5.84.

References and Notes

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(22) DNMR 4 was prepared by J. Brunelle and L. J. Letendre, and is a modification of a program originally written by G. Binsch and D. A. Kleier. We thank C. H. Bushweller for providing us with a copy of this program.
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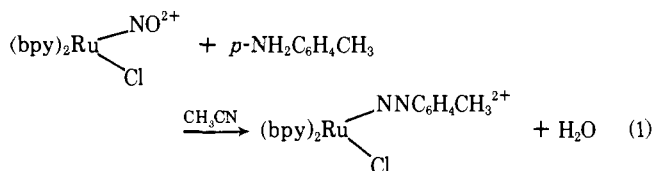# Diazotization of Aromatic Amines by Ruthenium Nitrosyl Complexes

William L. Bowden, William F. Little, and Thomas J. Meyer*

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514. Received September 30, 1976

Abstract: The ruthenium nitrosyl complex $[Ru(bpy)_2(NO)Cl]^{2+}$ (bpy is 2,2'-bipyridine) reacts with the aromatic amines p-$NH_2C_6H_4$-Y (-Y is -OCH₃, -CH₃, -H) in acetonitrile to give the corresponding diazonium complexes $[Ru(bpy)_2(N_2Ar)$-$Cl]^{2+}$ which have been isolated and characterized as hexafluorophosphate salts. The properties of the complexes are consistent with a considerable degree of diazonium ion character in the Ru–NNAr linkage including broad, sometimes structured $\nu(NN)$ stretching frequencies at 1980–2100 cm^{-1}. The bound ligands undergo a series of reactions including an irreversible one-electron reduction, thermal reactions in water with I⁻ and acetone, and diazo coupling with β-naphthol. Qualitative infrared studies in the $\nu(NN)$–$\nu(NO)$ stretching frequency region show that the rates of the diazotization reactions are sensitive to the natures of the nitrosyl complex and the amine, and that a series of stepwise reactions is probably involved in the overall reactions.

In an earlier communication we described preparations for a series of aryldiazo complexes[1] which were obtained as products of reactions between ruthenium nitrosyl complexes and aromatic amines, e.g., eq 1.[2] Both the chemistry involved in the net reactions (eq 1) and the electronic structure of the

$$(bpy)_2Ru\begin{array}{c} {}^{NO^{2+}} \\ \diagdown \\ {}_{Cl} \end{array} + p\text{-}NH_2C_6H_4CH_3$$

$$\xrightarrow{CH_3CN} (bpy)_2Ru\begin{array}{c} {}^{NNC_6H_4CH_3^{2+}} \\ \diagdown \\ {}_{Cl} \end{array} + H_2O \quad (1)$$

products have features of importance for chemical problems of a more general nature.

A series of reports has shown that the nitrosyl groups in complexes of the type $[Ru(bpy)_2(NO)L]^{n+}$ ($n = 2$, Br, N₃, NO₂; $n = 3$, H₂O, NH₃, py, CH₃CN) behave chemically much as does the nitrosonium ion (NO⁺). As examples the bound NO group has been found to react with the nucleophiles OH⁻ [3] and N₃⁻,[4] to add as an electrophile to activated aromatics,[5]

and to undergo reversible one-electron reduction.[6] The unusual reactivity of the bpy ions when compared with other metal nitrosyls can be attributed to a considerable degree of NO⁺ character in the formally (d⁶)Ru(II)–NO⁺ linkage which arises because of the relatively high formal oxidation state at the metal, the positive charge on the complexes, and competitive back-bonding with the 2,2'-bipyridine ligands.[6] The relatively high $\nu(NO)$ stretching frequencies for the complexes are consistent with this view,[7] as are the variations in $\nu(NO)$ as the group cis to NO is varied in the series N₃, Cl, NO₂, NH₃, py, and CH₃CN.[6] The NO group in the complexes can effectively be taken as a chemically modified form of the nitrosonium ion. The nitrosyl complexes, which are conveniently prepared under usual nitrosating conditions,

$$[Ru(bpy)_2(H_2O)Cl]^+ + NO_2^-$$

$$\xrightarrow{H^+} [Ru(bpy)_2(NO)Cl]^{2+} \ ^3$$
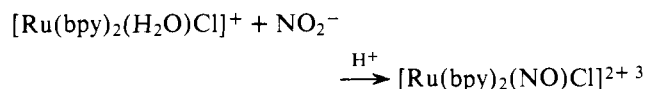
then represent reagents in which a useful but reactive inter-

Table I. Electronic Absorption Bands for the Complexes [Ru-(bpy)$_2$(p-N$_2$C$_6$H$_4$-Y)Cl]$^{2+}$ in Acetonitrile

-Y	λ_{max} (nm)[a]	$10^{-4}\epsilon$ (cm^{-1} M^{-1})
-H	345	2.4
	307	3.2
	292	3.7
	242	3.7
-CH$_3$	332	2.15
	307	3.1
	286	4.5
	238	3.2
-OCH$_3$	345	2.4
	308	3.7
	292	3.7
	242	3.7

[a] Relatively weak, low-energy shoulders appear on the lowest absorption band in the region 400–440 nm.

mediate (NO$^+$) is stored in a reasonably stable chemical form.

The net reaction in eq 1 involves diazotization of the aromatic amine within the coordination sphere of the metal complex. For purposes of comparison with related diazotization processes in organic chemistry, the stepwise details leading to the net reactions are of interest in that they may involve a series of known intermediates, but in this case intermediates which are bound to a metal center.

The electronic structures of the diazonium products of reactions like eq 1 are of interest in the context of developing an adequate description for the nature of the M–NNAr linkage. As for metal nitrosyls, ambiguities can arise[1a,8] as illustrated by limiting valence-bond structures for the ligand viewed as ArN$_2^+$ (I and II)

$$Ru^{II} \leftarrow N \equiv \overset{+}{N} Ar \qquad Ru^{II} = \overset{+}{N} = N_{\diagdown Ar}$$

I   **II**

$$\text{or as } ArN_2^-, \qquad Ru^{IV} - \bar{N} \diagdown N - Ar$$

III
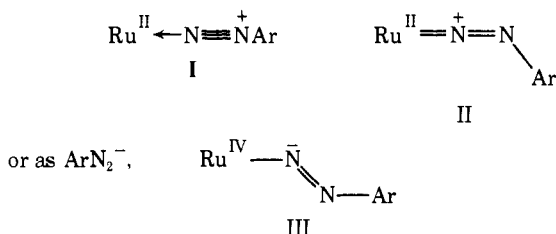
although a more satisfactory picture treatment can probably be developed based on the qualitative molecular orbital treatments developed recently for metal nitrosyls.[9] The relative importance of structures I and II would seem to depend on the extent of metal to ligand back-bonding and MNNAr bond angles between 120 and 180° are expected and have been found in x-ray crystallographic studies.[1a,8,10] Depending on the electron distribution within the Ru–NNAr group, the chemical and physical properties of metal and ligand are expected to vary widely.

Results and Discussion

Properties of the Diazonium Complexes. Bis-2,2'-bipyridine complexes of Ru(II) are known to undergo reversible one-electron oxidations to Ru(III) in the potential range −0.3 to 1.6 V vs. the saturated sodium chloride calomel electrode (SSCE) in acetonitrile containing 0.1 M supporting electrolyte.[11] As found earlier for related nitrosyl complexes, e.g., [Ru(bpy)$_2$(NO)Cl]$^{2+}$, the diazonium ions [Ru(bpy)$_2$(p-C$_6$H$_4$-Y)Cl]$^{2+}$ (Y = -OCH$_3$, -CH$_3$, -H) are not oxidized in the same medium out to potentials of 2.0 V. As for the nitrosyl complexes,[6] the diazonium complexes do undergo one-electron reductions, but electron transfer appears to be to the ligand, and these processes will be discussed in a later section.
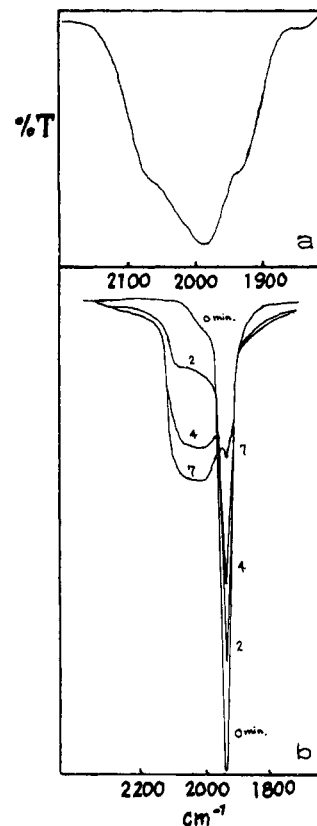

Figure 1. (a) Infrared spectrum of [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$CH$_3$)Cl](PF$_6$)$_2$ from 1800–2200 cm^{-1} in a KBr pellet. The shoulder at ~1930 cm^{-1} is from a small amount of [Ru(bpy)$_2$(NO)Cl](PF$_6$)$_2$ present as an impurity. (b) IR spectra for the reaction between [Ru(bpy)$_2$(NO)Cl]$^{2+}$ and p-NH$_2$C$_6$H$_4$OCH$_3$ in CH$_3$CN showing ν(NO) of the nitrosyl complex at 1930 cm^{-1} initially, followed by decreases in ν(NO) and increases in ν(NN): after mixing, after 2 min, after 4 min, and after 7 min (100 mg of [Ru(bpy)$_2$(NO)Cl](PF$_6$)$_2$ and 40 mg of p-anisidine in 10 mL of acetonitrile).

The electronic absorption spectra of the complexes in acetonitrile are summarized in Table I. Normally, (bpy)Ru^{II}< complexes have intense π*(bpy) ← dπ(Ru) charge transfer (CT) transitions in the visible region of the spectrum.[12,13] However, for the diazonium complexes, the first intense absorption bands appear in the ultraviolet (Table I). The absorption bands at λ_{max} 286–292 and 238–242 nm arise from ligand (bpy)-centered π* ← π transitions.[12] The intense absorption bands which appear in the near-ultraviolet (λ_{max} 307–308 and 332–345 nm) may arise from π*(bpy) ← d(Ru) transitions shifted to unusually high energies because of strong back-bonding from Ru(II) to the diazonium ligand. However, the band intensities are considerably higher than expected, and the transitions may be largely π*(N$_2$Ar) ← dπ(Ru) in character or composite bands including both types of transition. Similar absorption bands have been found for related nitrosyl complexes at 310 nm.[6]

The most notable feature of the IR spectra of the complexes is the appearance of broad, sometimes structured bands in the region 1980–2100 cm^{-1} either in KBr pellets or in solution (CH$_2$Cl$_2$ or CH$_3$CN) (Figure 1a). For example, for the complex [Ru(bpy)$_2$(p-NNC$_6$H$_4$OCH$_3$)Cl]$^{2+}$ a broad, somewhat structured band appears centered at 1980 cm^{-1} with a poorly defined shoulder of lower intensity at 2080 cm^{-1} in KBr. Similar band patterns appear where ArN$_2$- is p-CH$_3$C$_6$H$_4$N$_2$- and C$_6$H$_5$N$_2$- with bands centered at 2075 and 1983 cm^{-1} and at 2065 and 1987 cm^{-1}, respectively (in KBr). In the ^{15}N labeled complex [Ru(bpy)$_2$(p-^{15}NNC$_6$H$_4$OCH$_3$)Cl]$^{2+}$ prepared by the reaction between [Ru(bpy)$_2$(^{15}NO)Cl]$^{2+}$ and p-NH$_2$C$_6$H$_4$OCH$_3$, the same pattern appears but with each of

the components at 2080 and 1980 cm^{-1} shifted by 30 cm^{-1} to lower energy ($\sim$35 cm^{-1} calculated).

The observed shifts using the ^{15}N label support the assignment of the bands in the region 1950–2100 cm^{-1} as ν(NN) stretching frequencies. Interestingly, the ν(NN) bands and higher energy shoulders are at higher frequencies than ν(NO) in the related nitrosyl complex [Ru(bpy)$_2$(NO)Cl]$^{2+}$ by $\sim$50 and $\sim$140 cm^{-1}.

For both the nitrosyl and diazonium complexes the shifts in ν(NO) and ν(NN) when compared to NO$^+$ and ArN$_2^+$ salts, respectively, are $\sim$200 cm^{-1} indicating a lower bond order in the NO and N$_2$ linkages arising by back-bonding from the metal. However, the ν(NN) values appear to be the highest yet observed in compounds containing the M–NNAr group.[1a]
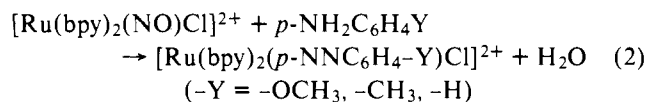
The origin of the band structure in the ν(NN) region is unclear. Multiple bands have been observed previously in diazonium complexes where their origin has been attributed to coupling between aromatic and ν(NN) modes[14-16] or to isomerism at the metal.[17] Given the work of Haymore and Ibers on the related compounds RuCl$_3$(N$_2$Ar)(PPh$_3$)$_2$, it is likely that the origin of the band structure lies in vibrational coupling between ν(NN) and phenyl vibrational modes.[17] It is unlikely that the origin of the two bands is an isomerism. For [Ru(bpy)$_2$(p-NNC$_6$H$_6$OCH$_3$)Cl]$^{2+}$ the relative intensities of the two ν(NN) bands are unchanged in a variety of media (KBr, dichloromethane, acetone, and acetonitrile), and both bands seem to appear concurrently and maintain constant relative intensities during the course of the diazotization reaction.

In summary, the physical properties of the diazonium complexes are similar to the properties of the related nitrosyl complex [Ru(bpy)$_2$(NO)Cl]$^{2+}$. The metal center is strongly influenced by the ArN$_2$– ligand apparently by back-bonding. The usual properties found in related complexes which arise from the filled t$_2$(d) levels (oxidation to Ru(III), low-lying π^*(bpy) $\leftarrow$ d(Ru) CT bands) are significantly modified. The ArN$_2$– ligand is also modified chemically compared to ArN$_2^+$ by back-bonding from the metal but because of the high ν(NN) stretching frequencies is expected to have chemical properties reminiscent of diazonium ions.[18]

The Diazotization Reactions. The reactions between [Ru(bpy)$_2$(NO)Cl]$^{2+}$ and several substituted anilines in acetonitrile were followed in the infrared in the region 2200–1900 cm^{-1}. As shown in Figure 1b for the reaction between [Ru(bpy)$_2$(NO)Cl]$^{2+}$ and p-NH$_2$C$_6$H$_4$OCH$_3$, the growth of the broad ν(NN) band of the diazonium product centered at 1980 cm^{-1} is accompanied by a concomitant decrease in ν(NO) for the nitrosyl reactant. Several qualitative observations were made on the nitrosyl–diazonium conversion based on IR studies: (1) If a stoichiometric or less than stoichiometric amount of amine was added, the ν(NN) band reached a maximum and remained constant for several hours, consistent with the stability of the diazonium complexes in acetonitrile. (2) With excess amine the diazonium band reached a maximum intensity and then gradually disappeared. (3) The rates of both the appearance and subsequent disappearance of the diazonium band appear to increase directly with the concentration of added amine.[19] (4) Using identical reaction conditions, the relative order of rates of diazotization for a series of para-substituted anilines p-NH$_2$C$_6$H$_4$–Y was found to be: –OCH$_3$ > CH$_3$ > H > Cl $\gg$ –NO$_2$. No diazonium product was observed with p-nitroaniline after a reaction time of 72 h. (5) The diazonium product of the reaction between p-NH$_2$C$_6$H$_4$OCH$_3$ and [Ru(bpy)$_2$(NO)Cl]$^{2+}$ is formed in the polar organic solvents acetonitrile, nitrobenzene DMF, and Me$_2$SO. In dichloromethane a reaction occurred as evidenced by a decrease in ν(NO), but a band attributable to ν(NN) did not appear. (6) In the reactions between p-NH$_2$C$_6$H$_6$OCH$_3$

and the nitrosyl complexes cis-[Ru(bpy)$_2$(NO)L]$^{n+}$ (n = 3, L = CH$_3$CN; n = 2, L = Cl, Br NO$_2$), ν(NN) bands characteristic of diazonium products appeared and the relative rates of appearance were in the order L = CH$_3$CN > NO$_2$ > Cl $\sim$ Br.[20] The cis-activating ligand effect is paralleled by increases in ν(NO) and in $E_{1/2}$ values for one-electron reduction at the nitrosyl group, in the same order.[6]

A number of conclusions can be drawn from the infrared experiments. In the absence of excess amine the diazotization reactions (eq 2) are quantitative in acetonitrile and the rate of diazotization appears to increase directly with amine concentration. The rate also increases with the electron donating ability of the para substituent –Y and with the NO$^+$ character of the nitrosyl group (as evidenced by ν(NO) and $E_{1/2}$ values for reduction). Since intensity decreases in ν(NO) and increases in ν(NN) occur simultaneously there is no evidence for the buildup of an intermediate or intermediates in polar organic solvents.

$$[Ru(bpy)_2(NO)Cl]^{2+} + p-NH_2C_6H_4Y$$
$$\rightarrow [Ru(bpy)_2(p-NNC_6H_4-Y)Cl]^{2+} + H_2O \quad (2)$$
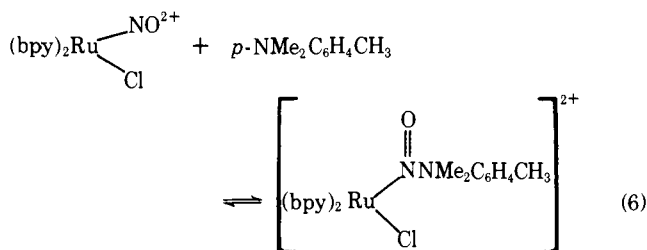$$(-Y = -OCH_3, -CH_3, -H)$$

The sensitivity of the diazotization reactions to the para substituent of the amine and to the NO$^+$ character of the nitrosyl group are not unexpected. The diazotization process must take place within the coordination sphere of the metal as shown by the retention of the ^{15}N label of [Ru(bpy)$_2$(^{15}NO)Cl]$^{2+}$ in [Ru(bpy)$_2$(p-^{15}NNC$_6$H$_4$OCH$_3$)Cl]$^{2+}$. The overall reactions presumably involve a series of steps. In the first step the amine as nucleophile must attack the nitrosyl group which functions as a Lewis acid, giving a Lewis acid–base adduct (eq 3). The reaction is analogous to the reactions
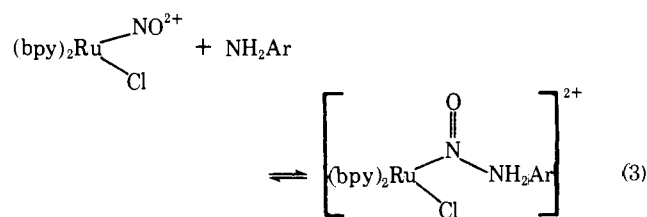
between (2,2'-bpy)nitrosyl complexes and OH$^-$ (eq 4 and 5).[3]
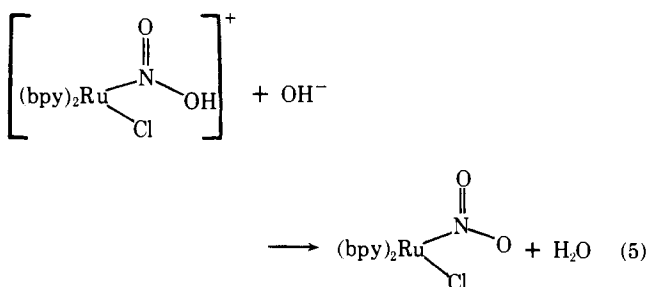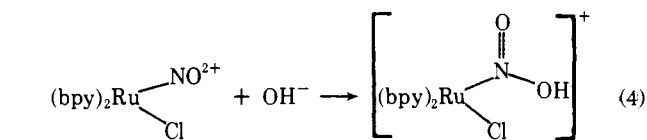
We have obtained independent evidence for reactions like eq 3. In acetonitrile, reversible reactions occur between [Ru(bpy)$_2$(NO)Cl]$^{2+}$ and tertiary amines (NR$_3$, p-NMe$_2$C$_6$H$_4$CH$_3$) (eq 6). The reactions involve the nitrosyl group as shown by IR (disappearance of ν(NO)) and UV–visible spectral changes (appearance of π^*(bpy) $\leftarrow$ dπ(Ru) bands at $\sim$480 nm). The nitrosyl complex reappears quantitatively upon the addition of acid. Addition of ether to solutions containing [Ru(bpy)$_2$(NO)Cl]$^{2+}$ and p-NMe$_2$C$_6$H$_4$CH$_3$ gave

$$(bpy)_2Ru{\overset{NO^{2+}}{\underset{Cl}{\big\langle}}} + p\text{-}NMe_2C_6H_4CH_3$$

$$\rightleftharpoons \left[(bpy)_2Ru{\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{N}}NMe_2C_6H_4CH_3}{\underset{Cl}{\big\langle}}}\right]^{2+} \quad (6)$$
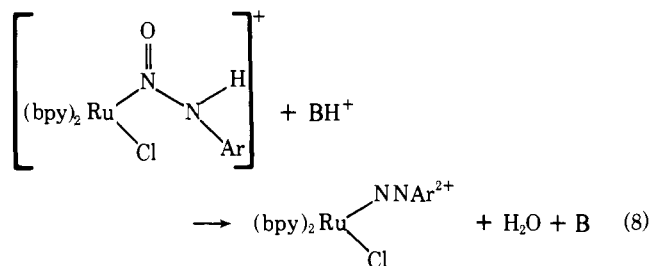
a solid product which was shown by IR (KBr pellet) to be a mixture of the starting nitrosyl complex and a second product with several bands in the region 1300–1600 cm^{-1} not assignable to ν(bpy) modes. Because of its lability we were unable to isolate the adduct as a pure solid.

The second step in the net diazotization reactions may involve deprotonation of the initial adduct to give a primary nitrosamine (eq 7), followed ultimately by formation of the di-
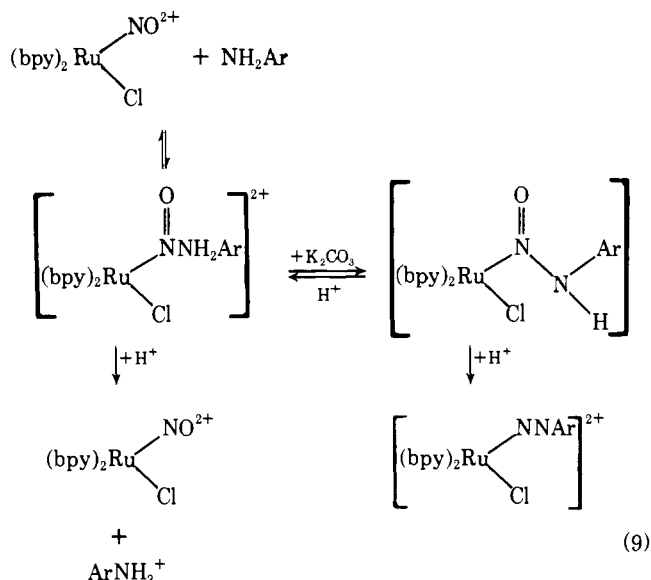
$$\left[(bpy)_2Ru{\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{N}}{\underset{NH_2Ar}{N}}}{\underset{Cl}{\big\langle}}}\right]^{2+} + B$$

$$\rightleftharpoons \left[(bpy)_2Ru{\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{N}}{-}{\underset{Ar}{N}}{\overset{H}{}}}{\underset{Cl}{\big\langle}}}\right]^{+} + BH^+ \quad (7)$$
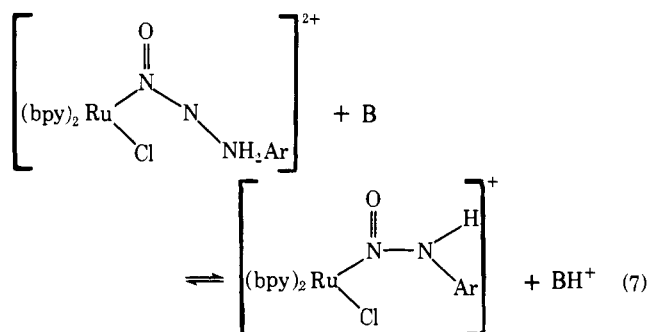
azonium product (eq 8). The proton transfer steps would

$$\left[(bpy)_2Ru{\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{N}}{-}{\underset{Ar}{N}}{\overset{H}{}}}{\underset{Cl}{\big\langle}}}\right]^{+} + BH^+$$

$$\longrightarrow (bpy)_2Ru{\overset{NNAr^{2+}}{\underset{Cl}{\big\langle}}} + H_2O + B \quad (8)$$
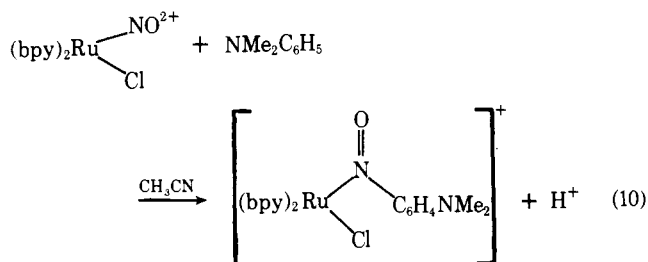
probably involve unreacted amine (B) and the corresponding ammonium ions (BH$^+$).

Evidence has been found for nitrosamines as intermediates in the formation of aryldiazonium ions, but they are transient intermediates since they rapidly eliminate OH$^-$ to give ArN$_2^+$.[21] Infrared and UV–visible spectral evidence and the reversibility of the reactions upon addition of acid all indicate that the reactions between [Ru(bpy)$_2$(NO)Cl]$^{2+}$ and the primary aromatic amines stop at the adduct stage (eq 3) in dichloromethane. Presumably the relatively low dielectric constant of dichloromethane is insufficient to support the ionic proton transfer steps in eq 7 and 8. When dissolved in acetone, treated with solid K$_2$CO$_3$, and precipitated by the addition of ether, the adduct formed between [Ru(bpy)$_2$(NO)Cl]$^{2+}$ and p-NH$_2$C$_6$H$_4$CH$_3$ with characteristic IR bands at 1570, 1490, 1380, and 680 cm^{-1} (KBr pellet) was converted into a product having bands at 1560, 1415, and 1270 cm^{-1} (KBr). Careful acidification of acetone solutions containing the latter material followed by precipitation with ether showed that first the adduct and then the nitrosyl complex could be regenerated. These observations are consistent with the scheme in eq 9. Unfortunately, the adduct and nitrosamine products have proven to be too labile for us to isolate as analytically pure solids.

An additional comment needs to be made about the diazotization reactions. Previously reported work has shown that in reactions between [Ru(bpy)$_2$(NO)L]$^{n+}$ and secondary or

$$(bpy)_2Ru{\overset{NO^{2+}}{\underset{Cl}{\big\langle}}} + NH_2Ar$$

$$\Updownarrow$$

$$\left[(bpy)_2Ru{\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{N}}NH_2Ar}{\underset{Cl}{\big\langle}}}\right]^{2+} \underset{H^+}{\overset{+K_2CO_3}{\rightleftharpoons}} \left[(bpy)_2Ru{\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{N}}{\underset{\overset{N}{\underset{H}{}}}{\overset{Ar}{}}}}{\underset{Cl}{\big\langle}}}\right]^{2+}$$

$$\big\downarrow +H^+ \qquad\qquad \big\downarrow +H^+$$

$$(bpy)_2Ru{\overset{NO^{2+}}{\underset{Cl}{\big\langle}}} \qquad \left[(bpy)_2Ru{\overset{NNAr^{2+}}{\underset{Cl}{\big\langle}}}\right]$$

$$+ \qquad\qquad (9)$$

$$ArNH_3^+$$

tertiary aromatic amines where diazotization cannot occur, net electrophilic attack occurs giving metal-bound nitrosoarenes as products (e.g., eq 10).[5] For the primary aromatic

$$(bpy)_2Ru{\overset{NO^{2+}}{\underset{Cl}{\big\langle}}} + NMe_2C_6H_5$$

$$\overset{CH_3CN}{\longrightarrow} \left[(bpy)_2Ru{\overset{\overset{\displaystyle O}{\underset{\displaystyle \|}{N}}C_6H_4NMe_2}{\underset{Cl}{\big\langle}}}\right]^{+} + H^+ \quad (10)$$
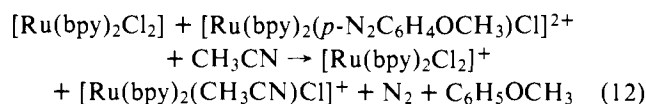
amines studied here, diazotization and electrophilic attack at the aromatic ring should be competitive processes. For the primary amines we find no evidence for nitrosoarene products under the conditions used. This observation is consistent with the fact that the diazotization reactions are noticeably more rapid than the electrophilic addition reactions using similar reaction conditions.[5]

Reactions of the Diazonium Ligands. Given the rather extensive reactivity of the nitrosyl group in (bpy)$_2$Ru^{II}< complexes and the similarities in physical properties between analogous nitrosyl and diazonium complexes, the reaction chemistry of the bound $-$N$_2$Ar group is clearly of interest. Qualitative experiments showed that the diazonium complexes reacted with a variety of nucleophiles (OH$^-$, N$_3^-$, etc.) including primary aromatic amines themselves as described in the previous section. Unfortunately, in most cases we were forced to work on a small scale and separation and identification of the organic products proved impractical. However, in certain cases we were able to characterize reaction products in some detail and these results are described below.
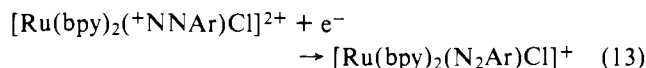
The diazonium complexes undergo irreversible one-electron reduction processes both chemically and electrochemically. Reduction is accompanied by gas evolution; the gas is presumably N$_2$. The details of the electron transfer chemistry have been described[22] and are discussed in a different context in a parallel communication.[23] As shown by cyclic voltammetry, the complex [Ru(bpy)$_2$(p-N$_2$C$_6$H$_5$CH$_3$)Cl]$^{2+}$ undergoes an irreversible one-electron reduction at $E_p = 0.08$ V vs. the SSCE in 0.1 M [N(n-C$_4$H$_9$)$_4$]PF$_6$–CH$_3$CN solution at 22 ± 2 °C. Electrolysis at -0.1 V gives $n = 1$ (by coulometry) and Ru(bpy)$_2$(CH$_3$CN)Cl$^+$ (as shown by cyclic voltammetry and UV–visible spectra) (eq 11). Noticeable gas evolution (presumably N$_2$) occurs during the electrolysis.

$$CH_3CN + [Ru(bpy)_2(p-N_2C_6H_6CH_3)Cl]^{2+} + e^-$$
$$\rightarrow [Ru(bpy)_2(CH_3CN)Cl]^+ + N_2$$
$$+ C_6H_5CH_3 \quad (11)$$
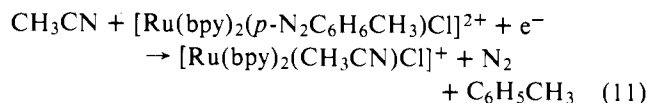
A spectrophotometric titration in CH_3CN of the reaction between $[Ru(bpy)_2(p-N_2C_6H_4CH_3)Cl]^{2+}$ and the chemical reductant $Ru(bpy)_2Cl_2$ gave a 1:1 stoichiometry and $Ru(bpy)_2Cl_2^+$ and $Ru(bpy)_2(CH_3CN)Cl^+$ as products (eq 12). GLC analysis of the product solution showed that anisole was also a product of the reaction (eq 12).

$$[Ru(bpy)_2Cl_2] + [Ru(bpy)_2(p-N_2C_6H_4OCH_3)Cl]^{2+}$$
$$+ CH_3CN \rightarrow [Ru(bpy)_2Cl_2]^+$$
$$+ [Ru(bpy)_2(CH_3CN)Cl]^+ + N_2 + C_6H_5OCH_3 \quad (12)$$

By analogy with the reversible one-electron reductions found for the related nitrosyl complexes,[6] reduction presumably occurs at levels largely $\pi^*(N_2Ar)$ in character (eq 13).

$$[Ru(bpy)_2(^+NNAr)Cl]^{2+} + e^-$$
$$\rightarrow [Ru(bpy)_2(N_2Ar)Cl]^+ \quad (13)$$

In contrast to the nitrosyl complexes where the reduced products are relatively stable, the reduced diazonium complexes undergo rapid decomposition (eq 14). There is no evidence for reversible electron transfer using cyclic voltammetry scan rates of up to 20 V/s.

$$[Ru(bpy)_2(N_2Ar)Cl]^+ + CH_3CN$$
$$\rightarrow [Ru(bpy)_2(CH_3CN)Cl]^+ + N_2 + Ar \quad (14)$$
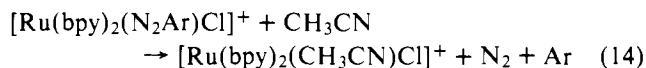
The observation of anisole as a product indicates that the radical $C_6H_4OCH_3$ once formed abstracts a hydrogen atom from solvent to give the hydrocarbon product.

In polar organic solvents the diazonium complexes react rapidly with potential two-electron reductants such as sodium borohydride, sodium dithionite, and stannous chloride, in certain cases without noticeable gas evolution. Although ligand-reduced products such as diimines ($Ru^{II}NH=NAr$) or hydrazines ($Ru^{II}NH_2NHAr$) might be expected from two-electron reductions,[21] once again we were plagued by the absence of a useful purification procedure and the products were not characterized.

The diazonium complexes are stable in aqueous solution for extended periods (several hours) at room temperature. Noticeable decomposition of the solutions begins at 60 °C as evidenced by gas evolution and a change in the color of the solutions from the pale yellow of the diazonium complexes to the deep red-brown color of $Ru(bpy)_2(H_2O)Cl^+$. Because we were working on a small scale, a precise determination of the organic products of thermal reactions was not possible. However, by heating $[Ru(bpy)_2(p-N_2C_6H_4CH_3)Cl]^{2+}$ in the presence of acetone, the expected hydrocarbon $C_6H_5CH_3$ was shown to be a product by GLC. Upon heating aqueous solutions of $[Ru(bpy)_2(p-N_2C_6H_4OCH_3)Cl]^{2+}$ in the presence of KI (catalytic amounts of I_2 may be necessary for the reaction to proceed), C_6H_5I was shown to be a product, again using GLC.

The reaction which shows most clearly that the reactivity properties of the bound diazonium group are similar to those of diazonium salts is the reaction between $[Ru(bpy)_2(p-N_2C_6H_4OCH_3)Cl]^{2+}$ and β-naphthol (eq 15). In aqueous methanol in the presence of K_2CO_3, the reaction occurs rapidly giving as products (as shown spectrophotometrically) $Ru(bpy)_2(OH)Cl$ and the expected azo-coupling product. The reaction shows that the ArN_2^+ group can be transferred intact by net electrophilic attack on a suitably activated aromatic system and is analogous to the reactions between the related nitrosyl complexes and secondary or tertiary aromatic amines which give nitrosoarenes as products (eq 10).
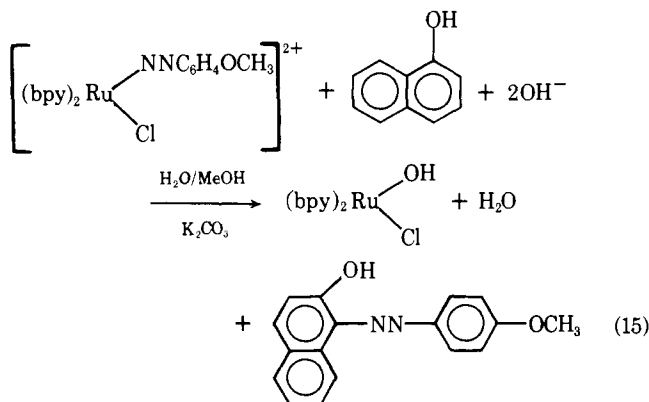
In summary, the relatively high thermal stability of the diazonium complexes in water indicates a considerable stabilization of the ArN_2^+ group by π-electron donation from Ru(II), an observation which is consistent with the $\nu(NN)$ IR data. On the other hand, the relatively high $\nu(NN)$ stretching frequencies when compared to other $M-N_2Ar$ systems help rationalize the azo-coupling reaction in which the bound diazonium group retains the reactivity of a diazonium ion. The one-electron reduction chemistry is consistent with reduction at largely π^* levels of the bound ArN_2^+ group and the instability of the reduced one-electron intermediates means that two and higher electron reduced products are probably inaccessible by simle one-electron transfer reactions.

Implications for Organic Synthesis. In principle, diazotization of aromatic amines by the nitrosyl complexes could find application in organic synthesis. The reactions can be carried out at room temperature in polar organic solvents and using appropriate conditions they are nearly quantitative. The metal-bound, diazotized products can be isolated and stored in the solid state for long periods. As for the analogous nitrosyl complexes, the diazonium complexes are potentially reagents in which a useful synthetic intermediate (ArN_2^+) is stored in a stable chemical form.

The bound diazonium group can be converted into the corresponding hydrocarbon by one-electron reduction followed by hydrogen-atom abstraction or by treatment with an α-hydrogen-containing ketone. In both of these reactions and in the diazo coupling reaction with activated aromatic systems the organic product is formed free of the coordination sphere of the metal complex. In water, the metal complex product of the reactions is $[Ru(bpy)_2(H_2O)Cl]^+$ or $Ru(bpy)_2(OH)Cl$ depending on the pH and either can be reconverted into the starting nitrosyl complex $[Ru(bpy)_2(NO)Cl]^{2+}$ in situ using known synthetic procedures.[3]

Experimental Section

Preparations. $[Ru(bpy)_2(p-N_2C_6H_4OCH_3)Cl](PF_6)_2$. The salt $[Ru(bpy)_2(NO)Cl](PF_6)_2^3$ (200 mg) was dissolved in acetonitrile (20 mL) and p-anisidine was added (40 mg). The solution was stirred for 10 min and a tan solid was then precipitated by slow addition to stirred ether. The precipitate was collected, air-dried, and extracted with dichloromethane (3 × 10 mL portions). The dichloromethane solution was precipitated by slow addition to low-boiling petroleum ether, collected, and air-dried. The solid was dissolved in reagent grade acetone, and a saturated solution of tetra-n-butylammonium chloride in acetone (3 mL) was added which precipitated the chloride salt of the complex. The resulting precipitate was collected, washed with

dichloromethane (10 mL), dissolved in distilled water, and precipitated by the addition of solid ammonium hexafluorophosphate. The precipitate was collected, air-dried, dissolved in acetone, filtered, and precipitated by adding to ether. The pale-yellow solid was collected and air-dried. The yield of the ruthenium diazonium salt [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)Cl](PF$_6$)$_2$, based on the nitrosyl starting material, was 75%.

Anal. Calcd for C$_{27}$H$_{23}$N$_6$OClRuP$_2$F$_{12}$: C, 37.02; H, 2.63; N, 9.61. Found: C, 36.55; H, 2.60; N, 9.43.

[Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$CH$_3$)Cl](PF$_6$)$_2$. The salt [Ru(bpy)$_2$(NO)Cl](PF$_6$)$_2$ (200 mg) was dissolved in acetonitrile (20 mL) and p-toluidine (40 mg) was added. The solution was stirred for 20 min and then added to ether to give a tan precipitate. The precipitate was then treated as in the preparation of the p-anisidine diazonium complex. The yield of the ruthenium p-tolyldiazonium salt, based on the salt [Ru(bpy)$_2$(NO)Cl](PF$_6$)$_2$, was 75%.

Anal. Calcd for C$_{27}$H$_{23}$N$_6$ClRuP$_2$F$_{12}$: C, 37.70; H, 2.65; N, 9.78; Cl, 4.18. Found: C, 37.66; H, 2.66; N, 9.78; Cl, 4.34.

[Ru(bpy)$_2$(N$_2$C$_6$H$_5$)Cl](PF$_6$)$_2$. The salt [Ru(bpy)$_2$(NO)Cl](PF$_6$)$_2$ (200 mg) was dissolved in acetonitrile (20 mL) and aniline (25 mg) was added. The solution was stirred for 24 h and then added to ether to give an orange precipitate. The precipitate was purified as in the preparation of [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)Cl](PF$_6$)$_2$ and a yield of 41% of the phenyldiazonium complex was obtained.

Anal. Calcd for C$_{26}$H$_{21}$N$_6$ClRuP$_2$F$_{12}$: C, 36.97; H, 2.49; N, 9.95. Found: C, 36.96; H, 2.67; N, 9.71.

Reaction of [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$CH$_3$)Cl]$^{2+}$ with KI. The salt [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$CH$_3$)Cl](PF$_6$)$_2$ (100 mg) was dissolved in acetone and a saturated solution of tetra-n-butylammonium chloride in acetone (3 mL) was added. The chloride salt, which precipitated, was collected, washed with dichloromethane, and dissolved in water (60 mL). To this solution was added a saturated aqueous solution of potassium iodide (10 mL). A solid formed, presumably the iodide salt, and the solution was distilled. The initial drops of distillate were cloudy in color and were extracted with diethyl ether. The extracts were reduced in volume to about 5 mL. This solution was then injected into a GLC (CT 193 °C). The iodide, p-iodotoluene was detected in the recorder trace and confirmed by its identical retention time with a known sample. While the yield determination of aryl iodide is inexact, because of the procedure involved, comparison with known concentrations of aryl halides suggests that the yield of iodide was only about 10% of the theoretical amount. The reaction of the diazonium complex with iodide ion in aqueous solution was not very reliable. There were numerous unsuccessful attempts to obtain the iodo aromatic using the same procedure, and as in the reaction of the free diazonium ion, the presence of triiodide ion may be necessary for the formation of the aryl iodide. In all cases the ruthenium product was shown to be Ru(bpy)$_2$I$_2$ by UV-visible spectral comparisons with a known sample.

Reaction of [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)Cl]$^{2+}$ with Aqueous Acetone. The salt [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)Cl]Cl$_2$ (250 mg) was dissolved in water (60 mL) and acetone (25 mL) was added, as well as 0.5 g of solid KI. A reddish solid was precipitated. The solution and precipitate were heated at reflux for 1 h. The solution became light red in color and a very dark solid was precipitated. The solution was extracted with benzene overnight, dried with Na$_2$SO$_4$, and reduced in volume. GLC analysis revealed the presence of anisole in the benzene extract (confirmed by comparison of retention time with a known sample). The dark solid was dissolved in CH$_2$Cl$_2$ and found to be Ru(bpy)$_2$I$_2$ from its characteristic UV-visible spectrum.

Reaction of [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)Cl]$^{2+}$ with β-Naphthol. The salt, [Ru(bpy)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)Cl](PF$_6$)$_2$ (100 mg), was dissolved in acetone (15 mL). To this was added a solution of β-naphthol in ethanol with a few grains of anhydrous K$_2$CO$_3$. After 5 min the solution was acidified with acetic acid and a reddish solid precipitated by adding to ether. The precipitate was collected and the red ethereal solution was evaporated to dryness and then taken up in benzene. The UV-visible spectrum of this material had absorption bands at 408, 455, and 540 nm, as did an authentic sample of the azo coupling product of β-naphthol and p-methoxybenzenediazonium chloride.

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(19) In order to decrease reaction times in the preparations of the diazonium complexes, excesses of the amines were used (Experimental Section). The lower than quantitative yields of the solid diazonium products (up to 75%; Experimental Section) can be attributed, in part, to the slower, subsequent reaction between the diazonium complexes and additional amine.
(20) Except for the case where L$^-$ = Cl$^-$, the diazonium products were not isolated and characterized. However, in all cases, broad, sometimes structured bands assignable to ν(NN) appear in the region 1950–2100 cm^{-1}. Interestingly, the ν(NN) band maxima for L = NO$_2^-$ and CH$_3$CN were centered at ~2070 and ~2100 cm^{-1}. Higher frequencies for ν(NO) compared to L$^-$ = Cl$^-$ are also found for the analogous nitrosyl complexes.[6]
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