Cobalt(salen)-Electrocatalyzed Reduction of Benzal Chloride. Dependence of Products upon Electrolysis Potential

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The products from the cobalt(salen)-electrocatalyzed reduction of benzal chloride have been studied over a wide range of electrode potentials. The products are bibenzyl (**10**), toluene (**11**), and stilbenes (**7**). The yield of **7** decreases with increasingly negative potential; yields of **11** and **10** exhibit more complex behavior: **11** generally increases and **10** decreases, but these trends are reversed at intermediate potentials. The reasons for the complex dependence of product composition upon electrode potential include a changeover from radical to carbanion mechanism and from catalyzed to direct reduction as the potential becomes more negative. This mechanistic information has been obtained by both addition of trapping agents to the electrolysis medium and interruption of electrolyses before completion.

A number of studies of the electrocatalytic reduction of alkyl halides by electrogenerated low-valent metal complexes have been reported in the literature.[2] We recently described an unusual example of such a reaction: the electrochemical reduction of cobalt(II)(salen) (**1**) to the corresponding Co(I) species (**2**) followed by electrocatalytic reduction of benzal chloride (**3**) by **2**.[3–5] A major product of this reaction is a mixture of *cis-* and *trans*-stilbenes (**7**). **7** is produced by a complex reaction sequence (Scheme 1) in which, briefly, **3** is converted into 1,2-dichloro-1,2-diphenylethane (**6**) by a series of reactions initiated by the action of **2** on **3** (eqs 2–5). **6** is then converted into **7** in a second, related but distinctly different, reaction sequence (Scheme 1, eqs 6–10). For this reason, we have described the conversion of **3** into **7** by **2** as a (as far as we know, unprecedented) "doubly electrocatalytic" process. We subsequently encountered other doubly electrocatalytic processes in a related study using nickel(I)(salen).[6]

A key intermediate in our proposed mechanistic scheme for the formation of **6** from **3** is the α-chlorobenzyl radical **5**. We postulated that **5** is not reducible at the potential at which the electrolysis was carried out (−1.7 V vs Ag/AgNO$_3$, which is the reduction potential of **1**) and presented voltammetric evidence suggesting that the reduction potential of **5** is actually *ca.* −2.0 V.[3] Nevertheless, because future studies involving synthetic applications of this reaction will be based on the reaction of **5** and related species with a variety of radical and carbanion traps, it was considered desirable to obtain further mechanistic information. In particular, we expected that the products of electrolysis of a mixture of **1** and **3** over a range of potentials spanning −2.0 V ought to be dependent upon the electrolysis potential. The present study set out to test this postulate. Other factors relevant to the planned future use of **5** in synthesis were also explored.

Results

Reaction mixtures were analyzed by gas chromatography–mass spectrometry (GC-MS). In general, the products consisted of mixtures of toluene (**11**), bibenzyl (**10**), *cis-* and *trans*-stilbene (**7**), and tributylamine in varying proportions. The latter substance arises from a side reaction of **2** with adventitious water to afford hydroxide ion, which then attacks the TBA cation in an E2 reaction. Tributylamine is easily separated from the other products by extracting the product mixture with 5% HCl. Electrolyses carried out from −1.7 to −2.3 V also produced two compounds of *m/e* 272 in amounts detectable by GC-MS but too small to permit isolation and characterization. One of these side-products is probably 1,2,3-triphenylpropane (**12**) (see Discussion).

In the course of these experiments, we discovered that our previous GC-MS analytical method[3] could not detect the presence of **11** in the reaction mixtures because its GC retention time is identical to that of the solvent, DMF. When the workup was modified to eliminate traces of DMF, we found that **11** is produced in substantial amounts not only under our original[3] electrolysis conditions but in fact at all potentials (Table 1). We have also improved the analytical procedure for *cis*-**7** and **10**, which have the same GC retention time under all conditions which we have tried (see Experimental Section). All electrolyses were carried out using an 8:1 mole ratio of **3** to **1**.

The composition of the electrolysis mixtures varies very substantially with the electrolysis potential (Table 1 and Figure 1). At −1.7 V, the most positive cathode potential studied, toluene (**11**), bibenzyl (**10**), and stilbene (**7**) are formed in equal amounts. Each of these products exhibits a different dependence upon potential. As the cathode potential is made more negative over the range from −1.7 to −2.1 V, the proportion of **11** steadily increases until it accounts for 80% of the product mixture at −2.1 V. As the potential is made even more negative, the yield of **11** sharply decreases and then increases again until it is almost the exclusive product. The dependence of bibenzyl (**10**) yield upon potential is more or less the inverse of that of **11**: it decreases steadily until −2.1 V, increases

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Scheme 1

$$\underset{\mathbf{1}}{\mathrm{Co(II)L_4}} + e^- \rightarrow \underset{\mathbf{2}}{\mathrm{Co(I)L_4^{-1}}} \tag{1}$$

$$\underset{\mathbf{3}}{\mathrm{C_6H_5CHCl_2}} + \mathbf{2} \rightarrow \underset{\mathbf{4a}}{\mathrm{C_6H_5CHClCo(III)L_4}} + \mathrm{Cl^-} \tag{2}$$

$$\mathbf{4a} + \mathbf{2} \rightarrow \mathrm{C_6H_5CH(Cl)Co(II)L_4^{-1}} + \mathbf{1} \tag{3}$$

$$\mathrm{C_6H_5CH(Cl)Co(II)L_4^{-1}} \rightarrow \underset{\mathbf{5}}{\mathrm{C_6H_5CHCl\cdot}} + \mathbf{2} \tag{4}$$

$$\mathbf{5} \rightarrow 1/2\ \underset{\mathbf{6}}{\mathrm{C_6H_5CHClCHClC_6H_5}} \tag{5}$$

Net reaction for formation of **6** [steps (1) - (5)]:

$$\mathrm{C_6H_5CHCl_2} + e^- \rightarrow 1/2\ \underset{\mathbf{6}}{\mathrm{C_6H_5CHClCHClC_6H_5}} + \mathrm{Cl^-}$$

$$\mathbf{6} + \mathbf{2} \rightarrow \mathrm{C_6H_5CHClCHCo(III)L_4C_6H_5} + \mathrm{Cl^-} \tag{6}$$

$$\mathrm{C_6H_5CHClCHCo(III)L_4C_6H_5} + \mathbf{2} \rightarrow (\mathrm{C_6H_5CHClCHCo(II)L_4C_6H_5})^{-1} + \mathbf{1} \tag{7}$$

$$(\mathrm{C_6H_5CHClCHCo(II)L_4C_6H_5})^{-1} \rightarrow (\mathrm{C_6H_5CHClCHC_6H_5})\cdot + \mathbf{2} \tag{8}$$

$$(\mathrm{C_6H_5CHClCHC_6H_5})\cdot \rightarrow \underset{\mathbf{7}}{\mathrm{C_6H_5CH{=}CHC_6H_5}} + \mathrm{Cl\cdot} \tag{9}$$

$$\mathrm{Cl\cdot} + \mathbf{2} \rightarrow \mathrm{Cl^-} + \mathbf{1} \tag{10}$$

Net reaction for formation of **7** [steps (6) - (10), plus 2 (1)]:

$$\mathrm{C_6H_5CHClCHClC_6H_5} + 2e^- \rightarrow \mathrm{C_6H_5CH{=}CHC_6H_5} + 2\,\mathrm{Cl^-}$$

Overall reaction for conversion of benzal chloride to stilbene:

$$\mathrm{C_6H_5CHCl_2} + 2e^- \rightarrow 1/2\ \mathrm{C_6H_5CH{=}CHC_6H_5} + \mathrm{Cl^-}$$

L_4 = *bis*(salicylideneethylenediamine)

Table 1. Products from Co(salen)-Electrocatalyzed Reduction of Benzal Chloride[a]

electrolysis potential (V)[b]	reactans	products (relative %)
−1.7	1 equiv of **1**	**7** (31); **8** (33); *cis*-**4** (12); *trans*-**4** (20); unk A[c] (tr); unk B[c] (tr)
−1.7	1 equiv of **1**	**7** (34); **8** (35); *cis*-**4** (12); *trans*-**4** (19); unk A[c] (tr); unk B[c] (tr)
−1.8	1 equiv of **1**	**7** (29); **8** (18); *cis*-**4** (21); *trans*-**4** (35); unk A[c] (tr); unk B[c] (tr)
−1.8	1 equiv of **1**	**7** (30); **8** (17); *cis*-**4** (19); *trans*-**4** (33); unk A[c] (tr); unk B[c] (tr)
−1.9	1 equiv of **1**	**7** (39); **8** (12); *cis*-**4** (13); *tans*-**4** (38); unk A[c] (tr); unk B[c] (tr)
−1.9	1 equiv of **1**	**7** (37); **8** (15); *cis*-**4** (12); *trans*-**4** (36); unk A[c] (tr); unk B[c] (tr)
−2.0	1 equiv of **1**	**7** (60); **8** (10); *cis*-**4** (9); *trans*-**4** (21); unk A[c] (tr); unk B[c] (tr)
−2.1	1 equiv of **1**	**7** (80); **8** (6); *cis*-**4** (4); *trans*-**4** (10); unk A[c] (tr); unk B[c] (tr)
−2.2	1 equiv of **1**	**7** (40); **8** (60); unk A[c] (tr); unk B[c] (tr)
−2.2	1 equiv of **1**	**7** (42); **8** (58); unk A[c] (tr); unk B[c] (tr)
−2.3	1 equiv of **1**	**7** (44); **8** (56); unk A[c] (tr); unk B[c] (tr)
−2.3	1 equiv of **1**	**7** (48); **8** (52); unk A[c] (tr); unk B[c] (tr)
−2.3	1 equiv of **1**	**7** (47); **8** (53); unk A[c] (tr); unk B[c] (tr)
−2.4	1 equiv of **1**	**7** (95); **8** (3); *cis*-**4** (tr); *trans*-**4** (tr)
−2.5	1 equiv of **1**	**7** (98); **8** (tr); *cis*-**4** (tr)
−1.7	1 equiv of **1**; 3 equiv of diethyl malonate	**7** (33); **8** (38); *cis*-**4** (9); *trans*-**4** (16); unk A[c] (tr); unk B[c] (tr)
−2.8	1 equiv of **1**; 3 equiv of diethyl malonate	**7** (83); **8** (17); **12b** (10)
−1.7	1 equiv of **1**; 2 equiv of D_2O	$C_6H_5CHD_2$ (65); $C_6H_5CHDCHDC_6H_5$ (30); *cis*-**4** (1); *trans*-**4** (3)
−1.7	1 equiv of **1**; 1 equiv of **13**	**7** (26); **8** (52); *cis*-**4** (6); *trans*-**4** (12)
−1.7	1 equiv of **1**; 5 equiv of **13**	**7** (24); **8** (76)

[a] Electrolyses carried out in DMF/0.1 M Bu_4NPF_6. [b] Potential vs Ag/0.1 M $AgNO_3$. [c] *m/e* = 272.

sharply at −2.2 V, and then gradually diminishes again as the potential is made even more negative. The yield of stilbene isomers (**7**) goes through a maximum at −1.8 V and then steadily decreases as the electrode potential is made more negative; no more than traces of these substances are observed at potentials negative of *ca.* −2.1 V. The sharp changes in yield of **7** and **10** on going from −2.1 to −2.2 V and of **7** from −1.7 to −1.8 V are reproducible. Finally, as mentioned above, two substances with *m/e* = 272 are produced in trace quantities over the potential range −1.7 to −2.3 V.

A number of additional electrolyses were interrupted before completion, in the hope of identifying reaction intermediates. Benzyl chloride (**8**) was found in all such incomplete electrolyses carried out at potentials ranging from −1.7 to −2.3 V. Interestingly, stilbene (**7**) is *not present* at the midpoint of electrolyses carried out over the potential range −1.7 to −2.1, even though it was

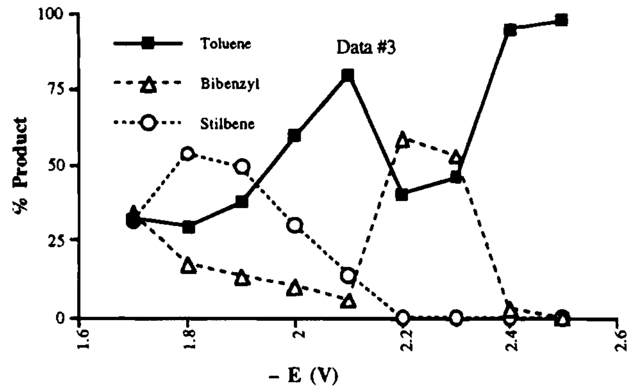


Figure 1. Dependence of products upon electrolysis potential (vs Ag/Ag 0.1 M $AgNO_3$ in CH_3CN) for the Co(salen)-electrocatalyzed reduction of benzal chloride (**1**) in DMF/0.1 M Bu_4NPF_6.

present in very substantial amounts in the end of such electrolyses. Conversely, **7** *is* present at intermediate stages of electrolyses at −2.2 and −2.3 V, whereas it was absent at the end. When **8** was substituted for **3** and electrolysis was carried out at −2.3 V, the products were **11** (95%) and **10** (5%). This result contrasts sharply with that observed with **3** at this potential. When **3** was replaced by stilbene (**7**) in the electrolysis, it was observed that **7** was reduced to **10** at −2.2 to −2.3 V, both in the presence and absence of **1**. **7** had previously been shown to undergo slow direct electrochemical reduction to **10** at −2.2 V.[6]

Trapping Agents. When an excess of deuterium oxide, D_2O, was added to an electrolysis carried out at −1.7 V, it was found by mass spectrometry that products **10** and **11** are doubly deuterated (**10**-D_2 and **11**-D_2, respectively). The stilbenes from this reaction are however *undeuterated*. The product composition from this reaction (65% **11**, 30% **10**, 4% **7**) was considerably different from the 32:34:32 ratio observed in the absence of D_2O. Examination of the electrolysis mixture at the midpoint demonstrated the presence of monodeuterated benzyl chloride (**8**-*D*).

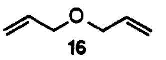
$C_6H_5CHD_2$ **11**-D_2 $C_6H_5CHDCHDC_6H_5$ **10**-D_2 C_6H_5CHDCl **8**-D

Diethyl malonate (**15a**) has been used to protonate electrochemically generated carbanions.[7] It is electroinactive at the potentials under investigation. **15a** was added in 2-fold excess to electrolyses carried out at −1.7 and −2.8 V. The electrolysis carried out at −1.7 V was unaffected by the addition of **15a**, whereas benzylmalonic ester **15b** was produced at −2.8 V. Finally, addition of an equivalent of allyl ether (**16**) to the medium increased the proportion of **10** in the product, primarily at the expense of **7** (**11**:**10**:**7** = 26:52:18); addition of five equiv of **16** continued this trend: **11**:**10**:**7** = 24:76:0.

Discussion

We previously proposed the mechanistic sequence shown in Scheme 1 to explain the formation of stilbene (**7**) from the electrochemical reduction of Co(II)(salen) (**1**) in the presence of benzal chloride (**3**) at −1.7 V.[3] The sequence of reactions is initiated by oxidative addition of Co(I)(salen) (**2**) to **3** (eq 2). The adduct (**4a**) is reduced by **2** to an unstable alkylCo(II) complex, which then decomposes to radical **5** (eqs 3, 4). Dimerization of **5** was suggested to afford dimer **6**, and **7** was produced by a second (and similar) electrocatalytic reductive elimination sequence on **6** (eqs 6−10). It was shown by independent synthesis of both diastereomers of **6** and subjection of each to the reaction conditions that this substance does indeed undergo Co(I)(salen)-electrocatalyzed nonstereoselective conversion to **7** in excellent yield.[5] The present experiments were carried out to better understand the processes leading to the products **7**, **10**, and **11**, as well as the dependence of each of these products upon experimental conditions.

$RCH(CO_2Et)_2$
15a, R = H
b, R = $C_6H_5CH_2$


16

$C_6H_5CH_2C_6H_4CH_2CH_2C_6H_5$
17

The products of this reaction exhibit an unusual dependence upon electrolysis potential (Figure 1). It appears that the overall smooth decrease in the yield of **10** and increase in the yield of **11** with increasingly negative potentials is subverted by another process (or processes) taking place in the intermediate potential region from −2.1 to −2.4 V. In order to understand what it (they) might be, it will be useful to consider the nature of the reactions taking place in each of a number of distinct potential regimes.

Electrolysis at −1.7 to −1.8 V. There now seems to be little doubt that the α-chlorobenzyl radical (**5**), the first cobalt-free intermediate in these reactions, has a reduction potential of *ca.* −2.0 V relative to our reference.[3,8] At potentials positive of −2.0 V, **5** is formed by eqs 2−4 of Scheme 1. It then reacts by two pathways: (a) dimerization to *dl*- and *meso*-dichlorodiphenylethane (**6**), which then undergoes clean electrocatalyzed conversion to a mixture of isomers of **7**,[5] and (b) hydrogen atom abstraction from DMF to afford benzyl chloride (**8**). The latter substance undergoes a sequence of reactions exactly analogous to eqs 2−4, affording the benzyl radical (**9**) (Scheme 2); once again, this can either dimerize to **10** or abstract a hydrogen atom from DMF to afford **11**. DMF is known to be a good hydrogen atom toward electrochemically generated radicals.[9,10] There is a relatively minor (but reproducible) change in the composition of the electrolysate on going from −1.7 to −1.8 V. This is probably a result of the higher flux of radical **5** at −1.8 V; the electrolysis at −1.7 V is carried out on the rising part of the wave for **1** and the electrolysis currents at this potential are relatively low. Since **5** is produced at higher concentration at −1.8 V, its bimolecular dimerization to **6**, and thus the eventual production of **7**, should also be enhanced. It was impossible to test this hypothesis by carrying out electrolysis at −1.6 V because the current is impractically low at this potential.

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[10] It is very likely that the hydrogen abstracted from DMF is supplied by one of the methyl groups, since the adjacent nitrogen could stabilize the resulting radical, but we have not isolated the products of H-atom abstraction.

Scheme 2

$$\underset{\mathbf{5}}{C_6H_5CHCl\cdot} + HCONMe_2 \rightarrow \underset{\mathbf{8}}{C_6H_5CH_2Cl} + HCON(Me)CH_2\cdot \tag{11}$$

$$\mathbf{8} + \mathbf{2} \rightarrow \underset{\mathbf{4b}}{C_6H_5CH_2Co(III)L_4} + Cl^- \tag{12}$$

$$\mathbf{4b} + \mathbf{2} \rightarrow C_6H_5CH_2Co(II)L_4^{-1} + \mathbf{1} \tag{13}$$

$$C_6H_5CH_2Co(II)L_4 \rightarrow \underset{\mathbf{9}}{C_6H_5CH_2\cdot} + \mathbf{2} \tag{14}$$

$$\mathbf{9} \rightarrow 1/2\ \underset{\mathbf{10}}{C_6H_5CH_2CH_2C_6H_5} \tag{15}$$

Net reaction for bibenzyl (**10**) formation by the radical path (steps (1)-(4) + (1) + (11)-(15):

$$C_6H_5CHCl_2 + 2\,e^- + HCONMe_2 \rightarrow 1/2\ C_6H_5CH_2CH_2C_6H_5 + 2\,Cl^- + HCON(Me)CH_2\cdot$$

$$HCON(Me)CH_2\cdot \rightarrow \text{decomposition products (unident.)}$$

$$\underset{\mathbf{9}}{C_6H_5CH_2\cdot} + HCONMe_2 \rightarrow \underset{\mathbf{11}}{C_6H_5CH_3} + HCON(Me)CH_2\cdot \tag{16}$$

Net reaction for toluene (**11**) formation by the radical path (steps (1)-(4) + (1) + (11)-(14) + (16):

$$C_6H_5CHCl_2 + 2\,e^- + 2\,HCONMe_2 \rightarrow C_6H_5CH_3 + 2\,HCON(Me)CH_2\cdot + 2\,Cl^-$$

$$\underset{\mathbf{9}}{C_6H_5CH_2\cdot} + \mathbf{7} \rightarrow [C_6H_5CH_2CH(C_6H_5)CHC_6H_5]\cdot \tag{17}$$

$$[C_6H_5CH_2CH(C_6H_5)CHC_6H_5]\cdot + HCONMe_2 \rightarrow \underset{\mathbf{12}}{C_6H_5CH_2CH(C_6H_5)CH_2C_6H_5} + HCON(Me)CH_2\cdot \tag{18}$$

$$\mathbf{5} + e^- \rightarrow \underset{\mathbf{13}}{C_6H_5CHCl^-} \tag{19}$$

$$C_6H_5CHCl^- + H^+ \rightarrow \mathbf{8} \tag{20}$$

$$\mathbf{8} + \mathbf{2} \rightarrow \underset{\mathbf{4b}}{C_6H_5CH_2Co(III)L_4} + Cl^- \tag{12}$$

$$\mathbf{4b} + \mathbf{2} \rightarrow C_6H_5CH_2Co(II)L_4^{-1} + \mathbf{1} \tag{13}$$

$$C_6H_5CH_2Co(II)L_4^{-1} \rightarrow \underset{\mathbf{9}}{C_6H_5CH_2\cdot} + \mathbf{2} \tag{14}$$

$$\mathbf{9} + \mathbf{1} \rightarrow C_6H_5CH_2^- + \mathbf{2} \tag{21}$$

$$C_6H_5CH_2^- + H^+ \rightarrow C_6H_5CH_3 \tag{22}$$

Net reaction for toluene formation by the carbanion path (steps (1)-(4) + (1)+ (12)-(14) + (19)-(22):

$$C_6H_5CHCl_2 + 4\,e^- + 2\,H^+ \rightarrow C_6H_5CH_3 + 2\,Cl^-$$

It must be stressed that there is no evidence for involvement of the benzylic carbanions **13** and **14** at these potentials. In particular, we showed previously that **13** reacts with malonic ester **15a** to produce **8** and malonate ion, which then react to afford benzylmalonic ester **15b**, whereas radical **5** does not react with **15a** to produce **15b**.[6] **15b** was not produced when **15a** was added to the medium at −1.7 V. On the other hand, how are we to account for the effect of D_2O on the electrolyses carried out at this potential? The deuterated products do not necessarily demand the intermediate formation of **13** and **14**. We believe that in this experiment **8**-*D* and **11**-D_2 may well be produced by direct attack of D_2O on alkylcobalt(III) intermediates **4a** and **4b**, respectively (Scheme 3). Scheffold has proposed a similar process to account for the effect of water on reactions known to involve alkylcobalt intermediates.[11] Reaction of water with **4a** or the corresponding alkylcobalt(II) species could thus afford **13** at a potential positive of the reduction potential of **5**. The fact that the stilbene (**7**) from this reaction is undeuterated is consistent with its formation by a free radical path (eqs 2−5 of Scheme 1). The results with allyl ether (**16**) support our conclusion that the reactive intermediates at −1.7 V are the radicals **5** and **9**. It was hoped to trap radical **5** with **16** and isolate a tetrahydrofuran product by cyclization of the intermediate adduct,[12] but no products other than **10** and **11** could be detected by TLC or GC-MS when **16** was added in excess. Allyl ether should, however, also be an excellent hydrogen atom donor, and indeed the two products **10** and **11** which we believe both result from hydrogen atom abstraction from DMF are enhanced by the addition of **16**. Furthermore, addition of this substance quenches the formation

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Scheme 3

$$C_6H_5CH(Cl)Co(III)L_4 + D_2O \rightarrow C_6H_5CH(Cl)Co(III)L_4(OD_2) \tag{23}$$

$$C_6H_5CH(Cl)Co(III)L_4(OD_2) \rightarrow \underset{\mathbf{8}\text{-}D}{C_6H_5CHDCl} + DOCo(III)L_4 \tag{24}$$

$$\mathbf{8}\text{-}D + \mathbf{2} \rightarrow C_6H_5CHDCo(III)L_4 + Cl^- \tag{25}$$

$$C_6H_5CHDCo(III)L_4 + D_2O \rightarrow C_6H_5CHDCo(III)L_4(OD_2) \tag{26}$$

$$C_6H_5CHDCo(III)L_4(OD_2) \rightarrow \underset{\mathbf{11}\text{-}D_2}{C_6H_5CHD_2} + DOCo(II)L_4 \tag{27}$$

$$C_6H_5CHDCo(III)L_4 + \mathbf{2} \rightarrow C_6H_5CHDCo(II)L_4{}^{-1} + \mathbf{1} \tag{28}$$

$$C_6H_5CHDCo(II)L_4{}^{-1} \rightarrow C_6H_5CHD\cdot + \mathbf{2} \tag{29}$$

$$C_6H_5CHD\cdot \rightarrow 1/2\ \underset{\mathbf{10}\text{-}D_2}{C_6H_5CHDCHDC_6H_5} \tag{30}$$

of **7** as would be expected if production of **7** is initiated by coupling of two **5** radicals (Scheme 1).

The proportion of **7** formed at these fairly positive potentials is less than that observed in a previous study.[3] However, that study employed a higher concentration of **3**. Production of **7** involves coupling of two **5** radicals; this bimolecular process should fall off relative to hydrogen atom transfer at lower concentrations.

Electrolyses at −1.9 to −2.1 V. As noted above, the reduction potentials of **5** and **9** are close to −2.0 V. As the electrolysis potential moves into this regime, reduction of these radicals to the corresponding carbanions **13** and **14** becomes increasingly significant. The changes are not discontinuous, however, because **5** and **9** are formed in solution, not at the electrode surface. They must be transported to the electrode in order for reduction to take place, but convection, acting competitively, can sweep them away from the electrode into bulk solution before they can be reduced. Thus, one sees a gradual decrease of the radical products bibenzyl and stilbene as the potential becomes more negative. Toluene is produced by both radical and carbanionic pathways in this potential range, and the proportion coming from the carbanion route becomes greater as the potential becomes more negative.

Electrolyses at −2.2 to −2.4 V. The smooth changes taking place over the range −1.9 to −2.1 V are interrupted in this potential range. This suggests that a new process has become operative. We believe that at least two new processes have to be considered. First of all, reduction of **7** to **10** begins taking place at −2.2 V; indeed, as noted previously, **7** is present in solution partway through these electrolyses, but not at the end of electrolysis. However, other changes must be taking place to account for the large amounts of **10** produced in this potential range, since one can see from Figure 1 that production of **7** just before −2.2 V is low and decreases with increasingly negative potentials. Independent experiments carried out in the absence of **1** showed that *direct* (uncatalyzed) electrochemical reduction of **3** begins at −2.2 V. This could readily account for the increased production of **10**. An increased proportion of its precursor **7** could arise because since the initial concentration of **3** is much higher than that of **1**. This, together with the fact that the direct electrolysis takes place at the electrode surface, rather than in bulk solution from thermal decomposition of an alkylcobalt(II) species, would produce a higher local concentration of radical **5**, which, as noted above, favors production of **6** and then, successively, **7** and **10**. It is likely that in this potential regime **7** is produced at least partly by a carbene mechanism (Scheme 4).[13]

Scheme 4

$$\underset{\mathbf{13}}{C_6H_5CHCl^-} \rightarrow C_6H_5CH{:} + Cl^- \tag{31}$$

$$C_6H_5CH{:} + C_6H_5CHCl^- \rightarrow C_6H_5CH(Cl)CH^-C_6H_5 \tag{32}$$

$$C_6H_5CH(Cl)CH^-C_6H_5 \rightarrow \mathbf{7} + Cl^- \tag{33}$$

Electrolysis at −2.4 to −2.5 V. At these potentials both direct and catalyzed reduction of **3** are taking place, but the former is undoubtedly more significant because of the higher concentration of **3**. Radical **5** is formed primarily at the electrode surface and therefore undergoes rapid reduction to the corresponding carbanion, which initiates a sequence leading to toluene. The latter is undoubtedly formed almost exclusively by a carbanion route via **13** and **14** (Scheme 2) at these potentials. Recall that addition of malonic ester to the medium in this potential region results in formation of benzylmalonic ester (**15b**), establishing that carbanion **13** is indeed present as an intermediate in this region. Note that traces of **7** (and **10**, which is produced from **7** at these potentials) are still being produced at −2.5 V, at least 0.5 V negative of the reduction potential of **5** and **9**. Almost certainly, **7** is being produced by the carbene mechanism in this potential region (Scheme 4).[12]

Side Products. As we have noted, electrolyses carried out from −1.7 to −2.3 V produced two compounds of *m/e* 272 in amounts insufficient to permit isolation and characterization. We suspect that one of these side products is 1,2,3-triphenylpropane (**12**), since the base peak in its mass spectrum is 91, which could be produced by cleavage of either of the terminal benzyl groups. **12** could be produced by attack of benzyl radical (**9**) on **7** (Scheme 2); as we have argued, **7** is an intermediate in these electrolyses at more positive potentials. The other substance of *m/e* 272 exhibits a much different mass spectrum, with a weaker peak at *m/e* 91. Attack of **10** could also take place on the aromatic ring of **7** to afford, ultimately, a product such as **17**. Attack on arene rings is frequently observed in radical chemistry.[14]

Conclusions. The complex electrochemical behavior of the benzal chloride−cobalt(salen) system in DMF is a

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(13) (a) Kirmse, W. *Carbene Chemistry;* Academic: New York, 1964; Chapter 8. (b) Hine, J. *Divalent Carbon;* Ronald Press: New York, 1964; Chapter 6.

(14) Fry, A. J.; Powers, T. A. *J. Org. Chem.* **1987**, *52*, 2498.

consequence of the relative reduction potentials of **1**, **3**, the two intermediate free radicals **5** and **9**, and stilbene (**7**), and even the relative concentrations of the reactants. The implications for future synthetic applications of this chemistry are clear: reactions in which one wishes to react **5** with free radical traps must be carried out at potentials positive of −2.0 V and in relatively dilute solution to minimize the dimerization of **5** to afford **6** and, ultimately, **7**. Hydrogen atom abstraction from the solvent may be expected to be troublesome under these conditions, but can be reduced by replacing DMF with a poorer hydrogen atom-donating solvent.[15] Potentials between −2.0 to −2.2 V must be used if it is desired to prepare carbanion **13** electrocatalytically. Because of the carbene path to **7** available to this species, trapping agents may have to be used at relatively higher concentrations to reduce competition from this path. We are exploring a number of implications for organic synthesis of these conclusions.[16]

Experimental Section

General. Dimethylformamide was distilled at aspirator vacuum from CaH_2 and stored over 3 Å molecular sieves which were activated by 5 min microwave heating, followed by 6 h at 400 °C. 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 (**3**) (Aldrich) was used as received after its purity had been established by NMR spectroscopy and GC-MS analysis. Co(II)(salen) (**2**) was prepared by a literature procedure.[17] Construction of the $Ag/AgNO_3$ reference electrode has been described previously.[18]

Product Analysis by GC-MS. A Hewlett-Packard Model 5988A gas chromatograph-mass spectrometer (GC-MS) was used for product analyses. The GC retention times of bibenzyl (**10**) and *cis*-stilbene (**7**) are identical under all conditions examined by us. Analyses of mixtures of **10** and *cis*-**7** were carried out in the following manner. A series of solutions of differing molar ratios was made. The ratio of the area (actually, numbers of ions) under the 182 and 91 peaks of **10** to that under the 178,179,180 cluster of peaks characteristic of *cis*-**7** was measured and plotted against the mole ratio of **10:7**. This calibration curve was used to calculate the **10:7** ratio in unknown mixtures. The GC-MS response factors of 1:1:1 mixtures of toluene (**11**), **10**, and *trans*-**7** and **11**, *cis*-**7**, and *trans*-**7** were also measured and used to construct a second calibration curve for determining the relative molar amounts of all products. Although *cis*-**7** and **10** come off the GC as a single peak, expansion of this peak on the time axis showed that the early portion of the peak consists primarily of *cis*-**7** and the late portion consists primarily of **10**.

Controlled-Potential electrolyses. Benzal chloride (**3**) (0.64 g, 4.0 mmol), Co(II)(salen (**1**) (0.163 g, 0.5 mmol), and Bu_4NPF_6 (2.00 g, 5.2 mmol) were placed in an oven-dried all glass electrolysis cell[19] equipped with magnetic stirrer and protected from light, and the cell was flushed with N_2. DMF (50 mL) was transferred by cannula into the cell under N_2 pressure and the contents of the cell were stirred and flushed with N_2 for 30 min. The cell contained a reticulated vitreous carbon (RVC) cathode and a carbon cloth electrode as anode. The cathode potential was adjusted to the appropriate value and electrolysis was carried out at 0 °C using a Bioanalytical Systems PWR-3 potentiostat. The initial current was typically *ca.* 60 mA; after 10−24 h, the current had decayed to less than 5 mA, at which point electrolysis was halted. The catholyte was extracted with three 50 mL portions of pentane, which were combined, washed with one 50 mL portion of 5% HCl and twice with water, and dried over $MgSO_4$.

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[15] We have recently found that acetonitrile is a good solvent for this purpose: the yields of **10** and **11** are very low compared to that of **7** in this solvent at −1.8 V (A. J. Fry, A. Uglialoro, and T. Phanijphand, research in progress).

[16] A reviewer raised the question of the likely magnitude of the uncompensated iR error in these electrolyses. The reduction potential of **1** is about the same in the preparative experiments as the measured voltammetric potential,[3] suggesting that the iR error is not large.

[17] Gilbert, W. C.; Taylor, L. T.; Dillard, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 2477.

[18] Fry, A. J.; Touster, J. *J. Org. Chem.* **1986**, *51*, 3905.

[19] Fry, A. J. *Synthetic Organic Electrochemistry*, 2nd ed.; Wiley: New York, 1989; p 323.