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C-C BOND FORMATION BY THE PHOTOINDUCED REACTIONS OF *cis*-DIALKYLCOBALT(III) COMPLEXES WITH BENZYL AND ALLYL BROMIDES

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The photocleavage 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), induces the selective C-C bond formation from benzyl and allyl bromides to yield 1,2-diphenylethane and 1,5-hexadiene, respectively. The monoalkylcobalt(II) complexes [$RCo(bpy)_2$]$^+$ formed by the photocleavage reactions are responsible for the selective reduction of benzyl and allyl bromides.

The mechanism of thermal cleavage of metal-carbon bond of transition-metal alkyl has extensively been studied and several pathways have been established.$^{1)}$ On the other hand, the photocleavage of metal-carbon bond of transition-metal alkyl is recently attracting growing attention.$^{2)}$ However, little is known for the photocleavage of cobalt-carbon bond of transition-metal alkyl involving reactions with substrates. We report here that the photocleavage 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)$^{3)}$ induces the selective reduction of benzyl and allyl bromides to yield 1,2-diphenylethane and 1,5-hexadiene, respectively. The successful detection of the reactive intermediates which are responsible for the selective reduction of benzyl and allyl bromides are also reported.

Irradiation of a degassed acetonitrile solution of *cis*-[$Me_2Co(bpy)_2$]$^+$ with the visible light from a Xenon lamp through a filter cutting off below 360 nm at 298 K resulted in the cleavage of the cobalt-carbon bonds to liberate methane and ethane in a 14 : 1 ratio (Eq. 1)$^{4)}$ which may be produced via a homolytic pathway.$^{5)}$ Photolysis of *cis*-[$Et_2Co(bpy)_2$]$^+$ in acetonitrile liberated ethane and ethylene in a 2 : 1 ratio with a trace amount of butane (Eq. 2)$^{6)}$ which indicates the involvement of a β-elimination pathway to yield ethane and ethylene in a 1 : 1 ratio, besides a homolytic pathway to yield mainly ethane with a trace amount of butane. In the photolysis of *cis*-[$(PhCH_2)_2Co(bpy)_2$]$^+$, the ratio of the coupling product

$$\underset{(1.0 \times 10^{-2}\ \mathrm{M})}{cis\text{-}[\mathrm{Me_2Co(bpy)_2}]^+} \xrightarrow[15\,\mathrm{h}]{h\nu} \underset{14}{\mathrm{CH_4}} \ \underset{:}{+}\ \underset{1}{\mathrm{C_2H_6}} \qquad (1\ \mathrm{M} = 1\ \mathrm{mol\ dm^{-3}}) \tag{1}$$

$$\underset{(1.0 \times 10^{-2}\ \mathrm{M})}{cis\text{-}[\mathrm{Et_2Co(bpy)_2}]^+} \xrightarrow[8\,\mathrm{h}]{h\nu} \underset{2}{\mathrm{C_2H_6}} \ \underset{:}{+}\ \underset{1}{\mathrm{C_2H_4}} + \underset{\mathrm{trace}}{\mathrm{C_4H_{10}}} \tag{2}$$

1,2-diphenylethane to toluene (Eq. 3) increased significantly compared with that

$$\begin{array}{llll} cis\text{-}[(PhCH_2)_2Co(bpy)_2]^+ & \xrightarrow[50\,h]{h\nu} PhCH_3 & + & PhC_2H_4Ph \qquad (3) \\ (4.5 \times 10^{-2}\ M) & \qquad\quad 1 & : & 1 \end{array}$$

of ethane to methane in the photolysis of *cis*-$[Me_2Co(bpy)_2]^+$ (Eq. 1), since benzyl radical is known to abstract a hydrogen from a solvent with a much slower rate than methyl radical.[7]

When the photolysis of *cis*-$[Me_2Co(bpy)_2]^+$ is carried out in the presence of benzyl bromide, the formation of the gaseous products (methane and ethane) observed in the absence of benzyl bromide (Eq. 1) is suppressed completely and *cis*-$[Me_2Co(bpy)_2]^+$ reacts with three mol of benzyl bromide to yield methyl bromide and 1,2-diphenylethane (Eq. 4) as shown in Fig. 1a.[8] Such a stoichiometry was observed

$$cis\text{-}[Me_2Co(bpy)_2]^+ + 3PhCH_2Br \xrightarrow{h\nu} 2MeBr + (3/2)PhC_2H_4Ph \qquad (4)$$

also in the photoinduced reaction of *cis*-$[Me_2Co(bpy)_2]^+$ with allyl bromide which gave 1,5-hexadiene as well as those of *cis*-$[Et_2Co(bpy)_2]^+$ with benzyl and allyl bromides. In contrast to the result in Fig. 1a, the photolysis of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ in the presence of benzyl bromide, the stoichiometry is changed to Eq. 5,

$$cis\text{-}[(PhCH_2)_2Co(bpy)_2]^+ + PhCH_2Br \xrightarrow{h\nu} (3/2)PhC_2H_4Ph \qquad (5)$$

where one mol of benzyl bromide is reduced by the photoinduced reaction with *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (Fig. 1b).

The homolytic cleavage of the cobalt-carbon bond of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ was confirmed by measuring the ESR spectra in acetonitrile under irradiation of the visible light at 77 K as shown in Fig. 2a, where the signal at $g = 2.0026$ for benzyl radical[9] is observed as well as the characteristic signals at $g_\perp = 2.28$ and $g_\parallel \cong 2.0$ expected for a monoalkylcobalt(II) complex $[PhCH_2Co(bpy)_2]^+$.[10,11] In the case of *cis*-$[Me_2Co(bpy)_2]^+$ (Fig. 2b), methyl radical, being much more reactive than benzyl radical,[7] is not detected but instead, $\dot{C}H_2CN$ ($g = 2.0028$)[12] which may be produced by the hydrogen abstraction of methyl radical from CH_3CN is observed in addition to $[MeCo(bpy)_2]^+$ ($g_\perp = 2.27$ and $g_\parallel \cong 2.0$). When benzyl bromide is added to an acetonitrile solution of *cis*-$[Me_2Co(bpy)_2]^+$,

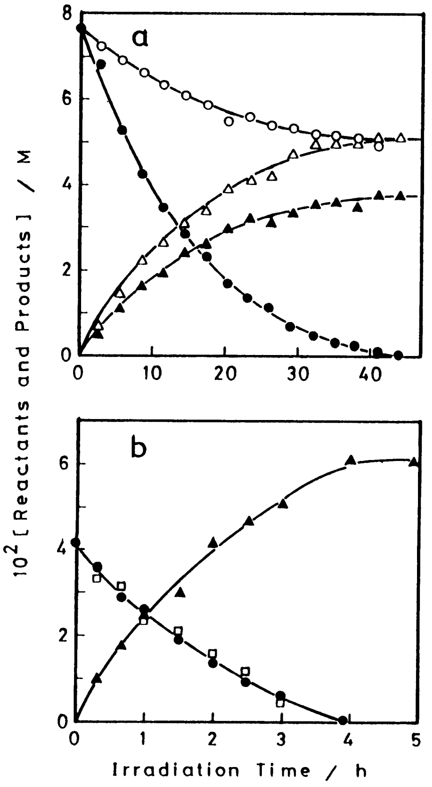
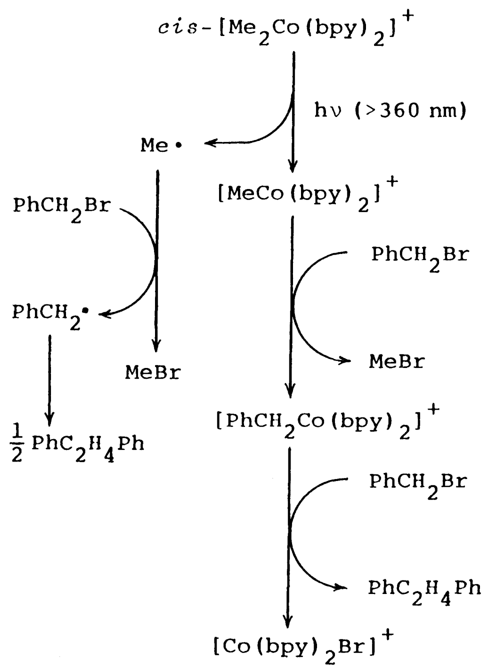
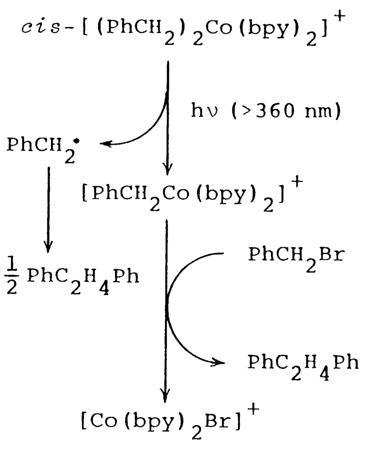


Fig. 1. Time course of the photoinduced reactions of (a) *cis*-$[Me_2Co(bpy)_2]^+$ with $PhCH_2Br$ and (b) *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with $PhCH_2Br$ in CD_3CN at 298 K; *cis*-$[Me_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), MeBr (△), PhC_2H_4Ph (▲), *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (□).



Scheme 1.



Scheme 2.

the ESR signal at $g_{\perp} = 2.14$ which may be assignable to $[Co(bpy)_2Br]^+$ as well as those of $[MeCo(bpy)_2]^+$ and benzyl radical is observed (Fig. 2c). In the *cis*-$[Me_2Co(bpy)_2]^+$-C_3H_5Br system as well, the photoinduced formation of $[MeCo(bpy)_2]^+$, $[Co(bpy)_2Br]^+$ and allyl radical ($g = 2.0026$)$^{9)}$ is detected by the ESR spectra at 77 K (Fig. 2d). The intensities of these ESR signals increased with irradiation time and disappeared completely when the samples were warmed up to room temperature and measured at 77 K.

The above observations (Figs. 1 and 2) are interpreted by Schemes 1 and 2. In Scheme 1, excitation of *cis*-$[Me_2Co(bpy)_2]^+$ leads to homolytic cleavage of the cobalt-carbon bond$^{5)}$ to produce $[MeCo(bpy)_2]^+$ and methyl radical. In the presence of benzyl bromide, methyl radical is converted to benzyl radical by the reaction with benzyl bromide as observed by the ESR spectrum in Fig. 2c,$^{13)}$ while a monoalkylcobalt(II) complex $[MeCo(bpy)_2]^+$ in which the alkyl group is considered as a carbanion ligand$^{10,11,14)}$ exchanges the alkyl group with benzyl bromide to produce [PhCH$_2$Co-

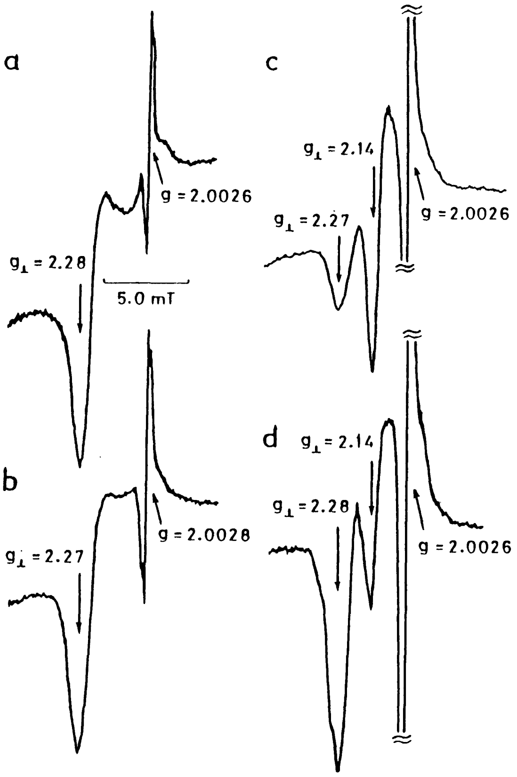


Fig. 2. ESR spectra observed in the photolysis at 77 K of (a) *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (4.5×10^{-2} M) for 8 h, (b) *cis*-$[Me_2Co(bpy)_2]^+$ (6.0×10^{-2} M) for 10 h, (c) *cis*-$[Me_2Co(bpy)_2]^+$ (6.0×10^{-2} M) in the presence of $PhCH_2Br$ (0.30 M) for 20 h, and (d) *cis*-$[Me_2Co(bpy)_2]^+$ (6.0×10^{-2} M) in the presence of C_3H_5Br (0.30 M) for 16 h; solvent, MeCN.

$(bpy)_2]^+$ having a more stable carbanion ligand, which reacts further with benzyl bromide to yield the coupling product 1,2-diphenylethane. Thus, Scheme 1 accounts for the 1 : 3 stoichiometry (Eq. 4) as well as the observation of $[MeCo(bpy)_2]^+$, $PhCH_2\bullet$, and $[Co(bpy)_2Br]^+$ (Fig. 2c). In the case of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$-$PhCH_2Br$ system, a similar sequence of steps to that in Scheme 1 accounts for the 1 : 1 stoichiometry (Eq. 5), since the exchange step of the alkyl group is apparently absent as shown in Scheme 2. In both Schemes, the benzyl radicals formed in the photoinduced reactions dimerize to give 1,2-diphenylethane predominantly.[7)]

Thus, the photoinduced formation of monoalkylcobalt(II) complexes is responsible for the selective C-C bond formation from benzyl and allyl bromides.

References

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8) A cobalt-containing product was identified as $[Co(bpy)_3]^{2+}$ which may be formed from $[Co(bpy)_2Br]^+$. The GC analysis of the products identified also trace amounts of toluene and ethylbenzene.

9) The computer simulated spectra using the ESR parameters of benzyl radical (W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4857) and allyl radical (R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963)) agreed well with the observed ESR spectra at g = 2.0026 in Fig. 1a (or 1c) and Fig. 1d, respectively.

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13) Methyl radical may not abstract a hydrogen from benzyl bromide since no methane has been formed in the presence of benzyl bromide.

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