Electron Transfer. 130. Reductions with Indium(I)[1]

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Received January 12, 1996[⊗]

Aqueous solutions of the hypovalent state indium(I) have been prepared by treatment of In(Hg) with silver triflate in acetonitrile, followed by dilution with oxygen-free water. These solutions are stable for over 5 h at 25 °C. $In^I(aq)$ reacts with oxidants of the type $[(NH_3)_5Co^{III}(Lig)]^{2+}$ ($In^I + 2Co^{III} \rightarrow In^{III} + 2Co^{II}$), and kinetic profiles are consistent with a two-step sequence proceeding with formation of the metastable state In^{II}, which reacts rapidly with Co^{III}. Rate ratios for reductions of halogeno-substituted oxidants point to predominance of halide-bridged paths for the chloro, bromo and iodo complexes. Reductions of carboxylato-substituted derivatives are slow but appear to entail inner-sphere precursors if aided by an O-donor group in a position favorable for chelation. In no case is there evidence for reaction via initial reduction of the ligand (the radical-cation mechanism) although the potential of the In(I,II) couple (−0.40 V) allows this path for carbonyl-substituted oxidants. Reductions by In(I), like those by Eu(II), make no significant use of bridging by heterocyclic donor nitrogen centers in pyridine and pyrazine complexes.

Compounds of unipositive indium have been known for almost a century,[2,3] but success in preparing and handling solutions of the aqua ion of this state has been limited. Anodization of indium wire electrodes in dilute $HClO_4$ by Taylor and Sykes[4] yielded solutions of $In^I(aq)$, but at concentrations less than 4×10^{-4} M. More recently, Dronskowski[5] generated more concentrated solutions of an In(I) species in 9 M aqueous HBr, but such preparations deposited slightly soluble InBr upon dilution with water. From potentiometric measurements, Biedermann and Wallin[3c,6] estimated formal potentials for the couples In(I,III) and In(0,I), but these experiments dealt with solutions in which the ratio $[In^{III}]/[In^I]$ exceeded 10^2. Aqueous solutions of In(I) have been described[7] as being quite unstable in the absence of high molarities of halide.

We here report the preparations of aqueous In(I) solutions having greater concentrations of this hypovalent center than those previously recorded and exhibiting substantially improved stability. Such solutions have been used to compare the rates at which In^+ reduces a series of $1e^-$ oxidants featuring an array of ligands which have been recognized to assume a variety of mediating roles in reductions by transition metal ions.[8] This appears to be the first mechanistic study of such reactions involving a *s*-electron donor.

Experimental Section

Materials. Indium powder (150 mesh), anhydrous acetonitrile, and anhydrous silver trifluoromethanesulfonate (silver triflate) were Aldrich products. Cobalt(III) complexes not available from previous studies[8] were prepared by literature methods.[9]

Preparation of Indium(I) Solutions. The method used was a modification of the procedure of Headridge,[7] but silver triflate was substituted for the more hazardous reagent anhydrous $AgClO_4$. All preparative operations and transfer of In(I) solutions were carried out under prepurified argon. A mixture of 12 g of Hg and 1.7 g of powdered indium metal was kept at 180−190 °C for 1 h. The resulting amalgam was cooled and then stirred with a solution of 500 mg of dry silver triflate in 6.0 mL of anhydrous acetonitrile for 12 h at 25 °C.

$$Ag(I) + In \xrightarrow{CH_3CN} Ag + In(I) \qquad (1)$$

After separation from the precipitated silver metal, $[In^I]$ in the supernatant was estimated by transferring a small aliquot to an aqueous solution having a measured excess of I_3^- and then estimating the loss of I_3^- spectrophotometrically at 353 nm ($\epsilon = 2.51 \times 10^4$ M^{-1} cm^{-1}).[10]

$$In^I + I_3^- \rightarrow In^{III} + 3I^- \qquad (2)$$

Typically, $[In^I]$ was 0.27−0.30 M (83−92% of the $[Ag^I]$ taken) and did not change perceptibly on standing for over 5 days. Aqueous solutions for kinetic experiments, prepared by 300-fold dilutions of the CH_3CN solutions with O_2-free water, were stable for over 5 h at 25 °C in the absence of added electrolyte, as well as in acetate buffers (pH 4.5) and in 0.13 M $LiClO_4$. These preparations decomposed slowly (17% loss in 5 min) in 0.06 M $HClO_4$ but were stable for more than 60 min in 0.13 M $LiClO_4$. In(I) solutions gave negative tests for Ag^+ and Hg_2^{2+}.

Stoichiometric Studies. Stoichiometric determinations were carried out under argon in 0.05 M $HClO_4$ and monitored at the low energy maximum of the Co(III) oxidant. Measured deficient quantities of In^I were added to a known excess of the oxidant. After 1.0 min reaction time, decreases in absorbance were compared with those resulting from addition of an excess of reductant. Such measurements were straightforward with the more rapidly reacting oxidants (the chloro-, bromo-, and iodo-substituted complexes) and yielded stoichiometries $\Delta[Co^{III}]/\Delta[In^I] \simeq 2.00 \pm 0.03$. This procedure was not successful for the more

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

[1] Sponsorship of this work by the National Science Foundation (Grant 9414113) is gratefully acknowledged.

[2] See, for example: Thiel, A. *Z. Anorg. Chem.* **1904**, *40*, 280.

[3] Reviews: (a) Wade, K.; Banister, A. J. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Ed.; Pergamon Press: Oxford, England, 1973; Vol. 1, p 1080. (b) Tuck, D. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 3, p 154. (c) Biedermann, G.; Wallin, T. *Acta Chem. Scand.* **1960**, *14*, 594.

[4] Taylor, R. S.; Sykes, A. G. *J. Chem. Soc. A* **1969**, 2419.

[5] Dronskowski, T. *Inorg. Chem.* **1994**, *33*, 5960.

[6] For earlier (less successful) attempts, see: (a) Hepler, L. G.; Hugus, Z. Z., Jr., Latimer, W. M. *J. Am. Chem. Soc.* **1953**, *75*, 5652. (b) Kangro, W.; Weingartner, F. *Z. Elektrochem.* **1954**, *58*, 505.

[7] Headridge, J. B.; Pletcher, D. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 475.

[8] See, for example: (a) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647. (b) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 1791.

[9] (a) Fan, F.-R. F., Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639. (b) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1925. (c) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.

[10] (a) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4546. (b) Taylor, R. S.; Sykes, A. G. *J. Chem. Soc. (A),* **1971**, 1628.

S0020-1669(96)00039-0 CCC: $12.00

slowly reacting complexes; with these, decomposition of In^I competed significantly with the redox reactions of interest.

Kinetic Experiments. Reactions, under argon, were examined at the high wavelength maximum of the Co^{III} complex, using either a Beckman Model 5260 recording spectrophotometer, a Cary 14 instrument, or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Ionic strength, which was regulated by addition of $LiClO_4$ and $HClO_4$, was maintained at 0.2 M. Excess quantities of oxidant were generally used and concentrations were most often adjusted so that no more than 10% of the latter was consumed in reaction. All rapid reactions yielded simple exponential curves, and rate constants in such cases were obtained by nonlinear least-squares fitting to the relationship describing first-order decay. Values obtained from replicate runs agreed to better than 5%. These reactions were first order in both redox partners. Profiles exhibited no indication of transients formed or destroyed on a time scale comparable to that of the Co(III)−In(I) reaction. For a number of the slower reactions, rate constants were calculated from initial rates, and in many instances only upper limits were estimated.

Results and Discussion

Although the present method for preparing In(I) solutions is patterned after that described by Headridge and Pletcher,[7] we have obtained, by substitution of silver triflate for anhydrous $AgClO_4$, concentrations of this hypovalent state 10 times greater than that reported (0.026 M) by these workers. Moreover our yields of In^I (83−92% of the Ag^I used) are superior to those listed in the earlier work (47−51%). We have made no effort to maximize the concentrations of In(I) but have encountered no indication that we are approaching an upper limit. Aqueous In^I solutions used in our kinetic runs are 3−4 times as concentrated as those used by Taylor and Sykes[4] and appear to be significantly more stable, possibly because traces of indium metal have been removed. Biedermann[3c] has shown that aqueous solutions having both In(I) and In(III) contain negligible concentrations of In(II).

Since the reductant solutions employed in the kinetic runs are 0.30−0.90% CH_3CN by volume (0.06−0.18 M), a key question is whether In(I) in these reagents exists mainly as an aqua cation or whether nitrile complexes are playing a significant part. The limited data available concerning the stability quotients of CH_3CN complexes of representative metal centers suggest a remarkable sensitivity to ionic radius. For Cu^+ (r = 0.91 Å),[11] $Q_{assn} \geq 10^{2.2}$,[12] whereas for Ag^+ (1.29 Å) Q drops to $10^{0.35}$.[13] The value for In^+ (1.5 Å)[14] may be reasonably assumed to fall below unity, corresponding to less than 6% conversion to the nitrile complex at $[CH_3CN] = 0.06$ M and less than 18% conversion at 0.18 M. Moreover, the rate of reduction of $[Co(NH_3)_5(N_3)]^{2+}$ by In^+ is seen (Table 1) to be unchanged when $[CH_3CN]$ is increased from 0.06 to 1.30 M, indicating even lower degrees of ligation within this range.

The stoichiometry observed for the more rapid conversions, 2.00 ± 0.03 mol of Co^{III} per mole of In^I, allows us to represent these reactions, and, by implication, the slower transformations in the series, as (3). All reactions for which complete profiles could be obtained feature only one kinetic component, are first order in each of the two redox partners, and proceed at rates independent of acidity in the range $[H^+] = 0.010{-}0.060$ M.

Table 1. Rate Constants for Oxidations of In(I) by Cobalt(III) Complexes[a] with Inorganic Bridging Ligands

$$In^I + 2Co^{III} \rightarrow In^{III} + 2Co^{II}$$

oxidant, $[(NH_3)_5Co(Lig^-)]^{2+}$	k, $M^{-1}\ s^{-1}$
Lig = F	≤0.008
Lig = Cl	7.9 ± 0.4
Lig = Br	$(5.4 \pm 0.5) \times 10^2$
Lig = I	$(5.2 \pm 0.2) \times 10^3$
Lig = NCS	0.09 ± 0.01
Lig = N_3	0.28
	0.28[b]
	0.29[c]
	0.27[d]

[a] Reactions were carried out at 25 °C; $\mu = 0.2$ M ($LiClO_4$); $[H^+] = 0.01{-}0.06$ M, $[CH_3CN] = 0.06$ M unless otherwise indicated. $[In^I] = (7.8{-}8.2) \times 10^{-4}$ M, $[Co^{III}] = (4{-}12) \times 10^{-3}$ M. Conversions were monitored at the low energy absorption maximum of the Co(III) oxidant. [b] $[CH_3CN] = 0.42$ M. [c] $[CH_3CN] = 0.84$ M. [d] $[CH_3CN] = 1.3$ M.

$$In^I + 2Co^{III} \rightarrow In^{III} + 2Co^{II} \qquad (3)$$

The observed kinetic picture, in conjunction with the 2:1 stoichiometry, is consistent with two-step reaction sequence in (4), proceeding through the metastable state In^{II}, which reacts with Co(III) much more rapidly than does In^I.

$$In^I \xrightarrow{Co^{III}} In^{II} \xrightarrow[rapid]{Co^{III}} In^{III} \qquad (4)$$

Rates of reaction of the halogeno-substituted oxidants (Table 1) are seen to be unusually sensitive to structural alteration. The iodo:chloro ratio ($k_I/k_{Cl} = 660$) for reductions by In^+ is greater than that reported for all other metal centers except cob(II)alamin (vitamin B_{12r})[15] and may be compared with the corresponding ratio ($k_I/k_{Cl} = 20$)[16] pertaining to reductions by the outer-sphere reagent $[Ru(NH_3)_6]^{2+}$. Since the model of Marcus[17] stipulates that such ratios should be very nearly independent of the identity of the reductant for outer-sphere processes, this difference may be taken to imply the predominance of an inner-sphere (halide-bridged) path for the initial step involving the iodo oxidant.[18] Analogous comparison of the ratio k_{Cl}/k_F (≥900) with that for the Ru(II) reductant (3.7)[19] points to a bridged route for $[(NH_3)_5CoCl]^{2+}$ as well.

Adin[20] has noted that the rate ratio for inner sphere reductions of $[(NH_3)_5CoN_3]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$ by metal-ion centers may be taken to reflect the degree of hardness of the reducing species. This ratio lies close to 10^4 for reductions by Cr^{2+}(aq) but falls nearly to unity for reductions[21] by $[Co(CN)_5]^{3-}$ and drops to 1/8 for vitamin B_{12r}.[15] On the basis of this criterion, the corresponding ratio for In^+ ($k_{N_3}/k_{NCS} = 3$) suggests that it is one of the softest of the aqua-substituted reductants, an inference which is in accord also with its affinity for bromide[5] and with the very large rate ratio observed here for its reactions with the iodo and chloro derivatives of $(NH_3)_5Co^{III}$.

In extending this study to include oxidants having organic bridging groups (Table 2), we find that a number of reactions proceed so slowly that oxidation of In^+ by H^+ in the supporting electrolyte[10b] becomes a serious complication. For most of the

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(11) (a) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988, p 1387. Indicated radii pertain to coordination number 6; use of radii applicable to lower CN's should not significantly change the estimate presented.

(12) The lower limit for monoligation is taken as the square root of Q_1Q_2 (pertaining to diligation). The latter product is reported as $10^{4.35}$: Hemmerich, P.; Sigwart, C. *Experimentia* **1963**, *19*, 488.

(13) Stelting, K. M.; Manahan, S. E. *Anal. Chem.* **1974**, *46*, 2118.

(14) The radius of In^+ is estimated by multiplying $r_{In(III)}$ (0.76 Å) by 1.64/1.03, the ratio of reported[11] radii for Tl(I) and Tl(III).

(15) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1984**, *24*, 1791.

(16) Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1686.

(17) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853; *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

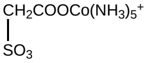
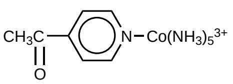
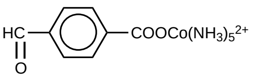
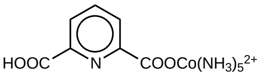
(18) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

(19) Daramola, G.; Ojo, J. F.; Olubuyide, O.; Oriaifo, F. *J. Chem. Soc., Dalton Trans.* **1982**, 2137.

(20) Adin, A.; Espenson, J. H. *Inorg. Chem.* **1972**, *11*, 686.

(21) See, for example: Candlin, J. P.; Halpern, J.; Nakamura, S. *J. Am. Chem. Soc.* **1963**, *85*, 2517.

Table 2. Rate Constants for Oxidations of In(I) by Cobalt(III) Complexes[a] with Organic Bridging Ligands

oxidant	k, $M^{-1}\,s^{-1}$
$(NH_3)_5Co(H_2O)^{3+}$	≤ 0.02
$(NH_3)_5Co(OAc)^{2+}$	≤ 0.002
$(NH_3)_5Co(C_2O_4H)^{2+}$ (**I**)	2.7
	2.5^b
	2.6^c
$(NH_3)_5Co(lactato)^{2+}$	≤ 0.007
$HC({=}O)COOCo(NH_3)_5^{2+}$ (**II**)	0.67
$CH_3C({=}O)COOCo(NH_3)_5^{2+}$ (**III**)	0.063
$C_6H_5C({=}O)COOCo(NH_3)_5^{2+}$ (**IV**)	≤ 0.02
 $\underset{SO_3}{\underset{\vert}{CH_2}}COOCo(NH_3)_5^{+}$ (**V**)	0.039
 (**VI**)	0.015
$(NH_3)_5Co(pyrazine)^{3+}$	0.057
 (**VII**)	≤ 0.004
	≤ 0.002

[a] Reactions were carried out at 25 °C; $\mu = 0.2$ M ($LiClO_4$); $[H^+] = 0.030$ M unless otherwise indicated; $[CH_3CN] = 0.06$ M; $[In^I] = (7.9-9.0) \times 10^{-4}$ M; $[Co^{III}] = 0.006-0.13$ M. [b] $[H^+] = 0.015$ M. [c] $[H^+] = 0.060$ M.

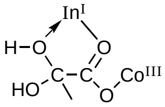
carboxylato-substituted complexes, only upper limits (in the range $0.002-0.007\ M^{-1}\,s^{-1}$) are listed, but marked acceleration is observed with the binoxalato ($HC_2O_4^-$) complex (**I**; $k_{In} = 2.6$) as well as perceptible, but less dramatic, increases with the glyoxalato (**II**; $k_{In} = 0.67$ and the pyruvato (**III**; $k_{In} = 0.063\ M^{-1}\,s^{-1}$) derivatives.

The rate enhancement for the HC_2O_4-substituted species brings to mind the marked quickening reported[22] for reduction of the same complex by Cr^{2+}, and, like the latter, is best attributed to a greater degree of conversion to the binuclear precursor complex resulting from chelation of the reductant by the oxalate function. However, the Cr^{2+} reduction proceeds preponderantly by a $[H^+]^{-1}$-proportional path, pointing to involvement of a much more active deprotonated form of the oxidant. We detect no hint of such a route for In^+ within the range $[H^+] = 0.015-0.060$ M, although at the lower acidity about 7% of this oxidant ($pK_A = 3.1$)[22] exists as $(NH_3)_5Co(C_2O_4)^+$. The implication here is that the reactivities of the $HC_2O_4^-$ and $C_2O_4^{2-}$ forms of the oxidant toward In^+ are similar enough to preclude kinetic differentiation by our experiments (although the deprotonated path may become detectable at higher pH values).

The more modest accelerations which appear to be associated with the α-carbonyl group in oxidants **II** and **III** have two possible sources. Since these complexes, like their parent acids,[23] are largely converted by aquation to *gem*-diols (**VIII**) (5),[24] we may again be seeing a reflection of chelation in the

$$-C({=}O)\,COOCo^{III} + H_2O \rightarrow \underset{\textbf{VIII}}{-C(OH)_2COOCo^{III}} \qquad (5)$$

precursor complex (**IX**), as is thought to occur with reductions of these carbonyl-substituted derivatives by Ti(III).[24] Alternatively, however, it may be asked whether the principal path for these reactions instead uses the carbonyl form of the oxidants, as is the case for reductions by Cr(II)[22] and Eu(II).[9a] It is recognized that these strongly reducing dipositive centers may operate by initial localized 1e reduction of the carbonyl function (the radical-cation mechanism),[25] and the very negative formal potential estimated by Latimer[6a] for the In(I,II) couple (−0.40 V), although highly approximate, suggests that this mechanistic variation might apply to In(I) as well.



IX

The indicated upper limit for reduction of the phenylglyoxylato complex (**IV**, $k_{In} \leq 0.02\ M^{-1}\,s^{-1}$) appears to dictate a choice. Its parent acid is known to be reduced much more easily than pyruvic acid[26] and to exists nearly completely in its (nonhydrated) keto form. The absence of appreciable acceleration may then be taken as evidence that the more rapid reductions of complexes **II** and **III** proceed mainly through the *gem*-diol forms. Moreover, the very slow reactions of the carbonyl-substituted complexes **VI** and **VII** (both of which are reduced rapidly by Cr^{II}),[9b] are in accord with the conclusion that reductive attack on the C=O function, which is prominent in reductions by Cr^{2+} and substantial in reductions by Eu^{2+},[9b] does not contribute significantly to the mechanistic picture for In^+.

This contrasting selectivity of Cr(II) and In(I) is notable since the two positive centers are subject to similar constraints imposed by orbital symmetry. Just as there is a mismatch of symmetry between the 5s orbital which is occupied by the reducing electron of In^+ and the π^* acceptor orbitals of the carbonyl group, so also is there a related mismatch between the e_g orbitals of octahedrally coordinated Cr(II) (one of which furnishes the reducing electron) and these carbonyl acceptor orbitals. It has been pointed out[8a] that electron transfer from Cr^{2+} to a carbonyl acceptor requires unsymmetric distortion of the ligand environment about the reductant, probably by stretching or breaking of a $Cr-OH_2$ bond above or below the acyl plane, a distortion aided by interaction with solvent molecules in the second coordination sphere. However, with In^+, which features a much lower charge density and is therefore much more weakly solvated, unsymmetric changes in the periphery of its solvation shell may have substantially less effect in easing the symmetry restriction to electron transfer.

In sum, the kinetic patterns emerging from our measurements point to a relatively narrow mechanistic perspective for electron transfer in Co(III)−In(I) systems. We find essentially no indication of outer-sphere transformations proceeding at a detectable pace, but the rate ratios pertaining to the halogeno-substituted oxidants argue strongly that In^+ is utilizing the bridging action of ligated chloride, bromide, and iodide. There is also evidence for redox mediation by O-donor bridges, especially when aided by the chelation involving O-donor neighboring groups, an effect considered to be highly characteristic of inner-sphere processes.[27] However, there is no hint of acceleration resulting from interaction of In^+ with reducible pendant functions even when such action may be feasible potentiometrically.[6a]

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(22) Price, H. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1.

(23) Ahrens, M.-L. *Z. Elektrochem.* **1969**, *72*, 691.

(24) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103.

(25) Gould, E. S. *Acc. Chem. Res.* **1985**, *18*, 22.

(26) Fleury, M. B.; Moiroux, J.; Fleury, D.; Dufresne, J.-C. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *81*, 365. Reduction potentials (1e, pH 0 vs NHE) reported by these workers are −0.268 V for pyruvic acid and +0.002 V for phenylglyoxylic acid.

(27) See, for example: Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321.

The situation with respect to N-donor bridges remains clouded. The azido, pyrazine, and 2,6-pyridinedicarboxylato derivatives of $(NH_3)_5Co^{III}$ are reduced by Cr^{2+} unusually rapidly ($k_{Cr} > 10^5$ M^{-1} s^{-1} in each case),[9a,21,28] all three through precursors featuring N−Cr bridging. With In^+ the rate for the N_3-bound oxidant is consistent with inner-sphere attack (Table 1), but bridging is at most marginal for the pyrazine complex and nondetectable for that of the 2,6-diacid (Table 2). We suspect that the apparent reluctance of In^+ to partake in redox bridging through heterocyclic nitrogen centers (as was noted for Eu^{2+} in an earlier comparison)[29] reflects, in large part, a series of vanishingly small association constant for the requisite N−In precursors.

Acknowledgment. The authors are grateful to Ms. Arla McPherson for technical assistance.

IC960039Y

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(28) Gould, E. S. *J. Am. Chem. Soc.* **1974**, *96*, 2373. Note that pyrazine and 2,6-pyridinedicarboxylate are among the most effective mediating groups reported for reductions by Cr(II).

(29) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673.