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Electron-Transfer Processes in the Electrophilic Cleavage of Cobalt-Carbon Bonds of Alkylcobalt(III) Complexes with Iodine

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Contribution of the electron-transfer processes in the cleavage of cobalt-carbon bonds of alkylcobalt(III) complexes *cis*-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$; bpy = 2,2′-bipyridine), *trans*-$[Me_2Co(DpnH)]$ (DpnH = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-1-olate), and $[RCo(DH)_2py]$ (R = Me, Et, $PhCH_2$; $(DH)_2$ = bis(dimethylglyoximato); py = pyridine) with iodine has been studied by detecting the products that could arise only via electron-transfer processes as well as by the kinetic comparison between the electrophilic reactions of iodine with alkylcobalt(III) complexes and the electron-transfer reactions of iodine with ferrocene derivatives in acetonitrile. The coupling products of alkyl groups of dialkylcobalt(III) complexes, derived from the corresponding dialkylcobalt(IV) complexes, are obtained in the cleavage reactions of dialkylcobalt(III) complexes with iodine, with alkyl iodides being the main products. The observed second-order rate constants for the cleavage reactions of alkylcobalt(III) complexes with iodine in acetonitrile at 298 K are compared with those of electron transfer from ferrocene derivatives to iodine, based on the Marcus theory of electron transfer.

Introduction

The mechanisms for electrophilic cleavage of cobalt-carbon bonds have been of considerable interest owning to the importance in understanding the enzymatic cleavage of those bonds.[2,3] The cleavage of the cobalt-carbon bond by electrophiles, which generally leads to the alkylation of attacking electrophiles, has generally been considered as a direct displacement of the cobalt atom by the attack of electrophiles at the α-carbon.[4-8] Recently some electrophilic cleavage reactions of cobalt-carbon bonds have been reconsidered as proceeding via electron-transfer processes.[9-11] However, it is often difficult to distinguish between these two mechanisms unless attempts are made to identify the products that could arise only via intermediates produced by electron-transfer processes. In this context, Fanchiang[12a] has recently reported the formation of CH_3Cl in the demethylation of methylcobalamin (CH_3-B_{12}) by iodine performed in the presence of Cl^-, suggesting that the CH_3Co^{IV} complex, formed by electron transfer from CH_3-B_{12} to I_2, is quenched by Cl^- to yield CH_3Cl instead of CH_3I. More direct evidence for the involvement of alkylcobalt(IV) complexes may be obtained by using *cis*-dialkylcobalt(III) complexes, *cis*-$[R_2Co(bpy)_2]^+$ (R = Me, Et; bpy = 2,2′-bipyridine), since the corresponding *cis*-dialkylcobalt(IV) complexes are known to be subjected to the unique reductive elimination of the alkyl groups to yield the coupling products R-R exclusively (eq 1).[13] Thus, the alkyl coupling products of *cis*-dialkylcobalt(III) complexes in the electrophilic cleavage of the cobalt-carbon bonds with iodine may be used as a nice probe to investigate the contribution of electron-transfer processes.

$$cis\text{-}[R_2Co(bpy)_2]^+ \xrightarrow{-e^-} R\text{-}R + [Co(bpy)_2]^{2+} \tag{1}$$

In this work,[14] we report evidence for the contribution of electron-transfer processes in the cleavage of cobalt-carbon bonds of dialkylcobalt(III) complexes with iodine by identifying the alkyl coupling products that could arise only via dialkylcobalt(IV) complexes. The degree of the contribution of electron-transfer processes is evaluated by the kinetic comparison between the cleavage reactions of various alkylcobalt(III) complexes with iodine and the electron-transfer reactions of ferrocene derivatives with iodine in acetonitrile (MeCN) using the Marcus theory of electron transfer.[15]

Experimental Section

Materials. Alkylcobalt(III) complexes *cis*-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, $PhCH_2$),[13,16] *trans*-$[Me_2Co(DpnH)]$,[17-19] and $[RCo(DH)_2py]$ (R = Me, Et, $PhCH_2$)[20] were prepared as described previously. The purity of the complexes was checked by elemental analysis. Anal. Calcd for $C_{22}H_{22}N_4O_4CoCl$ (*cis*-$[Me_2Co(bpy)_2]ClO_4$): C, 52.8; H, 4.4; N, 11.2. Found: C, 52.7; H, 4.6; N, 11.1. Anal. Calcd for $C_{24}H_{28}N_4O_4CoCl$ (*cis*-$[Et_2Co(bpy)_2]ClO_4$): C, 52.7; H, 5.2; N, 10.2. Found: C, 52.1; H, 5.1; N, 10.0. Anal. Calcd for $C_{34}H_{30}N_4O_4CoCl$ (*cis*-$[(PhCH_2)_2Co(bpy)_2]ClO_4$): C, 63.0; H, 4.7; N, 8.7. Found: C, 62.0; H, 4.6; N, 8.5. Anal. Calcd for $C_{13}H_{25}N_4O_2Co$ (*trans*-$[Me_2Co(DpnH)]$): C, 47.6; H, 7.7; N, 17.1. Found: C, 47.5; H, 7.7; N, 17.0. Anal. Calcd for $C_{14}H_{22}N_5O_4Co$ ($[MeCo(DH)_2py]$): C, 43.9; H, 5.8; N, 18.3. Found: C, 43.8; H, 5.8; N, 18.3. Anal. Calcd for $C_{15}H_{24}N_5O_4Co$ ([EtCo-

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Table I. Products Obtained by the One-Electron Oxidation of *cis*-$[R_2Co(bpy)_2]^+$ by $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ in the Absence and Presence of Oxygen in MeCN ($0.60\ cm^3$) at 298 K

cis-$[R_2Co(bpy)_2]^+$		oxidants and amt, 10^{-5} mol		products (yield,[a] %)
R	amt, 10^{-5} mol			
		O_2	$[Fe(bpy)_3]^{3+}$	
Me	2.1	0	94	C_2H_6 (100);[b] CH_4 (trace)
		O_2	$[Fe(phen)_3]^{3+}$	
	0.38	0	2.0	C_2H_6 (100);[b] CH_4 (trace)
	2.1	6.9	94	C_2H_6 (100); CH_4 (trace)
		O_2	$[Fe(bpy)_3]^{3+}$	
Et	2.0	0	94	C_4H_{10} (100);[b] C_2H_6 (trace); C_2H_4 (trace)
		O_2	$[Fe(phen)_3]^{3+}$	
	0.38	0	2.0	C_4H_{10} (98);[b] C_2H_6 (trace); C_2H_4 (trace)
	2.0	6.9	94	C_4H_{10} (100); C_2H_6 (trace); C_2H_4 (trace)
		O_2	$[Fe(phen)_3]^{3+}$	
$PhCH_2$	2.4	0	94	PhC_2H_4Ph (98);[b] $PhCH_3$ (trace)
	2.4	6.9	94	PhCHO (99); $PhCH_2O_2H$ (trace)

[a] Based on the amount of *cis*-$[R_2Co(bpy)_2]^+$. [b] Reference 13.

$(DH)_2py]$): C, 45.4; H, 6.1; N, 17.6. Found: C, 45.2; H, 6.0; N, 17.8. Ferrocene derivatives ferrocene, butylferrocene, amylferrocene, *tert*-amylferrocene, 1,1′-dimethylferrocene, and 1,1′-dibutylferrocene were obtained commercially and purified by sublimation or recrystallization from ethanol. Iodine was purified by vacuum sublimation three times. Bromine was refluxed and distilled with solid KBr, dried by shaking with an equal volume of concentrated H_2SO_4, and then distilled after the separation from H_2SO_4.[21] Reagent grade acetonitrile was purified by the standard procedure,[21] followed by redistillation from calcium hydride. Acetonitrile-d_3 was stirred with freshly activated molecular sieve 4A (Wako Pure Chemicals) and then transferred under vacuum into a dry, glass-stoppered bottle. Other reagents used for the product analyses were obtained commercially.

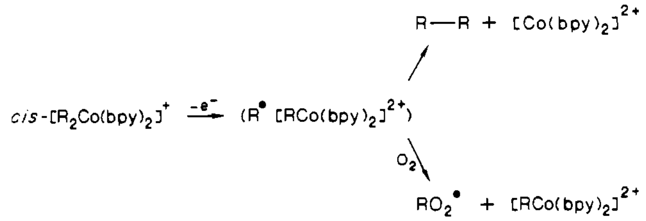
Product Analysis. Typically, iodine (30 μmol) was added to an NMR tube that contained an acetonitrile-d_3 ($0.5\ cm^3$) solution of the alkylcobalt(III) complex (30 μmol). The cleavage reaction of cobalt–carbon bond of the alkylcobalt(III) complex was monitored by using a Japan Electron Optics JNM-PS-100 ^1H NMR spectrometer (100 MHz). After completion of the reaction, the products were analyzed also by GLC using a Unibeads 1-S or a Gaskropak 54 column.

Stoichiometry. Spectral titrations were carried out by adding known quantities of a stock solution of iodine to a quartz cuvette containing a known aliquot of the alkylcobalt(III) complexes or ferrocene derivatives. After the reaction was complete, the electronic absorption spectrum was measured by using a Union SM-401 spectrophotometer. The amount of the triiodide ion (I_3^-) determined from the absorption band at $\lambda_{max} = 361$ nm ($\epsilon = 2.50 \times 10^4\ M^{-1}\ cm^{-1}$),[22] which was much more intense than those of the other absorbing species present in the solution, were plotted against the amount of I_2 added.

Kinetic Measurements. Kinetic measurements were carried out by using a Union-RA-103 stopped-flow spectrophotometer and a Union SM-401 spectrophotometer for the cleavage reactions of the cobalt–carbon bond of alkylcobalt(III) complexes with iodine or the electron-transfer reactions of ferrocene derivatives with iodine under deaerated conditions with half-lives of shorter than 10 s and longer than 10 s, respectively. The rates in MeCN at 298 K were determined by the increase in the absorbances at λ_{max} of the triiodide ion. All the kinetic measurements were carried out under pseudo-first-order conditions where the concentrations of iodine were maintained at >10-fold excess of the concentration of alkylcobalt(III) complexes or ferrocene derivatives. Pseudo-first-order plots for the reaction of iodine with alkylcobalt(III) complexes and ferrocene derivatives in MeCN were linear for more than 5 half-lives and the pseudo-first-order rate constants were determined by the least-squares curve fit, using a Union System 77 or NEC 9801 VM2 microcomputer.

Cyclic Voltammetry. Redox potentials of alkylcobalt(III) complexes and ferrocene derivatives in MeCN were determined by cyclic voltammetry at various sweep rates (20–1000 mV s^{-1}). The cyclic voltammograms were recorded on a Hokuto Denko model HA-301 potentiostat/galvanostat at 298 K using a platinum microelectrode and a standard NaCl calomel reference electrode (SCE) under deaerated conditions. The platinum microelectrode was routinely cleaned by soaking it in concentrated nitric acid, followed by repeated rinsing with water and acetone, and dried at 353 K prior to use. The anodic peak potential of alkylcobalt(III) complexes at a constant sweep rate was reproducible within ±20 mV. Little deterioration of the electrode was observed upon repeated scans, indicating that anodic oxidation leads to products without fouling of the electrode surface.

Scheme I



The redox potentials of ferrocene derivatives and $[RCo(DH)_2py]$ were determined as the average of anodic and cathodic peak potentials, since their electrochemical oxidation proceeds by reversible one-electron processes. In contrast, the anodic oxidation of dialkylcobalt(III) complexes was highly irreversible as characterized by the cyclic voltammogram, which showed an anodic wave with a well-defined current maximum but no coupled cathodic wave on the reverse scan even at sweep rates up to 1000 mV s^{-1}. A method of determining redox potentials in such irreversible systems, which has been reported to obtain the standard one-electron oxidation potentials of *cis*-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et)[13] based on the Marcus free energy relationship for electron-transfer reactions,[15,23] was applied to determine the value for *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ in MeCN at 298 K.

Results and Discussion

Cleavage Modes of Cobalt–Carbon Bonds upon the One-Electron Oxidation of Dialkylcobalt(III) Complexes. The modes for cleavage of cobalt–carbon bonds of alkylcobalt(IV) complexes are examined by determining the cleaved products in electron-transfer reactions from dialkylcobalt(III) complexes to strong one-electron oxidants such as $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) in the absence and presence of oxygen (Table I). In the case of *cis*-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$), the one-electron oxidation with $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ under deaerated conditions yields exclusively the coupling products of the alkyl groups.[13] When the one-electron oxidation of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ is carried out in the presence of oxygen, PhCHO is obtained instead of the coupling product, PhC_2H_4Ph. However, the same coupling products are obtained in the case of R = Me and Et in the absence and presence of oxygen. Such effects of oxygen on the one-electron oxidation of *cis*-$[R_2Co(bpy)_2]^+$ may be explained by Scheme I, where the cleavage of the two cobalt–carbon bonds upon the one-electron oxidation occurs in a stepwise manner. Namely, the one-electron oxidation of *cis*-$[R_2Co(bpy)_2]^+$ results in the cleavage of the one cobalt–carbon bond, followed by the reaction of the resulting alkyl radical with $[RCo(bpy)_2]^{2+}$ in the cage to yield the coupling product, R–R.

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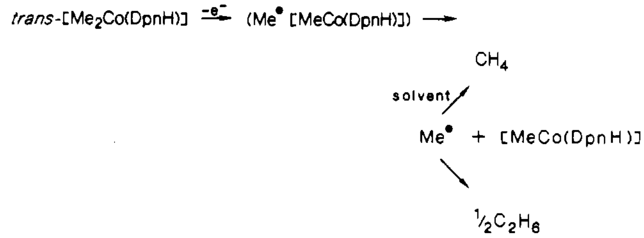
Scheme II



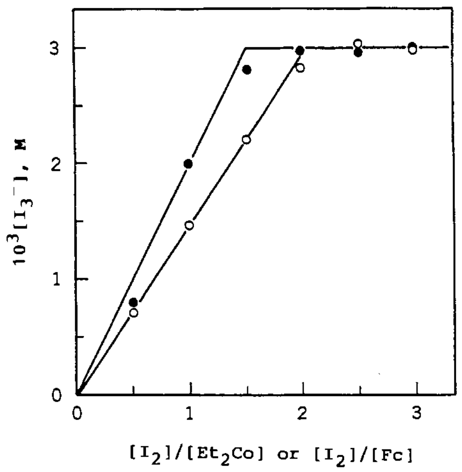


Figure 1. Plots of the concentration of triiodide ion, $[I_3^-]$, formed by the cleavage reaction of cobalt–carbon bond of *cis*-$[Et_2Co(bpy)_2]^+$ (Et_2Co) with iodine (○), and by the electron-transfer reaction from 1,1′-dimethylferrocene (Fc) to iodine (●) in MeCN vs the ratio of iodine to Et_2Co, $[I_2]/[Et_2Co]$, and the ratio of iodine to Fc, $[I_2]/[Fc]$, respectively.

In the case of R = $PhCH_2$, the benzyl radical formed by the initial cleavage of the cobalt–benzyl bond upon the one-electron oxidation may be stable enough to be trapped by oxygen to give the benzylperoxyl radical ($PhCH_2O_2^\bullet$), which may be further oxidized to yield benzaldehyde (PhCHO).[24,25]

The one-electron oxidation of *trans*-$[Me_2Co(DpnH)]$ is also known to result in the cleavage of the one cobalt–carbon bond to give methyl radical and $[MeCo(DpnH)]$.[17,23] In this case, however, the reaction of methyl radical with another cobalt–methyl bond may be disfavored, compared with the case of *cis*-$[R_2Co(bpy)_2]^+$, because of the trans configuration, and thereby methyl radical may diffuse outside of the cage to yield methane and ethane by the hydrogen abstraction from solvent and the radical coupling reaction, respectively (Scheme II).[17,23]

Electron-Transfer Processes in the Reactions of Alkylcobalt(III) Complexes with Iodine. All alkylcobalt(III) complexes react readily with iodine in MeCN to yield mainly alkyl iodide, cobalt(III) complexes, and triiodide ion. The stoichiometry of the cleavage reaction of cobalt-carbon bonds of alkylcobalt(III) complexes with iodine (Figure 1) is given by eq 2. This 1:2

$$RCo^{III} + 2I_2 \rightarrow RI + Co^{3+} + I_3^- \quad (2)$$

stoichiometry indicates that the cleavage of the cobalt–carbon bond of alkylcobalt(III) complexes by iodine occurs to yield RI and I^- (eq 3), the latter of which reacts further with excess I_2 to

$$RCo^{III} + I_2 \rightarrow RI + Co^{3+} + I^- \quad (3)$$

$$I^- + I_2 \rightarrow I_3^- \quad (4)$$

Table II. Product Yields in the Reactions of Alkylcobalt(III) Complexes (4.0×10^{-2} M) with Halogen ($[X_2] = 4.0 \times 10^{-2}$ M) in MeCN at 298 K

alkylcobalt(III) complex	X_2	products (yield,[a] %)
cis-$[Me_2Co(bpy)_2]^+$	I_2	CH_3I (99); CH_4 (trace); C_2H_6 (0.60)
cis-$[Me_2Co(bpy)_2]^+$	Br_2	CH_3Br (99); CH_4 (trace); C_2H_6 (0.24)
cis-$[Et_2Co(bpy)_2]^+$	I_2	C_2H_5I (97); C_2H_6 (trace); C_2H_4 (trace); C_4H_{10} (3.2)
cis-$[Et_2Co(bpy)_2]^+$	Br_2	C_2H_5Br (97); C_2H_6 (trace); C_4H_{10} (3.8)
cis-$[(PhCH_2)_2Co(bpy)_2]^+$	I_2	$PhCH_2I$ (100)
cis-$[(PhCH_2)_2Co(bpy)_2]^+$	Br_2	$PhCH_2Br$ (100)
trans-$[Me_2Co(DpnH)]$	I_2	CH_3I (99); CH_4 (0.34); C_2H_6 (0.06)
trans-$[Me_2Co(DpnH)]$	Br_2	CH_3Br (99); CH_4 (0.15); C_2H_6 (trace)
$[MeCo(DH)_2py]$	I_2	CH_3I (100)
$[EtCo(DH)_2py]$	I_2	C_2H_5I (100)

[a] Based on the amount of the alkylcobalt(III) complex.

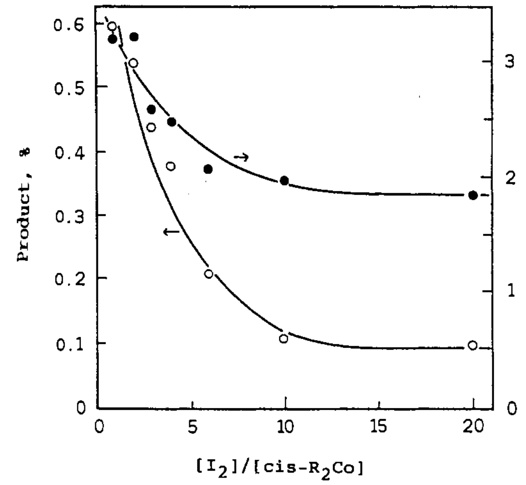


Figure 2. Plots of the gaseous products produced by the reaction of *cis*-$[R_2Co(bpy)_2]^+$ (*cis*-R_2Co) with iodine in MeCN vs the ratio of iodine to *cis*-R_2Co: R = Me, ethane (○); R = Et, butane (●).

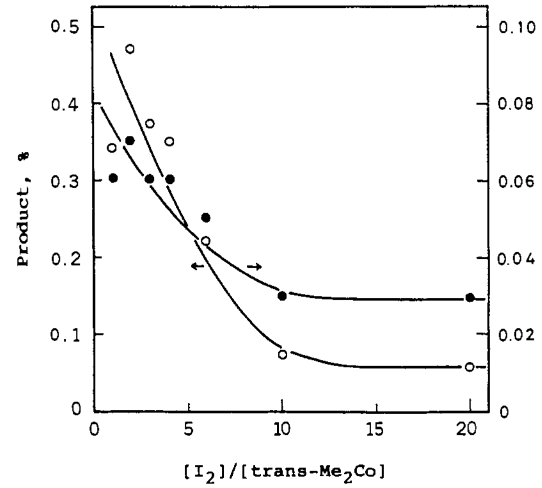


Figure 3. Plots of the gaseous products produced by the reaction of *trans*-$[Me_2Co(DpnH)]$ (*trans*-Me_2Co) with iodine in MeCN vs the ratio of iodine to *trans*-Me_2Co: methane (○); ethane (●).

produce I_3^- (eq 4).[26] In the case of *cis*-$[R_2Co(bpy)_2]^+$ (R = Me, Et) and *trans*-$[Me_2Co(DpnH)]$, minor gaseous products are produced in the cleavage of cobalt–carbon bonds with iodine as well as bromine. The yields are listed in Table II, where the main gaseous products from *cis*-$[R_2Co(bpy)_2]^+$ are the coupling products of the alkyl groups, i.e., ethane and butane for R = Me and Et, respectively, while *trans*-$[Me_2Co(DpnH)]$ yields more methane than the coupling product, ethane. In the case of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, however, the cleavage of the cobalt–carbon bonds with iodine and bromide yields only $PhCH_2I$ and $PhCH_2Br$,

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[24] Benzylperoxyl radical ($PhCH_2O_2^\bullet$) may decay by the bimolecular reaction to yield benzaldehyde, benzyl alcohol, and oxygen, or by the hydrogen abstraction from a solvent to produce benzyl hydroperoxide ($PhCH_2O_2H$). In fact, the homolysis of benzylcobalamin in the presence of oxygen has been reported to yield benzaldehyde and benzyl alcohol.[25] The absence of benzyl alcohol in the present case (Table I) may be ascribed to the further oxidation of benzyl alcohol by a strong oxidant, $[Fe(phen)_3]^{3+}$ or $[Fe(bpy)_3]^{3+}$.

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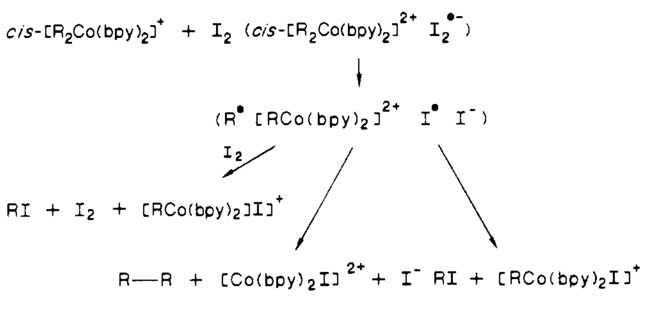
Scheme III



respectively (Table I). No gaseous products have been observed in the case of monoalkylcobalt(III) complexes, [RCo(DH)$_2$py] (R = Me, Et). With increasing mole ratio of iodine to cis-[R$_2$Co(bpy)$_2$]$^+$ (R = Me, Et), the yields of R–R decrease as shown in Figure 2. Similarly, the yields of methane and ethane decrease with an increase in the mole ratio of I$_2$ to $trans$-[Me$_2$Co(DpnH)] as shown in Figure 3.

The formation of the coupling products of alkyl groups of cis-[R$_2$Co(bpy)$_2$]$^+$ demonstrates clearly the involvement of an electron-transfer process in the cleavage of the cobalt–carbon bonds with iodine and bromine. Although the apparent quantities of the coupling products are small (Table II), the product distribution dependence on the alkyl group as well as the dependence on the excess I$_2$ concentration (Figures 2 and 3) suggests that the electron-transfer process is the main pathway for the cleavage of the cobalt–carbon bond as discussed below. As shown in Scheme III, electron transfer from cis-[R$_2$Co(bpy)$_2$]$^+$ to I$_2$ occurs to give the radical ion pair in which one cobalt–carbon bond of cis-[R$_2$Co(bpy)$_2$]$^{2+}$ as well as the I–I bond of I$_2^{\bullet-}$ is cleaved readily to produce the radical pair (R$^\bullet$ [RCo(bpy)$_2$]$^{2+}$ I$^\bullet$ I$^-$). In the case of R = Me and Et, the facile reaction of R$^\bullet$ with [RCo(bpy)$_2$]$^{2+}$ may give the coupling product R–R in competition with the radical coupling between R$^\bullet$ and I$^\bullet$ in the cage to yield RI (Scheme III). In the presence of excess I$_2$, the formation of the coupling product may be suppressed by the radical trap by I$_2$ to yield RI and I$^\bullet$,[27] the latter of which combines with I$^\bullet$ to regenerate I$_2$. In the case of R = PhCH$_2$, the reaction of PhCH$_2^\bullet$ with [PhCH$_2$Co(bpy)$_2$]$^{2+}$ to yield PhC$_2$H$_4$Ph may be too slow to compete with the radical coupling reaction between PhCH$_2^\bullet$ and I$^\bullet$, where benzyl iodide becomes the sole product, since the reaction of PhCH$_2^\bullet$ with [PhCH$_2$Co(bpy)$_2$]$^{2+}$ may be much slower than the corresponding reactions for R = Me and Et, judging from the effect of oxygen on the one-electron oxidation of cis-[R$_2$Co(bpy)$_2$]$^+$ (Scheme I).[28]

In the case of $trans$-[Me$_2$Co(DpnH)], the reaction of Me$^\bullet$ with [MeCo(DpnH)]$^+$ in the cage may be disfavored geometrically, compared with the case of cis-[R$_2$Co(bpy)$_2$]$^+$, and thereby, a free radical (Me$^\bullet$) escapes from the cage to yield methane and ethane (Scheme II) in competition with the radical coupling between Me$^\bullet$ and I$^\bullet$ in the cage to yield MeI. The escaped Me$^\bullet$ radical may be trapped by I$_2$ as shown in Scheme III for the case of cis-[R$_2$Co(bpy)$_2$]$^+$, and thus the yields of methane and ethane decrease with an increase in the mole ratio of I$_2$ to $trans$-[Me$_2$Co(DpnH)] as observed in Figure 3.

At this stage, however, the possibility of a competition between the one electron-transfer process (Scheme III) and the direct displacement of the cobalt atom by the attack of iodine at the α-carbon cannot be ruled out. Thus, in order to evaluate the degree of contribution of the electron-transfer processes (Scheme III) quantitatively, we have performed a kinetic comparison between the cleavage reactions of alkylcobalt(III) complexes with iodine and the electron-transfer reactions of ferrocene derivatives with iodine in MeCN at 298 K with the aid of the Marcus theory of electron transfer.

Table III. Observed Second-Order Rate Constants (k_{obs}) for Cleavage Reactions of Alkylcobalt(III) Complexes with Iodide in MeCN at 298 K, the One-Electron-Oxidation Potentials (E°_{ox} vs SCE) of Alkylcobalt(III) Complexes, and the Calculated Rate Constants (k_{calc}) for the Corresponding Electron-Transfer Reactions Based on the Marcus Theory

alkylcobalt(III) complex	E°_{ox}, V	k_{obs}, M^{-1} s^{-1}	k_{calc},[a] M^{-1} s^{-1}
cis-[Me$_2$Co(bpy)$_2$]$^+$	0.63[b]	2.4×10^4	8.8×10^2
cis-[Et$_2$Co(bpy)$_2$]$^+$	0.57[b]	1.2×10^4	5.0×10^3
cis-[(PhCH$_2$)$_2$Co(bpy)$_2$]$^+$	0.60	1.2×10^4	2.1×10^3
$trans$-[Me$_2$Co(DpnH)]	0.53[c]	2.5×10^6	4.1×10^2
[MeCo(DH)$_2$py]	0.88	3.1×10^{-2}	2.2×10^{-2}
[EtCo(DH)$_2$py]	0.82	2.7×10^{-1}	1.3×10^{-1}

[a] Calculated by using eq 11–13; see text. The k_{11} values are taken from ref 13, 23a, and 38. The k_{22} value is taken from ref 37. [b] Reference 13. [c] Reference 23a.

Kinetic Comparison between Cleavage Reactions of Cobalt–Carbon Bonds with Iodine and Electron-Transfer Reactions from Ferrocene Derivatives to Iodine. The rates of the cleavage reactions of alkylcobalt(III) complexes with iodine in MeCN at 298 K were monitored by the increase in the absorbance at λ_{max} (=361 nm) of the triiodide ion. The rate of formation of I$_3^-$ obeyed the pseudo-first-order kinetics in the presence of a large excess of I$_2$, and the pseudo-first-order rate constant is proportional to the I$_2$ concentration as shown in Figure 4. Thus, the rate can be expressed in terms of the clean second-order kinetics, showing a first-order dependence on the concentration of each reactant (eq 5), although the rates of reactions of halogen often include a

$$d[I_3^-]/dt = k_{obs}[RCo^{III}][I_2] \qquad (5)$$

second-order term in the halogen concentration.[29] The observed second-order rate constants k_{obs} were determined from 4–20 rate measurements to give average deviations from the mean values within ±5%, and the k_{obs} values are listed in Table III, together with the redox potentials of the alkylcobalt(III) complexes (see the Experimental Section).[13]

Ferrocene and its derivatives (Fc) are also oxidized readily to the corresponding ferrocenium ions (Fc$^+$), and the stoichiometry of the electron-transfer reaction (eq 6) has been determined from

$$2Fc + 3I_2 \rightarrow 2Fc^+ + 2I_3^- \qquad (6)$$

the spectroscopic measurements of the concentration of ferrocenium ion produced by changing the mole ratio of Fc to I$_2$ as shown in Figure 1. Such a stoichiometry indicates that the electron-transfer from Fc to I$_2$ occurs to give Fc$^+$ (eq 7) and I$_2^{\bullet-}$, the latter

$$Fc + I_2 \xrightarrow{k_{obs}} Fc^+ + I_2^{\bullet-} \qquad (7)$$

$$I_2^{\bullet-} \rightarrow I^\bullet + I^- \qquad (8)$$

$$Fc + I^\bullet \rightarrow Fc^+ + I^- \qquad (9)$$

of which is known to dissociate to produce I$^\bullet$ and I$^-$ (eq 8),[30,31] followed by the facile second electron-transfer reaction from Fc to I$^\bullet$ (eq 9).[32] The iodide ion reacts with excess I$_2$ to yield I$_3^-$ (eq 4).

The rate of formation of I$_3^-$ can also be expressed in terms of the second-order kinetics, showing a first-order dependence on the concentration of each reactant (eq 10) as shown in Figure 4.

$$d[I_3^-]/dt = k_{obs}[Fc][I_2] \qquad (10)$$

The observed second-order constants k_{obs} were determined from 10–20 rate measurements to give average deviations from the mean

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(27) The reaction of R$^\bullet$ with I$_2$ has been reported to occur with the diffusion-controlled rate; see: (a) Foldiak, G.; Schuler, R. H. *J. Phys. Chem.* **1978**, *82*, 2756. (b) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 2654.

(28) Only benzyl radical has a sufficient lifetime to be trapped by oxygen before the reaction with [PhCH$_2$Co(bpy)$_2$]$^{2+}$ to yield benzaldehyde.

(29) (a) Gielen, M. *Acc. Chem. Res.* **1973**, *6*, 198. (b) Fukuzumi, S.; Kochi, J. K. *Int. J. Chem. Kinet.* **1983**, *15*, 249. (c) Taylor, R. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tiffer, C. F. H., Ed., Elsevier: Amsterdam, 1972, Vol. 13.

(30) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1980**, *84*, 608.

(31) Ross, A. B.; Neta, P. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1979**, *NSRDS-NBS 65*, 42.

(32) The second electron transfer from Fc to I$^\bullet$ may be much faster than the initial electron transfer from Fc to I$_2$, since the electron affinity of I$^\bullet$ is 1.5 eV larger than that of I$_2$.[30]

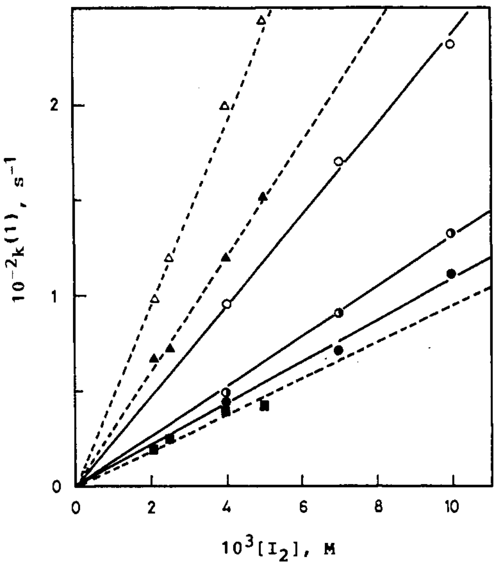


Figure 4. Plots of the observed first-order rate constants, $k^{(1)}$, for the cleavage reactions of alkylcobalt(III) complexes with iodine (—) and electron-transfer reactions from ferrocene derivatives to iodine (- - -) in MeCN at 298 K vs the concentration of iodine: *cis*-$[Me_2Co(bpy)_2]^+$ (○); *cis*-$[Et_2Co(bpy)_2]^+$ (◑); *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (●); butylferrocene (△); *tert*-amylferrocene (▲); ferrocene (■).

values within ±5%, and the k_{obs} values are listed in Table IV, together with the one-electron-oxidation potentials of the ferrocene derivatives.

A quantitative comparison between the cleavage of the cobalt–carbon bonds with I_2 and the electron-transfer reactions from Fc to I_2 can be achieved by comparing the k_{obs} values with those predicted by the Marcus theory for the rates of outer-sphere electron-transfer reactions.[15] The Marcus relation for the rate constant of electron transfer from a reductant (**1**) to an oxidant (**2**), k_{12}, is given by eq 11,[15] where k_{11} and k_{22} are the rate constants

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad (11)$$

for the corresponding self-exchanges of **1** and **2**, and K_{12} is the equilibrium constant for the electron-transfer reaction. The K_{12} value is obtained from the one-electron oxidation potential of the reductant (**1**), $E°_{ox}$, and the one-electron reduction potential of the oxidant (**2**), $E°_{red}$, by using eq 12, where w_p is the work term

$$\log K_{12} = (-2.3RT/F)(E°_{ox} - E°_{red} + w_p) \qquad (12)$$

required to bring the products together to the mean separation in the activation complex.[33-35] The parameter f in eq 11 is given by eq 13, in which Z, the frequency factor, is taken as 10^{11} M^{-1}

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (13)$$

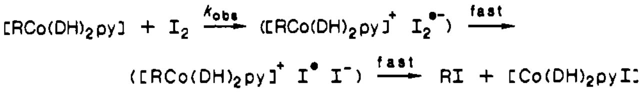
s^{-1}.[15] The reported values of self-exchange rate constants for Fc/Fc^+ ($k_{11} = 5.3 \times 10^6$ M^{-1} s^{-1})[36] and $I_2/I_2^{\bullet-}$ ($k_{22} = 8.5 \times 10^4$ M^{-1} s^{-1})[37] together with the equilibrium constant K_{12}, obtained from the one-electron oxidation potentials of Fc (Table IV), and the one-electron reduction potential of I_2 ($E°_{red} = 0.19$ V vs SCE)[36] constitute a satisfactory basis for accounting for the k_{obs} values in light of the Marcus relation, eq 11–13. The calculated electron-transfer rate constants ($k_{calc} = k_{12}$ in eq 11) are also listed in Table IV, where k_{obs} values agree well with the k_{calc} values. Such agreement indicates that the electron transfer from Fc to I_2 proceeds by an outer-sphere mechanism.

Table IV. Observed Second-Order Rate Constants (k_{obs}) for Electron-Transfer Reactions from Ferrocene Derivatives to Iodine in MeCN at 298 K, the One-Electron Oxidation Potentials of Ferrocene Derivatives ($E°_{ox}$ vs SCE), and the Corresponding Calculated Rate Constants (k_{calc}) Based on the Marcus Theory

ferrocene deriv	$E°_{ox}$, V	k_{obs}, M^{-1} s^{-1}	k_{calc},[a] M^{-1} s^{-1}
1,1′-dibutylferrocene	0.25	1.7×10^5	3.0×10^5
1,1′-dimethylferrocene	0.26	1.5×10^5	2.5×10^5
butylferrocene	0.31	4.6×10^4	8.9×10^4
amylferrocene	0.32	3.2×10^4	7.2×10^4
tert-amylferrocene	0.33	3.1×10^4	5.8×10^4
ferrocene	0.37	9.4×10^3	2.4×10^4

[a] Calculated by using eq 11–13; see text. All the k_{11} values are assumed to be the same as the value for ferrocene,[36] and the k_{22} value is taken from ref 37.

Scheme IV


$$[RCo(DH)_2py] + I_2 \xrightarrow{k_{obs}} ([RCo(DH)_2py]^+ \; I_2^{\bullet-}) \xrightarrow{fast} ([RCo(DH)_2py]^+ \; I^\bullet \; I^-) \xrightarrow{fast} RI + [Co(DH)_2pyI]$$

Similarly, the rate constants of electron transfer from alkylcobalt(III) complexes to I_2 can be calculated from the reported k_{11} values of alkylcobalt(III) complexes[13,38] and the one-electron-oxidation potentials in Table III by using eq 11–13. The calculated values (k_{calc}) are also listed in Table III, where the k_{obs} values of $[RCo(DH)_2py]$ (R = Me, Et) agree well with the corresponding k_{calc} values. Such agreement indicates that the rate-determining step for the cleavage of the cobalt–carbon bonds with I_2 is the electron transfer from $[RCo(DH)_2py]$ to I_2 as shown in Scheme IV. In contrast with the case of dialkylcobalt(IV) complexes, the $[RCo^{IV}(DH)_2py]^+$ complex is known to be rather stable,[39] and thus the cleavage of the cobalt–carbon bond may occur by the reaction with $I^\bullet$ in the cage to yield RI (Scheme IV).[40-42] In the case of dialkylcobalt(III) complexes, the k_{obs} values agree reasonably well with the corresponding k_{calc} value (Table III),[43] indicating that the electron-transfer process in Scheme III is the main pathway for the cleavage of the cobalt–carbon bonds with I_2, despite the small quantity of the coupling product of the alkyl group, derived from *cis*-$[R_2Co^{IV}(bpy)_2]^{2+}$. In the case of *trans*-$[Me_2Co(DpnH)]$, however, the k_{obs} value is significantly larger than the corresponding k_{calc} value (Table III).[44,45] Such a discrepancy between the observed and calculated values may indicate the contribution of an inner-sphere pathway for the electron-transfer process. At present, however, the contribution of the direct displacement of the cobalt atom by the attack of I_2 at the α-carbon[46] cannot be ruled out in such a case.

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(33) The work term for the reactants may be neglected since the reactants in the present case include neutral species. The importance of the work term for the charged species has been well documented.[34] In the present case, w_p is taken as –0.05 eV.[34,35]

(34) (a) Haim, A.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 476. (b) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416. (c) Adedinsewo, C. O.; Adegite, A. *Inorg. Chem.* **1979**, *18*, 3597.

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(36) Yang, E. S.; Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094.

(37) (a) Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2578. (b) Nord, G.; Pedersen, B.; Farver, O. *Ibid.* **1978**, *17*, 2233.

(38) Costa, G.; Puxeddu, A.; Tavagnacco, C.; Dreos-Garlatti, R. *Inorg. Chim. Acta* **1984**, *89*, 65.

(39) (a) Halpern, J.; Chan, M. S.; Hanson, J.; Roche, T. S.; Topich, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1606. (b) Halpern, J.; Topich, J.; Zamaraev, K. I. *Inorg. Chim. Acta* **1976**, *20*, L21.

(40) Alternatively, the nucleophilic attack of I^- may result in the cleavage of the cobalt–carbon bond to yield RI; see ref 41 and 42.

(41) (a) Vol'pin, M. E.; Levitin, I. Ya.; Sigan, A. L.; Halpern, J.; Tom, G. M. *Inorg. Chim. Acta* **1980**, *41*, 271. (b) Reisenhofer, E.; Costa, G. *Ibid.* **1981**, *49*, 121. (c) Levitin, I. Ya.; Sigan, A. L.; Vol'pin, M. E. *J. Organomet. Chem.* **1976**, *114*, C53.

(42) Magnuson, R. H.; Halpern, J.; Levitin, I. Ya.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1978**, 44.

(43) The agreement between the k_{obs} and k_{calc} values for *cis*-$[R_2Co(bpy)_2]^+$ is poorer than those for $[RCo(DH)_2py]$ probably because of the larger uncertainties in determining the $E°_{ox}$ values for the irreversible one-electron oxidation of *cis*-$[R_2Co(bpy)_2]^+$ than those for the reversible one-electron oxidation of $[RCo(DH)_2py]$.

(44) When the reported lowest limit of the k_{11} value of *trans*-$[Me_2Co(DpnH)]$ (the corresponding activation free energy is 2.1 kcal mol^{-1})[45] is used, the k_{calc} value is obtained as 1.0×10^4 M^{-1} s^{-1}, which is still 2.4×10^2 times smaller than the k_{obs} value.

(45) (a) Kochi, J. K. *Angew. Chem.* **1988**, *100*, 1331. (b) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5839.

(46) In this case, electron transfer may be viewed as occurring in concert with bond formation.