characterized by Booth, Chatt, and Chini[78] and later ascertained from an X-ray study[79] for a metal phosphine carbonyl complex of the congener platinum, *viz.*, $Pt_3\{P(C_6H_5)_2(CH_2C_6H_5)\}_3(CO)_3$; in this complex as in the hypothetical electronically equivalent neutral $Ni_3(CO)_6$ species, each metal atom has only a 16-electron count (*i.e.*, 2 electrons less than the required number for a closed-shell electronic configuration). The fact that other platinum phosphine cluster systems such as $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$[80] and $Pt_3\{P(C_6H_5)_3\}_4(CO)_3$[81] have also been shown from X-ray studies to contain analogous planar five-coordinated platinum atoms (*i.e.*, linked with one terminal ligand, two bridging carbonyl groups, and two other platinum atoms), whereas no corresponding complexes containing five-coordinated nickel atoms are known, is completely consistent with the expected large instability (and nonisolation to date) of the $Ni_3(CO)_6$ fragment or any other trinickel analog.

Further work is in progress on the derivative chemistry of these new cluster systems.

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Pulse Radiolysis of Aqueous Solutions of Pentacyanocobaltate(II). The Detection and Characterization of Pentacyanocobaltate(I)

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Abstract: Hydrated electrons, generated by pulse radiolysis of aqueous solutions of pentacyanocobaltate(II), react with the latter to form a transient species identified as pentacyanocobaltate(I), *i.e.*, $Co(CN)_5^{3-} + e^-_{aq} \rightarrow Co(CN)_5^{4-}$. The further reaction of pentacyanocobaltate(I) with water yields hydridopentacyanocobaltate(III), according to $Co(CN)_5^{4-} + H_2O \rightarrow Co(CN)_5H^{3-} + OH^-$. Kinetic measurements on the two successive reactions yielded the rate constants $1.2 \times 10^{10}\ M^{-1}\ sec^{-1}$ and $1.1 \times 10^5\ sec^{-1}$, respectively. The spectrum of $Co(CN)_5^{4-}$ is described and some aspects of its chemistry are discussed.

This paper describes pulse radiolysis studies on aqueous solutions of $Co(CN)_5^{3-}$, including kinetic measurements on the formation of $Co(CN)_5^{4-}$ according to eq 1 and on the further reaction of $Co(CN)_5^{4-}$

$$Co(CN)_5^{3-} + e^-_{aq} \xrightarrow{k_1} Co(CN)_5^{4-} \qquad (1)$$

with water to form $Co(CN)_5H^{3-}$ according to eq 2.[1]

$$Co(CN)_5^{4-} + H_2O \xrightarrow{k_2} Co(CN)_5H^{3-} + OH^- \qquad (2)$$

$Co(CN)_5^{4-}$ has previously been postulated as an intermediate in the chemical[2-4] and electrochemical[5] oxidations of $Co(CN)_5H^{3-}$, as well as in the electrochemical reduction of $Co(CN)_5^{3-}$.[6] However, this appears to be the first time that this species has been directly observed and spectrally characterized.

Experimental Section

Hydrated electrons (e^-_{aq}) were generated in the aqueous solutions by pulsed electron irradiation with the Argonne National Laboratory's ARCO linear accelerator (linac), in accord with the general procedures described elsewhere.[7,8] The electron pulses, of approximately 15-MeV energy and of 0.4-μsec duration, were attenuated by passing through quartz diffusors to vary the beam intensity and to achieve more uniform solution irradiation. The dose per pulse (determined by measuring the charge collected on a Faraday cup placed in front of the cell) was typically of the order of 1 krad, resulting in e^-_{aq} concentrations in the micromolar range. The irradiations were performed in a 5-cm cylindrical cell with Suprasil

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windows. Formation and decay of hydrated electrons and other transient species were followed spectrophotometrically using a 450-W xenon lamp as the analyzing light source. A Bausch and Lomb grating monochromator, followed by a photomultiplier (Hamamutsu TV R166 for wavelengths below 300 nm and RCA 1P28 for the 300–600-nm region) and an oscilloscope fitted with a Polaroid camera, were used to measure and record the absorption changes in the solution. By calibrating the Faraday cup while simultaneously monitoring the absorption of the hydrated electron, and using the known extinction coefficient of the latter ($\epsilon_{578\text{ nm}}$ $1.06 \times 10^4\ M^{-1}\ \text{cm}^{-1}$), absolute concentrations of e^-_{aq} and, hence, the conversion factors necessary to determine the molar extinction coefficients of other transient species could be computed.

Since electron irradiation of aqueous solutions produces other reactive species (notably H and OH) in addition to e^-_{aq}, it was necessary to adjust the conditions so as to eliminate interference from such species. At the prevailing pH (~13), H atoms were virtually completely converted to e^-_{aq} within the pulse time by the reaction $H + OH^- \rightarrow H_2O + e^-_{aq}$, for which $k = 2 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ [9] (corresponding to $t_{1/2} \sim 0.35\ \mu\text{sec}$). In those experiments in which the rate of reaction 1 was measured by monitoring the absorption of e^-_{aq}, interference from OH was eliminated by addition of *ca.* $10^{-2}\ M$ CH_3OH which reacts with OH according to $CH_3OH + OH \rightarrow CH_2OH + H_2O$, with a rate constant of $6 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ [9] (corresponding to $t_{1/2} \sim 0.1\ \mu\text{sec}$). In experiments in which the formation and decay of $Co(CN)_5^{4-}$ were monitored, the solutions contained approximately 0.1 M H_2 (corresponding to 100 atm of H_2 achieved by using a high-pressure irradiation cell)[8] to scavenge OH by the reaction $OH + H_2 \rightarrow H_2O + H$ ($k = 4.5 \times 10^7$,[9] corresponding to $t_{1/2} \sim 0.15\ \mu\text{sec}$). Since H atoms are rapidly converted to e^-_{aq} by the reaction with OH^- described above, effectively the only reactive species produced by electron irradiation under these conditions is e^-_{aq}.[10]

Solutions were prepared using triply distilled water which had been deaerated by successive evacuations and saturations with hydrogen, and preirradiated with a ^{60}Co γ source to destroy residual traces of oxygen and carbon dioxide. The final step of solution preparation was the injection (using the syringe technique)[11] into the irradiation cell already containing all the other solution components of the necessary additional small volume (*ca.* 0.1 cm^3) of a stock solution of *ca.* $10^{-2}\ M$ $Co(CN)_5^{3-}$ (prepared from AR grade $CoCl_2$ and KCN). The pulse radiolysis experiments were performed immediately after solution preparation in order to minimize the reaction of $Co(CN)_5^{3-}$ with water[12] or hydrogen.[13]

Sodium hydroxide and methyl alcohol were analytical grade reagents. Hydrogen gas (Matheson 99.95%, prepurified) was passed through a liquid nitrogen trap or (in the case of the high-pressure experiments) a catalytic deoxygenator.

Results

It was confirmed spectrophotometrically that the final yield of $Co(CN)_5H^{3-}$ corresponded to the initial hydrated electron concentration in accord with the overall stoichiometry defined by eq 1 and 2. Thus, in an experiment at pH 13 and 100 atm of H_2 (with $Co(CN)_5^{3-}$ in excess), the total initial e^-_{aq} concentration (including the primary e^-_{aq} yield as well as the yields of e^-_{aq} from the conversion of H and OH as described earlier) resulting from a 0.594-krad pulse was $3.9 \times 10^{-6}\ M$. At the end of the same experiment, the $Co(CN)_5H^{3-}$ concentration was determined from the absorbance change at 305 nm (2.07×10^{-3} for a 5-cm path), using the known extinction coefficients of $Co(CN)_5^{3-}$ and $Co(CN)_5H^{3-}$ at this wavelength (510 and 610 $M^{-1}\ \text{cm}^{-1}$, respectively), and found to be $4.1 \times 10^{-6}\ M$.

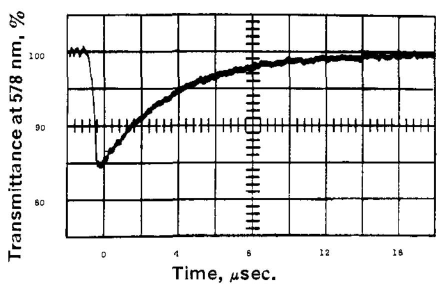

Figure 1. Typical oscillogram showing disappearance of e^-_{aq} (monitored at 578 nm) by reaction with $Co(CN)_5^{3-}$ (eq 1). Conditions correspond to experiment 4, Table I. (The pulse radiolysis is marked by the rapid initial transmittance decrease.)

Reaction of e^-_{aq} with $Co(CN)_5^{3-}$. The reaction between e^-_{aq} and $Co(CN)_5^{3-}$ (eq 1) was followed by monitoring the absorbance of e^-_{aq} at 578 nm ($\epsilon_{e^-_{aq}}$ $1.06 \times 10^4\ M^{-1}\ \text{cm}^{-1}$). Kinetic measurements at 20° encompassing the initial composition range, 0.5–2.0 μM e^-_{aq}, 11.5–29 μM $Co(CN)_5^{3-}$, and 0–3 $\times 10^{-4}\ M$ CN^-, yielded the second-order rate law described by eq 3. Since the initial $Co(CN)_5^{3-}$ concentration was generally at least ten times greater than that of e^-_{aq}, the observed kinetics were pseudo first order according to eq 4 (where D_{578} is the optical density at 578 nm due to e^-_{aq}).

$$-d[e^-_{aq}]/dt = -d[Co(CN)_5^{3-}]/dt = k_1[Co(CN)_5^{3-}][e^-_{aq}] \quad (3)$$

$$-d \ln [Co(CN)_5^{3-}]/dt = -d \ln D_{578}/dt = k_{obsd} = k_1[Co(CN)_5^{3-}] \quad (4)$$

A typical oscilloscope trace depicting the disappearance of e^-_{aq} is shown in Figure 1; first-order plots, derived froms uch traces, are shown in Figure 2. The kinetic results are summarized in Table I, where k_1 [$(1.2 \pm 0.2) \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$] is seen to be substantially independent of the initial concentrations of e^-_{aq}, $Co(CN)_5^{3-}$, and CN^-. k_1 exhibits only a small D_2O isotope effect (k_{H_2O}/k_{D_2O} ~1.2).

Table I. Kinetic Data for Reaction 1[a]

Expt no.	Initial concentrations, M: $10^5[Co(CN)_5^{3-}]$	$10^6 \cdot [e^-_{aq}]$	$[CN^-]$	$10^{-5} \cdot k_{obsd}$, sec^{-1}	$10^{-10}k_1$, M^{-1} sec^{-1}
1	1.2	1.5	1×10^{-3}	1.7	1.4
2	1.5	0.5	0	2.2	1.5
3	1.8	1.5	1×10^{-4}	2.3	1.3
4	2.0	1.3	1×10^{-5}	2.5	1.2
5	2.0	1.5	1×10^{-4}	2.5	1.2
6	2.0	1.5	3×10^{-4}	2.8	1.4
7	2.0	0.50	0	2.6	1.3
8	2.0	0.75	0	2.8	1.4
9	2.9	1.3	0	2.9	1.0[b]
10	2.9	1.5	0	2.6	0.9[b]
11	2.9	1.8	0	3.5	1.2[c]
12	2.9	2.0	0	3.0	1.0 (D_2O)

[a] Conditions unless otherwise noted: 20°, 0.10 M NaOH (pH 13), $10^{-2}\ M$ CH_3OH, 1 atm of H_2. [b] pH 7. [c] No CH_3OH added.

Reaction of $Co(CN)_5^{4-}$ with Water. The product of the reaction of e^-_{aq} with $Co(CN)_5^{3-}$ is a transient species, with an intense absorption centered on 280 nm (ϵ ~8000 $M^{-1}\ \text{cm}^{-1}$), which undergoes a further reaction to yield $Co(CN)_5H^{3-}$. It seems reasonable to identify the transient as the direct product of electron capture by $Co(CN)_5^{3-}$, *i.e.*, as $Co(CN)_5^{4-}$, and to interpret the second step as the reaction with water depicted by eq 2.

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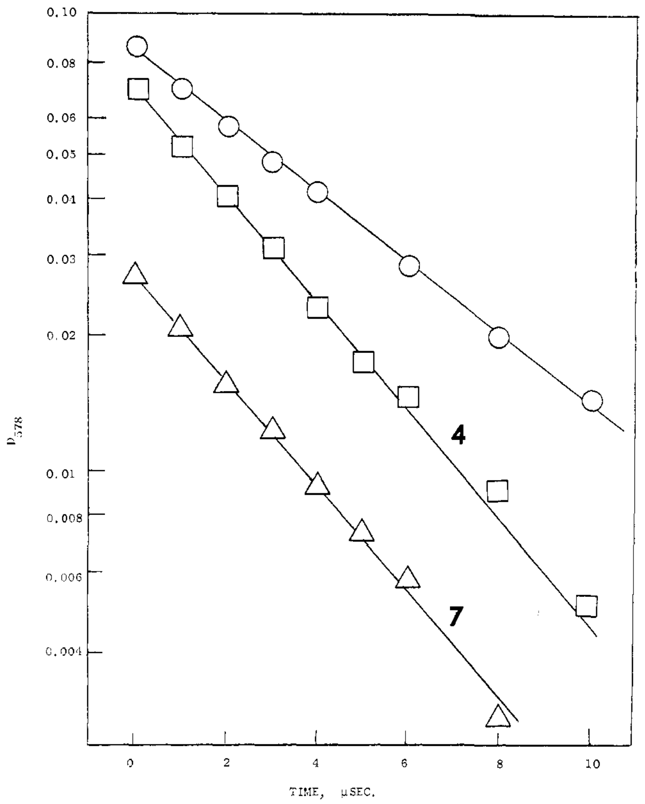

Figure 2. Representative pseudo-first-order rate plots for reaction 1. Experiment numbers correspond to Table I.

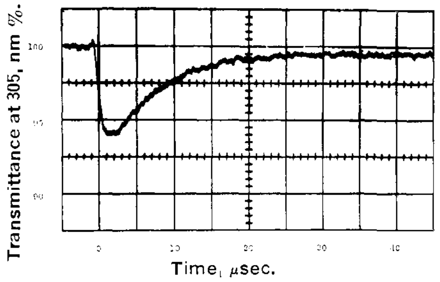

Figure 3. Oscillogram depicting disappearance of $Co(CN)_5^{4-}$ (monitored at 305 nm) by reaction with H_2O according to eq 2. Conditions correspond to experiment 5, Table II. (The pulse radiolysis is marked by the rapid initial transmittance decrease.)

The rate of reaction 2 was measured by monitoring the absorbance decrease in the 280–330-nm wavelength region where the absorbance of the $Co(CN)_5H^{3-}$ product is small compared to that of $Co(CN)_5^{4-}$. A typical oscilloscope trace from such an experiment is depicted in Figure 3. Several first-order plots derived from such traces are shown in Figure 4 and confirm the first-order rate law described by eq 5, where D_t is the absorbance value at time t and D_∞ is the final absorbance. The kinetic results are summarized in Table II, where $k_2[(1.1 \pm 0.1) \times 10^5\ sec^{-1}$ in $H_2O]$ is seen to be substantially independent of the initial $Co(CN)_5^{3-}$ and e^-_{aq} concentrations and of the wavelength of the analyzing light. The large decrease of k_2 (by a factor of 5.8 to a value of $(1.9 \pm 0.2) \times 10^4\ sec^{-1}$) in going from H_2O to D_2O is consistent with the proposed interpretation of this reaction as a proton-transfer process.

$$-d \ln [Co(CN)_5^{4-}]/dt = -d \ln [D_t - D_\infty]/dt = k_2 \quad (5)$$

Absorption Spectrum of $Co(CN)_5^{4-}$. By measuring the optical density changes accompanying reaction 1 at various wavelengths, it was possible to compute the spectrum of $Co(CN)_5^{4-}$ which is depicted in Figure 5. (The second reaction was sufficiently slow so as not to interfere seriously with these measurements.) The absorption of $Co(CN)_5^{4-}$ is considerably more intense than that of $Co(CN)_5^{3-}$ throughout the spectral region examined, including the vicinity of 280 nm where both species exhibit absorption maxima with extinction coefficients of *ca.* 8×10^3 and $5 \times 10^3\ M^{-1}\ cm^{-1}$, respectively.

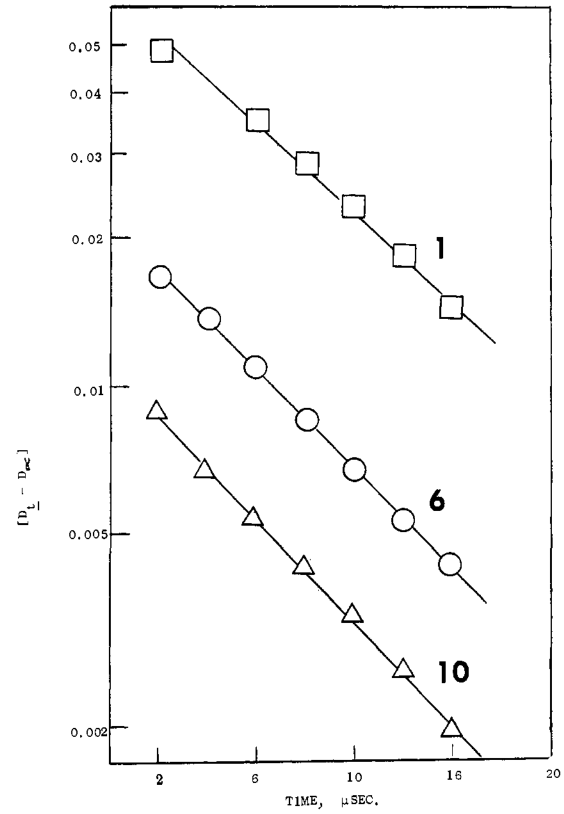

Figure 4. Representative first-order rate plots for reaction 2. Experiment numbers correspond to Table II.

Table II. Kinetic Data for Reaction 2[a]

Expt no.	Initial concentrations, M $10^4[Co(CN)_5^{3-}]$	Initial concentrations, M $10^6[Co(CN)_5^{4-}]$[b]	Wavelength of analyzing light, nm	$10^{-5}k_2$, sec^{-1}
1	0.3	3.6	280	1.1
2	0.3	4.1	285	1.1
3	0.3	3.9	305	1.1
4	0.5	1.4	280	1.1
5	0.8	3.1	305	1.1
6	3.0	3.4	290	1.1
7	3.0	3.4	300	1.0
8	3.0	3.9	305	1.1
9	3.0	3.6	310	1.2
10	3.0	3.5	330	1.1
11	0.2	3.7	305	0.20 (D_2O)
12	0.5	1.7	279	0.19 (D_2O)
13	0.5	1.8	305	0.17 (D_2O)

[a] Conditions: 20°, 100 atm of H_2 (~0.1 M). [b] Assumed to be equal to initial $[e^-_{aq}]$.

Discussion

Although the reverse of reaction 2, *i.e.*, reaction 6, has previously been postulated as a step in the chemical[2–4] and electrochemical[5] oxidations of $Co(CN)_5H^{3-}$, some uncertainty presently exists about the value of the rate constant (k_{-2}) for this reaction and, hence, about the pK_a of $Co(CN)_5H^{3-}$. Kinetic measurements on the oxidation of $Co(CN)_5H^{3-}$ by $Fe(CN)_6^{3-}$ (which obeys the rate law $-d[Co(CN)_5^{3-}]/dt = 1.2 \times 10^{-1}[Co(CN)_5H^{3-}][OH^-]$ M sec^{-1}, interpreted in terms of eq 6 as the rate-determining step) have yielded a value of 1.2×10^{-1} M^{-1} sec^{-1} for k_{-2} (at 20° and 1 M ionic strength).[4] This, in turn, yields an equilibrium quotient (k_2/k_{-2}) of *ca.* 1×10^6 for reaction 2, corresponding to a pK_a of *ca.* 20 for $Co(CN)_5H^{3-}$. A similar value of k_{-2} (9.7×10^{-2} M^{-1} sec^{-1} at 24°) has recently been determined by Lim and Anson from kinetic measurements on the reaction of $Co(CN)_5H^{3-}$ with $Hg(CN)_2$.[3] It should be noted, however, that these values of k_{-2} are too small to be compatible with the interpretation proposed by Hanzlik and Vlček for the reaction between $Co(CN)_5H^{3-}$ and benzoquinone, in terms of a mechanism also involving reaction 6 as a component step.[2] The origin and significance of this apparent discrepancy are presently unclear and warrant further investigation.

$$Co(CN)_5H^{3-} + OH^- \xrightarrow{k_{-2}} Co(CN)_5^{4-} + H_2O \qquad (6)$$

The $Co(CN)_5^{4-}$ ion, which we have detected and spectrally characterized for the first time, is isoelectronic with several other known five-coordinate d^8 complexes such as $Fe(CO)_5$, $Mn(CO)_5^-$, and $Ni(CN)_5^{3-}$.[14,15] With the possible exception of $Ni(CN)_5^{3-}$ (which, in the solid state, has been reported to exist in a square-pyramidal, as well as a distorted trigonal-bipyramidal, modification),[15] these species are all believed to have trigonal-bipyramidal configurations and it seems likely that this is the case also for $Co(CN)_5^{4-}$. Since the structure of $Co(CN)_5^{3-}$ is square pyramidal[16] and that of $Co(CN)_5H^{3-}$ presumably octahedral, it seems likely that both reactions 1 and 2 are accompanied by significant configurational changes. The value of k_{-2}, which seems remarkably low for a highly favorable proton-transfer reaction, may reflect this constraint.

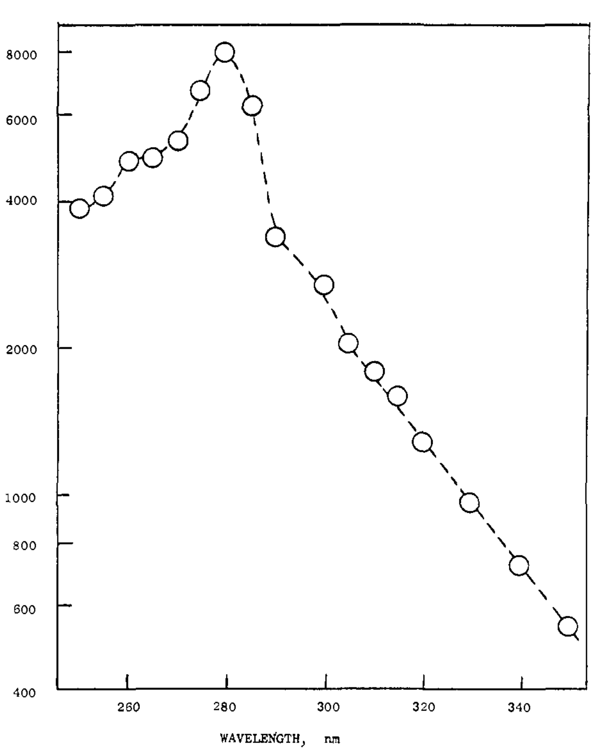

Figure 5. Absorption spectrum of $Co(CN)_5^{4-}$ computed from absorbance changes accompanying reaction 1 (corrected for absorbance change due to $Co(CN)_5^{3-}$ consumed).

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Photoreduction of Nitrogen Heterocycles. I. The Photoreduction of Phenazine: Evidence for Singlet-State Reactivity

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Abstract: The photoreduction of phenazine by isopropyl alcohol (IPA), triethylamine (TEA), and tri-*n*-butylstannane (TBS) has been studied by kinetic and flash-photolytic methods. All reactions produced 5,10-dihydrophenazine as the major reduction product. The three reactions were determined to proceed, at least mostly, from the nπ^* singlet excited state of phenazine. The reactions with TEA and TBS are much more efficient than the isopropyl alcohol reaction. The rate constants for the TEA and TBS reactions were determined to be $\geq 10^9$ l. mol^{-1} sec^{-1}, while that for the IPA reaction was found to be about 10^3 times slower.

Although kinetic and mechanistic studies of carbonyl photoreductions are legion,[1] relatively little effort has been devoted to such investigations of the photoreduction of nitrogen heterocycles.[2] This is surprising

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