Photoredox Reactions of *cis*-Dialkylcobalt(III) Complexes with Benzyl and Allyl Bromides

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Received June 5, 1986

When the photolysis of an acetonitrile solution of *cis*-dialkylcobalt(III) complexes *cis*-$[R_2CO(bpy)_2]ClO_4$ (R = Me and Et; bpy = 2,2′-bipyridine) was carried out in the presence of benzyl or allyl bromide by using visible light, *cis*-$[R_2Co(bpy)_2]ClO_4$ reacted with approximately three equivalent amounts of benzyl or allyl bromide to yield mainly the homocoupling products 1,2-diphenylethane or 1,5-hexadiene as well as a small amount of the cross-coupling product between the alkyl group of *cis*-$[R_2Co(bpy)_2]ClO_4$ and the benzyl or allyl group of the bromide. On the other hand, in the photoredox reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]$ with benzyl or allyl bromide, *cis*-$[(PhCH_2)_2Co(bpy)_2]$ reacted with an equivalent amount of benzyl or allyl bromide to yield only the homocoupling product in the case of benzyl bromide or comparable amounts of the homocoupling and cross-coupling products in the case of allyl bromide. Reaction schemes of the photoredox reactions are discussed on the basis of ESR measurements to detect the reactive intermediates as well as the quantum yield measurements.

Introduction

Thermal cleavage of metal–carbon bonds of transition-metal alkyls has been studied extensively since it is one of the key steps in transition-metal-catalyzed carbon–carbon bond formation which provides an attractive synthetic use.[1-3] Although some transition-metal alkyls are thermally stable, cleavage of metal–carbon bonds are known to be induced by the redox reactions with organic and inorganic oxidants.[4-9] Photoinduced cleavage of metal–carbon bonds of transition-metal alkyls which are stable thermally is recently attracting growing attention,[10,11] and such reactions of monoalkylcobalt(III) complexes, coenzyme B_{12} models, have been subjected to detailed scrutiny.[12-16] However, very little is known of photoredox reactions of transition-metal alkyls with organic oxidants that are inactive in thermal reactions. A combination of photoactivation of the metal–carbon bonds and the redox reactions with organic oxidants, especially with organic halides, may have potential utility for the formation of carbon–carbon bonds from transition-metal alkyls and organic halides.

In this study,[17] we report the photoinduced cleavage of cobalt–carbon bonds of *cis*-dialkylcobalt(III) complexes *cis*-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, and $PhCH_2$; bpy = 2,2′-bipyridine) as well as the photoredox reactions of *cis*-$[R_2Co(bpy)_2]ClO_4$ with benzyl or allyl bromide, which do not react in the dark, resulting in carbon–carbon bond formation from *cis*-$[R_2Co(bpy)_2]ClO_4$ and benzyl or allyl bromide. The photoredox reactions of other alkylcobalt(III) complexes with benzyl bromide are also reported. In the present study, we have succeeded in detecting the reactive intermediates by ESR measurements at 77 K. These intermediates provide a basis for understanding the reaction mechanism for carbon–carbon bond formation in the photoredox reactions.

Experimental Section

Materials. Alkylcobalt(III) complexes *cis*-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, and $PhCH_2$),[9,18] *trans*-$[Me_2Co(DpnH)]$ (DpnH =

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11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-1-olate),[19] and [RCo(DH)$_2$py] (R = Me and Et; (DH)$_2$ = bis(dimethylglyoximato); py = pyridine)[20] were prepared as described previously. The purity of the complexes was checked by the elemental analysis. Anal. Calcd for $C_{22}H_{22}N_4O_4CoCl$ (*cis*-[Me$_2$Co(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$_2$Co(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$_2$)$_2$Co(bpy)$_2$]ClO$_4$): C, 63.0; H, 4.7; N, 8.7. Found: C, 62.0; H, 4.6; N, 8.5. Both [Co(bpy)$_3$](ClO$_4$)$_2$ and [Co(bpy)$_3$]ClO$_4$ were prepared by following the literature method.[21] Benzyl and allyl bromides obtained from Wako Pure Chemicals were treated with a 5% aqueous NaHCO$_3$ solution and water successively. After the mixture was dried with MgSO$_4$, it was fractionally distilled in the dark under reduced pressure before use. Potassium ferrioxalate used as an actinometer was prepared according to the literature[22] and purified by recrystallization from hot water. Reagent grade acetonitrile was purified by the standard procedure,[23] 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. Other reagents used for the product analyses were obtained commercially.

Photochemical Reactions of Alkylcobalt(III) Complexes. Typically, benzyl bromide (31 μmol) was added to an NMR tube that contained an acetonitrile-d_3 (0.5 cm^3) solution of *cis*-[R$_2$Co(bpy)$_2$]ClO$_4$ (31 μmol). After the reactant solution in the NMR tube was thoroughly degassed by repeated freeze–pump–thaw cycles, the NMR tube was sealed under vacuum and then irradiated with visible light from a Ushio Model U1-501 Xenon lamp through a Toshiba glass filter (0–36) which transmits light of $\lambda > 360$ nm. The photochemical reaction was monitored by using a Japan Electron Optics JNM-PS-100 ^{1}H NMR spectrometer (100 MHz). After completion of the reaction, the products were analyzed also by GLC. The photodecomposition of *cis*-[R$_2$Co(bpy)$_2$]ClO$_4$ in the absence of benzyl or allyl bromide was also monitored by ^{1}H NMR, and the gaseous products were analyzed by GLC using a Unibeads 1-S column (1 m).

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[22] was used for the quantum yield determination of the photochemical reactions of *cis*-[R$_2$Co(bpy)$_2$]ClO$_4$ with benzyl and allyl bromides in acetonitrile. Under the conditions of actinometry experiments, both the actinometer and *cis*-[R$_2$Co(bpy)$_2$]ClO$_4$ solutions absorbed essentially all the incident light through a Toshiba C-39A glass filter which transmits light of 350 nm < λ < 470 nm. The quantum yields of the photochemical reactions of *cis*-[R$_2$Co(bpy)$_2$]ClO$_4$ with benzyl and allyl bromides were determined from the rate of disappearance of the absorption band due to *cis*-[R$_2$Co(bpy)$_2$]ClO$_4$ in MeCN (λ_{max} = 472, 495, and 502 nm for R = Me, Et, and PhCH$_2$, respectively) under degassed conditions by using a Schlenk tube equipped with a side arm fused to a square quartz cuvette (1- or 10-mm i.d.).

Electron Spin Resonance Measurements. Benzyl or allyl bromide was added to a quartz ESR tube that contained an MeCN solution of *cis*-[R$_2$Co(bpy)$_2$]ClO$_4$, and the ESR tube was thoroughly degassed by the repeated freeze–pump–thaw cycles before sealing. The ESR tube was then placed in a transparent Dewar which was maintained at 77 K and irradiated with visible light of $\lambda > 360$ nm. The ESR measurements were carried out by using a JEOL X-band spectrometer (JES-ME-2X). The g value and the hyperfine splitting constant (hfs) of the ESR spectra were calibrated by using an Mn^{2+} ESR marker. The spin concentration was determined by double integration of the ESR signals with 1,1′-diphenyl-2-picrylhydrazyl (DPPH) as a calibrant (±20%). The relative spin concentrations measured at various times of irradiation were readily determined to within ±5%.

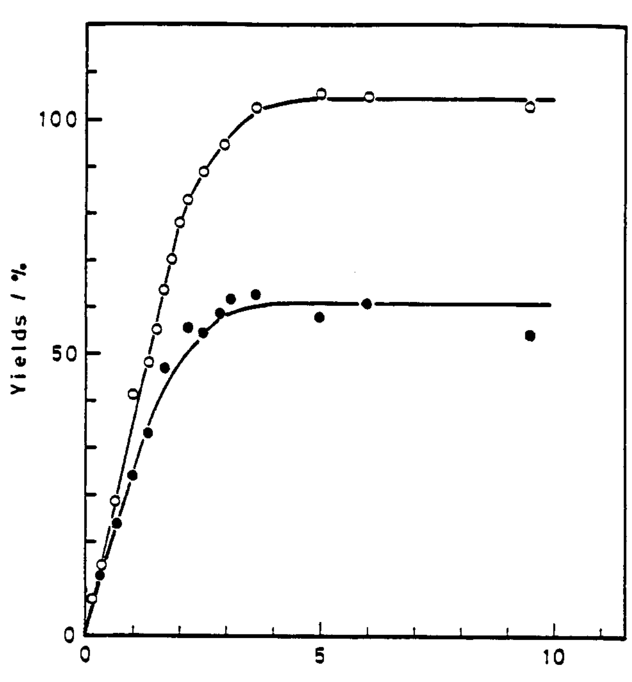

Figure 1. Yields of photodecomposition products of *cis*-[Et$_2$Co(bpy)$_2$]$^+$ (1.0 × 10^{-2} M) under an atmospheric pressure of oxygen in MeCN based on the cobalt complex plotted against the irradiation time: CH$_3$CHO (○) and C$_2$H$_4$ (●).

Results and Discussion

Photodecomposition of *cis*-[R$_2$Co(bpy)$_2$]ClO$_4$. The cobalt–carbon bond of *cis*-[Me$_2$Co(bpy)$_2$]ClO$_4$ was cleaved homolytically to produce methane and a small amount of ethane upon irradiation with visible light ($\lambda > 360$ nm) as shown by eq 1. In the photolysis of *cis*-[(PhCH$_2$)$_2$Co(bpy)$_2$]ClO$_4$, the cobalt–carbon bond was also cleaved homolytically, but the ratio of the coupling product of benzyl radicals (1,2-diphenylethane) to the product derived by the hydrogen abstraction from a solvent (toluene) increased significantly (eq 2), compared with the corresponding ratio of ethane to methane in the photolysis of *cis*-[Me$_2$Co(bpy)$_2$]ClO$_4$ (eq 1). Since the benzyl radical abstracts a hydrogen from a solvent at a much slower rate than the methyl radical,[24] the coupling process is much more favorable in the case of *cis*-[(PhCH$_2$)$_2$Co(bpy)$_2$]ClO$_4$ than [Me$_2$Co(bpy)$_2$]ClO$_4$.

$$\begin{array}{cccc} cis\text{-}[\mathrm{Me_2Co(bpy)_2}]^+ & \xrightarrow[15\ \mathrm{h}]{h\nu} & \mathrm{CH_4} + \mathrm{C_2H_6} & (1)\\ 1.0\times 10^{-2}\ \mathrm{M} & & 14 : 1 & \end{array}$$

$$\begin{array}{cccc} cis\text{-}[\mathrm{(PhCH_2)_2Co(bpy)_2}]^+ & \xrightarrow[50\ \mathrm{h}]{h\nu} & \mathrm{PhCH_3} + \mathrm{PhC_2H_4Ph} & \\ 4.5\times 10^{-2}\ \mathrm{M} & & 1 : 1 & (2) \end{array}$$

When an MeCN solution of *cis*-[Et$_2$Co(bpy)$_2$]$^+$ which has a β-hydrogen was irradiated with the visible light, ethane and ethylene were formed in a 2:1 ratio as well as a trace amount of butane (eq 3), indicating the involvement of a

$$\begin{array}{cccc} cis\text{-}[\mathrm{Et_2Co(bpy)_2}]^+ & \xrightarrow[8\ \mathrm{h}]{h\nu} & \mathrm{C_2H_6} + \mathrm{C_2H_4} + \mathrm{C_4H_{10}} & (3)\\ 1.0\times 10^{-2}\ \mathrm{M} & & 2 : 1 \quad \text{trace} & \end{array}$$

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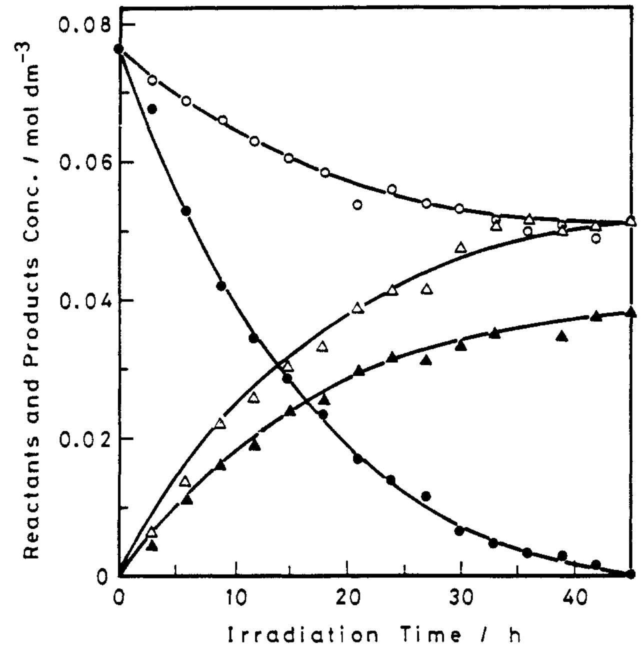

Figure 2. Time course of the photochemical reaction of *cis*-$[Me_2Co(bpy)_2]^+$ (7.7×10^{-2} M) with benzyl bromide (7.7×10^{-2} M) under a degassed condition in CD_3CN at 298 K: *cis*-$[Me_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), MeBr (△), and PhC_2H_4Ph (▲).

β-elimination pathway to yield ethane and ethylene in a 1:1 ratio (eq 4) besides a homolytic pathway to yield mainly

$$cis\text{-}[Et_2Co(bpy)_2]^+ \xrightarrow{h\nu} (C_2H_4\text{-}cis\text{-}[Et(H)Co(bpy)_2]^+) \rightarrow C_2H_4 + C_2H_6 + [Co(bpy)_2]^+ \quad (4)$$

ethane with a trace amount of the coupling product of ethyl radicals, i.e., butane. The product ratio of ethane to ethylene remained approximately constant throughout the irradiation. The involvement of a β-elimination pathway (eq 4) in addition to a homolytic pathway was confirmed by the photolysis of *cis*-$[Et_2Co(bpy)_2]^+$ under an atmospheric pressure of oxygen as shown in Figure 1. Thus, oxygen has essentially no effect on the formation of ethylene but can trap the ethyl radical to yield acetaldehyde as an oxidation product.[12d,25] The operation of a β-elimination pathway from a diethylcobalt(III) complex was reported also in the thermolysis of $[Et_2Co(acac)(PPhMe_2)_2]$ (acac = acetylacetonato).[1f] A cobalt-containing product was detected by monitoring the course of the photolysis in CD_3CN by ^1H NMR and characterized as $[Co(bpy)_3]^+$ by comparison with an authentic sample which was prepared by the reduction of $[Co(bpy)_3]^{2+}$ with $NaBH_4$.[21,26] The bis complex $[Co(bpy)_2]^+$ formed by the photoinduced β-elimination pathway (eq 4) may be converted to the tris complex, since thermodynamic considerations indicate that the tris complex is more stable than the mono- or bis(2,2′-bipyridine)cobalt(I) complexes.[27]

Photoredox Reactions of Alkylcobalt(III) Complexes with Benzyl and Allyl Bromides. When the photolysis of *cis*-$[Me_2Co(bpy)_2]^+$ is carried out in the presence of benzyl bromide under a degassed condition, formation of the gaseous products (methane and ethane) observed in the absence of benzyl bromide (eq 1) is suppressed completely. Instead, the coupling product from the benzyl group of benzyl bromide (i.e., 1,2-diphenylethane) is formed together with methyl bromide (Figure 2). The stoichiometry of the photochemical reaction is given by eq 5, where 1 mol of *cis*-$[Me_2Co(bpy)_2]^+$ reacts

$$cis\text{-}[Me_2Co(bpy)_2]^+ + 3PhCH_2Br \xrightarrow{h\nu} 2MeBr + {}^3/_2PhC_2H_4Ph + [Co(bpy)_2Br]^+ \quad (5)$$

with 3 mol of benzyl bromide.[28] Such a novel stoichiometry was observed also in the photoredox reactions of *cis*-$[Me_2Co(bpy)_2]^+$ with allyl bromide, where the coupling product from the allyl group of allyl bromide, i.e., 1,5-hexadiene, was formed as well as methyl bromide. Similarly, the photolysis of *cis*-$[Et_2Co(bpy)_2]^+$ in the presence of allyl bromide proceeds with a 1:3 stoichiometry to yield 1,5-hexadiene and ethyl bromide as shown in Figure 3, where it can be seen that after allyl bromide is consumed, photodecomposition of *cis*-$[Et_2Co(bpy)_2]^+$ starts to produce the gaseous products (ethane and ethylene) as observed in the absence of allyl bromide (eq 3). Thus, the presence of benzyl or allyl bromide changes the photoproducts derived from *cis*-$[R_2Co(bpy)_2]^+$ (R = Me and Et) from the gaseous products (methane, ethane, ethylene, etc.) in its absence to the corresponding alkyl bromide in the presence of benzyl or allyl bromide.

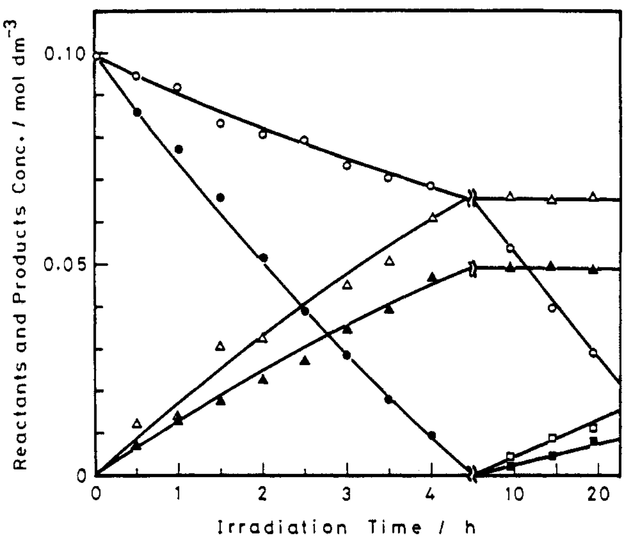

Figure 3. Time course of the photochemical reaction of *cis*-$[Et_2Co(bpy)_2]^+$ (9.9×10^{-2} M) with allyl bromide (9.9×10^{-2} M) under a degassed condition in CD_3CN containing D_2O (0.18 M) at 298 K: *cis*-$[Et_2Co(bpy)_2]^+$ (○), C_3H_5Br (●), EtBr (△), C_6H_{10} (▲), C_2H_6 (□), and C_2H_4 (■).

In contrast to the above results, when the alkyl group is the same between the reactants, i.e., photolysis of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ in the presence of benzyl bromide, the stoichiometry is changed to 1:1 as shown in Figure 4, where only the coupling product (1,2-diphenylethane) is produced as a main product (eq 6). Table I summarizes

$$cis\text{-}[(PhCH_2)_2Co(bpy)_2]^+ + PhCH_2Br \xrightarrow{h\nu} {}^3/_2PhC_2H_4Ph + [Co(bpy)_2Br]^+ \quad (6)$$

the product distributions from the photochemical reactions of various alkylcobalt(III) complexes with benzyl and allyl bromides including the minor products. In the photoredox

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[25] The *cis*-$[Et(H)Co(bpy)_2]^+$ complex formed by photoinduced elimination of ethylene form *cis*-$[Et_2Co(bpy)_2]^+$ (eq 4) may react also with oxygen to yield acetaldehyde, since the yield of ethane in the absence of oxygen (Figure 1) is approximately the same as that in the presence of oxygen (Figure 2).

[26] All the complexed ligand signals in $[Co(bpy)_3]^+$ appeared as broad singlets in the ^1H NMR spectrum; δ referenced to an internal standard Me_4Si: 39 (5,5′-H), 44 (3,3′-H), 62 (4,4′-H), and 108 ppm (6,6′-H).

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[28] A cobalt-containing product was identified by ^1H NMR as $[Co(bpy)_3]^{2+}$ (see ref 21).

Table I. Product Distribution in the Photochemical Reactions of Alkylcobalt(III) Complexes with Benzyl and Allyl Bromides under Degassed Conditions in Acetonitrile-d_3 at 298 K

reaction[a]			time, h	product, % based on the cobalt complex
cis-[$Me_2Co(bpy)_2$]$^+$ (7.7×10^{-2})	+	$PhCH_2Br$ (7.7×10^{-2})	45	PhC_2H_4Ph (49), $PhCH_3$ (1.3), PhEt (3.8)
cis-[$Et_2Co(bpy)_2$]$^+$ (9.9×10^{-2})	+	$PhCH_2Br$[b] (9.9×10^{-2})	24	PhC_2H_4Ph (48), $PhCH_3$ (0.4), PhPr (3.0)
cis-[$Me_2Co(bpy)_2$]$^+$ (5.9×10^{-2})	+	C_3H_5Br (5.9×10^{-2})	48	C_6H_{10} (48), C_3H_6 (2.2), C_4H_8 (4.2)
cis-[$Et_2Co(bpy)_2$]$^+$ (9.9×10^{-2})	+	C_3H_5Br[b] (9.9×10^{-2})	24	C_6H_{10} (49), C_3H_6 (1.8), C_5H_{10} (3.8)
cis-[$(PhCH_2)_2Co(bpy)2$]$^+$ (4.1×10^{-2})	+	$PhCH_2Br$ (4.1×10^{-2})	11	PhC_2H_4Ph (148), $PhCH_3$ (4.0)
cis-[$(PhCH_2)_2Co(bpy)_2$]$^+$ (4.1×10^{-2})	+	C_3H_5Br (4.1×10^{-2})	11	PhC_2H_4Ph (85), C_6H_{10} (36), PhC_4H_7 (34)
trans-[$Me_2Co(DpnH)$] (4.0×10^{-2})	+	$PhCH_2Br$ (4.0×10^{-2})	33	PhC_2H_4Ph (22), $PhCH_3$ (55)
[$MeCo(DH)_2py$] (0.10)	+	$PhCH_2Br$ (0.10)	71	$PhCH_3$ (6.4)
[$EtCo(DH)_2py$] (0.10)	+	$PhCH_2Br$ (0.10)	14	$PhCH_2$ (33)

[a] The concentrations of the reactants are shown in the parentheses. [b] In the presence of 0.18 M D_2O (see ref 43).

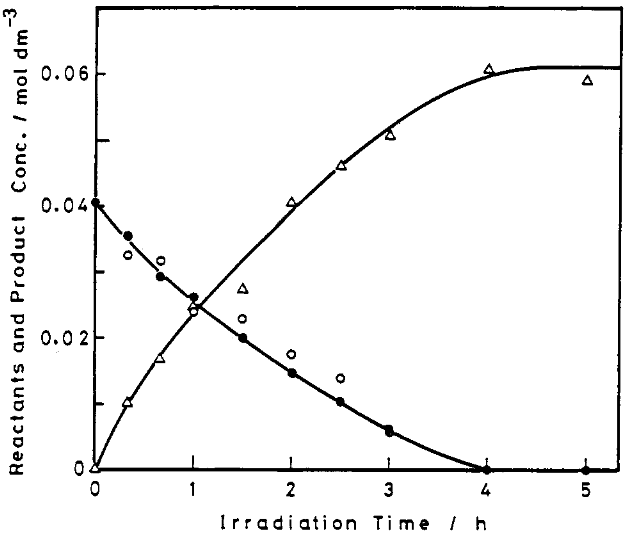

Figure 4. Time course of the photochemical reaction of *cis*-[$(PhCH_2)_2Co(bpy)_2$]$^+$ (4.1×10^{-2} M) with benzyl bromide (4.1×10^{-2} M) under a degassed condition in CD_3CN at 298 K: *cis*-[$(PhCH_2)_2Co(bpy)_2$]$^+$ (○), $PhCH_2Br$ (●), and PhC_2H_4Ph (△).

reactions of *cis*-[$Me_2Co(bpy)_2$]$^+$ and *cis*-[$Et_2Co(bpy)_2$]$^+$ with benzyl and allyl bromides, the coupling products (1,2-diphenylethane and 1,5-hexadiene, respectively) are mainly obtained, and small amounts of cross-coupling products (e.g., ethylbenzene in the case of the reactions of *cis*-[$Me_2Co(bpy)_2$]$^+$ with benzyl bromide) are formed as well as the products derived from hydrogen abstraction by benzyl and allyl radicals from a solvent (i.e., toluene and propene, respectively). The stoichiometry of these reactions is approximately 1:3 as shown by eq 5. In the case of the photoredox reactions of *cis*-[$(PhCH_2)_2Co(bpy)_2$]$^+$ with benzyl bromide, however, the stoichiometry is 1:1 (eq 6) to yield mainly the coupling product (1,2-diphenylethane) together with a small amount of toluene (Table I). When benzyl bromide is replaced by allyl bromide in the reaction with *cis*-[$(PhCH_2)_2Co(bpy)_2$]$^+$, the coupling products (1,2-diphenylethane and 1,5-hexadiene) are formed together with a comparable amount of the cross-coupling product between the benzyl and allyl group, i.e., 4-phenyl-1-butene (Table I). Thus, the photolysis of all the *cis*-dialkylcobalt(III) complexes in the presence of benzyl or allyl bromide results in the formation of carbon–carbon bonds to yield the coupling or cross-coupling products of the benzyl and allyl groups as the main products together with small amounts of products derived from hydrogen abstraction by the benzyl or allyl radical from a solvent.

Table II. Quantum Yields (Φ) for Photodecomposition of *cis*-[$R_2Co(bpy)_2$]$^+$ (R = Me, Et, and $PhCH_2$) in MeCN at 298 K[a]

cis-[$R_2Co(bpy)_2$]$^+$, M	additive	Φ
R = Me		
1.0×10^{-3}	none	0.012
1.0×10^{-3}	O_2[b]	0.014
R = Et		
1.0×10^{-3}	none	0.030
1.0×10^{-3}	O_2[b]	0.033
5.0×10^{-3}	none	0.030
5.0×10^{-3}	O_2[b]	0.030
1.0×10^{-3}	bpy[c]	0.029
1.0×10^{-3}	O_2,[b] bpy[c]	0.029
R = $PhCH_2$		
1.0×10^{-2}	none	0.022

[a] Under a degassed condition unless otherwise noted. [b] Under an atmospheric pressure of oxygen. [c] In the presence of 5.0×10^{-2} M 2,2′-bipyridine.

On the other hand, the photolysis of *trans*-[$Me_2Co(DpnH)$] in the presence of benzyl bromide gives mainly toluene. Thus, carbon–carbon bond formation in the case of *trans*-[$Me_2Co(DpnH)$] is much less efficient than the case of *cis*-[$R_2Co(bpy)_2$]$^+$ (Table I). Irradiation of monoalkylcobalt(III) complexes [$RCo(DH)_2py$] (R = Me and Et) in the presence of benzyl bromide gives only toluene with no appreciable amount of the coupling product, either.

Quantum Yields. The quantum yields (Φ) for photodecomposition of *cis*-[$R_2Co(bpy)_2$]$^+$ (R = Me, Et, and $PhCH_2$) were determined in the region of λ_{max} of the Co–C charge-transfer (CT) absorption. The magnitude of Φ observed (Table II), which is similar to that for photodecomposition of alkylcobaloximes,[12e] is typical for charge-transfer-induced excitation.[29] The quantum yield of photodecomposition of *cis*-[$Et_2Co(bpy)_2$]$^+$ is the largest among *cis*-[$R_2Co(bpy)_2$]$^+$ because of the involvement of a β-elimination step (eq 4) besides a homolytic pathway. The Φ value is independent of the concentration of *cis*-[$Et_2Co(bpy)_2$]$^+$ and is affected by neither the presence of oxygen, which is a typical triplet quencher, nor the addition of an excess amount of the ligand 2,2′-bipyridine (Table

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(29) Wehry, E. L. *Q. Rev., Chem. Soc.* **1967**, *21*, 213.

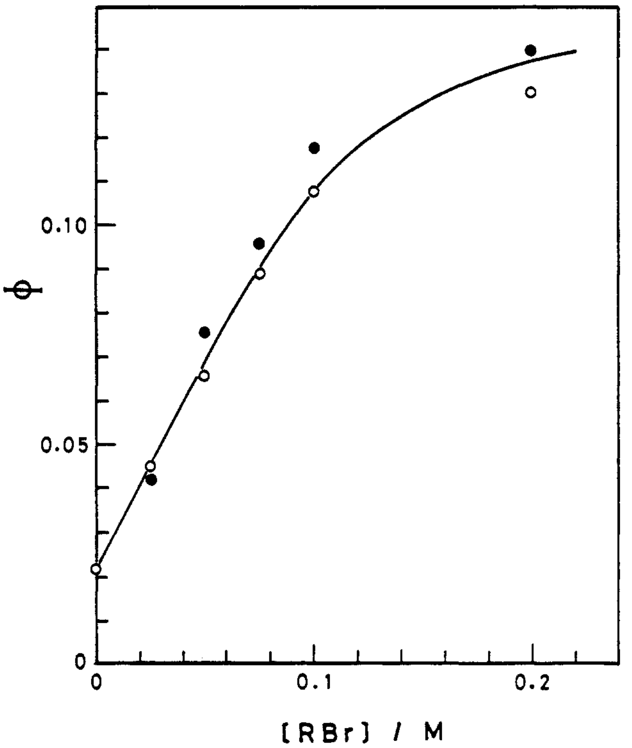

Figure 5. Plots of the quantum yield for photochemical reactions of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (1.0×10^{-2} M) with RBr [R = $PhCH_2$ (○) and C_3H_5 (●)] in the absence of oxygen in MeCN at 298 K vs. the concentration of the bromide.

II). Thus, the photodecomposition may be a unimolecular process via the singlet excited state without the dissociation of the 2,2′-bipyridine ligand.

In the presence of benzyl or allyl bromide, the Φ value for the photolysis of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ increases with increasing the concentration of benzyl or allyl bromide, approaching a constant value (Figure 5). Since the presence of benzyl or allyl bromide completely suppresses the photodealkylation process, *i.e.*, production of ethane and ethylene, which occurs in its absence as shown in Figure 3, the photochemical reactions in the absence and presence of benzyl or allyl bromide are neither independent of each other nor a competing process. Thus, the dependence of Φ on the bromide concentration (Figure 5) suggests that a common intermediate produced by the photochemical reaction in the absence and presence of the bromide reacts with the bromide by a bimolecular reaction.

Detection of Reactive Intermediates. For detection of the reactive intermediates produced in these photochemical reactions, the ESR spectra were measured in the course of photolysis of an MeCN solution of *cis*-$[R_2Co(bpy)_2]^+$ in the absence and presence of benzyl or allyl bromide at 77 K. In the photolysis of *cis*-$[R_2Co(bpy)_2]^+$ in the presence of benzyl bromide, the ESR signal due to benzyl radical is observed as shown in Figure 6a, where the computer simulation spectrum of benzyl radical using the ESR parameters reported in the literature[30] (g = 2.0026; $a(CH_2)$ = 1.40, $a(o\text{-H})$ = 0.30, $a(m\text{-H})$ = 0.15, and $a(p\text{-H})$ = 0.32 mT) with the line width (ΔH_{msl} = 0.39 mT) is indicated by the dotted line, showing reasonable agreement with the observed spectrum. In the presence of allyl bromide, the ESR spectrum of allyl radical (g = 2.0026, a_1 = 0.41 for one proton, a_2 = 1.40 for two equivalent protons, and a_2' = 1.48 mT for other two equivalent protons)[31] with the line width ΔH_{msl} = 0.50 mT is observed as shown in Figure 6b.

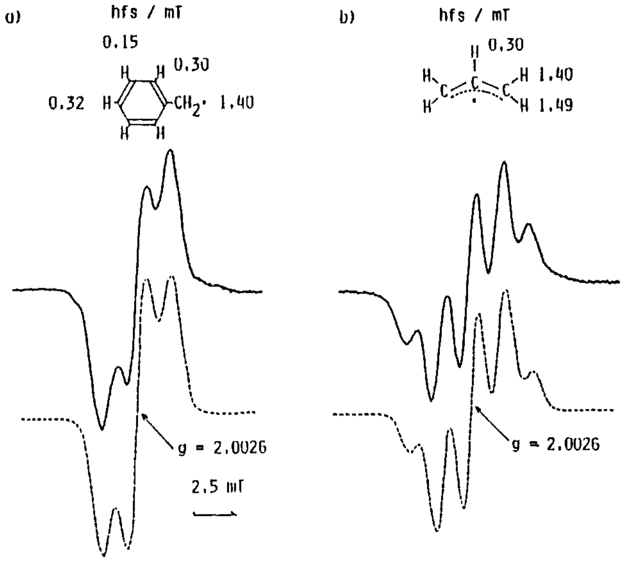

Figure 6. ESR spectra of (a) benzyl and (b) allyl radicals observed in the photolysis of *cis*-$[Et_2Co(bpy)_2]^+$ (5.0×10^{-2} M) in the presence of benzyl bromide (0.15 M) and allyl bromide (0.30 M), respectively, at 77 K (solvent, MeCN). The broken lines show the computer simulation spectra.

A cobalt(II) paramagnetic species is also observed in the wide magnetic region. In the photolysis of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, the isotropic signal at g = 2.0026 which is attributed to benzyl radical[32] is observed as well as the characteristic signal of a spin doublet possessing axial symmetry at $g_\perp$ = 2.28 and $g_\parallel \simeq 2.0$, which is expected for a monobenzylcobalt(II) complex, $[PhCH_2Co(bpy)_2]^+$, produced by the homolytic cleavage of the cobalt–carbon bond of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (Figure 7a). A similar anisotropic signal ($g_\perp$ = 2.27 and $g_\parallel \simeq 2.0$) that may be assigned to $[MeCo(bpy)_2]^+$ is also observed in the case of *cis*-$[Me_2Co(bpy)_2]^+$ (Figure 7b), where the isotropic sharp triplet signal at g = 2.0028 with $a(\alpha\text{-H})$ = 2.1 mT can be assigned to $\dot{C}H_2CN$ by comparison of the ESR parameters with those in the literature.[33] The $\dot{C}H_2CN$ radical may be produced by hydrogen abstraction by the methyl radical from CH_3CN, since the methyl radical formed initially by the homolytic cleavage of the cobalt–carbon bond of *cis*-$[Me_2Co(bpy)_2]^+$ is known to be much more reactive than the benzyl radical as noted above.[24]

When benzyl bromide is added to an MeCN solution of *cis*-$[Me_2Co(bpy)_2]^+$, the photolysis at 77 K results in the formation of the benzyl radical instead of $\dot{C}H_2CN$, and the signal intensity of benzyl radical in the presence of benzyl bromide (Figure 7c) is much stronger than that of $\dot{C}H_2CN$ in the absence of benzyl bromide (Figure 7b). In the presence of benzyl bromide, two anisotropic signals are observed at $g_\perp$ = 2.27 and 2.14 (Figure 7c); the former is the same as that observed in Figure 7b, being assigned to $[MeCo(bpy)_2]^+$, and the latter may tentatively be assigned to $[Co(bpy)_2Br]^+$. In the *cis*-$[Me_2Co(bpy)_2]^+$–C_3H_5Br system (Figure 7d) as well, the photolysis results in the formation of the allyl radical (g = 2.0026)[32] with a much stronger intensity than $\dot{C}H_2CN$ in the absence of allyl bromide (Figure 7b) as well as $[MeCo(bpy)_2]^+$ ($g_\perp$ = 2.27 and $g_\parallel \simeq 2.0$) and $[Co(bpy)_2Br]^+$ ($g_\perp$ = 2.14 and $g_\parallel \simeq 2.0$).

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[30] (a) Dixon, W. T.; Norman, R. O. C. *J. Chem. Soc.* **1964**, 4857. (b) Carrington, A.; Smith, I. C. P. *Mol. Phys.* **1965**, *9*, 137.

[31] Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

[32] The ESR signals at g = 2.0026 in parts a (or c) and d of Figure 7 are identical with those in parts a and b of Figure 6, respectively.

[33] Livingston, R.; Zeldes, H. *J. Magn. Reson.* **1969**, *1*, 169.

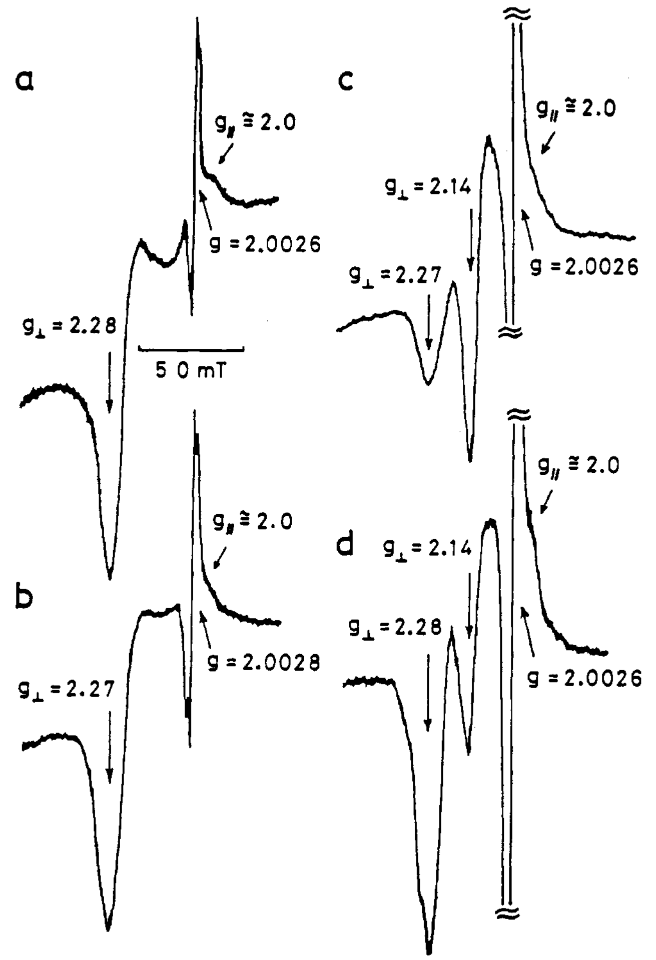

Figure 7. ESR spectra observed in the photolysis of (a) *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (4.5×10^{-2} M) for 8 h, (b) *cis*-$[Me_2Co(bpy)_2]^+$ (6.0×10^{-2} M) for 10 h, (c) *cis*-$[Me_2Co(bpy)_2]^+$ (6.0×10^{-2} M) in the presence of benzyl bromide (0.30 M) for 20 h, and (d) *cis*-$[Me_2Co(bpy)_2]^+$ (6.0×10^{-2} M) in the presence of allyl bromide (0.30 M) for 16 h at 77 K (solvent, MeCN).

No hyperfine structure of $[RCo(bpy)_2]^+$ and $[Co(bpy)_2Br]^+$ due to the cobalt nuclear spin ($I = {}^7/_2$) is observed in Figure 7, probably because paramagnetic centers are not diluted as reported in the case of the isothiocyanate complex of cobalt(II) with the tridentate ligand *N*-(2-(diphenylphosphino)ethyl)-*N'*,*N'*-diethylethylenediamine $[Co(NCS)_2(nnp)]$[34] as well as $[Co(NCS)(dpe)_2]ClO_4$ where dpe is 1,2-bis(diphenylphosphino)ethane,[35] which is known as a five-coordinate cobalt(II) complex with a square-pyramidal structure. No superhyperfine structure due to the alkyl group of $[RCo(bpy)_2]^+$ is observed, either, suggesting that little or no unpaired electron density is located on the alkyl group. In fact, the greater the $g_\perp$ value than the $g_\parallel$ value indicates that the unpaired electron is mainly located in the d_{z^2} orbital of cobalt(II) in a low-spin d^7 configuration.[35,36] Thus, the structure of $[RCo(bpy)_2]^+$ may be better described as $[R^- \cdots Co^{II}(bpy)_2]^+$ in which the Co–R bond is almost dissociated to produce the carbanion ligand as in the case of the reduced benzyl(pyridine)cobaloxime which has been reported to dissociate into the benzyl anion and (pyridine)cobaloxime.[37,38]

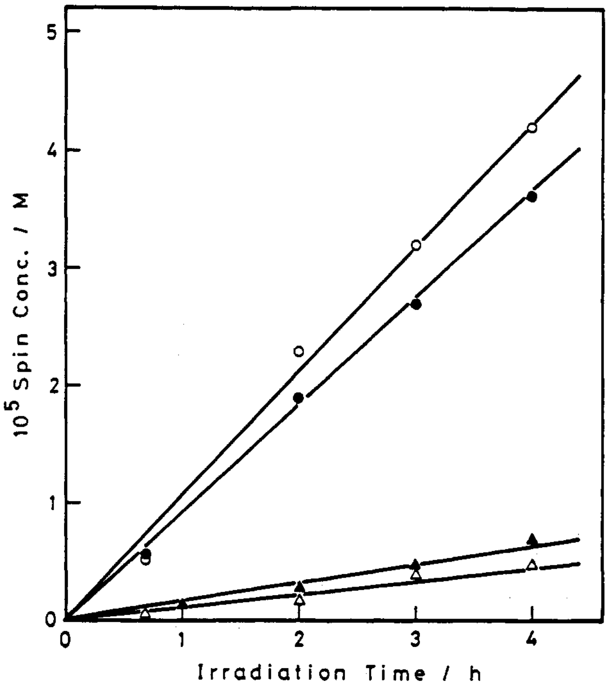

Figure 8. Plots of the spin concentrations of the paramagnetic species formed by the photolysis of *cis*-$[R_2Co(bpy)_2]^+$ (6.0×10^{-2} M) in the presence of benzyl bromide (0.18 M) vs. the irradiation time at 77 K: $PhCH_2\cdot$ (○), $[RCo(bpy)_2]^+$ (●), and $[Co(bpy)_2Br]^+$ (△) for R = Et, and $PhCH_2\cdot$ (▲) for R = Me.

The spin concentrations of both the benzyl radical and the monoalkylcobalt(II) complex produced by the photolysis of *cis*-$[R_2Co(bpy)_2]^+$ in the presence of benzyl bromide at 77 K increase linearly with the irradiation time, and the concentration of benzyl radical is approximately the same as that of the monoalkylcobalt(II) complex as shown in Figure 8 for the case of R = Et. Thus, both the benzyl radical and $[RCo(bpy)_2]^+$ may be formed at the same time by the initial photochemical step (eq 7). All the ESR

$$cis\text{-}[R_2Co(bpy)_2]^+ + PhCH_2Br \xrightarrow{h\nu} PhCH_2\cdot + [RCo(bpy)_2]^+ + RBr \quad (7)$$

signals in Figure 7 disappeared instantly when the samples were warmed up to room temperature, followed by the measurement at 77 K, indicating that the paramagnetic species observed in Figure 7 (the benzyl or allyl radical, $[RCo(bpy)_2]^+$, and $[Co(bpy)_2Br]^+$) are reactive intermediates involved in subsequent thermal reactions. On the disappearance of the ESR signals due to five-coordinate cobalt(II) species in Figure 7, an eight-line spectrum which is identical with that of $[Co(bpy)_3]^{2+}$ reported in the literature[39] was observed. Thus, $[Co(bpy)_3]^{2+}$ is the final product from *cis*-$[R_2Co(bpy)_2]^+$ in the photochemical reaction with benzyl or allyl bromide as confirmed by the ^1H NMR measurement,[28] suggesting that $[Co(bpy)_2Br]^+$ observed in part c or d of Figure 7, which may be the initial product (eq 15), is converted to $[Co(bpy)_3]^{2+}$ being the most stable form among the mono-, bis-, and tris(2,2'-bipyridine)cobalt(II) complexes.[29]

Reaction Schemes. On the basis of the above results, the reaction mechanism for the photoredox reactions of *cis*-$[R_2Co(bpy)_2]^+$ with benzyl and allyl bromides may be

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[34] Gatteschi, D.; Chilardi, C. A.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 3023.

[35] Nishida, Y.; Shimohori, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2406.

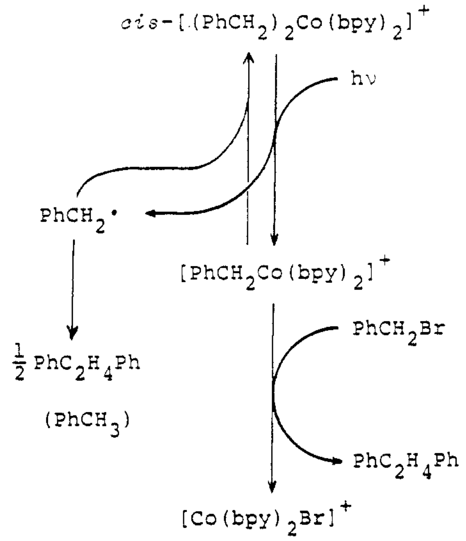
[36] Griffith, J. S. *Discuss. Faraday Soc.* **1958**, *26*, 81.

[37] (a) Hoshino, M.; Konishi, S.; Terai, Y.; Imamura, M. *Inorg. Chem.* **1982**, *21*, 89. (b) Rao, D. N. R.; Symons, M. C. R. *J. Organomet. Chem.* **1983**, *244*, C43; *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 423.

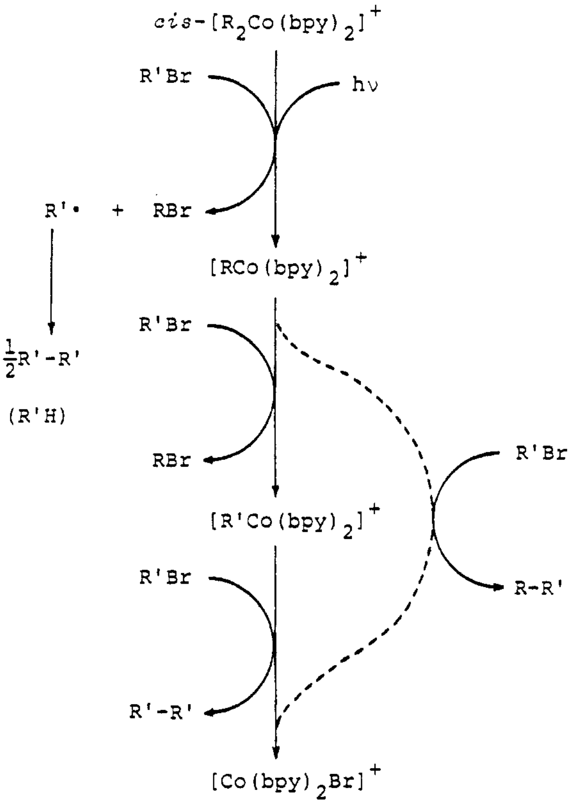
[38] (a) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3738. (b) Costa, G.; Puxeddu, A.; Reisenhofer, E. *J. Chem. Soc., Chem. Commun.* **1971**, 993. (c) Le Hoang, M. D.; Robin, Y.; Devynck, J.; Bied-Charreton, C.; Gaudemer, A. *J. Organomet. Chem.* **1981**, *222*, 311.

[39] (a) Mizuno, K.; Lunsford, J. H. *Inorg. Chem.* **1983**, *22*, 3484. (b) Berkoff, R.; Krist, K.; Gafney, H. D. *Ibid.* **1980**, *19*, 1.

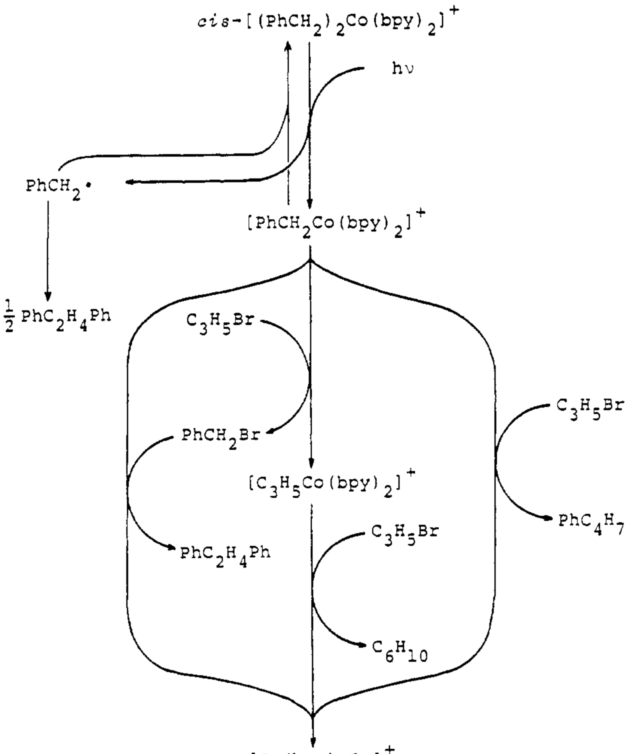
Scheme I



Scheme II



Scheme III



given by Schemes I–III. In the photoredox reactions of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide (Scheme I), which is the simplest case, excitation of *cis*-$[R_2Co(bpy)_2]^+$ leads to the homolytic cleavage of the cobalt–carbon bond to produce the benzyl radical and the monobenzylcobalt(II) complex $[PhCH_2Co(bpy)_2]^+$ as confirmed by the ESR measurement (Figure 7a). In the absence of benzyl bromide, the quantum efficiency is much lowered by the facile recombination of the benzyl radical with $[PhCH_2Co(bpy)_2]^+$. In the presence of benzyl bromide, however, $[PhCH_2Co(bpy)_2]^+$ in which the benzyl group is considered as the benzyl anion as discussed above may undergo a facile coupling reaction with benzyl bromide to yield 1,2-diphenylethane and $[Co(bpy)_2Br]^+$. Thus, the quantum yield is increased by the presence of benzyl bromide to prevent recombination between $[PhCH_2Co(bpy)_2]^+$ and the benzyl radical, approaching the limited Φ value with increasing bromide concentration (Figure 5).[40] When the reciprocal of the increase in the Φ value in the presence of benzyl or allyl bromide, i.e., $(\Phi - \Phi_0)^{-1}$ where Φ_0 is the quantum yield in the absence of benzyl or allyl bromide, was plotted against $[PhCH_2Br]^{-1}$ or $[C_3H_5Br]^{-1}$ by using the data in Figure 5, each plot gave a straight line with approximately the same intercept,[41] from which the quantum yield for the photocleavage of the Co–C bond of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ without the back reaction can be evaluated as 0.3 ± 0.1. On the other hand, benzyl radicals also give 1,2-diphenylethane by the coupling reaction together with a small amount of toluene by hydrogen abstraction from a solvent (Table I). According to Scheme I, the stoichiometry of the photoredox reaction is 1:1 (eq 6).

When the alkyl groups between the reactants (*cis*-$[R_2Co(bpy)_2]^+$ and R′Br) are different, the reaction scheme becomes more complicated (Scheme II). Excitation of *cis*-$[R_2Co(bpy)_2]^+$ (R = Me and Et) also leads to the homolytic cleavage of the cobalt–carbon bond to produce $[RCo(bpy)_2]^+$ and the alkyl radical (Figure 7b).[42] In the presence of R′Br (R′ = $PhCH_2$ and C_3H_5), the alkyl radical (Me· and Et·) may be converted to the more stable radical ($PhCH_2$· and C_3H_5·) by the reaction with R′Br as observed by the ESR spectra (Figure 6 and parts c and d of Figure

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[40] Such a saturation behavior of the rate with increasing concentration of benzyl or allyl bromide was confirmed also for the photochemical reaction of *cis*-$[Me_2Co(bpy)_2]^+$ with benzyl or allyl bromide; when the concentration of benzyl or allyl bromide was increased from 7.7 × 10^{-2} to 0.24 M, the initial rate monitored by ^{1}H NMR in CD_3CN as shown in Figure 2 was not changed appreciably.

[41] In the plots of $(\Phi - \Phi_0)^{-1}$ vs. $[PhCH_2Br]^{-1}$ and $[C_3H_5Br]^{-1}$ (the correlation coefficients are 0.98 and 0.99, respectively), the datum at the lowest concentration of benzyl or allyl bromide in Figure 5 was excluded since the experimental error in the $(\Phi - \Phi_0)^{-1}$ value is the largest.

[42] In the case of *cis*-$[Et_2Co(bpy)_2]^+$ which has a β-hydrogen, a β-elimination pathway is also involved in the photocleavage of the cobalt–carbon bond (eq 4).

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7). Thus, the photochemical reaction of *cis*-$[R_2Co(bpy)_2]^+$ with R′Br produces R′·, $[RCo(bpy)_2]^+$, and RBr (eq 7).[43] The benzyl and allyl radicals give mainly the coupling products (1,2-diphenylethane and 1,5-hexadiene, respectively) together with small amounts of byproducts derived from the hydrogen abstraction from a solvent (toluene and propene, respectively) as shown in Table II. The carbanion ligand in $[RCo(bpy)_2]^+$ may react readily with R′Br to produce the more stable carbanion ligand, and $[R'Co(bpy)_2]^+$ thus formed may undergo the coupling reaction with R′Br to yield R′–R′ and $[Co(bpy)_2Br]^+$. $[RCo(bpy)_2Br]^+$ may also participate in a cross-coupling reaction with R′Br, which is shown by the broken line in Scheme II, yielding R–R′ as a minor byproduct (ethylbenzene, propylbenzene, 1-butene, and 1-pentene for the *cis*-$[Me_2Co(bpy)_2]^+$–$PhCH_2Br$, *cis*-$[Et_2Co(bpy)_2]^+$–$PhCH_2Br$, *cis*-$[Me_2Co(bpy)_2]^+$–C_3H_5Br, and *cis*-$[Et_2Co(bpy)_2]^+$–C_3H_5Br systems, respectively). According to Scheme II, the stoichiometry of the photoredox reaction of *cis*-$[R_2Co(bpy)_2]^+$ with R′Br is 1:3 (eq 5), in contrast with the case in Scheme I.

The photoredox reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with allyl bromide (Scheme III) is the most complicated case, where the photocleavage reaction occurs to give $[PhCH_2Co(bpy)_2]^+$, which can undergo the exchange, coupling, and cross-coupling reactions with comparable rates, because of similar stabilities between the benzyl and allyl anions to yield 1,2-diphenylethane and 1,5-hexadiene as the homocoupling products as well as 4-phenyl-1-butene as the cross-coupling product (Table II). According to Scheme III, the stoichiometry is 1:1 as the case of Scheme I.

In conclusion, the photocleavage of the cobalt–carbon bond of *cis*-dialkylcobalt(III) complexes produces monoalkylcobalt(II) complexes as reactive intermediates in which the alkyl group has carbanion character, inducing the facile reduction of benzyl and allyl bromides to yield coupling and cross-coupling products depending on the stabilities of the carbanion ligands.

Registry No. *cis*-$[Me_2Co(bpy)_2]^+$, 71697-34-2; *cis*-$[Et_2Co(bpy)_2]^+$, 71697-32-0; *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, 104013-21-0; *trans*-$[Me_2Co(DpnH)]$, 105900-07-0; $[MeCo(DH)_2py]$, 23642-14-0; $[EtCo(DH)_2py]$, 25360-57-0; $PhCH_2Br$, 100-39-0; C_3H_5Br, 106-95-6; PhC_2H_4Ph, 103-29-7; C_6H_{10}, 592-42-7; PhC_4H_7, 768-56-9; $PhCH_3$, 107-35-7.

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[43] In the initial photochemical step in eq 7, the β-elimination pathway may also give the same species as the homolytic pathway by the facile reaction with R′Br in the presence of water, since the β-elimination pathway may be regarded as β-hydrogen transfer between the geminate radical pair following the homolytic cleavage of the cobalt–carbon bond; see: Tsou, T. T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* 1982, *104*, 623. However, the detailed mechanism is not clear at present.

Low-Temperature Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$: Establishment of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ as the Intermediate in the Rearrangement of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$

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Received June 3, 1986

Near-UV (355-nm) photolysis of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in alkane solution under 1 atm of CO or saturated with PPh_3 results in the nearly quantitative formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(L)SiMe_3$ (L = CO, PPh_3). The intermediate in this rearrangement is shown to be $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ by low-temperature IR, UV–vis, and NMR studies. Near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ at 77 K in a 1-pentene or 2-methyltetrahydrofuran matrix results in loss of CO as evidenced by the growth of an IR absorption due to free CO at 2132 cm^{-1}. A 16e $(\eta^5\text{-}C_5Me_5)Fe(CO)CH_2SiMe_2H$ cannot be trapped by the donor matrices, nor can it be detected under any conditions used. Rather, even at 77 K the β-H is transferred from the Si to the Fe as evidenced by the decline of the IR absorption at 2101 cm^{-1} associated with the Si-H bond. Although β-H transfer is the major photoprocess in alkane matrices at 77 K, the direct rearrangement of approximately 20% of the $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is evidence for radical formation as a minor primary photoprocess. The $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ resulting from β-H transfer is inert up to 225 K. The ^1H NMR of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ indicates that the complex is not fluxional even at the highest temperature at which it is chemically inert. This finding is consistent with the formulation of the $M(CH_2SiMe_2)$ unit as a metallasilacyclopropane. Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in a 1 M PEt_3 alkane solution at 200 K results only in the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$. Warming of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ to 225 K in the presence of 1 atm of CO or PEt_3 results in the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(L)SiMe_3$ (L = CO, PEt_3). The results confirm that $M(CH_2SiMe_2)(H)$ complexes are intermediates in the conversion of $M\text{–}CH_2SiMe_2H$ complexes to $M\text{–}SiMe_3$ complexes.

We would like to report the establishment of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ as the intermediate in the rearrangement of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (eq 1 and 2). A similar intermediate

0276-7333/87/2306-0365$01.50/0