

Reductive coupling of benzyl bromide catalyzed by a novel dicobalt complex having two salen units†

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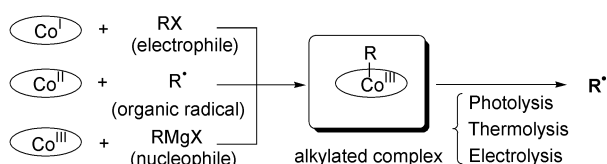
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A novel dicobalt complex $[\text{Co}^{\text{II}}_2\text{L}]$ has been synthesized, where $(\text{L})^{4-}$ is a dinucleating ligand derived by the 2 : 2 : 1 condensation of ethylenediamine, salicylaldehyde, and 5,5'-methylenebis(salicylaldehyde), and it has two N_2O_2 metal-binding sites which are linked to each other with a methylene spacer. This complex was characterized by UV-VIS, IR, and NMR as well as mass spectroscopy. Its redox behavior was investigated in dmf using cyclic voltammetry in comparison with that for the corresponding mononuclear complex $[\text{Co}(\text{salen})]$. The redox couples to $\text{Co}^{\text{III}}\text{--Co}^{\text{II}}$ and $\text{Co}^{\text{II}}\text{--Co}^{\text{I}}$ for $[\text{Co}^{\text{II}}_2\text{L}]$ were observed at +0.09 and -1.20 V vs. Ag–AgCl, respectively. These potentials are quite similar to those for $[\text{Co}(\text{salen})]$. The electro-generated $[\text{Co}^{\text{I}}_2\text{L}]^{2-}$ reacts with alkyl halide at each metal center to give an organocobalt complex. A further one-electron reduction of the compound yields an unstable intermediate that undergoes rapid decomposition by cleavage of the cobalt–carbon bond. The electrolysis of benzyl bromide at -1.40 V vs. Ag–AgCl in the presence of the dicobalt complex yields bibenzyl as the major product. On the other hand, when $[\text{Co}(\text{salen})]$ was used as a catalyst, toluene was obtained as the major product. The difference in the product distribution is due to the structural properties of the catalysts.

Introduction

A compound with a cobalt–carbon bond is a useful reagent for forming radical species. The cobalt–carbon bond can be cleaved homolytically in a simple fashion by photolysis, electrolysis, or thermolysis to form Co^{II} and the corresponding radical species as shown in Scheme 1.^{1,2} The application of the



Scheme 1

alkylated complex to organic synthesis is quite interesting from the viewpoint of a radical forming reagent.^{3–5} For example, we have been dealing with hydrophobic vitamin B_{12} derivatives which have ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B_{12} ,⁶ and succeeded in performing various organic reactions such as the 1,2 migration of functional groups, asymmetric reactions, and ring expansion reactions using a hydrophobic vitamin B_{12} derivative as a catalyst.^{7–19} Though many studies have used a compound with a cobalt–carbon bond, there is no example of a dicobalt complex with cobalt–carbon bonds employed as a catalyst. When we used a dicobalt complex it was possible to activate two molecules of the substrate at the same time to form two active species. Therefore, we designed a novel dicobalt complex having two $[\text{Co}(\text{salen})]$ units capable of forming two cobalt–carbon bonds at each metal center. The cobalt salen complex is widely known to form a stable cobalt–carbon bond.^{20,21}

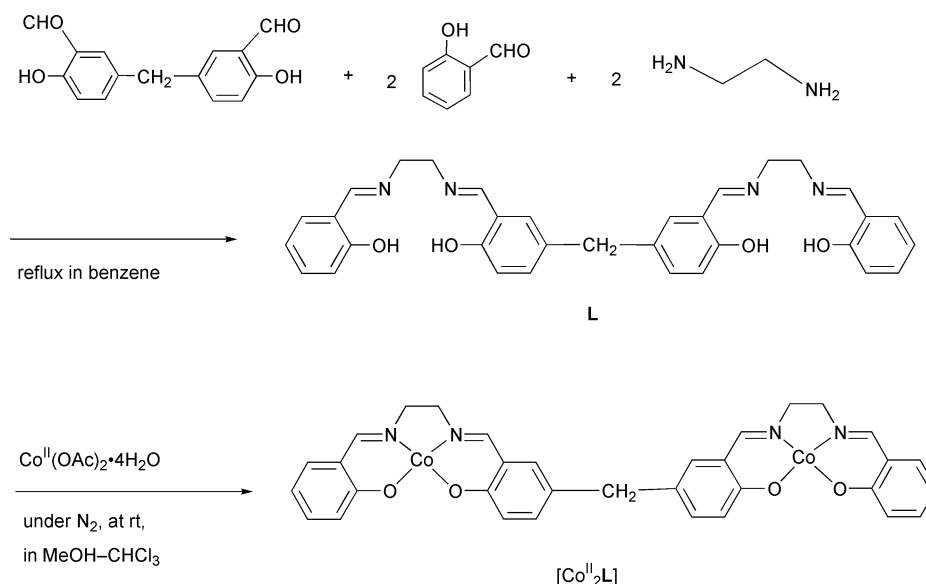
† Electronic supplementary information (ESI) available: ^1H NMR spectrum of ligand L and assignments; UV-VIS spectra of $[\text{Co}^{\text{II}}_2\text{L}]$ and $[\text{Co}^{\text{I}}_2\text{L}]$; ESR spectrum for the spin trapping. See <http://www.rsc.org/suppdata/dt/b0/b010022f/>

In this paper we report the synthesis, characterization, and redox behavior of a novel dicobalt complex, and the electro-reductive coupling reaction of benzyl bromide which has been shown to be catalyzed by the dicobalt complex.

Experimental

General analyses and measurements

Elemental analyses were obtained from the Service Centre of Elementary Analysis of Organic Compounds at Kyushu University. The ^1H , ^{13}C and 2-D NMR (COSY) spectra (in CDCl_3) were recorded on a Bruker AMX 500 spectrometer and the chemical shifts (in ppm) are referenced to SiMe_4 as the internal standard. The ESR spectrum was obtained on a JEOL JES-FE1G X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter. The FAB mass spectra were recorded on a JEOL JMS-HX110A, IR spectra on a JASCO IR-810 spectrophotometer using KBr disks and UV-VIS absorption spectra in chloroform or thf on a Hitachi U-3300 spectrophotometer at room temperature. The complexes of Co^{II} and Co^{I} were measured under anaerobic conditions to prevent auto-oxidation. The cobalt(I) complex was prepared *in situ* from the cobalt(II) complex by $\text{NaBH}_4/\text{PdCl}_2$ reduction under anaerobic conditions.²⁰ Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a BAS CV 50W electrochemical analyzer. A three-electrode cell equipped with a 1.6 mm diameter platinum wire and coil as the working electrode and counter electrode was used.⁹ An Ag–AgCl (3.0 M NaCl) electrode served as the reference. Non-aqueous solutions containing the cobalt complex (5.0×10^{-4} M) and tetra-*n*-butylammonium perchlorate (1.0×10^{-1} M) were deaerated prior to each measurement, and the inside of the cell was maintained under an argon atmosphere throughout. All the measurements were carried out at room temperature. The scan rate was varied over the range from 10 to 500 mV s^{-1} . The $E_{1/2}$ value of Fc^+/Fc was 0.54 V vs. Ag–AgCl with this set-up.



Scheme 2

Electrolysis of benzyl bromide

Electrolysis was carried out in a two-compartment cell equipped with platinum electrodes at room temperature under an argon atmosphere during irradiation with a 500 W tungsten lamp at a distance of 50 cm.⁹ The applied potential between the working and reference electrodes during the electrolysis was maintained constant with a Hokuto Denko HA-501 potentiostat/galvanostat and the reaction was monitored on a Hokuto Denko HF-201 coulomb/ampere-hour meter. Initial concentrations: $[\text{Co}^{\text{II}}_2\text{L}]$, 5.0×10^{-4} M; $[\text{Co}^{\text{II}}(\text{salen})]$, 1.0×10^{-3} M; benzyl bromide, 5.0×10^{-3} M; dmf solvent containing 0.05 M tetra-*n*-butylammonium tetrafluoroborate. The GLC analyses were carried out on a Shimadzu GC-9A apparatus equipped with a Shimadzu C-R6A chromatopac.

Materials

5,5'-Methylenebis(salicylaldehyde) was prepared by the method reported.²² All solvents and chemicals used in the syntheses were of reagent grade, used without further purification. For the electrochemical studies, dmf was stirred for one day in the presence of BaO under N_2 , then distilled at reduced pressure. NBu_4ClO_4 was purchased from Nakarai Chemicals (special grade) and dried at 60 °C under vacuum before use. NBu_4BF_4 was prepared based on a reported procedure.²³ *N*-Benzylidene-*tert*-butylamine *N*-oxide (PBN) was purchased from Aldrich and used without further purification. $[\text{Co}(\text{salen})]$ was prepared as described.²⁴

Synthesis of the ligand (L)

To a solution of 5,5'-methylenebis(salicylaldehyde) (8.96 g, 35 mmol) and salicylaldehyde (8.54 g, 70 mmol) in 200 mL of benzene, ethylenediamine (4.21 g, 70 mmol) in 50 mL of benzene was slowly added, and the reaction mixture refluxed for 30 min. It was cooled to room temperature and the precipitated polymeric product removed by filtration. The filtrate was concentrated to dryness, chloroform added, and the insoluble solid was filtered off again. The same procedures were repeated three times completely to remove the polymeric product. The filtrate was concentrated to dryness. The resulting product was washed with hot ethanol to remove a by-product ($\text{H}_2(\text{salen})$), affording the pure compound L (2.3 g, 12%). Found: C, 71.98; H, 5.87; N, 9.85%. $\text{C}_{33}\text{H}_{32}\text{N}_4\text{O}_4$ requires C, 72.24; H, 5.88; N, 10.21%. IR, $\tilde{\nu}/\text{cm}^{-1}$: 3450br (OH), 1630s (C=N) and 1280s (C-O) (KBr). ^1H NMR (500 MHz, CDCl_3 , SiMe_4): δ_{H} 3.81 (2 H, s, $\text{C}_6\text{H}_3\text{CH}_2\text{C}_6\text{H}_3$), 3.92 (8 H, s, $\text{NCH}_2\text{CH}_2\text{N}$), 6.85 (4 H, m, Ph),

6.93 (2 H, d, Ph), 6.98 (2 H, s, Ph), 7.08 (2 H, d-d, Ph), 7.23 (2 H, d, Ph), 7.30 (2 H, t, Ph), 8.29 (2 H, s, N=CH), 8.35 (2 H, s, N=CH), 13.06 (2 H, s, OH) and 13.23 (2 H, s, OH). ^{13}C NMR (125 MHz, CDCl_3 , SiMe_4): δ 39.7 ($\text{C}_6\text{H}_3\text{CH}_2\text{C}_6\text{H}_3$), 59.8 ($\text{NCH}_2\text{CH}_2\text{N}$), 116.9, 117.0, 118.4, 118.6, 118.7, 131.3, 131.4, 131.5, 132.4, 133.0 (Ph), 159.4, 161.0 (N=CH) and 166.5 (PhO). HRMS (FAB, m/z): calc. for $\text{C}_{33}\text{H}_{33}\text{N}_4\text{O}_4$, $[\text{MH}]^+$ 549.2502; found 549.2505.

Synthesis of $[\text{Co}^{\text{II}}_2\text{L}]$

All procedures were carried out using a standard Schlenk apparatus to avoid oxidation by atmospheric dioxygen. To a solution of L (82 mg, 0.15 mmol) in 10 mL of chloroform was dropwise added $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (78 mg, 0.32 mmol) in 10 mL of methanol. A reddish brown solid was immediately precipitated and the mixture stirred at room temperature for 1 h. The resulting solid was collected by filtration, washed with methanol and chloroform and dried *in vacuo* to afford a reddish brown powder (94 mg, 95%). Found: C, 58.40; H, 4.33; N, 8.14%. $\text{C}_{33}\text{H}_{28}\text{Co}_2\text{N}_4\text{O}_4 \cdot \text{H}_2\text{O}$ requires C, 58.25; H, 4.44; N, 8.23%. IR, $\tilde{\nu}/\text{cm}^{-1}$: 1640s (C=N) and 1310s (C-O) (KBr). HRMS (FAB, m/z): calc. for $\text{C}_{33}\text{H}_{28}\text{Co}_2\text{N}_4\text{O}_4$, $[\text{M}]^+$ 662.0774; found 662.0754.

Results and discussion

Preparations of the ligand and complex

The dinucleating ligand L was synthesized by the one-pot reaction of 5,5'-methylenebis(salicylaldehyde) and double the molar quantity of ethylenediamine and salicylaldehyde as shown in Scheme 2. Polymeric products and a monomeric one ($\text{H}_2(\text{salen})$) were also produced, but they could easily be separated from the desired dinucleating ligand due to the difference in their solubility in organic solvents. The IR analysis of L shows an intense $\tilde{\nu}(\text{C-N})$ band and broad $\tilde{\nu}(\text{O-H})$ band at 1630 and 3450 cm^{-1} , respectively. The structure of the ligand L was characterized by NMR and high resolution mass spectroscopies (HRMS).

The dicobalt complex $[\text{Co}^{\text{II}}_2\text{L}]$ was synthesized by the reaction between L and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in MeOH under anaerobic conditions, and isolated as a reddish brown powder in 95% yield. A satisfactory elemental analysis and FAB-MS spectrum have been obtained for the complex. The electronic spectra of the dicobalt complex with L in various oxidation states are similar to those of the corresponding mononuclear cobalt salen complexes.²⁵ They suggest an analogous coordination environment and geometry to those of $[\text{Co}(\text{salen})]$. The

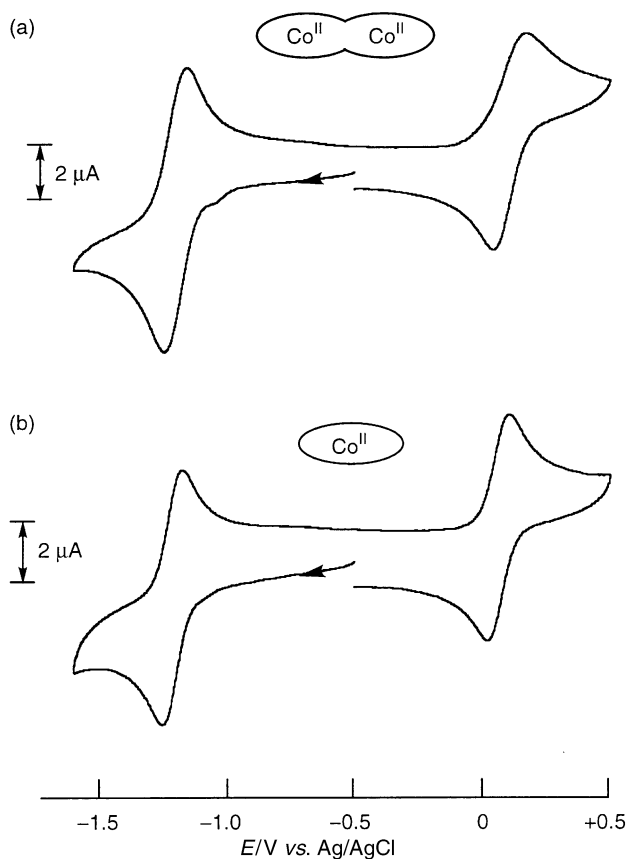


Fig. 1 Cyclic voltammograms of (a) $[\text{Co}^{\text{II}}_2\text{L}]$ and (b) $[\text{Co}^{\text{II}}(\text{salen})]$ in dmf containing 0.1 M NBu_4ClO_4 . Scan rate is 100 mV s^{-1} .

absorption spectrum of $[\text{Co}^{\text{II}}_2\text{L}]$ in deaerated acetonitrile showed the typical $[\text{Co}^{\text{II}}(\text{salen})]$ bands, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$) 350 (1.3×10^4), 408 (1.6×10^4), 493(sh) (3.1×10^3). The $[\text{Co}^{\text{II}}_2\text{L}]$ complex was reduced with $\text{NaBH}_4/\text{PdCl}_2/\text{NaOH}$ in deaerated thf to give a green solution containing $[\text{Co}^{\text{I}}_2\text{L}]^{2-}$, which showed a strong charge-transfer band at 703 nm ($1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). This is also a typical spectrum for the $[\text{Co}^{\text{I}}(\text{salen})]^-$ complex.²⁵

Electrochemistry of $[\text{Co}^{\text{II}}_2\text{L}]$

Cyclic voltammograms of $[\text{Co}^{\text{II}}_2\text{L}]$ and $[\text{Co}(\text{salen})]$ in dmf are shown in Fig. 1. The $\text{Co}^{\text{II}}\text{--Co}^{\text{I}}$ and $\text{Co}^{\text{III}}\text{--Co}^{\text{II}}$ redox couples for $[\text{Co}^{\text{II}}_2\text{L}]$ were observed at -1.20 and $+0.09 \text{ V vs. Ag--AgCl}$, respectively, very similar to those of the corresponding mononuclear complex $[\text{Co}^{\text{II}}(\text{salen})]$. The ratios between the anodic and cathodic peak currents, $i_{\text{pa}}:i_{\text{pc}}$, were almost unity and independent of the scan rate (from 10 to 500 mV s^{-1}) for the two redox couples in dmf. Plots of i_p ($= i_{\text{pa}} + i_{\text{pc}}$) vs. $\nu^{1/2}$ (ν is the scan rate, mV s^{-1}) were linear, and the separation between the anodic and cathodic peaks varied from 100 to 80 mV for the two redox couples, while the $E_{1/2}$ values remained constant within an accuracy of 5% regardless of the scan rate variation. The present electrochemical redox reactions in dmf are consistent with reversible one-electron transfer processes.²⁶ Therefore, the electron transfers occur independently at each cobalt with no interaction between the two metal centers. In order to provide an unambiguous assignment of the redox couples, coulometry studies were carried out at -1.3 and $+0.2 \text{ V vs. Ag--AgCl}$. The charge passed corresponded to two electrons at each potential.

Square-planar cobalt(i) complexes are strong nucleophiles and react with various organic halides to give organocobalt complexes.²⁷ The addition of benzyl bromide significantly changed the voltammetric pattern of the complex as shown in Fig. 2(a). In the presence of an excess of benzyl bromide a new peak appeared at a more cathodic potential for the $\text{Co}^{\text{II}}\text{--Co}^{\text{I}}$ reduction peak as shown in Fig. 2(b). This wave

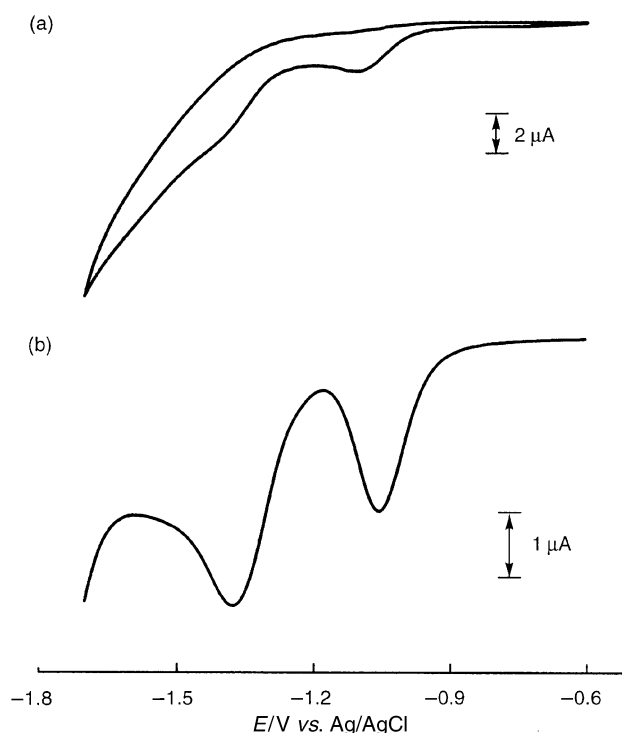
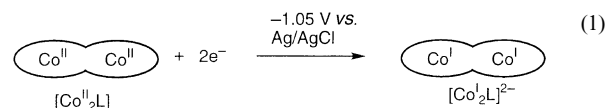
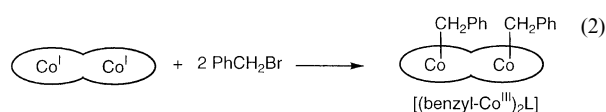


Fig. 2 (a) Cyclic voltammogram and (b) differential pulse voltammogram of $[\text{Co}^{\text{II}}_2\text{L}]$ in the presence of benzyl bromide in dmf. Initial concentrations: $[\text{Co}^{\text{II}}_2\text{L}]$, $1.0 \times 10^{-3} \text{ M}$; benzyl bromide, $1.0 \times 10^{-2} \text{ M}$; NBu_4ClO_4 , $1.0 \times 10^{-1} \text{ M}$. Scan rate: (a) 100 , (b) 20 mV s^{-1} .

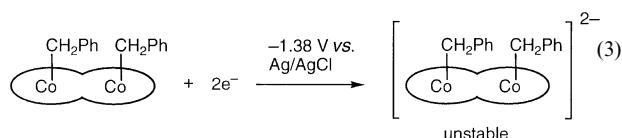
became irreversible, and shifted to a more negative potential (refer to eqn. 1). The disappearance of the oxidation peak for



$\text{Co}^{\text{I}}\text{--Co}^{\text{II}}$ suggests that the reaction of $[\text{Co}^{\text{I}}_2\text{L}]^{2-}$ with benzyl bromide gives benzyl- Co^{III} with a cobalt-carbon bond at both metal centers as shown in eqn. (2). Therefore, the new



peak at $-1.38 \text{ V vs. Ag--AgCl}$ is caused by the reduction of $[(\text{Co}^{\text{III}}\text{CH}_2\text{Ph})_2\text{L}]$ as shown in eqn. (3).



When the dialkylated complex $[(\text{Co}^{\text{III}}\text{CH}_2\text{Ph})_2\text{L}]$ is irradiated with visible light the cobalt-carbon bonds homolytically cleave to form the corresponding two radical species. If the radical parts are close to each other a coupling reaction will effectively occur. Based on this idea, we applied this complex as a catalyst for the reductive dimerization of the alkyl halide as shown in eqn. (4).

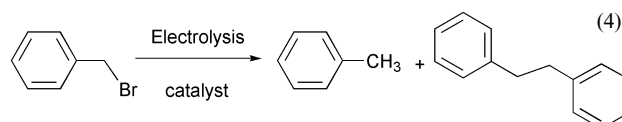


Table 1 Product analyses for the controlled-potential electrolyses of benzyl bromide catalyzed by $[\text{Co}^{\text{II}}_2\text{L}]$ and $[\text{Co}^{\text{II}}(\text{salen})]$ ^a

Catalyst	Electrolysis conditions		Product ratio ^c	
	Charge ^b / F mol ⁻¹	Conversion (%)	Toluene	Bibenzyl
$[\text{Co}^{\text{II}}_2\text{L}]$	0.7–1.3	39–75	24–33	67–76
$[\text{Co}^{\text{II}}(\text{salen})]$	0.7–1.5	51–87	67–87	13–33

^a Controlled potential electrolyses were carried out at -1.40 vs. Ag–AgCl under an argon atmosphere with irradiation by a 500 W tungsten lamp. Initial concentrations: $\text{Co}^{\text{II}}_2\text{L}$, 5.0×10^{-4} ; $[\text{Co}^{\text{II}}(\text{salen})]$, 1.0×10^{-3} ; NBu_4BF_4 , 5.0×10^{-2} ; PhCH_2Br , 5.0×10^{-3} M. ^b Electrical charge passed per mol of the substrate. ^c Products were analyzed by GC and GC-MS.

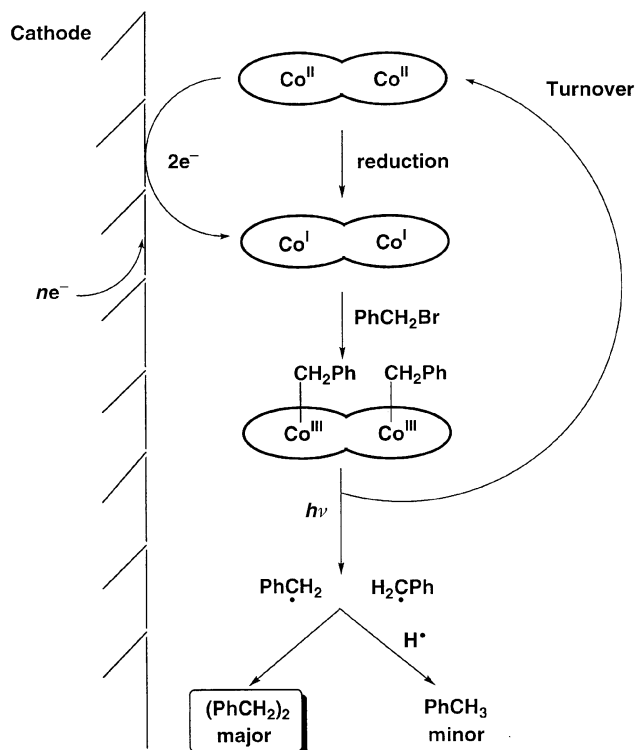


Fig. 3 Proposed mechanism for the electrolysis of benzyl bromide mediated by the dicobalt complex.

Electrolysis of benzyl bromide

The electrolysis of benzyl bromide at -1.4 V vs. Ag–AgCl in the presence of $[\text{Co}^{\text{II}}_2\text{L}]$ and irradiation by visible light yielded bibenzyl as a major product as shown in Table 1. On the other hand, when the corresponding mononuclear complex $[\text{Co}^{\text{II}}(\text{salen})]$ was used as a catalyst, toluene was obtained as the major product. No reaction occurred in the absence of the catalyst under the same conditions. In order to investigate the reaction mechanism, the electrolysis was examined by the spin-trapping technique with PBN.^{28,29} The electrolysis of benzyl bromide (5.0×10^{-3} M) was followed by ESR spectroscopy in the presence of $[\text{Co}^{\text{II}}_2\text{L}]$ (5.0×10^{-4} M) and PBN (3.9×10^{-1} M). The ESR signal attributable to the PBN spin adduct ($g = 2.006$, $A_N = 12.2$ G, $A_H = 2.4$ G; 10^4 G = 1 T) was observed during the electrolysis at -1.40 V vs. Ag–AgCl. Upon addition of PBN, the formation of toluene and bibenzyl was completely inhibited. This result indicates that the radical species are generated as electrolysis intermediates under the present conditions. A possible mechanism is shown in Fig. 3. The reaction is initiated by the formation of a $[\text{Co}^{\text{I}}_2\text{L}]^{2-}$ species generated from $[\text{Co}^{\text{II}}_2\text{L}]$ at -1.05 V vs. Ag–AgCl. The $[\text{Co}^{\text{I}}_2\text{L}]^{2-}$ species, which is a supernucleophile, reacts with benzyl bromide to yield

the alkylated complex. Upon irradiation by visible light the cobalt–carbon bonds of the alkylated complex then homolytically cleave to form benzyl radicals. The benzyl radicals are efficiently coupled before they diffuse out.

In conclusion, a novel dicobalt complex was synthesized and characterized by various spectroscopic methods. This complex catalyzed the dimerization of benzyl bromide under electrochemical conditions. This result provides a useful guideline for designing catalysts for dimerization reactions *via* radical intermediates.

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