J. Org. Chem. **1993**, *58*, 4919–4924

Electrocatalytic Reduction of Benzal Chloride by Cobalt(I)(salen). A Mechanistic Investigation

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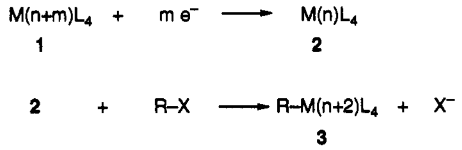
Received March 30, 1993

Benzal chloride (**6**) is converted to a mixture consisting primarily of *cis*- and *trans*-stilbene (**12**) by the action of electrochemically-generated cobalt(I)(salen)$^{-1}$ (**5**). The process involves a sequence involving electrocatalytic conversion of benzal chloride to a mixture of the stereoisomeric 1,2-dichloro-1,2-diphenylethanes (**10**), followed by electrocatalyzed conversion of the latter to **12**. Voltammograms of Co(II)(salen) (**4**) in the presence of varying amounts of **6** exhibit peaks both before and after that due to reduction of **4**. The voltammetric data and other chemical evidence is interpreted in light of a previously-suggested mechanism for stilbene formation.

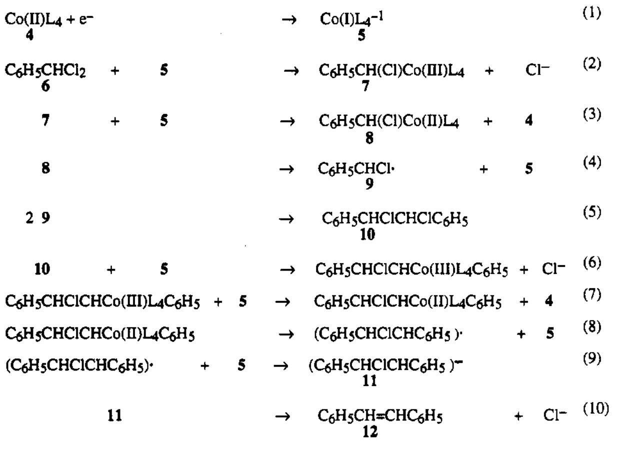
The electrochemical reduction of alkyl halides has been shown to be mediated by a variety of transition metal complexes, particularly those of cobalt, nickel, or iron.[1,2] Typically, the process involves reduction of the metal complex (**1**) to a reactive low-valent form (**2**), followed by oxidative addition of the latter into the carbon–halogen bond to generate an organometallic intermediate (**3**).



$$\underset{\mathbf{1}}{M(n+m)L_4} + m\,e^- \longrightarrow \underset{\mathbf{2}}{M(n)L_4}$$

$$\mathbf{2} + R{-}X \longrightarrow \underset{\mathbf{3}}{R{-}M(n+2)L_4} + X^-$$

Subsequent events depend on a number of factors: the electrolysis potential, the relative reduction potentials of **1**, **3**, and the alkyl halide, the stability of the **3** on the electrolysis time scale, and other experimental variables.[2] For example, **3** may be photochemically[3] or thermally labile. In such cases, rapid decomposition of **3** is observed, usually liberating the alkyl group as a free radical. Adduct **3** is often sufficiently stable to be isolated and studied by physical and spectroscopic techniques. Voltammetry of a mixture of an alkyl halide and **1** provides a convenient method for demonstrating the occurrence of the oxidative addition reaction (the alkyl halide must of course be electrochemically inactive at the potential at which **1** is reduced). A number of reports have appeared describing voltammetric experiments of this kind.[4] The reduction potential of **3** is generally negative of that of **1**. Hence, addition of an alkyl halide to the solution of **1** causes the reversible cyclic voltammetric wave of **1** to lose its reversibility (the anodic peak on the reverse scan disappears) and a new wave to appear at a more negative potential (reduction of **3**). Further chemistry can be induced by thermolysis, photolysis, or electrolysis at potentials corresponding to the latter wave, because the reduced form of **3** is usually more thermally unstable than **3** itself.[5]



Scheme I

$$\underset{\mathbf{4}}{Co(II)L_4} + e^- \rightarrow \underset{\mathbf{5}}{Co(I)L_4^{-1}} \qquad (1)$$

$$\underset{\mathbf{6}}{C_6H_5CHCl_2} + \mathbf{5} \rightarrow \underset{\mathbf{7}}{C_6H_5CH(Cl)Co(III)L_4} + Cl^- \qquad (2)$$

$$\mathbf{7} + \mathbf{5} \rightarrow \underset{\mathbf{8}}{C_6H_5CH(Cl)Co(II)L_4} + \mathbf{4} \qquad (3)$$

$$\mathbf{8} \rightarrow \underset{\mathbf{9}}{C_6H_5CHCl\cdot} + \mathbf{5} \qquad (4)$$

$$2\ \mathbf{9} \rightarrow \underset{\mathbf{10}}{C_6H_5CHClCHClC_6H_5} \qquad (5)$$

$$\mathbf{10} + \mathbf{5} \rightarrow C_6H_5CHClCHCo(III)L_4C_6H_5 + Cl^- \qquad (6)$$

$$C_6H_5CHClCHCo(III)L_4C_6H_5 + \mathbf{5} \rightarrow C_6H_5CHClCHCo(II)L_4C_6H_5 + \mathbf{4} \qquad (7)$$

$$C_6H_5CHClCHCo(II)L_4C_6H_5 \rightarrow (C_6H_5CHClCHC_6H_5)\cdot + \mathbf{5} \qquad (8)$$

$$(C_6H_5CHClCHC_6H_5)\cdot + \mathbf{5} \rightarrow \underset{\mathbf{11}}{(C_6H_5CHClCHC_6H_5)^-} \qquad (9)$$

$$\mathbf{11} \rightarrow \underset{\mathbf{12}}{C_6H_5CH{=}CHC_6H_5} + Cl^- \qquad (10)$$

L_4 = bis(salicylidene)ethylenediamine)

We recently examined the preparative-scale reduction of cobalt(II)(salen)[6] (**4**) in the presence of benzal chloride, $C_6H_5CHCl_2$ (**6**), and proposed[7] the mechanism shown in Scheme I. The reaction differs in several significant respects from previously studied processes involving **4** and simple alkyl monohalides. In particular, the initial organometallic intermediate **7** is *more easily* reduced than **4**. This causes the overall reduction to be electrocatalytic: **7** is reduced as soon as it is formed, and the resulting alkylcobalt(II) species **8** rapidly decomposes, regenerating Co(I)(salen)$^{-1}$ (**5**) which then continues the cycle. We hypothesized that the other product of the decomposition of **8** is the α-chlorobenzyl radical **9**. A critical feature of this mechanism was our postulate that **9** is not reducible at the potential at which the reduction of **4** is carried out. This assumption was required to explain the isolation of *cis*- and *trans*-stilbene (**12**) derived by dimerization of **9** as shown in Scheme I. In view of this assumption and others which are implicit in Scheme I, we felt that it was desirable to obtain further information. We have therefore carried out a voltammetric investigation of the interaction

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[1] E.g. (a) Gosden, C.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem.* 1981, *117*, 101. (b) Mubarak, M. S.; Peters, D. G. *J. Electroanal. Chem.* 1992, *332*, 127. (c) Fauvarque, J. F.; Chevrot, C.; Jutand, A.; François, M.; Perichon, J. *J. Organomet. Chem.* 1984, *264*, 273. (d) Lexa, D.; Mispelter, J.; Savéant, J.-M. *J. Am. Chem. Soc.* 1981, *103*, 6806.

[2] Scheffold, R. *Modern Synthetic Methods*; Wiley: New York, 1983; Vol. 3, p 355.

[3] Alelyunas, Y. W.; Fleming, P. E.; Finke, R. G.; Pagano, T. G.; Marzilli, L. G. *J. Am. Chem. Soc.* 1991, *113*, 3781.

[4] (a) Puxeddu, A.; Costa, G.; Marsich, N. *J. Chem. Soc., Dalton Trans.* 1980, 1489. (b) Pletcher, D. *Chem. Soc. Rev.* 1975, *4*, 471. (c) Duprilot, J.-M.; Bedioui, F.; Devynck, J.; Folest, J.-C.; Bied-Charreton, C. *J. Organomet. Chem.* 1985, *286*, 77. (d) Costa, G.; Puxeddu, A.; Reisenhofer, E. *J. Chem. Soc., Dalton Trans.* 1972, 1519.

[5] (a) Martin, B. D.; Finke, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 585. (b) Lexa, D.; Savéant, J.-M. *Acc. Chem. Res.* **1983**, *16*, 235.

[6] Salen = bis(salicyliden)ethylenediamine.

[7] Fry, A. J.; Sirisoma, U. N.; Lee, A. S. *Tetrahedron Lett.* **1993**, *34*, 809.

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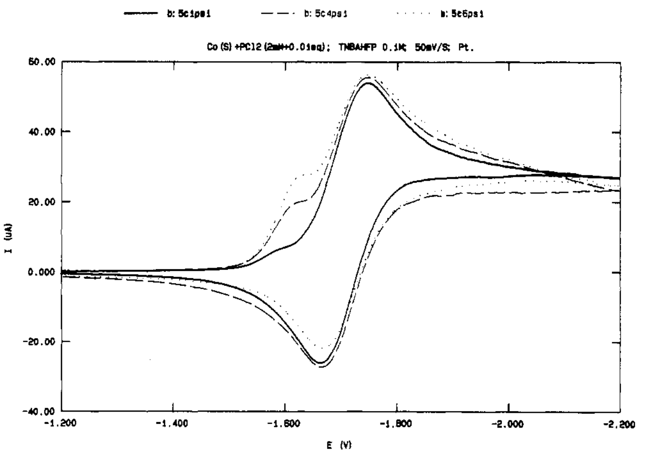

Figure 1. Cyclic voltammograms at 50 mV sec^{-1} of 2 mM Co(II)(salen) in DMF/0.1 M Bu_4NPF_6. Solid line: 0.02 mM benzal chloride. Dashed line: 0.06 mM benzal chloride. Dotted line: 0.12 mM benzal chloride.

between **5** and **6** and have also carried out a number of chemical experiments designed to obtain mechanistic information. We describe here our results, which provide clear support for the key features of the mechanism shown in Scheme I.

Results

Voltammetry. The voltammetric behavior of cobalt(II)(salen) (**4**) was examined in the presence of benzal chloride in dimethylformamide (DMF) containing tetra-*n*-butylammonium hexafluorophosphate (TBAHFP). Complex **4** exhibits a single quasireversible[8] cyclic voltammetric wave centered at −1.70 V vs Ag/0.1 M $AgNO_3$.[9] The voltammetric behavior of **4** was examined as increasing amounts of benzal chloride (**6**) were added. We define R_C as the mole ratio of benzal chloride to Co(II)(salen). Addition of 1 mol% of benzal chloride to the solution ($R_C = 0.01$) has a surprisingly large effect upon the voltammogram (Figure 1, solid line). A prewave appears at *ca.* −1.6 V. Its height is roughly 5–6% of that of the wave corresponding to reduction of **4**. As the concentration of **6** is increased, the height of the prewave continues to not only increase in height but to increase out of proportion to the relative amounts of the two species: when $R_C = 0.06$, the prewave and the original Co(II)(salen) reduction wave are of equal magnitude (dotted line in Figure 1). The prewave continues to increase with increasing benzal chloride concentration until the two waves finally merge at $R_C \cong 0.20$ (Figure 2). At this ratio the anodic wave on the reverse sweep associated with reoxidation of Co(I) has largely disappeared; in fact, it does so when R_C is 0.16 or greater. It is also significant that for $R_C \leq 0.12$, (a) the increase in size of the prewave with increasing concentration of **6** is *not* accompanied by an increase in the size of the original wave due to **4** and (b) the latter wave does not move toward more positive potentials throughout this range of concentrations of **6**, as one would expect for a wave associated with a following chemical reaction coupled to the reduction of **4**.[10]

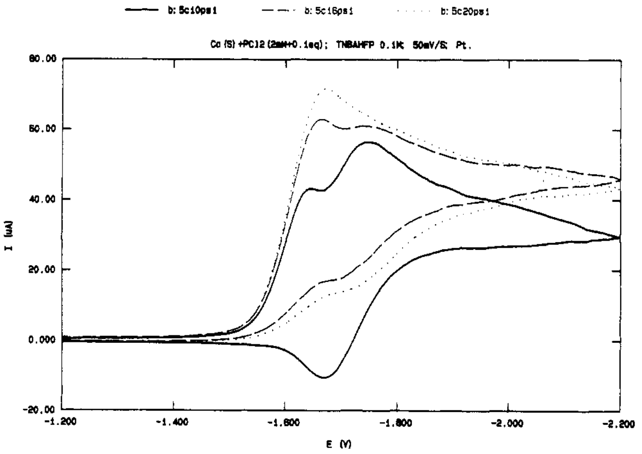

Figure 2. Cyclic voltammograms at 50 mV sec^{-1} of 2 mM Co(II)(salen) in DMF/0.1 M Bu_4NPF_6. Solid line: 0.20 mM benzal chloride. Dashed line: 0.32 mM benzal chloride. Dotted line: 0.40 mM benzal chloride.

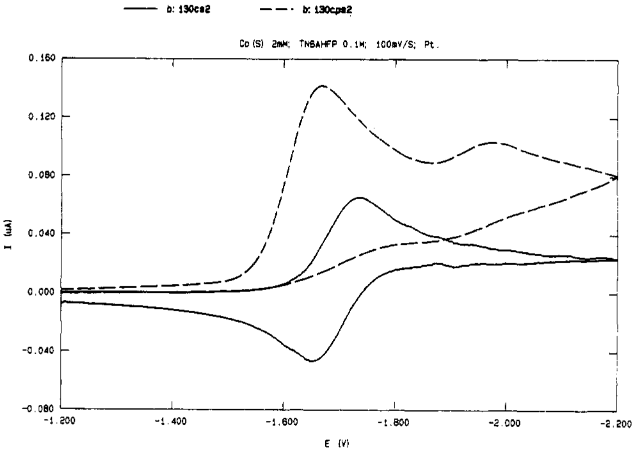

Figure 3. Solid line: cyclic voltammograms at 100 mV sec^{-1} of 2 mM Co(II)(salen) in DMF/0.1 M Bu_4NPF_6. Dashed line: benzal chloride (2 mM) added.

At values of R_C greater than 0.20, the composite wave increases in size and moves to more positive potentials. Both of these features are apparent in Figure 3, corresponding to $R_C = 1$. Of great significance is appearance of a new voltammetric wave at *ca.* −2 V at larger values of R_C. This second wave can be seen in Figure 3; it increases in size not only with increasing concentration of **6** but also with increasing scan rate (Figure 4).

Controlled Potential Electrolysis. Controlled potential electrochemical reduction of a solution of **4** in DMF/0.1 M TBAHFP at −1.7 consumes 1 faraday of charge per mole of **4** and produces a solution of the very air-sensitive Co(I) species **5**. If the solvent is not carefully dried, much more than the calculated amount of current is consumed and the electrolyte is converted to tributylamine. This is caused by a known electrocatalytic cycle in which **5** reduces water to hydrogen and hydroxide ion, which then attacks the supporting electrolyte in a Hofmann elimination.[11] When the electrolysis is repeated in the presence of added benzal chloride (**6**) (which is electroinactive before −2.3 V), additional charge is consumed over that required for reduction of **4** alone, and the amount of charge consumed increases with the amount of **6** present in the medium,[7]

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[8] (a) Samsel, E. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 585. (b) Opallo, M.; Behr, B.; Kapturkiewicz. *J. Electroanal. Chem.* **1985**, *182*, 427. (c) Brisard, G. M.; Manzini, M.; Lasia, A. *J. Electroanal. Chem.* **1992**, *326*, 317.

[9] The Ag/AgNO$_3$ reference electrode is +0.35 vs SCE (standard calomel electrode).

[10] See, e.g., Parker, V. D. *Acta Chem. Scand.* **1981**, *35B*, 259.

[11] Costa, G.; Puxeddu, A.; Reisenhofer, E. *J. Chem. Soc., Dalton Trans.* **1973**, 2034.

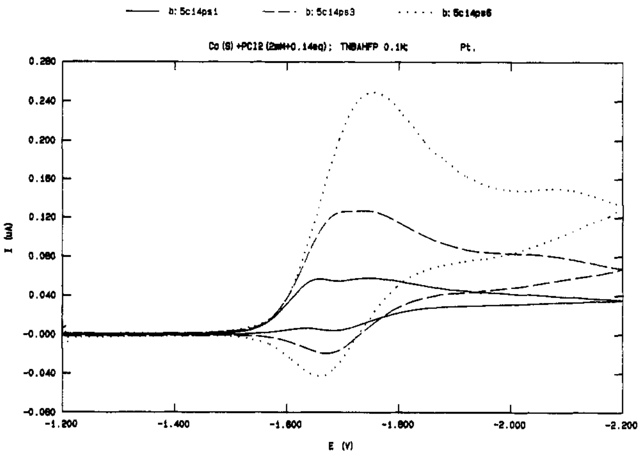


Figure 4. Cyclic voltammograms of a mixture of 2 mM Co(II)(salen) and 0.28 mM benzal chloride in DMF/0.1 M Bu_4NPF_6. Solid line: 50 mV sec^{-1}. Dashed line: 250 mV sec^{-1}. Dotted line: 1000 mV sec^{-1}.

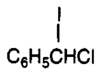
demonstrating the electrocatalytic behavior of the system. The major product in runs 1–3 is a mixture of *cis*- and *trans*-stilbenes (**12**), although small amounts of bibenzyl (**13**) and two hydrocarbons of mass 272 (Table I) are also formed. One of the two minor isomers is almost certainly 1,2,3-triphenylpropane (**14**) since its mass spectrum exhibits a very strong benzyl peak ($m/e = 91$); the m/e peak at 91 is very small in the other isomer.

$$\underset{\mathbf{6}}{C_6H_5CHCl_2} \xrightarrow[\text{Co(II)(salen)}]{e^-} \underset{\mathbf{12}}{C_6H_5CH{=}CHC_6H_5} + \underset{\mathbf{13}}{C_6H_5CH_2CH_2C_6H_5} + \underset{\mathbf{14}}{(C_6H_5CH_2)_2CHC_6H_5} + m/e\ 272$$

Identification of Intermediates. The conversion of two molecules of **6** to one of **12** with loss of four chlorine atoms is a deep-seated change and raises obvious mechanistic questions. We carried out a variety of experiments designed to identify the nature of some of the intermediates in this conversion. We initially considered that the isomers of **12** were produced by a carbene route[12] involving carbanion **15** (Scheme II) (see Discussion) and for this reason we were interested in the effect of a proton donor on the course of the electrolysis. Malonic ester is a useful proton donor toward electrochemically generated carbanion intermediates because it is electroinactive even at fairly negative potentials.[13] Addition of excess malonic ester to the medium quenched the formation of **12** only slightly (Table I, runs 4–6), demonstrating that **15** is not the primary precursor to **12**. Small amounts of toluene (**16**) were however produced in runs 5 and 6. We will return to these facts in the Discussion.

Our mechanistic hypothesis for the formation of **12** involves the intermediate formation of either or both of the stereoisomeric 1,2-diphenyl-1,2-dichloroethanes (**10**).[7] This hypothesis proved to be correct. The two isomers of **10** were synthesized by a literature procedure[14] and separated by fractional crystallization. Interruption of an electrolysis of a mixture of benzal chloride and **4** at the midpoint, followed by analysis by gas chromatography–mass spectrometry (GC-MS) demonstrated the presence of both isomers of **10** in the electrolysate. Furthermore, as we have previously reported, reduction of **4** in the presence of either isomer of **10** at a potential at which **10** is electroinactive produces the stilbenes **12** as the only products.[7]

Since interaction between low-valent cobalt complexes and alkyl halides is often presented as simply an electron-transfer process,[15] we were interested in the question whether the alkylcobalt(III)(salen) complex **7** is indeed an intermediate in these reactions. Kochi has reported that alkylcobalt(III) complexes react quantitatively with iodine to afford the corresponding alkyl iodides.[8a] A solution of **5** was prepared by electrochemical reduction of **4**. To this was added first **6** and then a solution of iodine in CH_2Cl_2. Workup afforded a mixture consisting of benzal chloroiodide (**17**) (13%), **6** (62%), benzyl chloride (8%), benzyl iodide (13%), **10** (1–2%), **12** (1–2%), and benzaldehyde (1%). Isolation of **17** is proof of the formation of an adduct (**7**) between **5** and **6**. The identity of **17** was confirmed by comparison with a sample synthesized by an independent route. **17** was synthesized by reaction between **6** and NaI in acetone.[16] A small amount of benzal iodide (**18**) was formed in the latter reaction. An authentic sample of geminal iodide **18** was prepared by reaction of diazotoluene with iodine.[17]

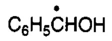


$$C_6H_5\overset{I}{C}HCl$$

17

$C_6H_5CHI_2$

18



$$C_6H_5\dot{C}HOH$$

19

Formation of **10** and **12** from the reaction between **5** and **6** provide further support for (a) eq 3 of Scheme I, that is, the presumption that intermediate **7** is reduced by **5**, this process leading quickly to formation of **10**, and (b) eqs 6–10 by which **10** is converted into **12** by the action of **5**. Benzyl chloride is presumably formed through hydrogen atom abstraction by **9** from the solvent (other work in this laboratory has shown that benzylcobalt(III)(salen) complexes slowly decompose to form benzyl radicals even at 0 °C) and benzyl chloride is then converted into benzyl iodide by attack of iodide ion. **17** is however not formed by attack of iodide on **6**; **6** does not react with iodide ion on the time scale of the iodination experiment.

Discussion

Our previously suggested[7] mechanism (Scheme I) for these reactions provides a context for discussing these results. Any discussion of the reactions taking place in an electrolytic reduction of a mixture of benzal chloride (**6**) and electrogenerated Co(I)(salen)$^{-1}$ (**5**) must begin with the question of the primary event upon encounter between **5** and **6**. There are three distinctly different processes which might occur (Scheme III). Paths A–C are equivalent in the overall sense: each results in formation of **9** with consumption of 1 electron/molecule of **6**. As eq 11 shows, they all explain the need for only catalytic quantities of

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(12) (a) Kirmse, W. *Carbene Chemistry*; Academic: New York, 1964; Chapt. 8. (b) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964; Chapters 3 and 8.

(13) (a) Little, R. D.; Fox, D. P.; Hijfte, L. V.; Dannecker, R.; Sowell, G.; Wolin, R.; Moëns, Baizer, M. M. *J. Org. Chem.* **1988**, *53*, 2287. (b) Mbarak, M. S.; Peters, D. G. *J. Org. Chem.* **1982**, *47*, 3397.

(14) Buckles, R. E.; Steinmetz, W. E.; Wheeler, N. G. *J. Am. Chem. Soc* **1950**, *72*, 585.

(15) Branchaud, B. P.; Detlefsen, W. D. *Tetrahedron Lett.* **1991**, *32*, 6273. (b) Giese, B.; Erdmann, P.; Göbel; Springer, R. *Tetrahedron Lett.* **1992**, *33*, 4545.

(16) Hsu, M. C.; Jwo, J. J. *J. Chin. Chem. Soc. (Taipei)* **1989**, *36*, 403.

(17) Larock, R. C. *Comprehensive Organic Transformations*; VCH Publishers: New York, 1989; p 347.

Table I. Products from Co(salen)-Catalyzed Electrochemical Reduction of Benzal Chloride[a]

run	reactants[b]	products (%)[c,d]
1	1 equiv of **6**	*cis*-**12** (45); *trans*-**12** (41); **13** (4); unk A (5); unk B(3)
2	2 equiv of **6**	*cis*-**12** (48); *trans*-**12** (36); **13** (5); unk A (6); unk B(4)
3	4 equiv of **6**	*cis*-**12** (51); *trans*-**12** (33); **13** (12); unk A (3); unk B(tr)
4	1 equiv of **6**; 1.5 equiv of diethyl malonate	*cis*-**12** (28); *trans*-**12** (48); **13** (16); unk A (3); unk B(4)
5	2 equiv of **6**; 3.0 equiv of diethyl malonate	*cis*-**12** (39); *trans*-**12** (30); **13** (13); unk A (5); unk B(3); **16** (7)
6	4 equiv of **6**; 6.0 equiv of diethyl malonate	*cis*-**12** (44); *trans*-**12** (30); **13** (10); unk A (3); unk B(3); **16** (9)

[a] Electrolyses were carried out in dimethylformamide/0.1 M Bu_4NPF_6 at −1.7 V vs Ag/$AgNO_3$. [b] All electrolyses contained 1.23 mmol of Co(II)(salen); the amounts of **6** and diethyl malonate used were the indicated multiples of this amount. [c] Yields were measured by comparison of GC-MS peak intensities with those produced by measured amounts of known standards. Bibenzyl and *cis*-stilbene exhibit identical GC retention times and the ratio of these two components was therefore determined by integration of the appropriate features in the 400-MHz NMR spectrum of the reaction mixture. [d] Unknowns A and B have parent mass spectral ions at *m/e* = 272; unknown A is probably 1,2,3-triphenylpropane. See Discussion.

Scheme II

$$\begin{array}{lcl}
\underset{\mathbf{9}}{C_6H_5CHCl\cdot} + e^- & \rightarrow & \underset{\mathbf{15}}{C_6H_5CHCl^-} \\
C_6H_5CHCl^- & \rightarrow & \underset{\mathbf{20}}{C_6H_5CH:} + Cl^- \\
C_6H_5CHCl^- + \mathbf{20} & \rightarrow & [C_6H_5CHClCHC_6H_5]^- \\
[C_6H_5CHClCHC_6H_5]^- & \rightarrow & C_6H_5CH{=}CHC_6H_5 + Cl^-
\end{array}$$

Scheme III

Path A:

$$\begin{array}{lcl}
\underset{\mathbf{5}}{CoI(salen)^{-1}} + \underset{\mathbf{6}}{C_6H_5CHCl_2} & \rightarrow & \underset{\mathbf{7}}{C_6H_5CH(Cl)Co(III)(salen)} + Cl^- \\
\mathbf{7} + e^- & \rightarrow & \underset{\mathbf{8}}{C_6H_5CH(Cl)Co(II)(salen)^{-1}} \\
\mathbf{8} & \rightarrow & \mathbf{9} + \mathbf{5}
\end{array}$$

Path B:

$$\begin{array}{lcl}
\mathbf{5} + \mathbf{6} & \rightarrow & \mathbf{7} + Cl^- \\
\mathbf{7} & \rightarrow & \mathbf{9} + \mathbf{4} \\
\mathbf{4} + e^- & \rightarrow & \mathbf{5}
\end{array}$$

Path C:

$$\begin{array}{lcl}
\mathbf{5} + \mathbf{6} & \rightarrow & \mathbf{9} + \mathbf{4} + Cl^- \\
\mathbf{4} + e^- & \rightarrow & \mathbf{5}
\end{array}$$

Net reaction for all three paths:

$$\mathbf{6} + e^- \rightarrow \mathbf{9} + Cl^- \qquad (11)$$

5. Paths A and B begin by oxidative addition of **5** to a carbon–halogen bond of **6** to afford the Co(III) complex **7**. In path A intermediate **7** is reduced to an alkylcobalt(II) species **8** which then undergoes facile thermal decomposition to the α-chlorobenzyl radical **9** and **5**. Alternatively, **7** might spontaneously decompose to **9** and **4**, and **4** would then be reduced back to **5** (path B). Path C involves electron transfer between **5** and **6** to produce **9** and **4** directly. Isolation of chloroiodide **17** in good yield from the iodination experiment (see Results) demonstrates that **7** is a discrete intermediate and permits us to exclude path B. The distinction between paths A and C is harder to make. There is no doubt that intermediate **7** is produced. It might however be formed by either an S_N2-like bimolecular substitution process or by electron transfer between **5** and **6** to generate radical **9**, providing that **9** immediately combines with **4** to generate **7**;[18] Co(II) species are in fact excellent radical traps.[19] We favor however an S_N2-like substitution mechanism for the oxidative addition because **6** is a benzylic halide, i.e., a good S_N2 substrate. We have, incidentally, written the adduct **7** as pentacoordinate because similar species are known to be extensively dissociated in dilute solution,[8a] but we have no information on the coordination state of cobalt. **7** may be hexacoordinate, bearing either a DMF molecule or chloride ion at its sixth coordination site.

Voltammetry. Further information on eqs 3 and 4 of Scheme I was obtained by voltammetry. As Figures 1–4 show, this system exhibits a number of unusual voltammetric features. In particular, both the prewave before the main wave for reduction of **4** at low concentrations of **6** and the postwave at *ca.* −2.0 V at high concentrations of **6** and relatively high scan rates require explanation. Chemical reactions coupled to electrochemical formation of a reactive intermediate generally give rise to a shift of the voltammetric wave to more positive potentials.[10] It is relatively rare for addition of a reactant to cause the appearance of a new wave at more positive potentials with the original wave remaining at the same potential, as is seen to occur in Figure 1. This phenomenon is known to occur only when certain very specific conditions are fulfilled.[20] The coupled chemical reaction must be rapid and the concentration of added reactant (here, **6**) must also be low. When these conditions are met, the concentration of the latter reactant can be totally depleted in the reaction layer immediately adjacent to the electrode; in effect, the rate of consumption of the reactant by chemical reaction exceeds the rate at which it is transported into the reaction layer by diffusion. The remaining electroactive species therefore behaves normally, i.e., its peak potential is unshifted. Unlike other alkylcobalt(III) complexes,[4a–c] **7** should be *easier* to reduce than its precursor **4**; benzylcobalt(III)(salen) is reduced at −1.61 vs Ag/$AgNO_3$[4d] and the additional chlorine atom in **7** should make it even easier to reduce than benzylcobalt(III)(salen). The fact that the prewave in Figures 1 and 2 grows disproportionately to the amount of added **6** is due to the catalytic nature of the **5**–**6** reaction sequence (Scheme I, eqs 2–5); in contrast, prewaves arising from ECE-type behavior grow in direct proportion to the concentration of the added reactant.[21] At higher concentrations of **6**, its concentration does not drop in zero in the reaction layer, and the main voltammetric reduction wave of **4** does shift to positive potentials with increasing **6** concentration (Figure 4). Literature rate constants of oxidative addition of Co(I) complexes into carbon–halogen bonds indicate that eq 2 of Scheme I should indeed by very fast.[11]

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[18] (a) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97. (b) Zhou, D.-L.; Walder, P.; Scheffold, R.; Walder, L. *Helv. Chim. Acta* **1992**, *75*, 995.

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[21] The observed reduction potential could be rather different from the thermodynamic formal potential of the radical,[22] but Wayner and Griller have offered data suggesting that the observed and formal redox potentials of benzylic radicals as measured by their photoelectrochemical method are similar.[23a,b]

Scheme IV

$$\underset{9}{C_6H_5CHCl\cdot} + e^- \rightarrow \underset{15}{C_6H_5CHCl^-}$$

$$15 + CH_2(CO_2Et)_2 \rightarrow \underset{21}{C_6H_5CH_2Cl} + {}^-CH(CO_2Et)_2$$

$$21 + {}^-CH(CO_2Et)_2 \rightarrow \underset{22}{C_6H_5CH_2CH(CO_2Et)_2} + Cl^-$$

Scheme V

$$(C_6H_5CHClCHC_6H_5)\cdot \rightarrow \underset{12}{C_6H_5CH{=}CHC_6H_5} + Cl\cdot \qquad (9a)$$

$$Cl\cdot + 5 \rightarrow Cl^- \qquad (10a)$$

We assign the wave at *ca* −2.0 V in Figures 3 and 4 to reduction of radical **9** to carbanion **15**.[21] The reduction potentials of a number of substituted benzyl radicals are about −1.9 to −2.1 V.[22,23] It might seem that a voltammetric wave ought not to be observable for an intermediate which is at low steady state concentration because it is undergoing rapid chemical reaction (dimerization) as we postulate for **9**. However, Savéant has shown that a voltammetric wave is readily observable for the α-hydroxybenzyl radical intermediate (**19** in the electrochemical reduction of benzaldehyde in protic media, even while **19** is undergoing rapid dimerization to afford the corresponding pinacol.[22] In fact, the voltammogram of the Co(II)(salen)–benzal chloride system under the conditions of Figure 3 closely resembles those recorded for benzaldehyde by Savéant.[22] The reason for the formation of radical-derived dimers (**10** and **12**) in these electrolyses and the failure of malonic ester to quench the formation of stilbene is now clear: electrolysis was carried out in a potential insufficiently negative to convert **9** to **15**, and stilbene is produced by the $9 \rightarrow 10 \rightarrow\rightarrow 12$ path, not by the carbene path of Scheme II.

Modifications to Scheme I. We previously advanced the series of reactions shown in Scheme I to account for the formation of stilbene from **6** (via **10**).[7] We now realize that eq 9, reduction of a β-chlorobenzyl radical to the corresponding carbanion (which would then eject chloride ion to form stilbene) is thermodynamically unfavorable at the potential at which our electrolyses are carried out; like **9** and other benzyl radicals, the reduction potential of the β-chlorobenzyl radical formed in eq 8 should be well negative of −1.7 V. We now favor decomposition of this radical into stilbene and a chlorine atom, followed by reduction of the latter to chloride ion (Scheme V, eqns 9a and 10a). The process shown in eq 9a is akin to the final step in the iodine-atom-catalyzed isomerization of stilbenes[24] and in intermediate steps in the allylic halogenation of alkenes by bromine atoms formed from *N*-bromosuccinimide or bromine at low temperatures and by chlorine atoms from *tert*-butyl hypochlorite.[25]

Role of Diethyl Malonate. Scheme I postulates a number of intermediates on the path from **6** to **12**. We have already presented our evidence for intermediates **5**, **7**, **9**, and **10** in these reactions. An equally important issue is the evidence for *absence* of a particular intermediate, carbanion **15**. Runs 4–6 of Table I demonstrate that addition of excess diethyl malonate to the medium slightly reduces, but does not quench, the formation of stilbene. This excludes a carbanionic route *via* phenylcarbene (**20**) (Scheme II) as the primary precursor to stilbene. On the other hand, it raises an interesting question as to just what the role of diethyl malonate is in runs 4–6. Table I shows that electrolysis in the presence of diethyl malonate reduces the yield of stilbene by about 10–15%. This decrease is compensated for by the formation of small amounts of toluene (**16**) and increased amounts of dibenzyl (**13**). We have also noted that small amounts of two trimeric hydrocarbons, mass 272, are produced in these reactions. Bibenzyl presumably arises by production during the electrolysis of small amounts of benzyl chloride (**21**); **21** would then be converted to bibenzyl by a path analogous to eqs 1–5 of Scheme I. The two trimeric hydrocarbons could arise by reaction of benzyl radical with stilbene, and **16** could also be generated via benzyl radical. However, what is the source of hydrogen in the formation of **21** (and ultimately, **13** and **16**)? We do *not* believe that **21** is produced by proton transfer from malonic ester to **15**. Our reasons for this belief are the following. First, we have already shown that **15** is produced only at much more negative potentials than that used in the electrolyses in Table I. Secondly, we recently found that malonic ester *does* quench the formation of stilbene during electrolysis of benzal chloride in the presence of nickel(II)(salen).[26] The difference between the cobalt and nickel chelates is the fact that the latter is reduced at −2.2 V, i.e., *negative* of the reduction potential of **9**, so that **9** is reduced to **15** as it is formed. Furthermore, quenching of stilbene formation by malonic ester in the reactions mediated by nickel(salen) is accompanied by formation of substantial amounts of benzylmalonic ester **22**, presumably by back-reaction between malonate ion and **21** (Scheme IV). We did not find any trace of **22** in runs 4–6 of Table I. We therefore suggest that the role of malonic ester is as a hydrogen atom donor toward **9**. The two carbonyl groups

$$\underset{9}{C_6H_5CHCl\cdot} + CH_2(CO_2Et)_2 \longrightarrow \underset{21}{C_6H_5CH_2Cl} + \cdot CH(CO_2Et)_2$$

in malonic ester should substantially stabilize a radical site at the central carbon atom.[27] The small amounts of **13** formed in runs 1–3 probably originate in hydrogen atom donation to **9** by the solvent DMF.[28]

Experimental Section

General. Dimethylformamide was distilled at aspirator vacuum from CaH_2 and stored over 3-Å molecular sieves. Bu_4NPF_6 was prepared by reaction between concentrated aqueous HPF_6 and an acetone solution of Bu_4NI, followed by recrystallization from ethanol. Benzal chloride was obtained from Aldrich Chemical Co. and used as received after verification of its purity by both NMR spectroscopy and mass spectral analysis using an Hewlett-Packard Model 5988 gas chromatograph–mass spectrometer. Co(II)(salen) was prepared by a literature procedure.[29]

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Cyclic voltammetry was carried out with the aid of a computerized system consisting of a Princeton Applied Research (PAR) VersaStat interfaced to a Gateway Systems 386SX computer, using the PAR Model 250 software to generate waveforms and to acquire and manipulate data. Voltammograms were plotted on a Hewlett-Packard ColorPro plotter.

The electrolysis cell was supplied by the Electrochemicals Co., Middletown, CT 06457 and consisted of a glass bottom and Teflon top machined to accept the counter electrode compartment and all cell utilities, including electrodes, nitrogen inlet, and sampling port; the cell utilities were contained in standard 14/20 adapters for ease of cell assembly. The counter electrode compartment consisted of a coarse porosity fritted disk set into the end of a glass tube and containing a methylcellulose gel[30] containing 0.1 M Bu_4NPF_6 to reduce mass transport between the working and counter electrode compartments. The cathode and anode were composed of Reticulated Vitreous Carbon (RVC) and carbon cloth, respectively. The construction of the $Ag/AgNO_3$ reference electrode has been described previously.[31] A standard taper adapter equipped with a large serum cap was installed in one of the cell ports, and two needles (one for nitrogen introduction and one for nitrogen escape) were inserted through the serum cap.

General Electrolysis Procedure. Co(I)(salen). The catholyte solution, 200 mL of 0.1 M Bu_4NPF_6 in DMF, was degassed by a stream of N_2 for 0.5 h. The cathode potential was adjusted to −1.7 *vs* $Ag/AgNO_3$ and the current was allowed to decay to a constant value. The potentiostat was turned off and Co(II)(salen) (4) (400 mg, 1.23 mmol) was added to the cathode compartment and dissolved by stirring with further degassing by N_2 for 0.5 h. Electrolysis was then carried out until the current had decayed to background, at which point the electrolysis had consumed 1.251 millifaradays (1.231 theor; 102% of the calculated current) and the deep green color of Co(I)(salen) (5) was evident. All other electrolyses were carried out in the same manner, with particular care to exclude light.

Iodination of (α-Chlorobenzyl)Co(III)(salen). A solution of **5** was prepared by the previous procedure. After the potentiostat was disconnected, **6** (158 μL, 1.23 mmol) was added, followed after 1 min by I_2 (0.6 g, 2.36 mmol). After 20 min the catholyte was extracted with hexane; the hexane extracts were then washed with H_2O and aqueous $NaHSO_3$ and dried over $MgSO_4$. The oily residue was analyzed by GC-MS and found to consist of a mixture of benzal chloroiodide (**17**) (13%), **6** (62%), **21** (8%), benzyl iodide (13%), and benzaldehyde (1%), together with small amounts of *cis*- and *trans*-(**12**) and *dl*- and *meso*-**10**.

Benzal Chloroiodide (17).[16] To a solution of NaI (10 g, 0.067 mol) in 125 mL of acetone were added 2.5 mL of **6** and 1 g of $FeCl_2{\cdot}4H_2O$. N_2 was passed through and the solution was refluxed for 2.5 h. A 5-mL portion of the mixture was treated with 5 mL of 25% aqueous $NaHSO_3$ and then extracted with hexane. After drying ($MgSO_4$) the hexane solution was analyzed by GC-MS. The product mixture consisted of **17** (61%), **6** (23%), benzal iodide (**18**) (3%), and **10** (9%).

Benzal Iodide (18). Benzaldehyde tosylhydrazone[32a] was prepared in pyridine[30b] and converted into the corresponding sodium salt and pyrolyzed at 80 °C at aspirator vacuum according to a standard protocol.[33] Diazotoluene distilled from the mixture as formed. It was immediately dissolved in CH_2Cl_2 and allowed to react with a solution of I_2 in CH_2Cl_2. The reaction mixture was washed with aqueous $NaHSO_3$, dried, and evaporated to afford authentic benzal iodide.[34] Its GC-MS retention time, mass spectral pattern, and ^1H NMR spectrum corresponded to the substance identified as **18** in the preceding experiment.

Acknowledgment. Financial support was provided by the National Science Foundation (grant no. CHE-9100943 to A.J.F.). Agnes S. Lee synthesized the stereoisomers of **10** and examined their electrocatalytic conversion to **12** as described in ref 7.

Supplementary Material Available: Cyclic voltammograms of cobalt(II)(salen) in the presence of benzal chloride, measured over a wider range of concentrations and scan rates than in Figures 1, 2, and 4 (3 pages). This material is contained in libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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