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Cathodic reductive couplings and hydrogenations of alkenes and alkynes catalyzed by the B_{12} model complex

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ABSTRACT

The reductive coupling and hydrogenation of alkenes were catalyzed by the B_{12} model complex, heptamethyl cobyrinate perchlorate (**1**), in the presence of acid during electrolysis at −0.7 V *vs.* Ag/AgCl in acetonitrile. Conjugated alkenes showed a good reactivity during electrolysis to form reduced products. The product distributions were dependent on the substituents at the C═C bond of the alkenes. ESR spin-trapping experiments using 5,5-dimethylpyrroline *N*-oxide (DMPO) revealed that the cobalt-hydrogen complex (Co—H complex) should be formed during the electrolysis and it functioned as an intermediate for the alkene reduction. The electrolysis was also applied to an alkyne, such as phenylacetylene, to form 2,3-diphenylbutane (racemic and meso) and ethylbenzene via styrene as reductive coupling and hydrogenated products, respectively.

1. Introduction

Electroorganic synthesis is currently expanding into various interdisciplinary fields because of its versatile application to molecular transformations as well as its sustainable and economic advantage [1,2]. Electroorganic synthesis is recognized as a green process in synthetic organic chemistry since the redox process of a substrate occurs due to an electric current without any chemical reagent and waste after the reaction. Furthermore, indirect electrolysis using a mediator facilitates the redox process of the substrate to lower the applied potential resulting in an efficient molecular transformation [3]. Various cobalt complexes were utilized as the mediator for the electroorganic synthesis. Among the cobalt complexes, heptamethyl cobyrinate perchlorate has been used for the B_{12}-dependent enzyme model complex and various B_{12}-mimic reactions were achieved using this B_{12} model complex during electrolysis [3,4]. The dechlorination of an organic halide and the 1,2-migration reaction of a functional group were performed as model reactions of the B_{12}-dependent enzymes, *reductive dehalogenase* and *methylmalonyl-CoA mutase*, respectively [5–8]. In these reactions, electrochemically-formed Co(I) species reacted with the substrate to form an alkylated complex with the cobalt-carbon σ-bond as the reaction intermediate. The alkylated complex is a key intermediate for the B_{12} dependent enzymatic reactions [9–13]. Recently, a B_{12} inspired unique reaction for alkene reduction was reported by us [14]. In the reaction, the photochemically produced Co(I) species of the B_{12} derivative could react with a proton to form the cobalt-hydrogen complex (Co—H complex), then the Co—H complex was considered to catalyze the alkene reduction. Similar alkene reductions catalyzed by the B_{12} derivatives were also reported by the A. Fischli and W. Donk groups using Zn and Ti(III) citrate as the reducing reagent, respectively [15,16]. We have now developed a new electroorganic synthesis using the B_{12} derivative for alkene reduction in the presence of acid. The reactive Co(I) species should be formed by a green electrochemical technique. Furthermore, the direct reduction of alkenes requires an extremely negative potential over −2 V *vs.* SCE in an organic solvent [17,18], while the alkene reduction may occur at a more positive potential in the presence of the B_{12} complex since the Co(I) species of the B_{12} complex can be formed at the potential and reacts with a proton to form the Co—H complex as a reactive intermediate for the alkene reduction. In the present paper, we report the electrochemical reductive coupling and hydrogenation of alkenes catalyzed by the B_{12} model complex in the presence of acid as shown in Fig. 1. Two examples of the alkyne reduction are also reported.

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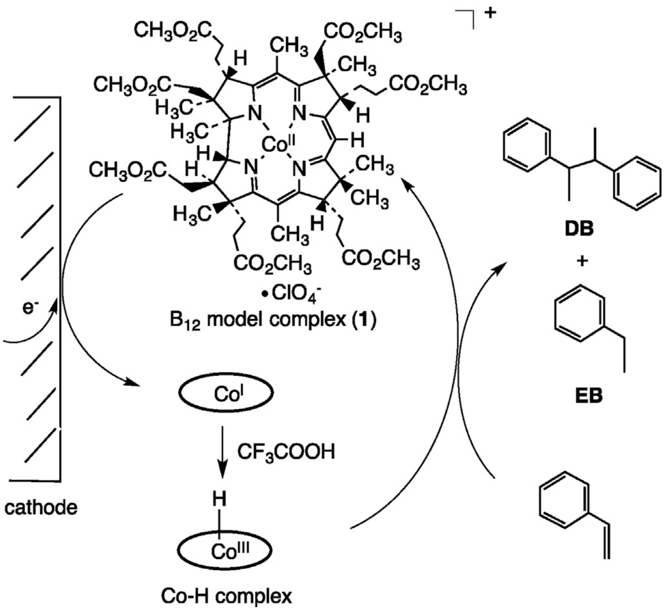

Fig. 1. Electrolysis of styrene catalyzed by B_{12} model complex (**1**) in the presence of acid.

2. Results and discussion

2.1. Cyclic voltammometry study

The cyclic voltammogram (CV) of **1** was obtained in acetonitrile using a glassy carbon working electrode. The Co(II)/Co(I) redox couple was observed at −0.61 V *vs*. Ag/AgCl as shown in Fig. 2. The addition of a styrene did not change the voltammetric pattern, which implies that the Co(I) species of **1** does not react with styrene. In contrast, the voltammetric pattern dramatically changed with the addition of trifluoroacetic acid (TFA) as shown in Fig. 2 (red lines). Supernucleophilic Co(I) species may react with a proton to form the cobalt-hydrogen complex, i.e., the Co—H complex [19,20]. The subsequent addition of styrene increased the cathodic current around −0.7 V *vs*. Ag/AgCl, which implies that styrene may react with the Co—H complex and the catalytic reduction of styrene should occur around −0.7 V *vs*. Ag/AgCl in the presence of **1** and acid.

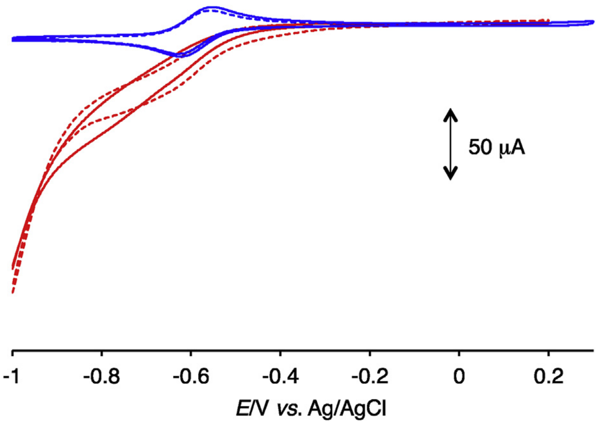

Fig. 2. CVs of **1** (1 mM) in CH_3CN containing of 0.1 M *n*-Bu_4NClO_4 under N_2 (solid blue line) and in the presence of 0.05 M styrene (dotted blue line), 0.5 M TFA (solid red line), and 0.05 M styrene and 0.5 M TFA (dotted red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Electrochemical reduction of alkenes

Based on the CV studies, the bulk electrolysis of styrene was carried out in the presence of TFA ($pK_a = 12.65$ in CH_3CN [21]) and a catalytic amount of **1** using a divided cell equipped with a carbon felt working electrode and zinc counter electrode. The results are summarized in Table 1. 2,3-Diphenylbutanes (**DB**) (racemic and meso) and ethylbenzene (**EB**) were formed from styrene as reductive coupling and hydrogenated products, respectively (entry 1 in Table 1). Without the catalyst **1** or acid, the reaction did not proceed (entries 5 and 6 in Table 1). The direct reduction of styrene occurred at −2.8 V *vs*. $Ag/AgNO_3$ in CH_3CN on a platinum electrode [22]. The B_{12} derivative **1** significantly accelerated the styrene reduction at the positive applied potential. It should be noted that the conventional hydrogenation of alkenes catalyzed by the cobalt complexes was performed using H_2 gas (3–6 atm) [23]. In contrast, the electrochemical method reported here required no H_2 gas for the reaction and the reaction proceeded under normal atmosphere at room temperature.

The imine/oxime type cobalt complex (**2**) (Fig. 7), which is a well-known functional model of B_{12} [24], showed a very low reactivity toward the styrene reduction (entry 7 in Table 1), but vigorous hydrogen evolution was observed during the electrolysis. The imine/oxime type cobalt complexes are known as good proton reduction catalysts [25,26] and the intermediate Co—H complex should be used for hydrogen production in the imine/oxime type cobalt complex and not used for styrene reduction during the electrolysis. The hydrogen evolution by the B_{12} derivative, cobyrinic acid, combined the use with titanium oxide as a photosensitizer, was recently reported by us and the turnover number of the cobalt complex for hydrogen evolution was only 1 per hour, while reduction of the arylalkenes efficiently proceeded with the 100 turnover number per hour based on the cobalt complex [14]. These results imply that the Co—H complex of the B_{12} derivative has a low reactivity for hydrogen evolution, but has a high reactivity for alkene reduction.

The products yields were dependent on the type of acid. No reaction occurred using the relatively weak acid, acetic acid ($pK_a = 22.3$ in CH_3CN [21]), under the same conditions (entry 2 in Table 1). Using a strong acid, *p*-toluensulfonic acid (*p*-TsOH) ($pK_a = 8.7$ in CH_3CN [21]), also decreased the product yields (entry 4 in Table 1). To allow the reaction to occur using acetic acid as a

Table 1
Electrolysis of styrene catalyzed by B_{12} model complexes (**1** and **2**).[a]

Entry	Catalyst	Acid (p*Ka* in CH_3CN)	Products yield[b]/%	
			DB (Racemic and meso)	EB
1	**1**	TFA (12.65)	34, 34	15
2	**1**	AcOH (22.3)	0, 0	0
3[c]	**1**	AcOH (22.3)	34, 34	16
4	**1**	*p*-TsOH (8.7)	9, 9	3
5	None	TFA (12.65)	0	0
6	**1**	None	0	0
7	**2**	TFA (12.65)	11, 11	Trace

[a] Conditions: [cobalt complex] = 5×10^{-4} M; [styrene] = 5×10^{-2} M; [acid] = 5×10^{-1} M; [*n*-Bu_4NClO_4] = 1×10^{-1} M using a carbon felt cathode at room temperature under N_2. Applied potentials were −0.7 V *vs*. Ag/AgCl for 3 h.
[b] Yield of products was based on the initial concentration of the substrate.
[c] Applied potential was −1.2 V *vs*. Ag/AgCl for 4 h, [acetic acid] = 1 M.

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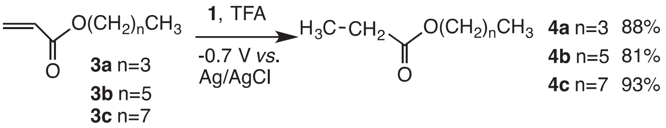
proton source, a more negative applied potential, −1.2 V *vs.* Ag/AgCl with twice the acid concentration was required (entry 3 in Table 1).

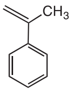
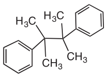
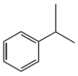
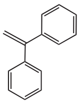
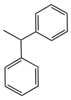
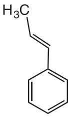
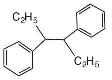
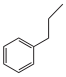
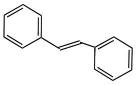
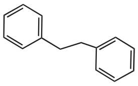
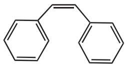
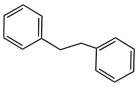
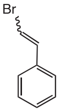
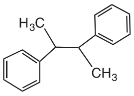
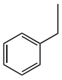
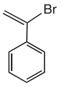
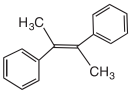
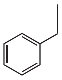
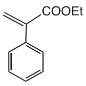
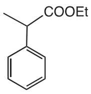
The reaction was also applied to various styrene derivatives (Table 2). The selectivity of the products was dependent on the substituents on the C=C bond. α-Methyl styrene produced a 63% yield of 2,3-dimethyl-2,3-diphenylbutane and 11% yield of 2-propylbenzene at −0.7 V *vs.* Ag/AgCl as reductive coupling and hydrogenated products, respectively (entry 1 in Table 2). α-Phenyl styrene afforded only a hydrogenated product, 1,1-diphenylethane, in 45% yield (entry 2 in Table 2) under the same reaction conditions. The bulky phenyl group of α-phenyl styrene may disturb the coupling reaction. Direct electrolysis of α-phenyl styrene required more negative applied potential at −2.6 V *vs.* SCE in DMF to form 1,1-diphenylethane [18]. Therefore, it is clear that B$_{12}$ derivative **1** significantly accelerated reduction of substrate at positive applied potential. A substituent at the β-position on the C=C bond of the alkene decreased the substrate reactivity and the reaction of β-methylstyrene (*E* form) or β-bromostyrene (*E* and *Z* mixtures) or *E* and *Z* stilbenes required a more negative applied potential of −1.2 V *vs.* Ag/AgCl. At this potential, the product distributions were changed for β-substituted styrenes. A hydrogenated product, 1-propylbenzene, was obtained in 52% yield and the coupling products, 2,3-diphenylhexane (racemic and meso), were obtained in only 30% yield from β-methylstyrene (entry 3 in Table 2). From *E* and *Z* stilbenes, 1,2-diphenyl ethanes were obtained in 35% and 53% yields, respectively (entries 4 and 5 in Table 2). In the case of β-bromostyrene, the debromination was coupled with the C=C bond reduction and the corresponding hydrogenated product, ethylbenzene, was obtained in 58% yield and the coupling products, 2,3-diphenylbutanes (racemic and meso), were obtained in 10% yield (entry 6 in Table 2). The product selectivity was different from that of the styrene reduction (entry 1 in Table 1). The difference in the product distributions could be caused by the difference in the applied potential from −0.7 V *vs.* Ag/AgCl for styrene to −1.2 V *vs.* Ag/AgCl for β-bromostyrene. The interesting reaction occurred in α-bromostyrene, and 2,2-diphenyl 2-butenes (*E* and *Z* mixtures) were obtained in 55% yield as the main products (entry 7 in Table 2). A similar reaction occurred using the B$_{12}$–TiO$_2$ hybrid photocatalytic system [14]. Ethyl 2-phenylacrylate was reduced to the hydrogenated product, ethyl 2-phenylpropionate, in 47% yield (entry 8 in Table 2).

The scope of substrate was examined using a variety of alkenes. The C=C bond of the unsaturated esters, alkyl acrylates (**3a-3d**), was reduced to form alkyl propionates (**4a-4d**) in moderate yields as shown by Eqs. (1) and (2).



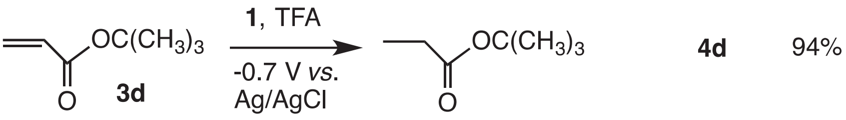
(1)

Table 2
Electrolysis of styrene derivatives catalyzed by **1**.[a]

Entry	Substrate	Product	Yield[b]/%
1			63
			11
2			45
3[c]			15/15 (racemic/meso)
			52
4[c]			35
5[c]			53
6[c]	 (*E* and *Z* mixture)		5/5 (racemic/meso)
			58
7			28/28 (*E*/*Z*)
			17
8			47

[a] Conditions: [cobalt complex] = 5 × 10^{-4} M; [styrene] = 5 × 10^{-2} M; [*n*-Bu$_4$NClO$_4$] = 1 × 10^{-1} M using a carbon felt cathode at room temperature under N$_2$. Applied potentials were −0.7 V *vs.* Ag/AgCl for 3 h.
[b] Yield of products were based on the initial concentration of the substrate.
[c] Applied potential was −1.2 V *vs.* Ag/AgCl.

In contrast, the nonconjugated alkenes, such as allylbenzene or vinylcyclohexane, did not react under standard conditions (electrolysis at −0.7 V *vs.* Ag/AgCl, TFA = 0.5 M) as shown in Eq.



(2)

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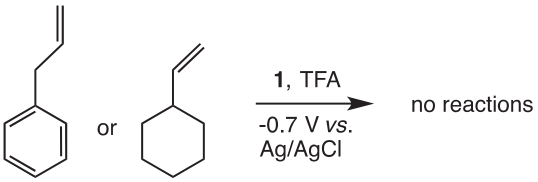
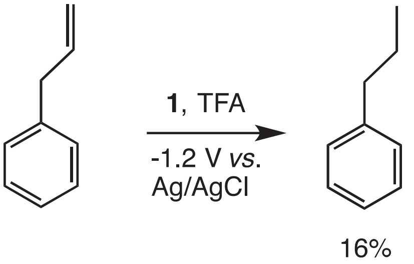
(3), but a small amount of 1-propylbenzene was obtained from the allylbenzene electrolysis at −1.2 V *vs.* Ag/AgCl as shown by Eq. (4).

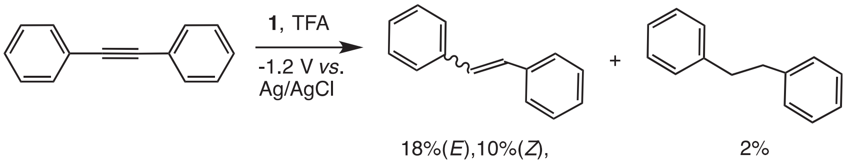


(3)



(4)

The reaction was also applied to the alkyne group. Electrolysis of phenylacetylene at −0.7 V *vs.* Ag/AgCl afforded no reduced products in the presence of **1** and TFA, but afforded 54% of 2,3-diphenylbutanes (racemic and meso), 39% of ethylbenzene, and small amount of styrene at −1.2 V *vs.* Ag/AgCl as shown by Eq. (5). From the time course of the electrolysis, phenylacetylene should be first reduced to styrene and the further reduction of styrene could produce the 2,3-diphenylbutanes (racemic and meso) and ethylbenzene as shown in Fig. 3. The difference in the product distribution from that of the reduction of styrene (entry 1 in Table 1, applied potential is −0.7 V *vs.* Ag/AgCl) could be caused by the applied potential. The electrolysis at a more negative potential, −1.2 V *vs.* Ag/AgCl, increased the yield of the hydrogenated product similar to the electrolysis of *β*-substituted styrenes (entries 3–6 in Table 2).



(6)

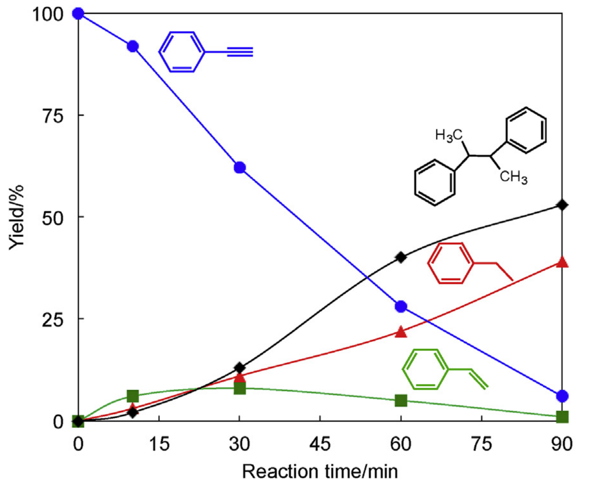
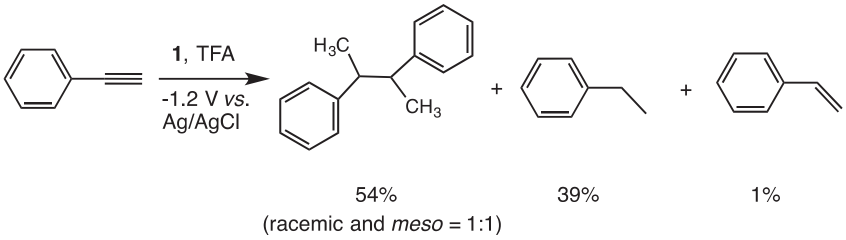


Fig. 3. Electrolysis progress at −1.2 V *vs.* Ag/AgCl showing the disappearance of phenylacetylene (blue) by **1** in the presence of TFA and the appearance of reduction products (2,3-diphenylbutenes: black, ethylbenzene: red, styrene: green); [**1**] = 5 × 10^{-4} M; [phenylacetylene] = 5 × 10^{-2} M; [TFA] = 5 × 10^{-1} M; [*n*-Bu_4NClO_4] = 1 × 10^{-1} M in CH_3CN under N_2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

From diphenylacetylene, *E* and *Z* stilbenes and 1,2-diphenylethane were obtained as shown by Eq. (6). It was noted that all alkenes and alkynes used here required acid in the reaction catalyzed by **1**. The controlled reaction without acid provided no reduced product in the all substrates.

Based on these results, we proposed the reaction mechanism shown in Fig. 4. The Co(I) species of B_{12} may react with a proton to form the cobalt-hydrogen intermediate, Co(III)—H. It is likely that the Co(III)—H complex provides the hydrogen radical, and the hydrogen radical could then attack the β-position of the alkene avoiding steric hindrance of the benzene ring in the styrene derivatives to form the α-radical intermediate. If R is H or a methyl



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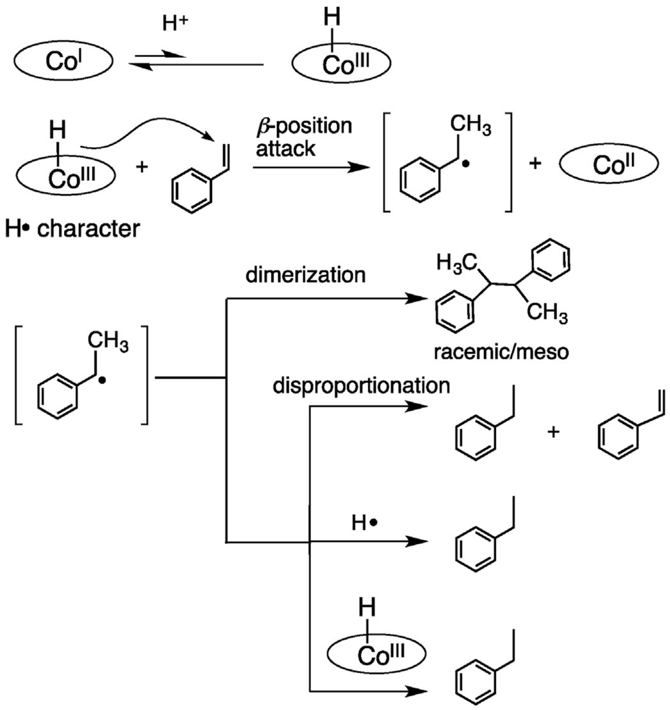

Fig. 4. Proposed mechanism for electrolysis of styrene catalyzed by **1** in the presence of acid.

group, the radical coupling preferentially occurred to form a coupling product. The hydrogenated product, ethylbenzene, could be formed by three pathways from the substrate radical. Disproportionation, hydrogen radical abstraction, and a second reaction with the Co—H complex from the substrate radical are possible for the ethylbenzene formation mechanism. If R is an electron-withdrawing group, further reduction of the radical by the cathode to form the carbanion intermediate is shown in Fig. 5. Protonation should afford a hydrogenated product when R is CO_2Et. When R is Br, the carbanion may lead to a carbene with the elimination of the bromide ion [14], and the short-lived carbene could react with the carbanion to form 2,3-diphynylbutane (*E* and *Z*).

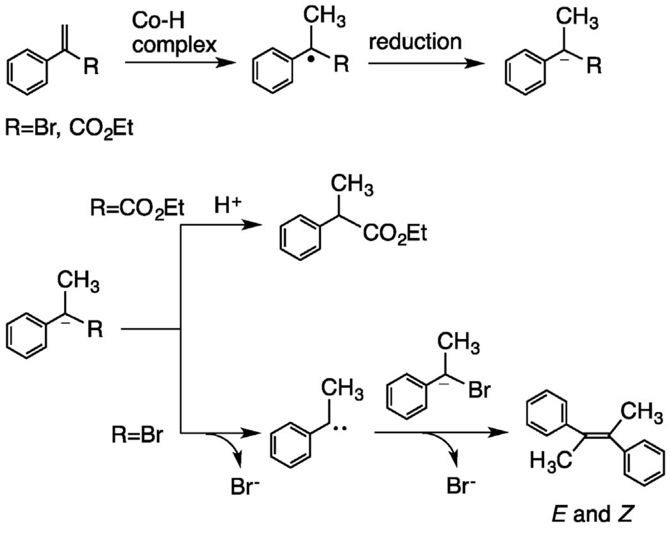

Fig. 5. Proposed mechanism for electrolysis of styrene derivatives with electron withdrawing group at α-position catalyzed by **1** in the presence of acid.

2.3. Co—H complex detection by spin-trapping experiment in ESR

The electrolysis of styrene was carried out in the presence of a spin-trapping reagent, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO). ESR signals of two DMPO trapping species were observed during the electrolysis of styrene catalyzed by **1** at −0.7 V *vs*. Ag/AgCl in the presence of TFA. The ESR signal was ascribed to the hydrogen radical trapped DMPO, DMPO-H (g = 2.009, A_N = 14.9 G, A_H = 19.7 G), combined with the carbon-centered radical trapped DMPO, DMPO-C (g = 2.008, A_N = 15.0 G, A_H = 21.4 G) as shown in Fig. 6(a). The obtained ESR parameters were similar to values already reported [27]. The DMPO-H signal disappeared using deuterated TFA (TFA-d_1) instead of TFA as shown in Fig. 6(b). These results suggested that the Co—H complex existed during the electrolysis and provided a hydrogen radical. These ESR experimentvs supported our proposal that the Co(III)—H complex of the B_{12} derivative could have a hydrogen radical character and catalyze the alkene and the alkyne reduction.

3. Conclusion

In summary, we have developed for the first time the electrolysis of alkenes and alkynes by the B_{12} model complex in the presence of acid. The reductive coupling and hydrogenation of alkenes proceeded at a positive applied potential compared to that of the direct reduction of alkenes. The electrolysis was applied to a variety of alkenes and the conjugated alkenes especially afforded a moderate yield of products. The B_{12} derivative showed a good catalysis for the reaction, and the Co—H species of the B_{12} complex was proposed as an intermediate for the reaction. The bioinspired electroorganic synthesis shown here can be applied to the sustainable production of fine chemicals with the possible expense of energy economy. Ongoing work in our laboratory is focused on the application of this chemistry to other organic syntheses.

4. Experimental section

4.1. Reagents and materials

The solvents and chemicals used in the syntheses were of reagent grade and used without further purification. The acetonitrile solvent for the electrolysis was a special dry grade purchased from Kanto Chemicals. Tetra-*n*-butylammonium perchlorate (n-Bu_4NClO_4) was purchased from Nakalai Chemicals (special grade) and dried at room temperature under vacuum before use. The preparative TLC (silica gel 60 F_{254}) was purchased from Merck. Heptamethyl cobyrinate perchlorate (**1**) (Fig. 1) was synthesized by a previously reported method [28,29]. The cobalt complex, [Co(III){(C_2C_3)(DO)(DOH)pn}Br_2], (C_2C_3)(DO)(DOH)pn is 4,10-dipropyl-5,9-diazatrideca-4,9-diene-3,10-dione dioxime), (**2**) (Fig. 1) was prepared according to the literature [24].

4.2. Apparatus and characterization

The NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Center of Advanced Instrumental Analysis of Kyushu University. The UV-vis absorption spectra were measured by a Hitachi U-3300 spectrophotometer at room temperature. The MALDI-TOF mass spectra were obtained by a Bruker autoflex II using 6-aza-2-thiothymine as the matrix. The GC-mass spectra were obtained using a Shimadzu GC-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 μm). Hydrogen gas was analyzed by a Shimadzu 14-B gas chromatograph equipped with a SHINCARBON ST packed column (Shimadzu GLC). The cyclic voltammograms (CV) were obtained

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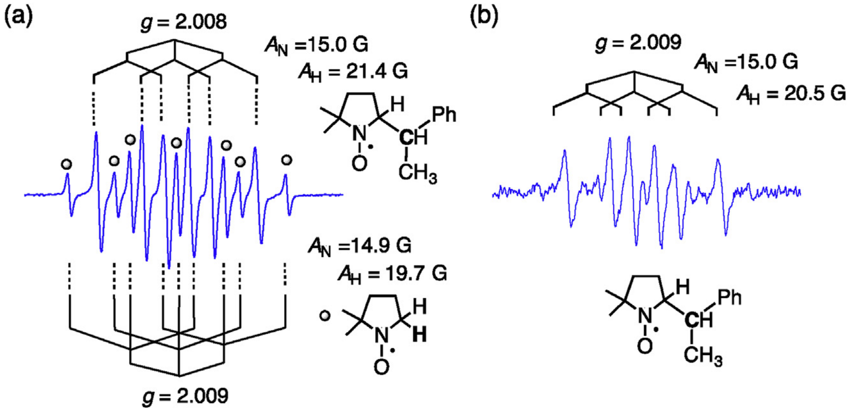

Fig. 6. ESR spectra of **1** during the electrolysis of styrene at −0.7 V *vs*. Ag/AgCl in CH_3CN under N_2; [**1**] = 5×10^{-4} M; [styrene] = 5×10^{-2} M; [TFA] = 5×10^{-1} M; [DMPO] = 5×10^{-1} M; [*n*-Bu_4NClO_4] = 1×10^{-1} M in the presence of TFA (a) and in the presence of TFA-d_1 (b).

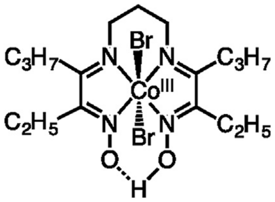

Fig. 7. Structure of the imine/oxime type cobalt complex, [Co(III){(C_2C_3)(DO)(DOH)pn}Br_2].

using a BAS CV 50W electrochemical analyzer. A three-electrode cell equipped with a 1.6-mm diameter glassy carbon rod and platinum wire as the working and counter electrodes, respectively, was used. An Ag/AgCl (3.0 M NaCl) electrode served as the reference. The $E_{1/2}$ value of the ferrocene-ferrocenium (Fc/Fc^+) was 0.40 V *vs*. Ag/AgCl with this setup.

4.3. General bulk electrolysis

The controlled-potential electrolysis of the alkene was carried out in a divided cell equipped with a carbon felt cathode and a zinc plate anode (1×3 cm^2) at −0.7 V *vs*. Ag/AgCl in the presence of **1** at room temperature in 0.1 M *n*-Bu_4NClO_4 containing acetonitrile. The applied potential between the working and reference electrodes during the electrolysis was maintained constant using a Hokuto Denko HA BF-501A potentiostat, and the electrical quantity was also recorded by it. The concentrations of the catalyst and substrate were 5.0×10^{-4} M and 5.0×10^{-2} M, respectively. After the electrolysis, the electrolyte solution was passed through silica gel with the $CHCl_3$ eluent, then analyzed by GC-MS. Authentic samples of the products from the catalytic reactions (Tables 1 and 2) except for those listed below were purchased from Aldrich or Tokyo Kasei Kogyo (TCI). The 2,3-diphenylhexanes (racemic and meso) (**DH**) were synthesized by reported methods [30], and the mixture of the racemic and meso compound was separated by preparative TLC using hexane as the eluent. 1,1-Diphenylethane, butyl propionate (**4a**), and octyl propionate (**4c**) were synthesized by hydrogenation of 1,1-diphenylethylene, butyl acrylate (**3a**), and octyl acrylate (**3c**) using Pd/C under 1atm H_2, respectively. Ethyl 2-phenylacrylate was synthesized by the acid-catalyzed esterification of 2-phenylacrylic acid in ethanol.

4.3.1. **DH** (meso)

White solid. GC-MS, $M^+ = 238$; ^1H NMR ($CDCl_3$, δ/ppm), 0.55 (t, $J = 7.2$Hz, 6H, CH_3), 1.28–1.44 (m, 4H, CH_2), 2.60–2.62 (m, 2H, CH), 7.21–7.36 (m, 10H, Ph), ^{13}C NMR ($CDCl_3$, δ/ppm), 12.55, 27.80, 54.65, 126.37, 128.58, 128.83, 144.95.

4.3.2. **DH** (racemic)

Colorless liquid. GC-MS, $M^+ = 238$; ^1H NMR ($CDCl_3$, δ/ppm), 0.77 (t, $J = 7.6$Hz, 6H, CH_3), 1.54–1.66 (m, 4H, CH_2), 2.74–2.76 (m, 2H, CH), 6.88–7.21 (m, 10H, Ph), ^{13}C NMR ($CDCl_3$, δ/ppm), 12.76, 26.24, 53.68, 126.00, 127.83, 129.46, 143.46.

4.3.3. 1,1-Diphenylethane

Colorless liquid. GC-MS, $M^+ = 182$; ^1H NMR ($CDCl_3$, δ/ppm), 1.74 (d, $J = 7.3$Hz, 3H, CH_3), 4.27 (q, $J = 7.3$Hz, 1H, CH), 7.25–7.39 (m, 10H, Ph), ^{13}C NMR ($CDCl_3$, δ/ppm), 22.44, 45.33, 126.58, 128.19, 128.92, 146.92.

4.3.4. Butyl propionate **(4a)**

Colorless liquid. GC-MS, $M^+ = 130$; ^1H NMR ($CDCl_3$, δ/ppm), 0.95 (t, $J = 7.3$Hz, 3H, CH_3), 1.16 (t, $J = 7.6$Hz, 3H, CH_3), 1.38–1.41 (m, 2H, CH_2), 1.60–1.66 (m, 2H, CH_2), 2.35 (q, $J = 7.6$Hz, 2H, CH_2), 4.09 (t, $J = 7.0$Hz, 2H, CH_2), ^{13}C NMR ($CDCl_3$, δ/ppm), 9.45, 13.98, 19.47, 27.94, 31.07, 64.47, 174.86.

4.3.5. Octyl propionate **(4c)**

Colorless liquid. GC-MS, $M^+ = 186$; ^1H NMR ($CDCl_3$, δ/ppm), 0.89–0.92 (t, $J = 7.3$Hz, 3H, CH_3), 1.15–1.18 (t, $J = 7.6$Hz, 3H, CH_3), 1.30–1.31 (m, 10H, CH_2), 1.63–1.66 (m, 2H, CH_2), 2.33–2.37 (q, $J = 7.6$Hz, 2H, CH_2), 4.07–4.10 (t, $J = 6.9$Hz, 2H, CH_2), ^{13}C NMR ($CDCl_3$, δ/ppm), 9.54, 14.44, 23.01, 26.31, 28.02, 29.05, 29.55, 29.60, 32.16, 64.87, 174.97.

4.3.6. Ethyl 2-phenylacrylate

Colorless liquid. GC-MS, $M^+ = 176$; ^1H NMR ($CDCl_3$, δ/ppm), 1.33 (t, $J = 7.2$Hz, 3H, CH_3), 4.3 (q, $J = 7.2$Hz, 2H, CH_2), 5.89 (s, 1H, CH), 6.35 (s, 1H, CH), 7.34–7.41 (m, 5H, Ph), ^{13}C NMR ($CDCl_3$, δ/ppm), 14.62, 61.51, 126.86, 128.48, 128.51, 128.69, 137.19, 141.99, 167.23.

4.4. Spin-trapping experiment by ESR

The ESR spectra were obtained using a Bruker EMX-Plus X-band spectrometer at room temperature. The ESR spectra for the DMPO spin-trapping products were observed during the electrolysis of styrene (5.0×10^{-2} M) at −0.7 V *vs*. Ag/AgCl using a carbon felt electrode in the presence of DMPO (5×10^{-1} M), **1** (5.0×10^{-4} M) and TFA (5.0×10^{-1} M) in dry acetonitrile under nitrogen. The settings for the ESR measurements were a frequency of 9.87 GHz,

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power of 1.0 mW, center field of 3515 G, sweep width of 150 G, modulation amplitude of 1.0 G, time constant of 40 ms, and sweep time of 20 s.

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