Electron-transfer Reactions from *cis*-Dialkylbis(2,2′-bipyridyl)cobalt(III) Complexes to Organic Oxidants†

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One-electron oxidation of *cis*-$[CoR_2(bipy)_2]ClO_4$ (R = Me or Et; bipy = 2,2′-bipyridine) by organic oxidants (2,3-dichloro-5,6-dicyano-*p*-benzoquinone, 2,3-dicyano-*p*-benzoquinone, tetracyanoethylene, and tetracyano-*p*-quinodimethane) in acetonitrile results in the cleavage of the pair of cobalt–alkyl bonds to yield the coupled products (R–R) exclusively. A transient absorption band observed in the electron-transfer reaction of $[CoEt_2(bipy)_2]^+$ with tetracyanoethylene is shown to arise from a charge-transfer complex formed between $[CoEt_2(bipy)_2]^+$ and tetracyanoethylene as a reaction intermediate. The logarithm of the rate constants (log *k*) for these electron-transfer reactions in acetonitrile at 298 K is linearly correlated with the difference in the redox potentials between $[CoR_2(bipy)_2]^+$ and oxidants with a slope of $-F/2.3RT$ (*F* is the Faraday constant). Based on the linear Gibbs energy relationship, mechanisms for the electron-transfer reactions are discussed with the aid of the Marcus theory, and the lifetimes of *cis*-$[CoR_2(bipy)_2]^{2+}$ are estimated as $\leqslant 8 \times 10^2$ ns.

The mechanisms of cleavage of metal–carbon bonds have been of considerable interest owing to the importance in understanding the role of organometallic compounds in a variety of catalytic reactions.[1,2] Especially, cleavage of the cobalt–alkyl bonds in alkylcobalt(III) complexes upon oxidation has extensively been studied.[3–8] Although both mono- and di-alkylcobalt(III) complexes are known, examples of the latter are fewer and relatively little is known concerning their reactivities towards oxidants.[9] For example, *trans*-dialkylcobalt(III) complexes are reported to be readily oxidized by inorganic oxidants such as Hg^{2+}, Ag^+, Zn^{2+}, Pb^{2+}, and $[IrCl_6]^{2-}$, resulting in the fission of only one cobalt–alkyl bond.[10–12] However, little is known of the cleavage of cobalt–alkyl bonds in *cis*-dialkylcobalt(III) complexes. Moreover, no cleavage of such bonds in *trans*- or *cis*-dialkylcobalt(III) complexes by organic oxidants has so far been reported.

In this work [13] we report the electron-transfer reactions of *cis*-dialkylcobalt(III) complexes, $[CoR_2(bipy)_2]^+$ (R = Me or Et; bipy = 2,2′-bipyridine), with some organic oxidants such as tetracyanoethylene (tcne), where the *cis* complexes have been found to undergo facile reductive coupling of a pair of alkyl ligands upon oxidation, in contrast with the case of *trans*-dialkylcobalt(III) complexes.[10–12] The mechanisms of these reactions as well as the lifetime of *cis*-$[CoR_2(bipy)_2]^{2+}$ formed upon one-electron oxidation will be discussed based on a linear Gibbs energy relationship {*i.e.* the logarithm of the rate constant *vs.* the difference in the redox potentials between *cis*-$[CoR_2(bipy)_2]^+$ and the organic oxidants} with the aid of the Marcus theory.[14]

Experimental

Materials.—The *cis*-dialkylcobalt(III) complexes, $[CoR_2(bipy)_2]ClO_4$ (R = Me or Et), were prepared according to the literature.[15] Tetracyanoethylene, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, and 7,7,8,8-tetracyano-*p*-quinodimethane were obtained commercially and purified by the standard method.[16] 2,3-Dicyano-*p*-benzoquinone was prepared from the corresponding hydroquinone according to the literature.[17] The preparation of tris(phenanthroline)iron(III) perchlorate, $[Fe(phen)_3][ClO_4]_3$, was described elsewhere.[18] Reagent grade acetonitrile (Wako Pure Chemicals) was purified by the standard procedure,[16] followed by redistillation from calcium hydride.

Oxidation of cis-*Dialkylbis*(2,2′-*bipyridyl*)*cobalt*(III).—In a typical experiment, the oxidant 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (20 μmol) was weighed into a round-bottom flask (30 cm³) containing acetonitrile (2.0 cm³). The flask was capped with a rubber septum and filled with nitrogen by pumping and refilling through a syringe needle. Then, a MeCN solution (0.10 cm³) of $[CoEt_2(bipy)_2]ClO_4$ (3.8 μmol) was introduced into the flask by using a hypodermic syringe. The contents were equilibrated at 298 K for 30 min and thoroughly mixed. The gaseous products were analysed by gas chromatography using a 2-m Unibeads 1S column. After the addition of an equivalent amount of perchloric acid to the product mixture, the $[Co(bipy)_2]^{2+}$ complex was isolated as the perchlorate salt by the slow addition of diethyl ether (Found: C, 42.5; H, 3.1; N, 9.4. Calc. for $C_{20}H_{16}Cl_2CoN_4O_8$: C, 42.1; H, 2.8; N, 9.8%).

Spectral titrations were carried out by adding known quantities of a stock solution of $[CoR_2(bipy)_2]^+$ to a quartz cuvette containing a known aliquot of the oxidant in excess. After the reaction was complete, the absorption spectrum was measured using a Union SM-401 spectrophotometer. The amounts of the radical anions of oxidants determined from the absorbances at $\lambda_{max.}$ (for radical anion of tetracyanoethylene $\lambda_{max.}$ 475 nm, ε 5.67×10^4 dm² mol⁻¹,[19] of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone $\lambda_{max.}$ 585 nm, ε 5.46×10^4 dm² mol⁻¹,[20] of 2,3-dicyano-*p*-benzoquinone $\lambda_{max.}$ 585 nm, ε 3.63×10^4 dm² mol⁻¹,[20] and of 7,7,8,8-tetracyano-*p*-quinodimethane $\lambda_{max.}$ 842 nm, ε 4.35×10^5 dm² mol⁻¹ [21]) were plotted against the amount of $[CoR_2(bipy)_2]^+$ added. The least-squares slope was 1.0 ± 0.1.

Kinetic Measurements.—Kinetic measurements were carried out by using a Union RA-103 stopped-flow spectrophotometer and a Union SM-401 spectrophotometer for electron-transfer reactions from $[CoR_2(bipy)_2]^+$ to organic oxidants under deaerated conditions with half-lives of shorter than 10 s and longer than 100 s, respectively. Reaction rates were monitored by the increase in the absorbances at $\lambda_{max.}$ of the radical anions of oxidants[19–21] under pseudo-first-order conditions in the

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† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

presence of more than a 10-fold excess of oxidant. Pseudo-first-order rate constants were determined by least-squares curve fitting using a Union System 77 microcomputer.

Cyclic Voltammetry.—Redox potentials of $[CoR_2(bipy)_2]^+$ in MeCN were determined by cyclic voltammetry at various sweep rates (20—1 000 mV s^{-1}), based on the method described in detail elsewhere.[22,23] The cyclic voltammogram was recorded on a Hokuto Denko model HA-301 potentiostat/galvanostat at 298 K using a platinum microelectrode and a standard NaCl calomel reference electrode (s.c.e.) under deaerated conditions. The platinum microelectrode was routinely cleaned by soaking in concentrated nitric acid, followed by repeated rinsing with water and acetone, and drying at 353 K prior to use. The anodic peak potential of $[CoR_2(bipy)_2]^+$ 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.

Results and Discussion

Reductive Coupling of a Pair of Alkyl Ligands in cis-$[CoR_2(bipy)_2]^+$ *upon One-electron Oxidation.*—*cis*-Dialkylbis(2,2′-bipyridyl)cobalt(III) complexes undergo facile cleavage of the pair of cobalt–alkyl bonds upon one-electron oxidation by tetracyanoethylene (tcne), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (ddbq), 2,3-dicyano-*p*-benzoquinone (dcbq), 7,7,8,8-tetracyano-*p*-quinodimethane (tcnq), and $[Fe(phen)_3]^{3+}$ in MeCN. The cleavage products are listed in Table 1, where yields of alkanes (R–R) from the coupled alkyl radicals approach 100% except for ethane from tcne (92%). In any case, no detectable RH or R$-$H has been observed upon one-electron oxidation. Spectral titration and the product analysis indicated that one equivalent of the radical anion of the oxidant was formed per equivalent of $[CoR_2(bipy)_2]^+$ (see Experimental section), and the stoicheiometry of the reaction is as shown by equation (1), where ox denotes the oxidant.

$$[CoR_2(bipy)_2]^+ + ox \longrightarrow R\text{–}R + [Co(bipy)_2]^{2+} + ox^{\bullet -} \quad (1)$$

The strikingly selective formation of R–R (Table 1) indicates that facile reductive elimination proceeds from $[CoR_2(bipy)_2]^{2+}$ formed by the one-electron transfer from $[CoR_2(bipy)_2]^+$ to the oxidant. Similar facile reductive elimination has been reported for *cis*-dialkyl(2,2′-bipyridyl)iron(III) and the corresponding iron(II) complex upon one- and two-electron oxidation, respectively.[24,25]

On the other hand, the present result is in marked contrast with the mode of cleavage of the cobalt–alkyl bond in *trans*-dialkylcobalt(III) complexes of macrocyclic chelates such as dimethylglyoxime upon one-electron oxidation where homolytic cleavage of only one cobalt–alkyl bond occurs to yield the products derived from alkyl radicals, *i.e.* a mixture of RH, R$-$H, and R-R depending on the experimental conditions.[12] The thermal decomposition of related *cis*-dialkylcobalt(III) complexes such as *cis*-$[CoR_2(acac)(PPhMe_2)_2]$ (acac = acetylacetonate) has been reported to give the β-elimination products, *i.e.* RH and R$-$H.[26] Thus, both the *cis* configuration and the high oxidation state (IV) of cobalt seem to be essential for selective reductive coupling of the alkyl ligands in dialkylcobalt complexes.

Table 1. Yields of the product based on the amount of *cis*-$[CoR_2(bipy)_2]^+$ (R = Me and Et) employed (3.8 μmol) in the reactions with some oxidants (20 μmol) in MeCN (2.0 cm^3) at 298 K

Oxidant	*cis*-$[CoMe_2(bipy)_2]^+$ Ethane (%)	*cis*-$[CoEt_2(bipy)_2]^+$ Butane (%)
tcne	92	97
ddbq	100	99
dcbq	100	100
$[Fe(phen)_3]^{3+}$	100	98

Redox Potentials of cis-$[CoR_2(bipy)_2]^+$.—In order to understand electron-transfer reactions from $[CoR_2(bipy)_2]^+$ to oxidants [equation (1)], the redox potentials of both $[CoR_2(bipy)_2]^+$ and the oxidants are indispensable. The redox potentials of oxidants $E^{\ominus}(ox\text{–}ox^{\bullet -})$ used in this study (Table 1) are well known since the cathodic electrochemistry of these oxidants is reversible.[27] On the other hand, electrochemical oxidation of monoalkylcobalt(III) complexes with dimethylglyoxime and Schiff-base ligands is also known to proceed by a reversible one-electron process to afford relatively stable monoalkylcobalt(IV) complexes with a half-life of about several minutes at 298 K in MeCN, and thereby the redox potentials of monoalkylcobalt(III) complexes have been determined from the cyclic voltammograms.[28] In contrast, the anodic electrochemistry of dimethylcobalt(III) complexes with macrocyclic ligands is reported to be highly irreversible.[12] In the present case as well, the electrochemical oxidation of $[CoR_2(bipy)_2]^+$ was highly irreversible as characterized by the cyclic voltammogram which shows a cathodic wave with a well defined current maximum but no coupled anodic wave on the reverse scan even at sweep rates up to 1 000 mV s^{-1}. Such an irreversible oxidation of $[CoR_2(bipy)_2]^+$ indicates that the follow-up reaction of $[CoR_2(bipy)_2]^{2+}$, *i.e.* the reductive coupling of the alkyl ligands [equation (1)], may be fast on the time-scale of the cyclic voltammetry measurements.

A method of determining redox potentials in such irreversible systems has recently been established based on the Gibbs energy relationship for electron-transfer reactions,[22,23] which as given by Marcus[14] is shown in equation (2), where $\Delta G_{ex.}^{\ddagger}$ is the Gibbs

$$\Delta G^{\ddagger} = \Delta G_{ex.}^{\ddagger}\,[1 + (\Delta G_{et.}^{\ominus}/4\Delta G_{ex.}^{\ddagger})]^2 \quad (2)$$

activation energy for self-exchange of electrons between $[CoR_2(bipy)_2]^+$ and $[CoR_2(bipy)_2]^{2+}$ when the standard Gibbs energy of electron transfer, $\Delta G_{et.}^{\ominus}$ $\{= F[E^{\ominus}(CoR_2^{2+}\text{–}CoR_2^{+}) - E]\}$, where F is the Faraday constant and E the electrode potential, is equal to zero. It should be noted that the application of equation (2) is limited to a region $-4\Delta G_{ex.}^{\ddagger} < \Delta G_{et.}^{\ominus} < 4\Delta G_{ex.}^{\ddagger}$.[29] In this region the transfer coefficient β is expressed as a function of $\Delta G_{et.}^{\ominus}$ by differentiating equation (2) with respect to $\Delta G_{et.}^{\ominus}$ yielding equation (3), from which can be derived a relation between the

$$\beta = \tfrac{1}{2} + \tfrac{1}{8}(\Delta G_{et.}^{\ominus}/\Delta G_{ex.}^{\ddagger}) \quad (3)$$

oxidation peak potential $E^{p}(CoR_2^{2+}\text{–}CoR_2^{+})$ and the standard redox potential $E^{\ominus}(CoR_2^{2+}\text{–}CoR_2^{+})$ when $E = E^{p}(CoR_2^{2+}\text{–}CoR_2^{+})$, equation (4). According to equation (4), the standard

$$E^{p}(CoR_2^{2+}\text{–}CoR_2^{+}) = E^{\ominus}(CoR_2^{2+}\text{–}CoR_2^{+}) + 4\,(1 - 2\beta)\Delta G_{ex.}^{\ddagger}/F \quad (4)$$

redox potential $E^{\ominus}(CoR_2^{2+}\text{–}CoR_2^{+})$ can be evaluated from the intercept of the linear correlation between $E^{p}(CoR_2^{2+}\text{–}CoR_2^{+})$ and 4 (1 − 2β) and the β value is obtained from the width of the anodic wave, $E^{p}(CoR_2^{2+}\text{–}CoR_2^{+}) - E^{p/2}(CoR_2^{2+}\text{–}CoR_2^{+})$, using equation (5).[30] Linear plots of $E^{p}(CoR_2^{2+}\text{–}CoR_2^{+})$ *vs.* 4 (1 − 2β) for $[CoR_2(bipy)_2]^+$

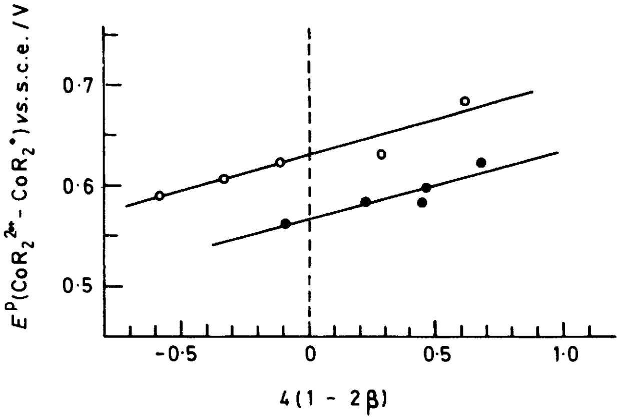

Figure 1. Oxidation peak potentials $E^p(CoR_2^{2+}–CoR_2^+)$ vs. s.c.e. of *cis*-$[CoR_2(bipy)_2]^+$ [R = Me (○) and Et (●); 5.0 × 10^{-3} mol dm^{-3}] in MeCN containing 0.10 mol dm^{-3} $NBu^n_4ClO_4$ plotted as a function of the transfer coefficient β, 4 (1 − 2β), based on the Marcus–Gibbs energy relationship [equation (2)], see text

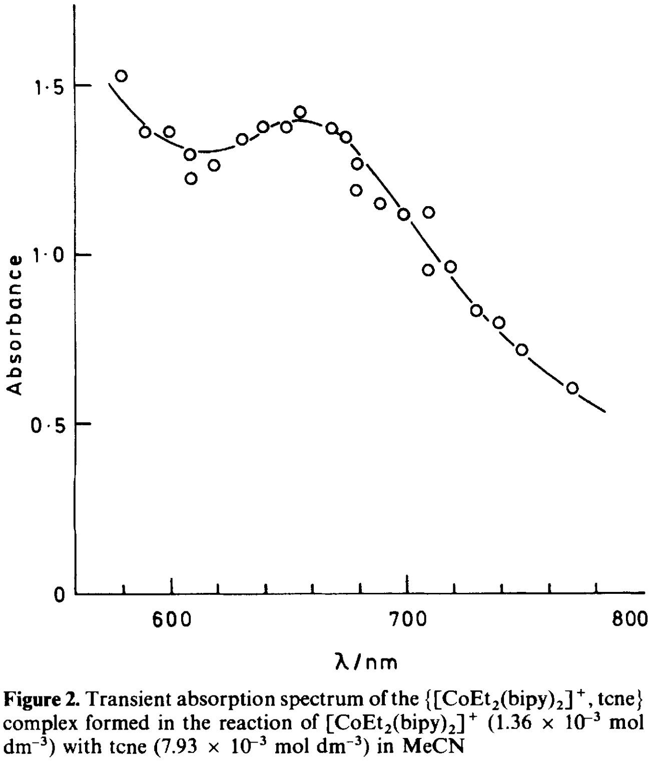

Figure 2. Transient absorption spectrum of the {$[CoEt_2(bipy)_2]^+$, tcne} complex formed in the reaction of $[CoEt_2(bipy)_2]^+$ (1.36 × 10^{-3} mol dm^{-3}) with tcne (7.93 × 10^{-3} mol dm^{-3}) in MeCN

$$E^p(CoR_2^{2+}–CoR_2^+) - E^{p/2}(CoR_2^{2+}–CoR_2^+) = 1.857RT/\beta F \quad (5)$$

(R = Me or Et) in MeCN containing 0.10 mol dm^{-3} $NBu^n_4ClO_4$ are shown in Figure 1. Then, from the intercepts and slopes in Figure 1 the standard redox potentials $E^\ominus(CoR_2^{2+}–CoR_2^+)$ vs. s.c.e. and the $\Delta G_{ex.}^\ddagger$ values were determined as follows: R = Me, $E^\ominus(CoMe_2^{2+}–CoMe_2^+)$ 0.63 V, $\Delta G_{ex.}^\ddagger$ 6.9 kJ mol^{-1}; R = Et, $E^\ominus(CoEt_2^{2+}–CoEt_2^+)$ 0.57 V, $\Delta G_{ex.}^\ddagger$ 6.7 kJ mol^{-1}.

Formation of a Charge-transfer Complex as a Reaction Intermediate.—Mixing of a MeCN solution of $[CoEt_2(bipy)_2]^+$ (1.36 × 10^{-3} mol dm^{-3}) with tcne (7.93 × 10^{-3} mol dm^{-3}) in the stopped-flow spectrophotometer results in an instant appearance of a new absorption band with a broad but distinctive absorption maximum centered at 660 nm (Figure 2), followed by its decay. The decay coincided with an increase in absorbance at 457 nm due to tcne.[5] Since the initial absorbance at 660 nm was proportional to the concentrations of $[CoEt_2(bipy)_2]^+$ and tcne, the new absorption band may be assignable to an intermolecular charge-transfer (c.t.) complex formed between $[CoEt_2(bipy)_2]^+$ and tcne with a 1:1 stoicheiometry [equation (6)]. Similar new absorption bands

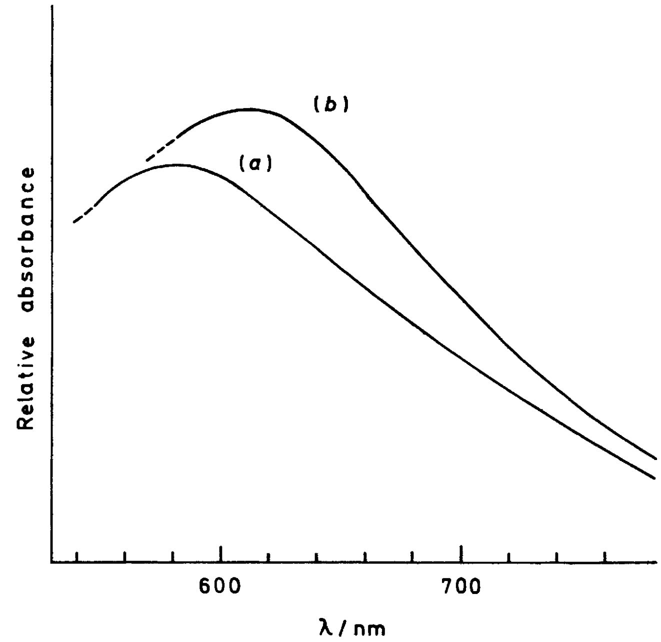

Figure 3. Absorption spectra of (*a*) $[CoMe_2(bipy)_2]^+$–*p*-chloranil and (*b*) $[CoEt_2(bipy)_2]^+$–*p*-chloranil complexes in dimethylformamide

$$[CoEt_2(bipy)_2]^+ + \text{tcne} \rightleftharpoons \{[CoEt_2(bipy)_2]^+, \text{tcne}\} \quad (6)$$

which may also arise from c.t. complexes were observed ($\lambda_{max.}$ 580 and 610 nm for R = Me and Et, respectively) upon mixing a dimethylformamide solution of $[CoR_2(bipy)_2]^+$ (1.7 × 10^{-3} mol dm^{-3}) with *p*-chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone) (1.0 × 10^{-1} mol dm^{-3}), as shown in Figure 3. The c.t. spectra of the $[CoR_2(bipy)_2]^+$ complexes in the presence of other organic oxidants in Table 1 such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone have not been recorded because of significant overlaps with the absorption bands due to the radical anions of the oxidants[20,21] formed upon electron transfer from $[CoR_2(bipy)_2]^+$ to the oxidants [equation (1)].

In order to confirm the assignment of c.t. complexes, the transition energies of these absorption bands ($h\nu_{max.}$) were compared with those of known c.t. complexes formed between organometallic σ donors (dialkylmercury compounds HgR_2) and tcne[31] by plotting the $h\nu_{max.}$ values against the difference in the redox potentials between the organometallic donor (MR) and the organic oxidant (ox), which is related to the Gibbs energy change for electron transfer from MR to ox, $\Delta G_{et.}^\ominus$, by equation (7); the redox potentials of HgR_2, tcne, and *p*-chloranil

$$\Delta G_{et.}^\ominus/F = E^\ominus(MR^+–MR) - E^\ominus(ox–ox^{\bullet -}) \quad (7)$$

have been reported[27,31] and those of $[CoR_2(bipy)_2]^+$ were determined as described above. The plot of $h\nu_{max.}$ vs. $E^\ominus(MR^+–MR) - E^\ominus(ox–ox^{\bullet -})$ is shown in Figure 4, where both the

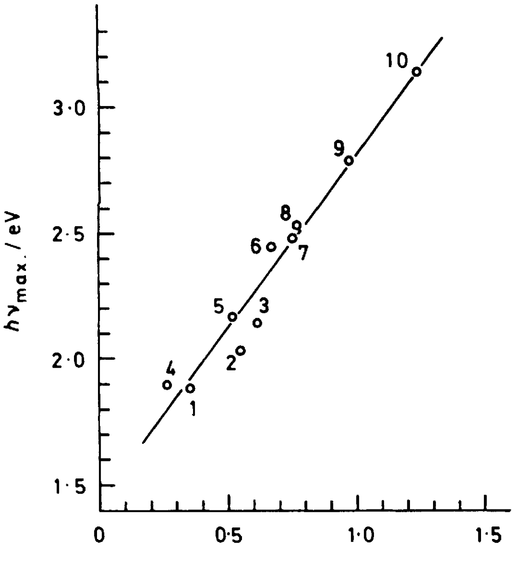

Figure 4. Plot of the transition energies ($h\nu_{max.}$) of the MR–tcne and MR-*p*-chloranil complexes (MR = $[CoR_2(bipy)_2]^+$ and HgR_2[31]) *vs.* the difference in the redox potentials between the organometallic donor (MR) and the organic oxidant (ox), $E^{\circ}(MR^+–MR) - E^{\circ}(ox–ox^{\cdot -})$: (1) $[CoEt_2(bipy)_2]^+$–tcne, (2) $[CoEt_2(bipy)_2]^+$–*p*-chloranil, (3) $[CoMe_2(bipy)_2]^+$–*p*-chloranil, (4) $HgBu^t_2$–tcne, (5) $HgPr^i_2$–tcne, (6) $HgMeBu^t$–tcne, (7) $HgEt_2$–tcne, (8) $HgMePr^i$–tcne, (9) HgMeEt–tcne, and (10) $HgMe_2$–tcne

$[CoEt_2(bipy)_2]^+$–tcne and $[CoR_2(bipy)_2]^+$–*p*-chloranil systems lie on the same linear correlation as the HgR_2–tcne system. Thus, the $[CoEt_2(bipy)_2]^+$–tcne and $[CoR_2(bipy)_2]^+$–*p*-chloranil complexes may be classified as c.t. complexes in which $[CoR_2(bipy)_2]^+$ act as σ donors, providing novel examples of organotransition metals acting as σ donors, while π complexes of organotransition metals are known.[32,33]

Kinetics and Mechanism.—The rates of the electron-transfer reactions from $[CoR_2(bipy)_2]^+$ to organic oxidants in MeCN at 298 K were monitored by the increase in the absorbance at $\lambda_{max.}$ of the radical anions of oxidants.[19–21] The rate equation can be expressed in terms of the second-order kinetics, showing a first-order dependence on the concentration of each reactant [equation (8)], which was confirmed under pseudo-first-order

$$d[ox^{\cdot -}]/dt = k_{obs.}[CoR_2{}^+][ox] \quad (8)$$

conditions in the presence of large excesses of the oxidants. The observed rate constants $k_{obs.}$ were determined from 4 to 20 replicate measurements to give average deviations from the mean values within ±5% (Table 2), together with the redox potentials of the oxidants[27,31] and $[CoR_2(bipy)_2]^+$. The rate constant for the reaction of $[CoR_2(bipy)_2]^+$ with *p*-chloranil has not been determined accurately since the rate of formation of the *p*-chloranil radical anion was too slow to compete with the decomposition of the radical anion. From the temperature dependence of $k_{obs.}$ for the reactions of $[CoR_2(bipy)_2]^+$ with dcbq, measured at 298, 308, and 318 K, the activation parameters ($\Delta H^‡$ and $\Delta S^‡$) have been determined: R = Me, $\Delta H^‡$ 59 ± 5 kJ mol^{-1}, $\Delta S^‡$ −13 ± 17 J K^{-1} mol^{-1}; R = Et, $\Delta H^‡$ 49 ± 5 kJ mol^{-1}, $\Delta S^‡$ −4 ± 17 J K^{-1} mol^{-1}. The $\Delta S^‡$ values are close to zero, within the experimental errors, typical for electron-transfer reactions.[29]

The logarithms of rate constants $k_{obs.}$ in Table 2 were plotted against the difference in the redox potentials between $[CoR_2(bipy)_2]^+$ and the oxidants, $E^{\circ}(CoR_2{}^{2+}–CoR_2{}^+) - E^{\circ}(ox–ox^{\cdot -})$ {which is related to the standard Gibbs energy change for electron transfer from $[CoR_2(bipy)_2]^+$ to the oxidants, $\Delta G_{et.}{}^{\circ}$, by equation (7)}, as shown in Figure 5, where a linear correlation is observed [equation (9)]. It is interesting to

$$\log k_{obs.} = -15.3[E^{\circ}(CoR_2{}^{2+}–CoR_2{}^+) - E^{\circ}(ox–ox^{\cdot -})] + 6.2 \quad (9)$$

compare these results with the rate constants for the forward electron transfer from $[CoR_2(bipy)_2]^+$ to the oxidants, which can be calculated as a function of $\Delta G_{et.}{}^{\circ}$ by using the Marcus theory of electron-transfer reactions [equation (10)],[14] where

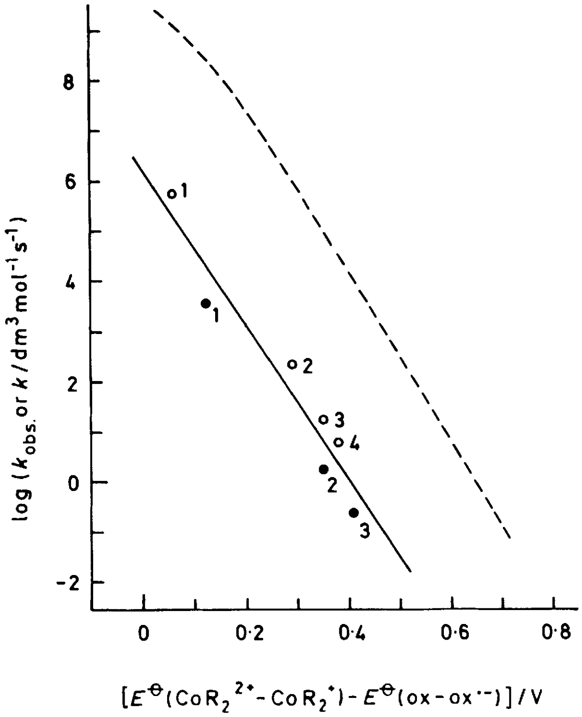

Figure 5. Plot of log $k_{obs.}$ for electron-transfer reactions from $[CoR_2(bipy)_2]^+$ [R = Me (●) and Et (○)] to the organic oxidants (Table 2) *vs.* the difference in the redox potentials between $[CoR_2(bipy)_2]^+$ and the oxidants, $E^{\circ}(CoR_2{}^{2+}–CoR_2{}^+) - E^{\circ}(ox–ox^{\cdot -})$. Numbers refer to the oxidants in Table 2. The broken line shows the calculated rate constants (k) for the forward electron transfer from $[CoR_2(bipy)_2]^+$ to the oxidants based on the Marcus theory [equation (10)], see text

Table 2. Rate constants $k_{obs.}$ of the electron-transfer reactions from *cis*-$[CoR_2(bipy)_2]^+$ (R = Me and Et) to some organic oxidants and their redox potentials (*vs.* s.c.e.) in MeCN at 298 K

			$k_{obs.}/dm^3\ mol^{-1}\ s^{-1}$	
Reaction	Organic oxident	$E^{\circ}(ox–ox^{\cdot -})$/ V	R = Me (0.63 V)*	R = Et (0.57 V)*
1	ddbq	0.51	3.2×10^3	5.5×10^5
2	dcbq	0.28	1.8	2.3×10^2
3	tcne	0.22	2.5×10^{-1}	1.9×10
4	tcnq	0.19	—	6.1

* The values in parentheses denote the redox potentials of *cis*-$[CoR_2(bipy)_2]^+$ which were determined from the analysis of the cyclic voltammograms (see Figure 1 and text).

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\,[1 + (\Delta G_{\mathrm{et.}}^{\ominus}/4\Delta G_0^{\ddagger})]^2 \qquad (10)$$

$\Delta G_0^{\ddagger}$ is the intrinsic barrier for electron transfer from $[\mathrm{CoR_2(bipy)_2}]^+$ to the oxidants when $\Delta G_{\mathrm{et.}}^{\ominus} = 0$, which corresponds to $\Delta G_{\mathrm{ex.}}^{\ddagger}$ in the case of self-exchange of electrons between $[\mathrm{CoR_2(bipy)_2}]^+$ and $[\mathrm{CoR_2(bipy)_2}]^{2+}$ [equation (4)]. According to the Marcus theory,[14] the intrinsic barrier $\Delta G_0^{\ddagger}$ can be calculated as the average of $\Delta G_{\mathrm{ex.}}^{\ddagger}$ for the self-exchange of electrons between $[\mathrm{CoR_2(bipy)_2}]^+$ and $[\mathrm{CoR_2(bipy)_2}]^{2+}$, and that between the oxidants and their radical anions. The $\Delta G_{\mathrm{ex.}}^{\ddagger}$ values for the $[\mathrm{CoR_2(bipy)_2}]^+$–$[\mathrm{CoR_2(bipy)_2}]^{2+}$ system have already been evaluated from an analysis of the cyclic voltammograms as described above ($\Delta G_{\mathrm{ex.}}^{\ddagger}$ 6.8 ± 0.1 kJ mol^{-1} for R = Me and Et). On the other hand, the $\Delta G_{\mathrm{ex.}}^{\ddagger}$ values for the tcne–tcne$^{\bullet-}$, tcnq–tcnq$^{\bullet-}$, dcbq–dcbq$^{\bullet-}$, and ddbq–ddbq$^{\bullet-}$ systems have been reported to be approximately the same (8.8 ± 0.1 kJ mol^{-1}).[31,34] Then, the $\Delta G_0^{\ddagger}$ value in equation (10) is 7.8 kJ mol^{-1}. Thus, the $\Delta G^{\ddagger}$ values can be calculated from equations (4) and (10) by using $\Delta G_0^{\ddagger}$ together with the values of the redox potentials of $[\mathrm{CoR_2(bipy)_2}]^+$ and the oxidants in Table 2. When $\Delta G_{\mathrm{et.}}^{\ominus} > 4\Delta G_0^{\ddagger}$, however, equation (10) may no longer be valid,[29] and in this case $\Delta G^{\ddagger}$ is approximately equal to $\Delta G_{\mathrm{et.}}^{\ominus}$.[35] The calculated dependence of log k [$=Z\exp(-\Delta G^{\ddagger}/RT)$, where Z is the collision frequency, 1×10^{11} dm^3 mol^{-1} s^{-1}][14] on the difference in the redox potentials between $[\mathrm{CoR_2(bipy)_2}]^+$ and the oxidants, $E^{\ominus}(\mathrm{CoR_2}^{2+}\text{–}\mathrm{CoR_2}^+) - E^{\ominus}(\mathrm{ox\text{–}ox^{\bullet-}})$ $(=\Delta G_{\mathrm{et.}}^{\ominus}/F)$, is shown as the broken line in Figure 5, where the calculated rate constants (k) for the forward electron transfer from $[\mathrm{CoR_2(bipy)_2}]^+$ to the oxidants run parallel to the observed rate constants ($k_{\mathrm{obs.}}$), but are much larger by approximately four orders of magnitude. Such a large discrepancy as well as the observed Brönsted slope [equation (9)] which is close to $-F/2.3RT$ (-16.9 at 298 K) suggests that the forward electron transfer from $[\mathrm{CoR_2(bipy)_2}]^+$ to the oxidants is not the rate-determining step, and thereby the follow-up reaction may be the rate-determining step, since the calculated rate constant k provides the lowest limit for the forward electron transfer and a Brönsted slope smaller than $-F/2.3RT$ would be expected if the forward electron transfer is the rate-determining step.[14]

Based on the above discussion on the linear correlation between log $k_{\mathrm{obs.}}$ and $E^{\ominus}(\mathrm{CoR_2}^{2+}\text{–}\mathrm{CoR_2}^+) - E^{\ominus}(\mathrm{ox\text{–}ox^{\bullet-}})$ (Figure 5) as well as the observation of a c.t. complex as a reaction intermediate (Figure 2), the mechanisms of the reactions of $[\mathrm{CoR_2(bipy)_2}]^+$ with the oxidants [equation (1)] may be as in equations (11)—(13) and the observed rate constant

$$cis\text{-}[\mathrm{CoR_2(bipy)_2}]^+ + \mathrm{ox} \overset{K_{\mathrm{c.t.}}}{\rightleftharpoons} \{cis\text{-}[\mathrm{CoR_2(bipy)_2}]^+, \mathrm{ox}\} \qquad (11)$$

$$\{cis\text{-}[\mathrm{CoR_2(bipy)_2}]^+, \mathrm{ox}\} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{cis\text{-}[\mathrm{CoR_2(bipy)_2}]^{2+}, \mathrm{ox}^{\bullet-}\} \qquad (12)$$

$$\{cis\text{-}[\mathrm{CoR_2(bipy)_2}]^{2+}, \mathrm{ox}^{\bullet-}\} \xrightarrow{k_d} \mathrm{R\text{–}R} + [\mathrm{Co(bipy)_2}]^{2+} + \mathrm{ox}^{\bullet-} \qquad (13)$$

$k_{\mathrm{obs.}}$ as in equation (14). Under the condition $k_{-1} \gg k_d$ (*i.e.* the reaction following electron transfer is the rate-determining step), equation (14) reduces to (15), where $K_{\mathrm{et.}}$ $(=k_1K_{\mathrm{c.t.}}/k_{-1})$ is

$$k_{\mathrm{obs.}} = k_d k_1 K_{\mathrm{c.t.}}/(k_d + k_{-1}) \qquad (14)$$

$$k_{\mathrm{obs.}} = k_d K_{\mathrm{et.}} \qquad (15)$$

the formation constant for the radical ion pair $\{[\mathrm{CoR_2(bipy)_2}]^+, \mathrm{ox}^{\bullet-}\}$. The log $K_{\mathrm{et.}}$ value can be related to the standard Gibbs energy change for electron transfer, $\Delta G_{\mathrm{et.}}^{\ominus}$,[35] and thereby expressed as a function of the difference in the redox potentials between $[\mathrm{CoR_2(bipy)_2}]^+$ and the oxidants as shown in equation (16), where w_p is the work term required to bring the products

$$\log K_{\mathrm{et.}} = -F[E^{\ominus}(\mathrm{CoR_2}^{2+}\text{–}\mathrm{CoR_2}^+) - E^{\ominus}(\mathrm{ox\text{–}ox^{\bullet-}})]/2.3RT + w_p/2.3RT \qquad (16)$$

$[\mathrm{CoR_2(bipy)_2}]^{2+}$ and ox$^{\bullet-}$ to their mean separation in the activated complex.[35] Then, from equations (15) and (16) a linear correlation between log $k_{\mathrm{obs.}}$ and $E^{\ominus}(\mathrm{CoR_2}^{2+}\text{–}\mathrm{CoR_2}^+) - E^{\ominus}(\mathrm{ox\text{–}ox^{\bullet-}})$ is derived with a slope of $-F/2.3RT$ which is -16.9 at 298 K [equation (17)]. Thus, the linear plot between log $k_{\mathrm{obs.}}$ and $E^{\ominus}(\mathrm{CoR_2}^{2+}\text{–}\mathrm{CoR_2}^+) - E^{\ominus}(\mathrm{ox\text{–}ox^{\bullet-}})$ in Figure 5 [equation (19)] accords well with equation (17) which is

$$\log k_{\mathrm{obs.}} = -16.9[E^{\ominus}(\mathrm{CoR_2}^{2+}\text{–}\mathrm{CoR_2}^+) - E^{\ominus}(\mathrm{ox\text{–}ox^{\bullet-}})] + \log k_d - (w_p/2.3RT) \qquad (17)$$

derived from the reaction mechanism [equations (11)—(13)].

By comparing equation (9) with (17), the log $k_{\mathrm{obs.}}$ value when $E^{\ominus}(\mathrm{CoR_2}^{2+}\text{–}\mathrm{CoR_2}^+) - E^{\ominus}(\mathrm{ox\text{–}ox^{\bullet-}}) = 0$ provides the lowest limit of the k_d value for the reductive elimination of the pair of alkyl ligands in *cis*-$[\mathrm{CoR_2(bipy)_2}]^{2+}$ (log $k_d \geqslant 6.2$). When equation (17) is applied to the reaction of *trans*-$[\mathrm{CoMe_2(L)}]$ [L = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioximate(1−)] with $[\mathrm{IrCl_6}]^{2-}$,[12] by substituting the observed rate constant (4.0×10^2 dm^3 mol^{-1} s^{-1})[12] and the redox potentials (*vs.* s.c.e.) of *trans*-$[\mathrm{CoMe_2(L)}]$ (0.53 V)[36] and $[\mathrm{IrCl_6}]^{2-}$ (0.43 V)[37] into equation (17), the log k_d value is evaluated as $\geqslant 4.3$, in good agreement with the reported value (log k_d = 5.0).[12] Such agreement indicates that the lowest limit of k_d evaluated from equation (17) may provide a good estimate of the lifetime τ of *cis*-$[\mathrm{CoR_2(bipy)_2}]^{2+}$ ($\tau \sim 0.8$ μs for R = Me and Et). Then, it is interesting to compare the lifetime of *cis*-$[\mathrm{CoR_2(bipy)_2}]^{2+}$ with that of *trans*-$[\mathrm{CoMe_2(L)}]^+$ ($\tau \sim 10$ μs).[12] The shorter lifetime of *cis*-$[\mathrm{CoR_2(bipy)_2}]^{2+}$ may be ascribed to the facile elimination of the pair of alkyl ligands in the *cis*-dialkylcobalt(IV) complexes [equation (13)], compared with the homolytic cleavage of one of the alkyl ligands in the *trans*-dimethylcobalt(IV) complex.[12]

References

1 J. K. Kochi, 'Organometallic Mechanisms and Catalysis,' Academic Press, New York, 1978.

2 P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, 1976, **76**, 219; R. R. Schrock and G. W. Parshall, *ibid.*, p. 243; M. C. Baird, *J. Organomet. Chem.*, 1974, **64**, 289; P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, **2**, 271.

3 J. M. Pratt and P. J. Craig, *Adv. Organomet. Chem.*, 1973, **11**, 331; D. Dodd and M. D. Johnson, *J. Organomet. Chem.*, 1973, **52**, 1; M. D. Johnson, *Acc. Chem. Res.*, 1978, **11**, 57.

4 Y-T. Fanchiang, *Inorg. Chem.*, 1982, **21**, 2344; 1983, **22**, 1693; *Organometallics*, 1983, **2**, 121; Y-T. Fanchiang and J. M. Wood, *J. Am. Chem. Soc.*, 1981, **103**, 5100; H. P. C. Hogenkamp, N. A. Kohlmiller, R. Howsinger, T. E. Walker, and N. A. Watwiyoff, *J. Chem. Soc., Dalton Trans.*, 1980, 1668.

5 J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, 1964, **86**, 2311; P. Abley, E. R. Dockal, and J. Halpern, *ibid.*, 1973, **95**, 3166; J. Topich and J. Halpern, *Inorg. Chem.*, 1979, **18**, 1339.

6 V. E. Magnuson and J. H. Weber, *J. Organomet. Chem.*, 1974, **74**, 135; I. Ya. Levitin, A. L. Sigan, and M. E. Vol'pin, *ibid.*, 1976, **114**, C53.

7 J. H. Espenson, W. R. Bushey, and M. E. Chmielewski, *Inorg. Chem.*, 1975, **14**, 1302; J. H. Espenson and T. D. Sellers, jun., *J. Am. Chem. Soc.*, 1974, **96**, 94; J. H. Espenson and J. Shveima, *ibid.*, 1973, **95**, 4468; H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *ibid.*, 1974, **96**, 2378.

8 R. Dreos, G. Tauzher, N. Marsich, and G. Costa, *J. Organomet. Chem.*, 1975, **92**, 227; G. Costa, G. Mestroni, and C. Cocevar, *Chem. Commun.*, 1971, 706; R. H. Magnuson, J. Halpern, I. Ya. Levitin, and M. E. Vol'pin, *J. Chem. Soc., Chem. Commun.*, 1978, 44.

9 M. W. Witman and J. H. Weber, *Inorg. Chim. Acta*, 1977, **23**, 263.
10 J. H. Dimmit and J. H. Weber, *Inorg. Chem.*, 1982, **21**, 1554; M. W. Witman and J. H. Weber, *ibid.*, 1976, **15**, 2375; 1977, **16**, 2512.
11 J. H. Espenson, H. L. Fritz, R. A. Heckman, and C. Nicolini, *Inorg. Chem.*, 1976, **15**, 906.
12 W. H. Tamblyn, R. J. Klingler, W. S. Hwang, and J. K. Kochi, *J. Am. Chem. Soc.*, *1981*, **103**, 3161.
13 S. Fukuzumi, K. Ishikawa, and T. Tanaka, *Chem. Lett.*, 1984, 421.
14 R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853; *Annu. Rev. Phys. Chem.*, 1964, **15**, 155.
15 G. Mestroni, A. Camus, and E. Mestroni, *J. Organomet. Chem.*, 1970, **24**, 775.
16 D. D. Perrin, W. L. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, New York, 1966.
17 J. Cason, C. F. Allen, and S. Goodwin, *J. Org. Chem.*, 1948, **13**, 403; A. G. Brook, *J. Chem. Soc.*, 1953, 5040.
18 S. Fukuzumi, N. Nishizawa, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3482; M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, 1961, **83**, 1830.
19 O. W. Webster, W̃. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, 1962, **84**, 3678.
20 Y. Iida, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1777.
21 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.
22 S. Fukuzumi, K. Hironaka, N. Nishizawa, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2220.
23 R. J. Klingler, S. Fukuzumi, and J. K. Kochi, *Am. Chem. Soc. Symp. Ser.*, 1983, **211**, 117; R. J. Klingler and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 4790.
24 T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1978, **100**, 1634; W. Lau, J. C. Huffman, and J. K. Kochi, *Organometallics*, 1982, **1**, 155.
25 T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1104; A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Am. Chem. Soc.*, 1965, **87**, 4562; 1968, **90**, 1878.
26 T. Ikariya and A. Yamamoto, *J. Organomet. Chem.*, 1976, **120**, 257.
27 D. H. Evans, 'Encyclopedia of Electrochemistry of the Elements, Organic Section,' eds. A. J. Bard and H. Lund, Marcel Dekker, New York, 1978, ch. XII-1 and refs. therein; Y. Iida and H. Akamatsu, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 231.
28 J. Halpern, M. S. Chan, J. Hanson, T. S. Roche, and J. A. Topich, *J. Am. Chem. Soc.*, 1975, **97**, 1606; I. Levitin, A. L. Sigan, and M. E. Vol'pin, *J. Chem. Soc., Chem. Commun.*, 1975, 469.
29 L. Eberson, *Adv. Phys. Org. Chem.*, 1982, **18**, 79.
30 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
31 S. Fukuzumi, C. L. Wong, and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 2928.
32 T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, 1971, **93**, 3350, 3360.
33 Y-T. Fanchiang, *J. Chem. Soc., Chem. Commun.*, 1982, 1369.
34 M. A. Komarynsky and A. C. Wahl, *J. Phys. Chem.*, 1975, **79**, 695; A. Yamagishi, *ibid.*, 1976, **80**, 1271.
35 R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.
36 R. J. Klingler and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 4186.
37 C. L. Wong and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 5593.

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