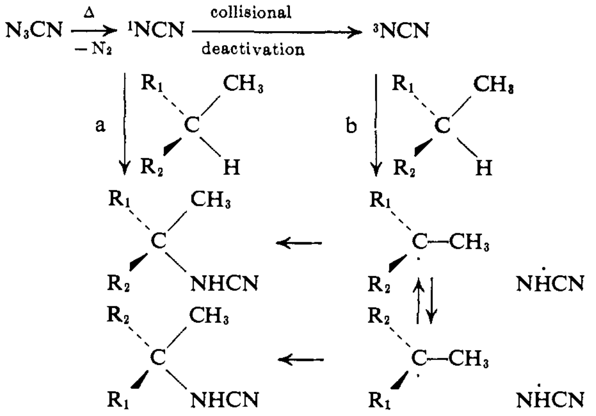
readily deactivated, through collisions with a suitable inert solvent, to triplet NCN which is incapable of stereospecific insertion[3] *into C–H bonds.* In the absence of a solvent, singlet NCN is in all probability the reactive species also in other reactions such as additions to aromatic[10] and olefinic[11] double bonds since these are in general less energetic processes than insertion.

The results reported here point to Scheme I in which path a is followed in the absence of a solvent, path b in methylene bromide, and a combination of a and b in methylene chloride.[12]

Scheme I



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(10) F. D. Marsh and H. E. Simons, *J. Am. Chem. Soc.*, **87**, 3529 (1965).

(11) A. G. Anastassiou, *ibid.*, **87**, 5512 (1965).

(12) Within the frame of this mechanism, equilibration between the stereoisomeric radicals is a rapid process compared with recombination.

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Parallel Single- and Double-Bridged Activated Complexes in Electron-Transfer Reactions[1]

Sir:

Although a double-bridged activated complex would appear to provide a reasonable path for an electron-transfer reaction,[2] such a path has been demonstrated only in the *cis*-$Cr(N_3)_2^+$–Cr^{2+} exchange reaction.[3] A search for a double-bridged activated complex has also been made in the *cis*-$Co(en)_2(OH_2)_2^{3+}$–Cr^{2+} and *cis*-CrF_2^+–Cr^{2+} systems,[4,5] but the experimental evidence indicates that transition states with a single bridging ligand are dominant in these cases.

In contrast with these results, we have found that the reaction of *cis*-$Co(NH_3)_4(N_3)_2^+$ (and of *cis*-$Co(en)_2(N_3)_2^+$) with chromium(II) proceeds *via* parallel single- and double-bridged activated complexes.

$$Cr^{2+} + cis\text{-}Co(NH_3)_4(N_3)_2^+ \begin{cases} \xrightarrow{k_d} cis\text{-}Cr(N_3)_2^+ \\ \xrightarrow{k_s} CrN_3^{2+} \end{cases} \tag{1}$$

Furthermore, we have demonstrated that, after the *cis*-$Cr(N_3)_2^+$–Cr^{2+} exchange which proceeds *via* the diazido-bridged transition state is substantially complete,[3] it is possible to detect the *cis*-$Cr(N_3)_2^+$–Cr^{2+} reaction that makes use of a single azide bridge.

When chromium(II) was added to an *excess* of *cis*-$Co(NH_3)_4(N_3)_2^+$, both CrN_3^{2+} and *cis*-$Cr(N_3)_2^+$ were produced.[6,7] The ratio [*cis*-$Cr(N_3)_2^+$]/[CrN_3^{2+}] was 0.6 ± 0.1 at 0° in 0.010 to 0.10 *M* perchloric acid. This ratio was found to be reasonably reproducible if the cobalt(III) complex was in excess. However, when an *excess* of chromium(II) was added to *cis*-$Co(NH_3)_4(N_3)_2^+$, the yield of *cis*-$Cr(N_3)_2^+$ appeared to be variable. In general the yield of *cis*-$Cr(N_3)_2^+$ was found to decrease with increasing [Cr^{2+}], and with increasing contact times between the excess chromium(II) and the *cis*-$Cr(N_3)_2^+$ produced in the *cis*-$Co(NH_3)_4(N_3)_2^+$–Cr^{2+} reaction. These results suggested chromium(II) catalysis of the aquation of *cis*-$Cr(N_3)_2^+$ *via* the single-bridged electron-transfer path[9]

$$cis\text{-}Cr(N_3)_2^+ + Cr^{2+} \longrightarrow [cis\text{-}N_3CrN_3Cr^{3+}]^* \longrightarrow CrN_3^{2+} + Cr^{2+} + N^{3-} \tag{2}$$

A direct test of reaction 2 was made by preparing *cis*-$Cr(N_3)_2^{+}$[10] and allowing it to react with chromium(II).

Table I. Kinetics of the Chromium(II)-Catalyzed Aquation of *cis*-$Cr(N_3)_2^+$ ([$HClO_4$] = 0.20 *M*, [*cis*-$Cr(N_3)_2^+$] = 3–4 × 10^{-5} *M*)[a]

15°		25°	
[Cr^{2+}], *M* × 10^3[b]	*k*, M^{-1} sec^{-1}	[Cr^{2+}], *M* × 10^3[b]	*k*, M^{-1} sec^{-1}
1.26	4.6	1.24	8.2
2.92	4.4	1.66	7.7
2.92	4.7	2.28	7.5
5.84	4.4	2.68	7.4
1.14	4.8[c]	2.87	7.6
2.32	4.4[c]	2.13	7.5[c]
2.58	4.4[c,d]	2.61	7.5[c]
Average	4.5	Average	7.6

[a] Except as noted, *cis*-$Cr(N_3)_2^+$ was prepared *in situ* by the *cis*-$Co(NH_3)_4(N_3)_2^+$–Cr^{2+} reaction. [b] Measured at the completion of the reaction from the increase in absorbance at 418 mμ upon reaction with oxygen. [c] *cis*-$Cr(N_3)_2^+$ prepared as indicated in footnote 10. [d] [$HClO_4$] = 0.080 *M*.

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(1) This work was supported by the National Science Foundation, Grant GP 2001.

(2) H. Taube, *Advan. Inorg. Radiochem.*, **1**, 1 (1959).

(3) R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962).

(4) W. Kruse and H. Taube, *ibid.*, **82**, 526 (1960).

(5) Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960).

(6) The separation of *cis*-$Cr(N_3)_2^+$ and CrN_3^{2+} was achieved by ion-exchange chromatography.[3] At the concentrations used, *both* complexes were adsorbed on the resin (Dowex 50X-8, 50–100 mesh). Elution with 0.2 and 1.5 *M* perchloric acid, followed by spectrophotometric measurements at 275 mμ (ε 5900) and 270 mμ (ε 3700), yielded the concentrations of *cis*-$Cr(N_3)_2^+$ and CrN_3^{2+}, respectively.

(7) Hydrazoic acid was also formed under these conditions. The amount of hydrazoic acid formed was estimated from the absorbance at 260 mμ in the fraction that passed directly through the column, and was found to be comparable to the CrN_3^{2+} formed. This observation indicates that the chromium(II)–hydrazoic acid reaction,[3,8] although rapid, does not compete with the faster chromium(II)–*cis*-$Co(NH_3)_4(N_3)_2^+$ reaction. Furthermore, although it is possible that electron transfer occurs first *to* the azide bridge, the production of hydrazoic acid demonstrates that the electron is ultimately transferred to the cobalt(III) center.

(8) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2861 (1962).

(9) Chromium(II) and azide ion are shown as products of reaction 2. However, in the presence of excess chromium(II), hydrazoic acid is rapidly reduced.[3,8] The rate of this reaction was *not* measured. However, the following blank experiments were carried out to ascertain the effect of this reaction on the measurements presented in Table I. Hydrazoic acid in 0.20 *M* perchloric acid was generated *in situ* by the rapid reaction ($k > 10^3$ M^{-1} sec^{-1}) of chromium(II) (~2 × 10^{-3} *M*) with *trans*-$Co(NH_3)_4(N_3)_2^+$ (~3 × 10^{-5} *M*), and the absorbance at 275 mμ was measured as a function of time. No change in absorbance was observed after the mixing time of 10 sec, and we conclude that, under these conditions, any changes in absorbance due to the chromium(II)–hydrazoic acid reaction are too small to interfere with reaction 2. Furthermore, as expected, we conclude that *cis*-$Cr(N_3)_2^+$ is not formed in the *trans*-$Co(NH_3)_4(N_3)_2^+$–Cr^{2+} reaction.

Table II. Rate Constants for Some Reactions of Chromium(II) at 0°

Reaction	k_d[a] M^{-1} sec^{-1}	k_s[b,h] M^{-1} sec^{-1}	k_d/k_s[h]	ΔH^*, kcal mole^{-1}	ΔS^*, cal mole^{-1} deg^{-1}	Ref
cis-Cr(N$_3$)$_2^+$ + Cr^{2+}	60[c]	1.9[d]	31	8.1	−27	This work
CrN$_3^{2+}$ + Cr^{2+}	...	1.3	...	9.6	−22.8	...[e]
cis-CrF$_2^+$ + Cr^{2+}	...	1.2×10^{-3}	<0.01	13	−24	...[f]
CrF^{2+} + Cr^{2+}	...	3.2×10^{-3}[d]	...	13.7	−20	...[f]
cis-Co(NH$_3$)$_4$(N$_3$)$_2^+$	>10^3	>10^3	0.6[g]	...	...	This work
cis-Co(en)$_2$(N$_3$)$_2^+$	>10^3	>10^3	0.2[g]	...	...	This work

[a] Rate constant for reaction proceeding *via* a double-bridged activated complex. [b] Rate constant for reaction proceeding *via* a single-bridged activated complex. [c] Reference 3. [d] Extrapolated value. [e] Reference 11. [f] Reference 5. [g] From the ratio [*cis*-Cr(N$_3$)$_2^+$]/[CrN$_3^{2+}$] produced. [h] If the values of k_s are corrected for the symmetry number factor, the values of k_d/k_s must be multiplied by 2.

It was found that chromium(II) indeed catalyzes the aquation of *cis*-Cr(N$_3$)$_2^+$. Kinetic measurements were carried out by following the decrease in absorbance at 275 mμ, and the results are summarized in Table I. Identical results (see Table I) were obtained when *cis*-Cr(N$_3$)$_2^+$ was prepared *in situ* by treating *cis*-Co(NH$_3$)$_4$(N$_3$)$_2^+$ with an excess of chromium(II): following the very rapid *cis*-Co(NH$_3$)$_4$(N$_3$)$_2^+$–Cr^{2+} reaction ($k >$ 10^3 M^{-1} sec^{-1} at 15°), the slower chromium(II)-catalyzed aquation of *cis*-Cr(N$_3$)$_2^+$ was observed.

In Table II we present a summary of rate constants for some related reactions of chromium(II). One feature of interest is the large variation in the relative importance of double- and single-bridged transition states. The complexes *cis*-Cr(N$_3$)$_2^+$ and *cis*-CrF$_2^+$ display extreme behaviors. In the former case, the path that features two azide bridges is by far the dominant one. In the latter case, the exchange reaction mediated by two fluoride bridges could not be detected in spite of a thorough search.[5] The complexes *cis*-Co(NH$_3$)$_4$(N$_3$)$_2^+$ and *cis*-Co(en)$_2$(N$_3$)$_2^+$ exhibit an intermediate behavior, and both single- and double-bridged paths provide substantial contributions to the over-all reaction. The decrease of k_d/k_s upon substitution of ammonia by ethylenediamine suggests that fairly mild modifications in the structures of the reactants may affect the relative importance of single- and double-bridged transition states. However, no rationalization can be offered, at the present stage of development of the subject, for the observed effects, and we hope that further experimentation will uncover some of the factors conducive to favoring one mechanism over the other.

It was noted previously, in comparing the rates of exchange of CrN$_3^{2+}$ and CrF^{2+} with Cr^{2+}, that the enthalpy of activation was primarily responsible for the difference in rates.[11] Similarly, the difference in the rates of the chromium(II)-catalyzed aquations of *cis*-Cr(N$_3$)$_2^+$ and *cis*-CrF$_2^+$ is predominantly an enthalpy effect.

Finally, we note that the rates of the reactions of chromium(II) with CrN$_3^{2+}$ and with *cis*-Cr(N$_3$)$_2^+$ (catalyzed aquation) are remarkably similar, suggesting that the nonbridging ligand effects of water and azide in *cis* positions are of comparable magnitude. Analogous results were obtained in previous work: the rate constants for the iron(II) reductions of *cis*-Co(NH$_3$)$_4$(OH$_2$)N$_3^{2+}$ and *cis*-Co(NH$_3$)$_4$(N$_3$)$_2^+$ differ by less than a factor of 2.[12,13]

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[10] We found the reaction of chromium(II) with *cis*-Co(NH$_3$)$_4$(N$_3$)$_2^+$, followed by ion-exchange separation, a convenient way of preparing *cis*-Cr(N$_3$)$_2^+$ solutions.

[11] R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964).

[12] A. Haim, *J. Am. Chem. Soc.*, **85**, 1016 (1963); **86**, 2352 (1964).

[13] On the basis of the present work, it may be necessary to revise the previous suggestion[12] regarding the double-bridged mechanism for the *cis*-Co(NH$_3$)$_4$(N$_3$)$_2^+$–Fe^{2+} reaction. This suggestion was made by taking cognizance of the relatively large increase in rate observed upon substitution of *cis*-NH$_3$ by N$_3^-$ in Co(NH$_3$)$_5$N$_3^{2+}$. However, it may be more appropriate to consider the change in rate upon substitution of H$_2$O by N$_3^-$ in *cis*-Co(NH$_3$)$_4$(OH$_2$)N$_3^{2+}$. The mild decrease in rate[12] coupled with the results of the present work would suggest that both *cis*-Co(NH$_3$)$_4$(OH$_2$)N$_3^{2+}$ and *cis*-Co(NH$_3$)$_4$(N$_3$)$_2^+$ make use, at least in part, of a single azide bridge.

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Nuclear Magnetic Resonance Spectroscopy. III. Structure of Phenyldiazonium Ion from ^{15}N–H Coupling Study[1]

Sir:

Nuclear spin–spin interaction between ^{15}N and ^{1}H makes nmr spectroscopy a method of great potential for elucidation of the structure of organic compounds containing two or more nitrogen atoms. In pmr spectra ^{15}N (spin = $^1/_2$) produces a sharp doublet for the proton directly bonded to the nitrogen; the corresponding signal for ^{14}N–*H* is usually a single broad peak because ^{14}N possesses quadrupole moment and spin = 1. The large coupling (~90 cps) between directly bonded ^{15}N and ^{1}H is of particular advantage in pmr spectra. The measurement of the area under the doublet due to ^{15}N–*H* and the singlet due to ^{14}N–*H* may be used for a quantitative estimation of the relative amounts of ^{15}N and ^{14}N in compounds under investigation.

We have used pmr spectroscopy of ^{15}N-labeled compounds for studying the possibility of the isotope rearrangement (Ia ⇄ Ib) during the generation or reactions of phenyldiazonium ion (I).

$$\underset{\text{Ia}}{(C_6H_5{}^{15}N\equiv N)^+} \rightleftharpoons \underset{\text{Ib}}{(C_6H_5N\equiv {}^{15}N)^+}$$

Phenyldiazonium chloride was prepared from ^{15}N-aniline by diazotization with unlabeled sodium nitrite and subjected to the reactions outlined in Scheme I. The pmr spectra of the resulting compounds II and III recorded on a Varian A-60A spectrometer

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[1] Part II: A. K. Bose, M. S. Manhas, and E. R. Malinowski, *J. Am. Chem. Soc.*, **85**, 2795 (1963); Part I: E. R. Malinowski, M. S. Manhas, G. H. Müller, and A. K. Bose, *Tetrahedron Letters*, 1161 (1963).