2. With the addition of 2 mM of nickel(II) salen, the catalytic electrolyses give benzyl radicals, which would couple efficiently to afford more bibenzyl. Meanwhile, the yield of benzyl ether which is produced via benzyl anion intermediates, drops significantly. The increase of substrate concentration to 20 mM does not have a large impact on the product distribution. The formation of benzyl alcohol (as well as benzyl ether) in a small amount indicates that the direct reduction still takes place to some extent. All these results are comparable to the previous report for the electrochemical reduction of benzyl iodide.[29] More interestingly, both 1-methyl-2-(phenylmethyl)benzene and 1-methyl-4-(phenylmethyl)benzene were also found in the products from catalytic reductions, strongly suggesting a radical pathway for the reaction mechanism.[30] Analogous CPE data were obtained as well for the direct and catalytic reduction of 1-bromomethylnaphthalene in the total product yields of around 90%.

With nickel(II) salen and organic halide mixed in a molar ratio of 1:10, the catalytic electrolysis of 1-bromooctane gives a total product yield of merely 76%, as revealed by our previous studies.[23] This total product yield is much lower than that for catalyzed reduction of benzyl bromide (94%) or 1-bromomethylnaphthalene (89%), indicating that the S$_N$2 nucleophilic reaction between species **3** and 1-bromooctane is significant,[19] likely due to less steric hindrance. Nevertheless, total recovery yields of starting materials for electrolyses of benzyl bromide and 1-bromomethylnaphthalene seem similar, making it impossible to draw a conclusion with regard to which substrate reacts more efficiently with **3** for the alkylation of nickel(II) salen catalyst. We resorted to cyclic voltammetry for further investigation.

Comparison of cyclic voltammograms for the nickel(II) salen catalyst after reactions with organic halides.— To obtain further insight into the modification of nickel(II) salen catalysts, we examined the

corresponding cyclic voltammograms before and after CPEs with a final reoxidation electrolysis at 0 V.[19,23] Figs. 2I–2III display CVs recorded at a scan rate of 100 mV s^{-1} with a glassy carbon electrode in DMF containing 0.050 M TMABF$_4$ for nickel(II) salen before and after CPEs with the organic halides. There are huge decreases in the redox peak currents for reduction of nickel(II) salen after CPE of 10 mM solution of 1-bromooctane, as shown in Fig. 2I (Curve B). Moreover, a second pair of redox waves appears at a more negative potential, due to reduction of alkylated catalyst. The changes become more prominent after CPE of 20 mM 1-bromooctane. As pointed out earlier,[19,23] these characteristic CV features are due to the alkylation of nickel(II) salen catalysts.

Much less decreases in peak currents can be observed for reduction of nickel(II) salen after CPEs of benzyl bromide (Fig. 2II) or 1-bromomethylnaphthalene (Fig. 2III). However, the appearance of a second cathodic wave is more obvious after the electrolyses of 20 mM benzyl bromide than that for 1-bromomethylnaphthalene, suggesting a more efficient reaction between **3** and benzyl bromide. Additionally, these CVs are compared in Fig. 2IV for the catalyst before and after CPEs of the three substrates. It becomes more clear that the degree of alkylation for nickel(II) salen follows the sequence of 1-bromooctane > benzyl bromide > 1-bromomethylnaphthalene in the catalytic reduction, likely due to the steric effects.

Least significant alkylation should be expected if the bulky organic halide, α-bromodiphenylmethane, is employed as the substrate. Unfortunately, nickel(I) salen-catalzyed CPE of α-bromodiphenylmethane is not feasible because its reduction potential is much more positive than that of nickel(II) salen. Consequently, a different method was used to study its reaction with **3**. A solution containing 2.0 mM of nickel(II) salen was first electrolyzed by one-electron reduction to form both the metal-reduced **2** and the ligand-reduced **3**. Subsequently, an equal molar amount of organic halide was added for the reactions. Fig. 3 shows that the CV peak currents for reduction of nickel(II) salen decrease after alkylation by various substrates. The magnitude of this change follows the order of 1-bromooctane > benzyl bromide > 1-bromomethylnaphthalene > α-bromodiphenylmethane, which agrees well with the corresponding steric effects caused by the substrates for aforementioned nucleophilic substitution. Results demonstrate that the structure of organic halide plays an important role in the alkylation of nickel(II) salen during the catalytic process.

Table II. Coulometric data and product distributions for CPE of 1-bromomethylnaphthalene at reticulated vitreous carbon cathodes in DMF containing 0.050 M TMABF$_4$ under various experimental conditions.

| Substrate (mM) | Ni(II) Salen (mM) | E (V) | n | Product Distribution (%) | | | | Total |
				10	**11**	**12**	**13**	
10	0	−1.95	0.96	46	18	30	TA[a]	94
10	2	−1.55	1.02	50	33	8	TA	91
20	2	−1.55	0.98	52	30	7	TA	89

10 = 1-methylnaphthalene; **11** = 1,2-bis(1-naphthyl)ethane; **12** = bis(1-naphthylmethyl) ether; **13** = 1-naphthalenemethanol.
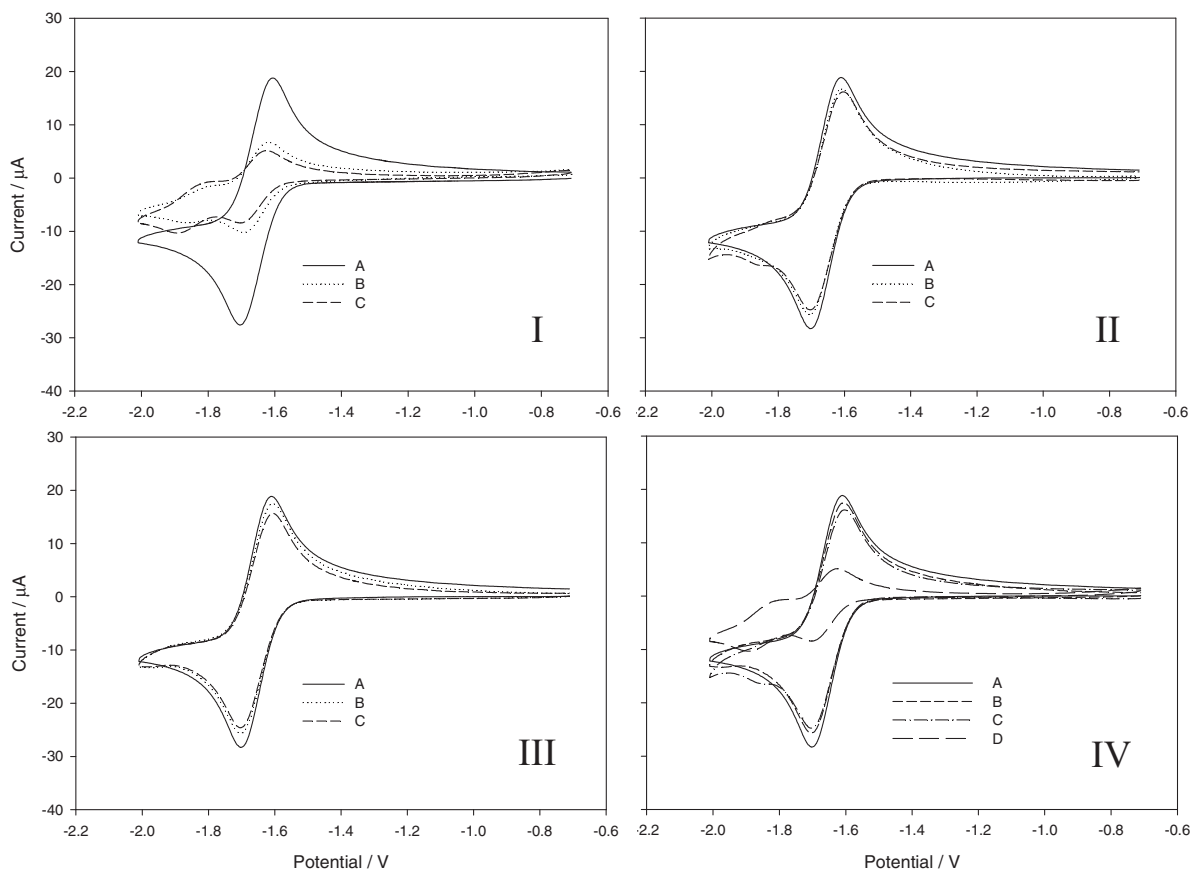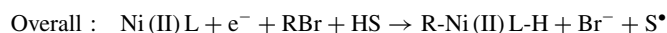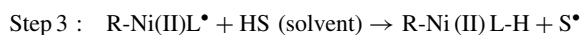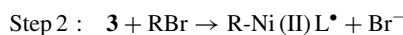[a]TA = trace amount.

Figure 2. Cyclic voltammograms recorded with a glassy carbon electrode (3-mm-diameter) at 100 mV s^{-1} in DMF containing 0.050 M TMABF$_4$ for 2.0 mM of nickel(II) salen before (A) and after CPEs of (B) 10 mM or (C) 20 mM of substrates (I = 1-bromooctane; II = benzyl bromide; III = 1-bromomethylnaphthalene) as well as CVs (IV) for 2.0 mM of nickel(II) salen before (A) and after CPEs of 20 mM of (B) 1-bromomethylnaphthalene, (C) benzyl bromide, and (D) 1-bromooctane.

Computational studies of the electrochemically induced nucleophilic reaction.— To understand the energies associated with the nucleophilic reactions involving benzyl bromide, 1-bromomethylnaphthalene, and α-bromodiphenylmethane, we have performed theoretical studies using density functional theory with the standard B3LYP functional (Becke's three-parameter exchange

Figure 3. Cyclic voltammograms recorded with a glassy carbon electrode (3-mm-diameter) for 2.0 mM of reduced nickel(II) salen in DMF containing 0.050 M TMABF$_4$ at a scan rate of 100 mV s^{-1} before (A) and after reaction with 2.0 mM of (B) 1-bromooctane, (C) benzyl bromide, (D) 1-bromonaphthalene, or (E) α-bromodiphenylmethane.

functional,[31] together with the correlation functional of Lee et al.[32]) for the following stepwise and overall reactions:

Step 1 :   Ni (II) L (**1**) + e$^-$ → **3**

Step 2 :   **3** + RBr → R-Ni (II) L$^{\bullet}$ + Br$^-$

Step 3 :   R-Ni(II)L$^{\bullet}$ + HS (solvent) → R-Ni (II) L-H + S$^{\bullet}$

Overall :   Ni (II) L + e$^-$ + RBr + HS → R-Ni (II) L-H + Br$^-$ + S$^{\bullet}$

We utilized the 6-31+G(2d,f) basis set[33,34] 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 all reactants, products, and intermediates. Solvation effects were included by a continuum solvation model (integral equation formalism, polarizable continuum model, IEF-PCM[35,36]) based on the use of 36.7 as the dielectric constant and 0.948 as the density for DMF. Frequency calculations were carried out directly on the optimized structures at 298.15 K using the same basis set and conditions to determine internal energies (E), enthalpies (H), and Gibbs free energies (G) for all species, corrected for zero-point and thermal energies. Results were used to calculate ΔE and ΔG values for each mechanistic step and then for the overall reaction. All calculations were carried out with the aid of Gaussian 09 suite of electronic structure programs.[37]

Listed in Table III are the ΔE and ΔG values for the overall nucleophilic reactions between nickel(II) salen and the three aromatic organic halides. The ΔG values indicate that thermodynamically, the reaction should be most favored for benzyl bromide and least favored for α-bromodiphenylmethane. These theoretical data are consistent with our experimental results, as the steric effects caused by the substrates according to their bulkiness (benzyl bromide
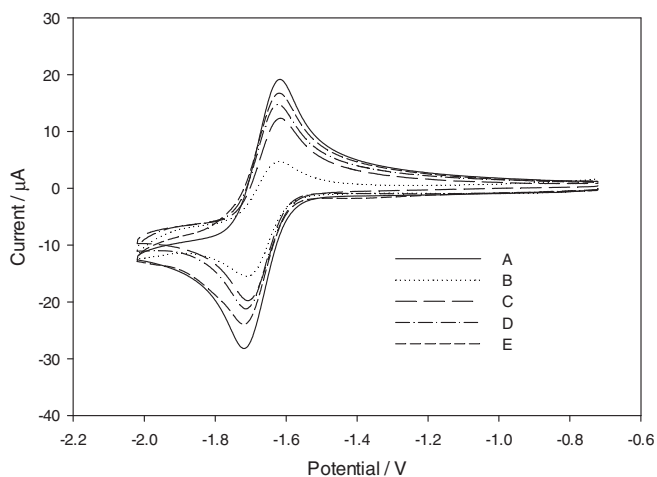
Table III. Theoretical ΔE and ΔG values calculated by Gaussian 09 for the overall nucleophilic reactions between nickel salen and organic halides.

Substrate	ΔE (KJ mol^{-1})	ΔG (KJ mol^{-1})
Benzyl bromide	−274	−261
1-Bromomethylnaphthalene	−274	−257
α-Bromodiphenylmethane	−245	−227

< 1-bromomethylnaphthalene < α-bromodiphenylmethane) would have an impact on the nucleophilic substitutions. For purposes of verification, follow-up single-point calculations were carried out with

a larger 6-311+G(2d,f) basis set[38−40] (roughly triple-zeta + diffuse functions + 2f,1g on Ni, and 2d,1f on C, N, and O) and the same ranking of the relative (uncorrected) energies was confirmed. The detailed mechanism will be discussed below.

Mechanistic features.— The mechanism for the direct reduction of benzyl bromide or 1-bromomethylnaphthalene involving carbanion intermediates should be similar to that for benzyl iodide[29] and needs no further discussion. On the basis of established mechanistic pathways[17−20,22] and our current findings, a possible mechanism for the nickel(I) salen-catalyzed reduction of the two aryl halides is proposed in Scheme 2. The electrogenerated metal-reduced nickel(I)
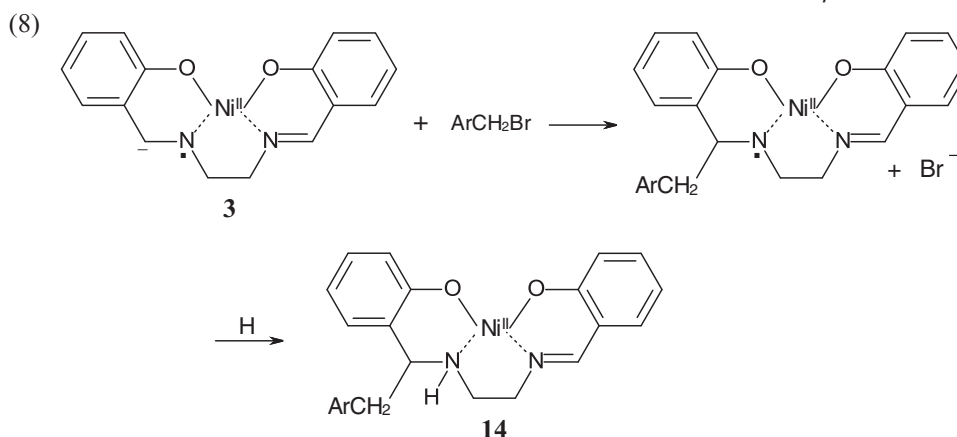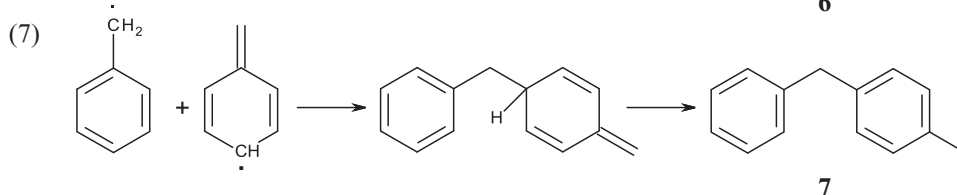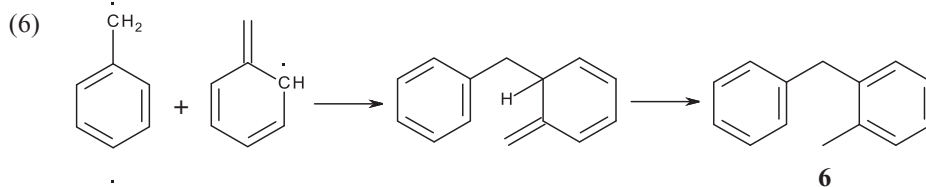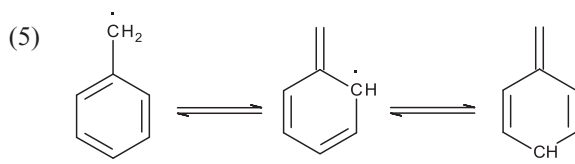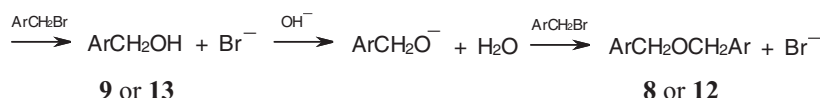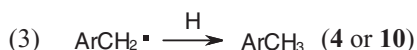
Scheme 2.

salen (**2**) or the ligand-reduced radical−anion (**3**) can transfer one electron to the substrate, which undergoes reductive cleavage of the carbon−bromine bond to form the corresponding radical and regenerates nickel(II) salen (**1**) (reaction 1). The aryl radicals can couple with each other to give the dimers (reaction 2) or abstract hydrogen atom from solvent (reaction 3). Because a reticulated vitreous carbon cathode is often not an equipotential surface, it is unavoidable for some aryl radicals to be further reduced to anions,[41] which go through reaction 4 to yield alcohol (**9** or **13**) and ether (**8** or **12**). Benzyl radical has two resonance structures, which can couple with the primary radical to generate both 1-methyl-2-(phenylmethyl)benzene (**6**) and 1-methyl-4-(phenylmethyl)benzene (**7**) (reactions 5–7). The formation of these isomers, which was not reported in a previous study,[29] is another strong evidence that radical intermediates are involved in the catalytic reduction.

The ligand-reduced nickel(II) salen **3** could undergo nucleophilic reaction with benzyl bromide or 1-bromomethylnaphthalene to produce the alkylated nickel(II) salen (**14**) (reaction 8). However, this side reaction should not be significant due to steric effects. On the other hand, when 1-bromooctane or α-bromodiphenylmethane is employed as the substrate, reaction 8 would become more or even less prominent for the same reasons. Alternatively, the formation of **14** may also be caused by the reaction of substrate radicals with **3**[19] or nickel(II) salen. The corresponding mechanism can possibly explain our experimental results according to the reactivity of substrate radicals. Nevertheless, we believe this pathway is less likely for two reasons. First, the electrochemical reduction of 1-iodooctance catalyzed by a dimethylated nickel(II) salen showed minimal alkylation of the catalyst.[22] Second, we electrolyzed benzyl iodide to produce benzyl radical in the presence of nickel(II) salen and also found no catalyst-substrate adduct. These studies suggest that the radical incorporation into nickel(II) salen should be insignificant. A more thorough mechanistic investigation is currently being carried out in our group.

Conclusions

In summary, the reduction of several selected organic halides by electrogenerated metal-reduced nickel(I) salen (**2**) or ligand-reduced nickel(II) salen radical−anion (**3**) involves mainly radical intermediates. The catalyst species **3** can also undergo direct nucleophilic reaction with the substrates to form alkylated nickel(II) salen, as revealed by previous and present studies. The CV and CPE data obtained in this investigation further illustrate that steric effect could significantly affect these S_N2 reactions. It would be more difficult for **3** to attack bulky organic halide substrate and consequently, the loss of catalytic activity for nickel(II) salen should be minimal. The reaction efficiency follows the sequence of 1-bromooctane > benzyl bromide > 1-bromomethylnaphthalene > α-bromodiphenylmethane for the corresponding nucleophilic substitution by **3**.

Acknowledgment

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