38-7; $Fe(CO)_2PMe_3(N_4Me_2)$, 76299-42-8; $Fe(CO)_2PMe_2Ph(N_4Me_2)$, 78328-92-4; $Fe(CO)_2PBu_3(N_4Me_2)$, 78328-93-5; $Fe(CO)_2PEt_2Ph(N_4Me_2)$, 78328-94-6; $Fe(CO)_2PMePh_2(N_4Me_2)$, 78328-95-7; $Fe(CO)_2P(OEt)_3(N_4Me_2)$, 78328-96-8; $Fe(CO)_2P(OMe)_3(N_4Me_2)$, 76299-41-7; $Fe(CO)_2PH_2Ph(N_4Me_2)$, 78328-97-9; $Fe(CO)_2P(c\text{-}Hx)_3(N_4Me_2)$, 78328-98-0; $Fe(CO)_2PPh_3(N_4Me_2)$, 76299-43-9; $Fe(CO)_2AsMe_3(N_4Me_2)$, 78328-99-1; $Fe(CO)_2AsEt_3(N_4Me_2)$, 78329-00-7; $Fe(CO)_2AsMe_2Ph(N_4Me_2)$, 78329-01-8; $Fe(CO)_2(4\text{-}CNpy)(N_4Me_2)$, 78329-02-9; $Fe(CO)_2Me_3CNC(N_4Me_2)$, 78329-03-0; $Fe(CO)(Me_3CNC)_2(N_4Me_2)$, 78329-04-1; BF_3, 7637-07-2; $Fe(Me_3CNC)_3(N_4Me_2)$, 78329-05-2.

Supplementary Material Available: Listings of rate constants for reaction 1 as a function of $Fe(CO)_3(N_4Me_2)$ concentration, ligand concentration, and temperature (2 pages). Ordering information is given on any current masthead page.

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Electron Transfer. 49. Redox Catalysis by Pyridinecarboxylic Acids in Which Conjugation Is Interrupted[1]

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Received January 6, 1981

The reductions of $Co(NH_3)_5py^{3+}$ and $Co(en)_3^{3+}$ with Eu^{2+} are strongly catalyzed by a number of carboxylate derivatives of pyridine in which the carboxyl group is separated from the ring by a saturated fragment of one to four atoms. The effectiveness of this group of "interrupted catalysts", each of which features a —C(=O)O— or —C(=O)N— group in the 4-position of the pyridine ring, exceeds that of a series of fully conjugated carboxylato catalysts described earlier.[12] Such effectiveness depends mainly on the ease with which these catalysts undergo 1e reduction to radical intermediates, cat· (k_1 in sequence 1). Observed enhancements of k_1 resulting from interposition of "insulating" side chains are attributed to intervention of homoallylic intermediates of types VIII and IX, in which europium is bound to the carboxyl but interacts with the pyridine ring as well. Catalytic potency in this series is quite insensitive to the length of the insulating chain but is found to decrease when branching is introduced or, more markedly, when a peptide linkage is incorporated into this chain. The isonicotinoyl derivatives of glycolic and lactic acids (I and II) are somewhat more effective than the *N*-(carboxymethyl) catalyst, $Inic^+CH_2COOH$ (VII) and, at the same time, suffer much less serious attrition under conditions of use. Arguments are presented that this improvement in recycling properties reflects more strongly negative values of $E°_{cat}$ for 1e reductions of ester catalysts I and II, leading to lower steady-state concentrations of the catalytic radical intermediates (cat·) in reaction mixtures where these catalysts are operating.

The various substituted pyridines which markedly catalyze the outer-sphere reductions of cobalt(III) complexes[3] appear to fall into two categories. In the first class are compounds in which a carboxyl or related function (ester, amide, or nitrile) lies in direct conjugation with the ring nitrogen. The second group consists of bipyridyls, fused bipyridyls, and dipyridylethylenes in which the two ring nitrogens are in conjugation. Catalysts in both groups operate through preliminary reduction to a radical, "cat·" (sequence 1), but the carboxyl derivatives

$$\text{cat} \underset{M^{3+},\ k_{-1}}{\overset{M^{2+},\ k_1}{\rightleftharpoons}} \text{cat}\cdot \xrightarrow[k_2]{Co^{III}} \text{cat} + Co^{II} \qquad (1)$$

$$M = Eu, V, Cr$$

are generally the more effective catalysts for their side chains can assume the role of "lead-in groups", thus allowing the initial reduction (k_1) to proceed via a facile inner-sphere path, whereas all catalytic steps with the bipyridyl-related catalysts are necessarily outer sphere.[3a,b] Note that the most powerful catalysts thus far encountered are derived from 2,4-pyridinedicarboxylic acid, in which both carboxyl groups are conjugated with the hetero nitrogen.[3c,4]

The impetus for the present work was our finding that certain carboxylato derivatives of pyridine, in which the carboxyl group was separated from the ring by a saturated fragment, were, when ligated to Co^{III}, remarkably effective mediators for inner-sphere reduction by Eu^{2+} and, further, that such reactions were strongly autocatalytic.[5] Since the initial step in autocatalytic sequences of this sort is the 1e reduction of the ligand released as a result of the primary electron transfer (i.e., the same process as that initiating catalytic sequence of (1)) it appeared likely that these ligands featuring interrupted conjugation would, when uncoordinated, catalyze elelctron transfer to such sluggish oxidants as $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and $Co(py)(NH_3)_5^{3+}$. We here compare the action exhibited by several members of this more recent class of catalysts.

Experimental Section

Inorganic Materials. Solutions of $Eu(ClO_4)_2$, the primary reductant, were prepared as described.[6] (Pyridine)pentaamminecobalt(III) perchlorate, $Co(NH_3)_5py(ClO_4)_3$,[7] and tris(ethylenediamine)cobalt(III) perchlorate, $Co(en)_3(ClO_4)_3$,[8] the primary oxidants, were prepared by published procedures.

Catalysts. Isonicotinate esters of α- and β-hydroxy acids were prepared by a procedure analogous to that of Irikura and co-workers[9] in which aqueous solutions of sodium isonicotinate and the sodium salt of the appropriate chloro- or bromo-substituted aliphatic acid were mixed, brought to pH 8, and then kept at 85 °C for 5 h. The mixture was then cooled, the desired carboxyalkyl isonicotinate precipitated by addition of HCl, and the product recrystallized from dilute aqueous $HClO_4$.

Isonicotinylglycine (V) was prepared by the procedure of Gardner and co-workers.[10] *N*-(2-Carboxybenzyl)isonicotinamide (VI) was

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[1] Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] On leave from Vivekananda College, Mylapore, Madras, India.

[3] See, for example: (a) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1942. (b) Fanchiang, Y.-T.; Gould, E. S. *Ibid.* **1977**, *16*, 2516. (c) Fanchiang, Y.-T.; Heh, J. C.-K; Gould, E. S. *Ibid.* **1978**, *17*, 1142.

[4] Singh, A. N.; Radlowski, C. A.; Reed, J. W.; Krishnamurthy, V. V.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 211.

[5] Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1289.

[6] (a) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2329. (b) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673.

[7] Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929.

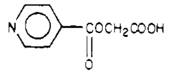
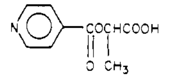
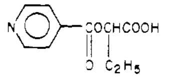
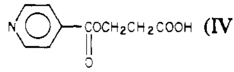
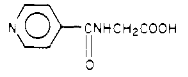
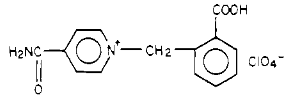
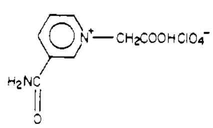
[8] (a) Work, J. B. *Inorg. Synth.* **1946**, *2*, 221. (b) Loar, M. K.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3689.

[9] Irikura, T.; Sata, S.; Kasuga, K.; Abe, Y.; Tamada, T. Japanese Patent 2707, 1967; *Chem. Abstr.* **1967**, *67*, 90691*m*.

[10] Gardner, T. S.; Wenis, E.; Lee, J. *J. Org. Chem.* **1954**, *19*, 753.

0020-1669/81/1320-3172$01.25/0

Table I. Analyses of Catalysts Featuring Interrupted Conjugation

	% C		% H	
	calcd	found	calcd	found
 (I)	53.0	52.8	3.87	3.97
 (II)	55.4	53.7	4.62	4.85
 (III)	57.4	57.6	5.26	4.08
 (IV)	55.4	54.5	4.62	4.55
 (V)	53.3	53.4	4.44	4.41
 (VI)	47.1	48.3	3.65	3.95
	34.3	34.4	2.86	3.10

prepared by a method adapted from that of Hajdu and Sigman.[11]

Analyses (Galbraith Laboratories) of the catalysts used appear in Table I.

Rate Measurements. Rates were estimated from measurements of decreases in absorbance at the low-energy Co(III) maximum (475 or 465 nm) with the use of a Cary 14 or Beckman 5260 spectrophotometer as described.[6b,12] Reactions were carried out in 1.0 M $HClO_4$ under pseudo-first-order conditions with either Co(III) or Eu^{2+} in greater than fivefold excess. Reactions were first order in Eu^{2+}, very nearly first order in catalyst, and with Eu^{2+} in excess (and Eu^{3+} added) were first order in Co(III). Reactions were followed for at least 5 half-lives. Catalytic attrition in the presence of excess reductant, as described for several of the most active catalysts,[4,13] was slight or, in most cases, imperceptible; however, for a number of experiments with $Co(en)_3^{3+}$ in excess, an appreciable decrease in specific rate during the course of a single run, due to the accumulation of Eu^{3+}, an inhibitor (see following section), was noted. When either of these effects was evident, half-life periods were extrapolated to zero time, and the resulting limiting values were used to calculate specific rates. In the absence of such complications, rate constants evaluated from successive half-values within a single run generally agreed to within 6%. Specific rates obtained from replicate runs agreed to within 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Nicotinylglycolic acid ($3\text{-pyCOOCH}_2\text{COOH}$) and *N*-(carboxymethyl)pyridine (py^+CH_2COOH) showed no catalytic activity at concentrations as great as 10^{-3} M, whereas 3-carbamoyl-1-(carboxymethyl)pyridine (Nic^+CH_2COOH) exhibited marginal activity.

Results and Discussion

The catalytic sequence of (1) leads, on application of the steady-state approximation to the radical intermediate, cat·, to the rate law of (2)[12] in which the k_{un} term, pertaining to

$$\text{rate} = \frac{k_1 k_2[\text{Co}^{\text{III}}][\text{Eu}^{2+}][\text{cat}]}{k_{-1}[\text{Eu}^{3+}] + k_2[\text{Co}^{\text{III}}]} + k_{un}[\text{Co}^{\text{III}}][\text{Eu}^{2+}] \quad (2)$$

the uncatalyzed reaction component, is very nearly neglibible in the system at hand. As in earlier systems,[3,12] the kinetic picture mirrors the competition between Co(III) and Eu^{3+} for the radical intermediate. If Co(III) is in deficiency and Eu^{3+} is added, the k_{-1} term in the denominator is dominant, leading to a first-order dependence on Co^{III} and inhibition by Eu^{3+}, but with the oxidant in large excess, reaction rates become nearly independent of Co(III).

Table II. Representative Kinetic Data for the Europium(II) Reduction of (Pyridine)pentaamminecobalt(III), $(NH_3)_5(py)Co^{3+}$, as Catalyzed by Isonicotinylglycolic Acid, $4\text{-pyCOOCH}_2\text{COOH}$

$10^3 \times$ $[Co^{III}]$, M	$10^3 \times$ $[Eu^{2+}]$, M	$10^2 \times$ $[Eu^{3+}]$, M	$10^6 \times$ [cat], M	$10^2 \times$ k,[a] s^{-1}
1.11	15.9	0	0	0.10
1.50	15.9	3.2	23.0	4.3
1.50	15.9	3.2	11.6	2.6
1.50	15.9	3.2	5.8	1.32
1.50	8.0	3.2	23.0	2.3
1.50	32.0	3.2	23.0	7.0
1.50	15.9	6.4	23.0	2.7
1.50	15.9	12.8	23.0	1.23
8.2	1.6	0	72.0	3.1
8.2	1.6	0	48.0	2.2
12.3	2.4	0	24.0	1.32
12.3	2.4	0	12.0	0.74
8.8	1.6	0	24.0	1.27
12.3	3.2	0	24.0	1.28

[a] Pseudo-first-order rate constants at 25 °C. Reactions were carried out in 1.0 M $HClO_4$.

Representative kinetic data for the reduction of $Co(NH_3)_5py^{3+}$, as catalyzed by isonicotinylglycolic acid (I), are assembled in Table II. With Co(III) in deficiency, plots of pseudo-first-order rate constants vs. the quotient $[\text{cat}][\text{Eu}^{2+}]/[\text{Eu}^{3+}]$ give values of k_1k_2/k_{-1} as slopes. With Co(III) in excess, plots of rate constants vs. [cat] yield, as slopes, values of k_1. Steady-state experiments such as those constituting this study do not yield individual values of k_2 and k_{-1}, only their ratio.

The resulting kinetic parameters for catalysts in the present series are summarized in Table III, together with several values pertaining to "fully conjugated" catalysts (from earlier work) which are included for comparison. Where possible, parameters pertaining to two oxidants, $Co(NH_3)_5py^{3+}$ and $Co(en)_3^{3+}$, have been entered. As expected, k_1, the specific rate for reduction of the catalyst, is independent of the oxidant taken. Among the carboxylate catalysts, there is very little variation in the ratio k_2/k_{-1} (for a given oxidant), but this ratio is found to be much greater with methyl viologen (MV) which is devoid of lead-in donor groups and therefore cannot utilize an inner-sphere path for k_{-1}.

The effectiveness of the various carboxylate catalysts is thus determined mainly by their values of k_1, which are seen to span wide ranges, both for the conjugated catalysts and for the "interrupted" catalysts (the final seven entries in Table III). Indeed, aside from the extraordinarily active derivatives of 2,4-pyridinedicarboxylic acid,[14] the interrupted catalysts appear to be, as a group, no less effective than the conjugated. Note that despite the incorporation of "insulating fragments", each active catalyst features a —C(=O)O— or a —C(=O)N— group in the 4-position of a pyridine ring; when this group is shifted to the 3-position or is removed from the ring, catalytic power becomes marginal or disappears completely. The effectiveness of these catalysts is doubtless related, at least in part, to the ease with which isonicotinyl-related systems undergo reduction.[5,15]

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(11) Hajdu, J.; Sigman, D. S. *Biochemistry* **1977**, *16*, 2841.

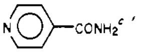
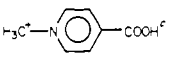
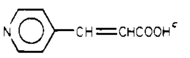
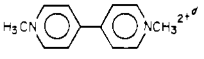
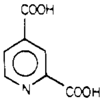
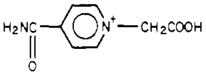
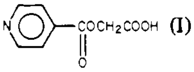
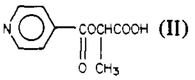
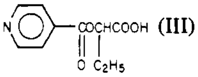
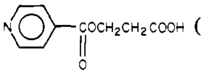
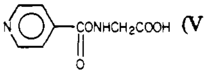
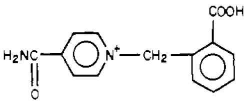
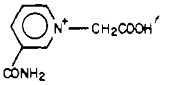
(12) Fanchiang, Y.-T.; Carlson, R. R.; Thamburaj, P. K.; Gould, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 1073.

(13) Radlowski, C. A., Chum, P.-W.; Hua, L.; Heh, J.; Gould, E. S. *Inorg. Chem.* **1980**, *19*, 401.

(14) The most reactive electron-transfer catalyst of this type thus far reported is the N-methylated dimethyl ester of 2,4-pyridinedicarboxylic acid[4] which reacts with Eu^{2+} at a specific rate near 2.4×10^4 M^{-1} s^{-1} (25 °C, 1 M $HClO_4$) but deteriorates very rapidly during use. Values of k_1 for other pyridinedicarboxylato derivatives have been reported by Fanchiang.[3c]

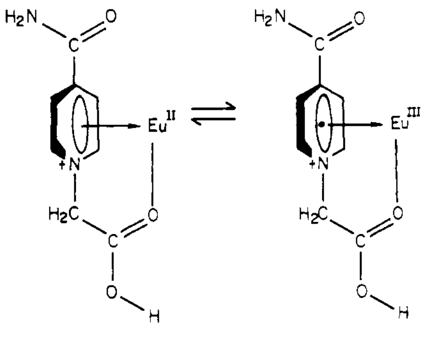
(15) See, for example: Bruhlmann, U.; Hayon, E. *J. Am. Chem. Soc.* **1974**, *96*, 6169.

Table III. Catalyzed Europium(II) Reductions of Cobalt(III) Complexes. Composite Rates and Kinetic Parameters

conjugated catalysts	oxidant[a]	k_1k_2/k_{-1}[b]	k_1	k_2/k_{-1}
	(py)Ro $(en)_3Co$	15.4 0.16	2.0	7.6 0.078
	(py)Ro $(en)_3Co$	115 1.31	16	7.7 0.081
	(py)Ro $(en)_3Co$	3.1×10^2 4.7	28 28	11.0 0.17
 (MV)	(py)Ro $(en)_3Co$	 2.6×10^2	0.76 0.66	 3.9×10^2
	(py)Ro	2.3×10^4[e]	1.7×10^3	13
"interrupted" catalysts	**oxidant[a]**	**k_1k_2/k_{-1}[b]**	**k_1**	**k_2/k_{-1}**
 (VII)	(py)Ro	8.9×10^2[e]	170	5.2
 (I)[g]	(py)Ro $(en)_3Co$	4.3×10^3 49	3.5×10^2 3.8×10^2	12.3 0.13
 (II)	(py)Ro	2.7×10^3	3.0×10^2	8.8
 (III)	(py)Ro $(en)_3Co$	144 1.52	25	5.6
 (IV)	(py)Ro $(en)_3Co$	3.6×10^2 3.8	10^2	3.6
 (V)	(py)Ro	8.4	0.7	12
 (VI)	(py)Ro	6.3×10^2	95	6.6
	(py)Ro	2.5	0.33	7.6

[a] (py)Ro = (pyridine)pentaamminecobalt(III); $(en)_3Co$ = tris(ethylenediamine)cobalt(III). [b] Values of k_1 and the quotient k_1k_2/k_{-1} (see (1)) are in $M^{-1} s^{-1}$. The ratio k_2/k_1 is dimensionless. Reactions were carried out in 1.0 M $HClO_4$ at 25 °C. [c] Reference 12. [d] Reference 3b. [e] Corrected for catalyst deterioration during individual runs (see ref 4). [f] Marginal catalyst. The acid having no $-CONH_2$ group (py^+-CH_2COOH) exhibits no catalytic activity. [g] The 3-isomer of this acid, $3-pyCOOCH_2COOH$, does not exhibit catalytic activity.

The most striking result of this study is that incorporation of a carboxyl-bearing side chain can accelerate the one-electron reduction of the activated pyridine rings (as indicated by k_1 values) by factors as great as 10^2. This enhancement is far too large to be attributed to an inductive effect nor can it result from any combination of conjugative interactions of the usual kind. We suspect instead that these reductions pass through intermediates of types VIII and IX, in which europium is bound to the side-chain carboxyl and interacts, at the same time, with the pyridine ring. Such "homoallylic" species, although infrequently encountered,[16] are analogous to those proposed[5,17] as intermediates in the very rapid Cr^{2+} reductions of the $(NH_3)_5Co^{III}$ complexes of these same carboxylic acids, the primary products from which have been characterized as $-COOCr^{III}$ complexes.



VIII IX

We find values of k_1 to be quite insensitive to the length of the chain separating the carboxyl group from the activated ring, i.e., only minor variations in k_1 are observed as this insulating chain is extended from one member (complex VII) to three (I, II, and VI) and, further, to four (complex IV). Scale models have been constructed for intermediate IX and for analogous species which are taken to intervene in reductions of catalysts I–VI. In each instance, close contact between Eu(III) and the π-electron region of the pyridine ring may be

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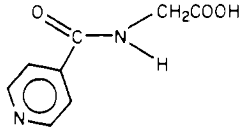
(16) See, for example: (a) Story, P. R.; Clark, B. C., Jr. *Carbonium Ions* **1972**, *3*, Chapter 23. (b) Itoh, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1968**, *90*, 1843.

(17) Srinivasan, V. S.; Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 2094.

achieved by suitable twisting of the side chain. Comparisons of such models may thus be considered to be in accord with the lack of kinetic selectivity within this series if it is assumed further that interaction between the two functions takes place mainly through space rather than through the insulating chain.

The reactivity pattern for Eu(II) reductions of the pyridine derivatives in this study contrasts markedly with that governing the Cr^{2+} reductions of the $(NH_3)_5Co^{III}$ complexes of this same group of acids.[17] Chromium(II) reduction of the Co^{III} complex of $Inic^+CH_2COOH$ (VII) is found to be unexpectedly rapid,[5] but electron-transfer rates fall off quite sharply with elongation of the chain between functions, suggesting that interaction through the chain has assumed a much more important role in the latter series.[18]

The k_1 value for isonicotinylglycine (V), the only interrupted catalyst with an amide function in the side chain, falls well below the values for all other members of the series. It is likely that this compound, like a large number of known N-alkylated amides,[19] exists preferentially as the trans conformer (X) in



X

which interaction between the pyridine ring and a carboxyl-bound metal ion is ruled out. Rotation aroung the peptide linkage to allow formation of an intermediate analogous to IX would be expected to contribute as much as 18 kcal/mol[19] extra to ΔG^* associated with the homoallylic route, making this path virtually inoperative.

Note finally that catalytic deterioration, which has been found to be extensive when many of the more reactive electron-transfer catalysts are utilized in conjunction with Eu^{2+},[4,13] is not a serious problem in the systems at hand. Thus, the isonicotinoyl derivatives of glycolic and lactic acids (I and II) are seen to be somewhat more effective than the N-carboxymethyl catalyst VII and, at the same time, exhibit much more favorable recycling characteristics. Attrition of catalyst VII has been shown[4] to occur mainly through bimolecular disproportionation of the radical intermediate, cat·. We may then reasonably infer that this second-order process is significantly more important for the intermediate from VII than for those from the ester catalysts I and II, implying, in turn, that the radical from reduction of VII disproportionates at the greater specific rate or that it achieves a higher steady-state concentration. We favor the latter alternative in view of existing evidence that rate constants for disproportionation of substituted pyridinyl radicals in strongly acid solution fall slightly below the diffusion-controlled limit and exhibit relatively little kinetic response to structural alteration.[4,20] An increase in the steady-state concentration of cat· in systems of this type reflects a shift in the formal 1e potential, E°_{cat}, to a less strongly negative value.[21] Attempted direct electrochemical comparisons of such potentials for the catalysts at hand have encountered the difficulty that these molecules in acid media undergo irreversible 2e reduction (rather than the desired reversible 1e reduction) at metal electrodes.[22] Past experience[23] indicates, however, that cat· radicals of this type can be generated by pulse radiolysis in Eu^{2+}-free systems and that these react with $py(NH_3)_5Co^{3+}$ at measurable specific rates. The latter correspond to values of k_2 indicated in sequence 1 and, in conjunction with experimental quotients k_1k_2/k_{-1} (Table III), should allow us to estimate the ratios k_1/k_{-1} and thus values of $E^\circ_{cat\cdot}$.[12] Work is proceeding in this direction.

Registry No. I, 78307-89-8; II, 78328-72-0; III, 78307-90-1; IV, 78307-91-2; V, 2015-20-5; VI, 78307-93-4; VII, 78307-95-6; $(Nic^3CH_2CO_2H)ClO_4^-$, 78307-97-8; (py)Ro, 31011-67-3; $(en)_3Co$, 14878-41-2; Eu^{2+}, 16910-54-6.

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(18) The lesser role of through-space interaction in the reductions by Cr^{2+} has been attributed tentatively to a mismatch of orbital symmetry between the e_g orbitals of octahedrally coordinated Cr(II) and the $4B_2$ orbital associated with the pyridine ring in the homoallylic transition state.[17]

(19) See, for example: Robin, M. B.; Bovey, F. A.; Basch, B. In "The Chemistry of Amides"; Zabicky, J., Ed.; Wiley-Interscience: New York, 1970; pp 19–34.

(20) See, for example: (a) Hayon, E.; Simic, M. *J. Am. Chem. Soc.* **1973**, *95*, 1029. (b) Kosower, E. M.; Teuerstein, A.; Burrows, H. D.; Swallow, A. J. *Ibid.* **1978**, *100*, 5185.

(21) With the assumption that we have reasoned correctly, the greater ease with which catalyst VII undergoes reduction may reflect poorer stabilization of its oxidized form by solvation. Protonated forms of the other members of this series derive an extra measure of stabilization via hydrogen bonding in solution ($PyH^+ \cdots OH_2$), but this cannot be the case when the pyridine ring is N-alkylated.

(22) Singh, A. N., unpublished experiments, Kent State University, 1980. The 2e reductions of these catalysts at metal electrodes are in accord with the report[13] that cat· radicals of the type considered here are stronger 1e oxidants than the aromatics from which they are derived.

(23) See, for example: Cohen, H.; Meyerstein, D. *Isr. J. Chem.* **1974**, *12*, 1049.