(16) It is unlikely that **6** and **8** interconvert; cf. ref 3, note 11.

(17) (a) Repetition of case 2 using **5** prepared with CH_3O^- CH_3OH gave **10** with 4.29% net retention. (In this experiment, **10**, $C_2H_5 = CH_3$, was formed with 0.1% net retention.) Close agreement with results obtained using **5** prepared with $C_2H_5O^-$–C_2H_5OH eliminates the possibility that **10**, formed solvolytically *during the preparation* of **5** has biased the observed stereochemistry. (b) Exclusion of $C_6H_5(CH_3)C{=}N_2$ as a racemizing intermediate (from **6** or **8** by loss of ethanol) is necessary because **10** is formed by reaction of $C_6H_5(CH_3)C{=}N_2$ and $(C_2H_5)_3O^+BF_4^-$.[18] However, nitrogen-evolution controls show that the latter reaction occurs either very slowly, or not at all, at −22° to −27°; i.e., conditions under which reactions of **3** or **5** with $(C_2H_5)_3O^+BF_4^-$ are fast and near quantitative. (c) Alternative mechanisms which feature bimolecular reactions of **5** with itself, or with oxonium ions derived from **10**, are inconsistent with the similar stereochemical results of direct and inverse addition experiments (Table I, note *a*, and runs 2 and 3). Specifically, such mechanisms predict more inversion for **10** formed in direct addition. This is not observed.

(18) R. A. Moss, C. E. Powell, and K. M. Luchter, unpublished observation.

(19) Both reactions are less stereoconservative in the presence of HMPA, consistent with their ionic nature.

(20) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N.Y., 1968, especially pp 449–452.

(21) Separations were measured from Dreiding models.

(22) Reasons for excluding alkyldiazonium ions in eq 3 or 4 are discussed in R. A. Moss, *Acc Chem. Res.*, **7**, 421 (1974).

(23) Parallel reactions of the syn analogues are almost identical: **6** → **10**, 78% (overall) retention, Table I, case 4; **4** → 1-phenylethyl 2-naphthoate, 73% retention.[3]

(24) R. A. Moss, M. J. Landon, K. M. Luchter, and A. Mamantov, *J. Am. Chem. Soc.*, **94**, 4392 (1972).

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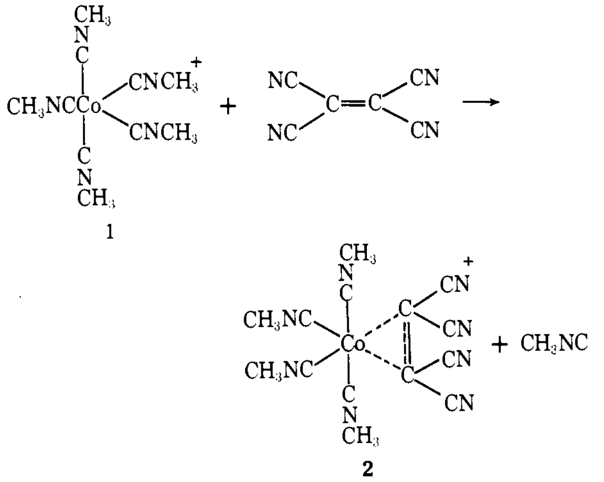
Evidence for Radical Intermediates in the Addition of Tetracyanoethylene to Pentakis(methyl isocyanide)cobalt(I)

Sir:

A number of reports of the involvement of free radicals in reactions of both d^8 and d^{10} transition metal complexes has recently appeared.[1-7] The involvement of electron-transfer steps is most probable in cases where the specific metal concerned is known to undergo one-electron transfer to give a stable complex with a d^7 or d^9 electronic configuration. Consequently, of the various group 8 metal complexes with a d^8 electronic configuration, those of Co(I) are the most likely to undergo a one-electron oxidation, since Co(II) is the most commonly encountered d^7 ion within this group. Many previous studies of Co(I) reactions have stressed the role of Co(I) as a nucleophile;[8] here are presented data which suggest that outer-sphere electron-transfer may also be involved in reactions of Co(I) complexes.

The reaction of tetracyanoethylene with $[Co(CNCH_3)_5][PF_6]$ (**1**)[9] in a variety of solvents including acetone, dichloromethane, and acetonitrile produces via eq 1 the yellow cation **2** which has been isolated as the hexafluorophosphate in yields of 90% (Anal. found for $C_{14}H_{12}CoN_8PF_6$, C, 33.93; H, 2.49; N, 22.36. Ir (Fluorolube mull) 2275, 2255, 2230 cm^{-1} ($\nu_{C\equiv N}$); ^1H NMR (CD_3COCD_3) τ 6.26 (6 H, $^2J_{NH} = 2.4$ Hz), 6.12 (6 H, $^2J_{NH} = 2.4$ Hz). Mixing the reactants of eq 1 produced a transient brown color. The evidence reported below suggests that the transient arises via reaction 2, an outer sphere, electron-transfer step and that this is followed by reaction 3 which generates the final products. Both of the products of reaction 2—tetracyanoethylene radical anion[10] and $Co(CNCH_3)_5^{2+}$[11]—are known, isolable species. Thermodynamically, the electron transfer of eq 2 is favored as demonstrated by electrochemical measurements. In acetonitrile solution with 0.1 M $(n\text{-}Bu)_4NClO_4$ as supporting electrolyte and an aqueous calomel reference electrode, tetracyanoethylene undergoes a one-electron reduction with a half-wave potential of +0.22 V. Under similar conditions $Co(CNCH_3)_5^+$ undergoes a one-electron oxidation with a half-wave potential of +0.10 V. Cyclic voltammetry demonstrates that this process is quasi-reversible with equal anodic and cathodic peak currents but with the peak separation of 120 mV. The identity of the electrochemical oxidation product as $Co(CNCH_3)_5^{2+}$ has been established; this complex undergoes one-electron reduction with a half-wave potential of +0.10 V.



(1)

$$Co(CNCH_3)_5^+ + (CN)_2C{=}C(CN)_2 \rightarrow Co(CNCH_3)_5^{2+} + (NC)_2C{=}C(CN)_2^- \quad (2)$$

$$Co(CNCH_3)_5^{2+} + (NC)_2C{=}C(CN)_2^- \rightarrow \mathbf{2} + CNCH_3 \quad (3)$$

Through the use of a flow system in conjunction with electron spin resonance (ESR) spectroscopy it has been possible to detect the tetracyanoethylene radical anion during reaction **1**. When a 5 mM dichloromethane solution of **1** and a 5 mM dichloromethane solution of tetracyanoethylene are mixed in a flow system with a flow rate of 25 ml/min through a tube with 3 mm i.d., it has been possible to detect the characteristic 11-line ESR spectrum[12] (a(N) = 1.5 g) of the tetracyanoethylene radical anion. This could only be observed under the conditions of rapid flow. When the flow was stopped, the ESR spectrum of the radical anion vanished. No ESR signal due to $Co(CNCH_3)_5^{2+}$ could be observed. The inability to observe such a signal is not surprising in view of the low concentration and the line width of the ESR spectrum of $Co(CNCH_3)_5^{2+}$. The observation of the ESR spectrum of the tetracyanoethylene radical appears to be the result of eq 1 only. Under similar circumstances the reactions of methyl isocyanide, pentakis(methyl isocyanide)cobalt(II), or **3** with tetracyanoethylene do not produce the tetracyanoethylene radical anion.

Finally the separate occurrence of reaction 3 has been verified. When $[Co(CNCH_3)_5]^{2+}$ and $K[(NC)_2C{=}C(CN)_2]$[9] are mixed in acetonitrile solution **2** is formed in greater than 85% yield.

Although tetracyanoethylene undergoes addition to a variety of d^8 and d^{10} metal complexes,[14] the reaction reported here is the first in which the transient appearance of radicals has been observed. By way of comparison the addition of tetracyanoethylene to $Rh(CNR)_4^+$ has been examined; products analogous to **2** are formed.[13] However, no evidence for paramagnetic intermediates has been found and electrochemical examination of these and other Rh(I) complexes does not reveal the existence of any one-electron oxidation processes.

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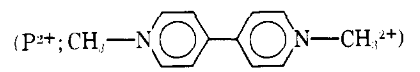
Electron Transfer Quenching of Excited States of Metal Complexes

Sir:

Quenching of the excited states of tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+*}$, by electron transfer has been demonstrated for several electron acceptors.[1-4] Such reactions are potentially of value in energy conversion processes. Likely candidates for a systematic study of such reactions are transition metal complexes because of their often high absorptivity in the visible and their ability to undergo facile electron transfer. Nearly all of the work in this area has utilized the redox properties of $Ru(bpy)_3^{2+*}$. Even though the $Ru(bpy)_3^{2+}$ system has some remarkable properties, it is clear that fundamental studies need to be carried out on a series of excited states of different orbital origins, and with different lifetimes and absorptivities. We report here a preliminary account of our initial work on the redox quenching of a series of metal complex excited states.

In order to extend the work on $Ru(bpy)_3^{2+*}$ we have investigated the reactions between the MLCT (d → π*) excited states of a series of ruthenium(II) chelates and the quenchers paraquat



in 0.10 M $[N(n\text{-}Bu)_4][ClO_4]$-acetonitrile, and $Fe(H_2O)_6^{3+}$ in 1.0 M aqueous $HClO_4$. The complexes differ with regard to excited state lifetimes and visible absorption properties (Table I). Flash photolysis studies[3] show that initial excited state quenching is followed by a back-thermal electron transfer reaction (Scheme I). The rate constants for the quenching step were determined by luminescence quenching using Stern-Volmer plots and excited state lifetimes (Table I). Rates for the back-reaction were obtained from flash photolysis by observing the recovery of the bleaching of the Ru(II) chelate (eq 3) following the quenching step (eq 2).

Scheme I

$$Ru(phen)_3^{2+} \xrightarrow{h\nu} Ru(phen)_3^{2+*} \quad (1)$$

$$Ru(phen)_3^{2+*} + Fe(H_2O)_6^{3+} \xrightarrow{k_q} Ru(phen)_3^{3+} + Fe(H_2O)_6^{2+} \quad (2)$$

$$Ru(phen)_3^{3+} + Fe(H_2O)_6^{2+} \xrightarrow{k_b} Ru(phen)_3^{2+} + Fe(H_2O)_6^{3+} \quad (3)$$

In all cases the initial quenching step is at, or near, the diffusion-controlled limit. The rates for the back-reaction between $Fe(H_2O)_6^{2+}$ and $Ru(phen)_3^{3+}$ or $Ru(terpy)(bpy)(NH_3)^{3+}$ are in excellent agreement with values obtained earlier by Cramer and Braddock[5] using the stopped-flow technique.

The f-f excited states of Eu^{3+} and Eu(III) chelates are known to be relatively long lived in solution.[6] They are of interest in terms of redox quenching since they conceivably can act as oxidizing rather than reducing agents, and since electrons must be transferred to relatively deeply buried f levels. Luminescence quenching of the excited states of

Table I. Kinetic and Spectral Data

Complex[a]	Absorption bands Photolyzed λ_{max}, nm (ϵ)[b]	Aqueous (Fe^{3+} as quencher)[c] τ_0 (μs)	k_q ($M^{-1}\,s^{-1}$)	k_b ($M^{-1}\,s^{-1}$)	Nonaqueous (Paraquat as quencher)[d] τ_0 (μs)	k_q ($M^{-1}\,s^{-1}$)	k_b ($M^{-1}\,s^{-1}$)
$Ru(bpy)_3^{2+}$[e]	450 (1.38×10^4)	0.624	2.9×10^9	9.5×10^5	0.85	2.4×10^9	8.1×10^9
$Ru(phen)_3^{2+}$	422 (1.76×10^4) 447 (1.84×10^4)	0.81	2.5×10^9	8.5×10^5	0.50	2.9×10^9	1.3×10^{10}
$Ru(terpy)(bpy)(NH_3)^{2+}$	462 (8.8×10^3)	0.43	3.1×10^9	1.1×10^4	*f*	*f*	*f*
$Ru(bpy)_2(CN)_2$	445 (9.0×10^3)	0.36	*g*	*g*	0.34	9.2×10^9	2.2×10^{10}
$Eu(phen)_3^{3+}$	270 (~5×10^5) 580 (~400)				740	3.7×10^7[h]	6.0×10^8[h]
Pd(OEP)	390 (1.7×10^5) 510 (1.6×10^4) 544 (5.0×10^4)				360	1.5×10^9	1.4×10^9

[a] Key: bpy is 2,2′-bipyridine; phen is 1,10-phenanthroline; terpy is 2,2′,2″-terpyridine; OEP is octaethylporphyrin. [b] In acetonitrile except for Pd(OEP) which is in isobutyronitrile. [c] In 1.0 M $HClO_4$. [d] In 0.1 M $[N(n\text{-}Bu)_4][ClO_4]$ (TBAP)–acetonitrile except for Pd(OEP) which is in isobutyronitrile. [e] Data from ref. 3. [f] Not stable in acetonitrile. [g] Upward curving Stern–Volmer plot indicates a static quenching phenomenon similar to the Cu^{2+}–$Ru(phen)_2(CN)_2$ system reported by J. Demas, *J. Am. Chem. Soc.*, 96, 3663 (1974). [h] NPh_3 as quencher, 0.01 M TBAP. For Stern–Volmer quenching λ_{ex} 580 nm to ensure metal centered excited state. Flash photolysis λ_{ex} 270 nm is necessary because ϵ at 580 nm is not large enough to populate a significant amount of excited state.