Nitrosoarene Complexes of Ruthenium. Nitrosation of Activated Aromatic Compounds by the Coordinated Nitrosyl Group

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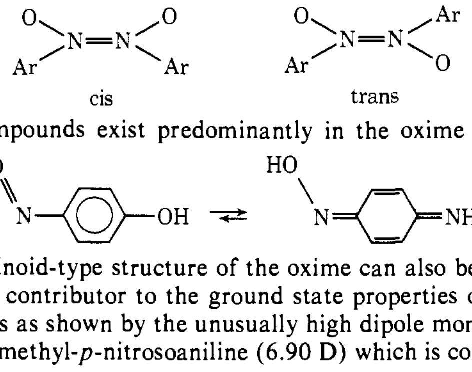
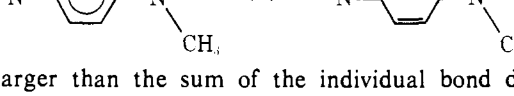
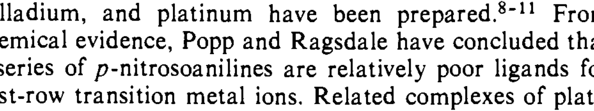
Abstract: The nitrosyl complexes $Ru(bpy)_2(NO)X^{2+}$ (X is Cl or NO_2) (bpy is 2,2′-bipyridine) react with the aromatic amines, $C_6H_5NRCH_3$ (R is H or CH_3), in acetonitrile at room temperature to give the *p*-nitrosoarene complexes, $Ru(bpy)_2(N(O)C_6H_4NRCH_3)X^+$. The phenoxide ion can also be nitrosated by the coordinated nitrosyl group. A series of nitrosoarene complexes containing nonactivated aromatic rings, $Ru(bpy)_2(p\text{-}N(O)C_6H_4Y)Cl^+$ (Y is H, CH_3, or NO_2), has also been prepared by solvent displacement from a labile, solvent-bound intermediate. An ^{15}N labeling experiment using $Ru(bpy)_2(^{15}NO)Cl^{2+}$ and the anilines has shown that the ^{15}N is retained in the product, and that the bound $\nu(NO)$ stretching vibrations occur at 1284 cm^{-1} (R = H) and 1286 cm^{-1} (R = CH_3). In the nitro-nitrosoarene complex, $Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2^+$, the coordinated nitro group is converted into nitrosyl by acid, and the reverse, nitrosyl → nitro, conversion is achieved by base. The kinetics of the nitro → nitrosyl reaction have been studied in 1.0 *M* aqueous NaCl, and the rate law is first order in complex and first order in acid.

Nitrosobenzene and its derivatives are potentially interesting ligands since there is a possible ambiguity with regard to the site of binding (at N or O), and the compounds have low-lying π^* systems[1-4] which may be accessible for back-bonding. The properties of nitrosoarene compounds are themselves somewhat complicated.[5,6] Many of the compounds dimerize in the solid state and in solution; both cis and trans dimers are known.[7] If there are ionizable protons, the compounds exist predominantly in the oxime form.[5,6]


cis trans



The quinoid-type structure of the oxime can also be an important contributor to the ground state properties of nitrosoarenes as shown by the unusually high dipole moment for *N,N*-dimethyl-*p*-nitrosoaniline (6.90 D) which is considerably larger than the sum of the individual bond dipoles. Monomeric nitrosoarenes are green because of a low energy absorption band which has been assigned to a n → π^* transition.[2] Absorption bands also appear at higher energies which have been assigned to $\pi \rightarrow \pi^*$ transitions.[1]



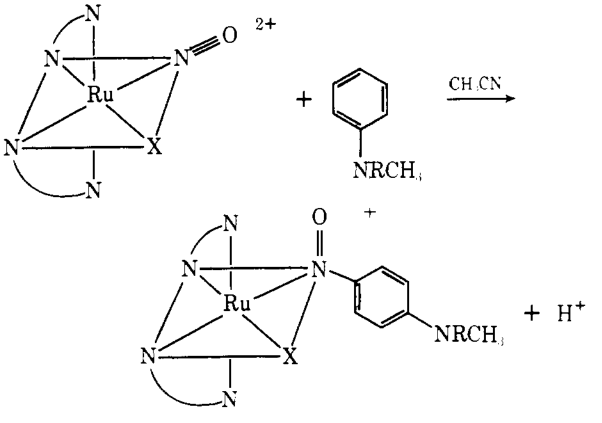
Nitrosoarene complexes of copper, nickel, cobalt, zinc, palladium, and platinum have been prepared.[8-11] From chemical evidence, Popp and Ragsdale have concluded that a series of *p*-nitrosoanilines are relatively poor ligands for first-row transition metal ions. Related complexes of platinum and palladium appear to be more stable.[9-11] The structure of a nitrosobenzene complex of palladium, $Pd(C_6H_5NO)_2Cl_2$, has been determined by x-ray crystallography, and the nitrosoarene group found to be N bound.[12] However, the mode of nitrosoarene binding may vary from system to system. It has been suggested that first-row transition metal complexes are O bound,[8] and the dimeric photoproduct of the reaction between $Fe(CO)_5$ and $C_6H_5NO_2$, $[Fe(CO)_3(C_6H_5NO)]_2$,[13] has been shown to have bridging C_6H_5NO groups with the N and O atoms bound to separate iron atoms.[14]

Activated aromatic systems react with the nitrosonium ion (NO^+) to give *p*-nitrosoarenes, even though the nitrosonium ion is a relatively weak electrophile.[15] The reactions occur by direct nitrosation (as for *N,N*-dimethylaniline or phenoxide ion) or by Fischer-Hepp rearrangement of an *N*-nitrosamine intermediate (as for *N*-methylaniline).[15]

In an appropriate coordination environment (one in which the $\nu(NO)$ stretching frequency is relatively high), the coordinated nitrosyl group has been shown to react chemically as the nitrosonium ion.[16-23] In particular, in complexes like *cis*-$Ru(bpy)_2(NO)Cl^{2+}$ (bpy is 2,2′-bipyridine) the nitrosyl group has been found to react with nucleophiles like OH^- and N_3^-,[16,17] and to diazotize primary aromatic amines.[21] We now find that the analogy in reactivity between coordinated nitrosyl and nitrosonium ion is extended to aromatic nitrosation and have prepared and characterized a series of mononitrosoarene complexes of ruthenium. Part of this work has appeared in a preliminary communication.[24]

Results and Discussion

The nitrosyl complexes, $Ru(bpy)_2(NO)X^{2+}$ (X is Cl or NO_2), react with *N,N*-dimethylaniline and *N*-methylaniline in acetonitrile at room temperature to give the corresponding nitrosoarene complexes (eq 1). Under preparative



(1)

(X is Cl or NO_2; R is H or CH_3)

Table I. Elemental Analysis Data for the Nitrosoarene Complexes

Complex	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N	Color
$[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)Cl]PF_6$	45.16	3.49	11.29	45.33	3.52	11.16	Blue-green
$[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2]PF_6 \cdot H_2O$	43.52	3.61	12.69	43.57	3.49	12.41	Royal blue
$[Ru(bpy)_2(N(O)C_6H_4NHCH_3)Cl]PF_6 \cdot H_2O$	43.20	3.47	11.20	43.06	3.32	10.99	Blue
$[Ru(bpy)_2(N(O)C_6H_4NHCH_3)NO_2]PF_6$	43.78	3.23	13.23	43.60	3.26	13.08	Blue-violet
$[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO](PF_6)_3$	32.68	2.53	9.53	32.45	2.60	9.46	Orange
$[Ru(bpy)_2(N(O)C_6H_4OH)Cl]PF_6 \cdot H_2O$	42.45	3.13	9.52	41.95	3.03	9.44	Blue-violet
$[Ru(bpy)_2(N(O)C_6H_4CH_3)Cl]PF_6$	45.31	3.22	9.79	45.17	3.19	9.69	Orange-red
$[Ru(bpy)_2(N(O)C_6H_5)Cl]PF_6$	44.58	2.98	9.98	44.29	3.02	9.84	Orange-red
$[Ru(bpy)_2(N(O)C_6H_4NO_2)Cl]PF_6 \cdot H_2O$	40.83	2.62	10.99	40.44	2.68	10.80	Red-brown

conditions, the reactions appear to be fairly rapid and nearly quantitative. The blue color of the nitrosoarene complexes appears upon mixing the reactant solutions and yields of >80% were obtained after chromatography on Kieselguhr.

The facile aromatic nitrosation reaction (eq 1) is apparently limited to highly activated aromatic amines, at least under mild conditions. No evidence for reaction between $Ru(bpy)_2(NO)Cl^{2+}$ and either phenol, anisole, or ferrocene was observed after up to 4 hr in acetonitrile at room temperature. However, when anhydrous K_2CO_3 is added to an acetonitrile solution containing phenol and the nitrosyl complex, a rapid reaction occurs giving the coordinated nitrosophenol complex (eq 2).

$$Ru(bpy)_2(NO)Cl^{2+} + C_6H_5O^- \rightarrow Ru(bpy)_2(N(O)C_6H_4OH)Cl^+ \quad (2)$$

By analogy with the simple nitrosation of phenol itself, the reaction almost surely involves prior loss of a proton giving the highly activated phenoxide ion (eq 2). Anisole remained unreactive upon the addition of K_2CO_3. Thus $[Ru(bpy)_2(NO)Cl]^{2+}$ behaves as a weak electrophile with reactivity comparable to that of the aryldiazonium ion (as in azo coupling reactions).

Nitrosoarene complexes of less strongly activated aromatic systems can be prepared directly by ligand displacement reactions. In earlier papers, synthetic work has been described in which selective substitution can be obtained in complexes of bis-2,2′-bpy complexes of ruthenium(II).[17,25] The reactions proceed via a labile, solvent-bound intermediate (eq 4) which is generated by reaction between free azide ion and a nitrosyl complex (eq 3).

$$Ru(bpy)_2(NO)Cl^{2+} + N_3^- + S \rightarrow Ru(bpy)_2(S)Cl^+ + N_2 + N_2O \quad (3)$$

(S is acetone or methanol)

$$Ru(bpy)_2(S)Cl^+ + ArNO \rightarrow Ru(bpy)_2(N(O)Ar)Cl^+ + S \quad (4)$$

(Ar is C_6H_5, p-$C_6H_4CH_3$, p-$C_6H_4NO_2$, p-$C_6H_4N(CH_3)_2$)

An alkylnitroso complex of ruthenium(II), $[Ru(NH_3)_5(NOCH_2C(CH_3)_2OH)]^{2+}$, was prepared recently by radiolysis of $Ru(NH_3)_5NO^{3+}$ in aqueous *tert*-butyl alcohol.[26] The reaction is thought to proceed by the attack of *tert*-butyl alcohol radicals, $CH_2C(CH_3)_2OH$, on the reduced nitrosyl complex, $Ru(NH_3)_5NO^{2+}$.[26] In principle, the radiolysis experiment may also provide a general synthetic route to both alkyl- and aryl-nitroso complexes.

Isolation of the nitro complexes, $Ru(bpy)_2(N(O)C_6H_4NRCH_3)NO_2^+$ (R is -H or $-CH_3$), opens a route to bisnitrosoarene complexes. Earlier work has shown that the nitrite group, when bound to bis(2,2′-bpy)Ru(II), is converted into nitrosyl in acidic solution.[16] Treatment of a nitro-nitrosoarene complex with acid (eq 5), followed by reaction with an aromatic amine, apparently gives the bisnitrosoarene product (eq 6).

$$Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2^+ + 2H^+ \rightarrow Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO^{3+} + H_2O \quad (5)$$

$$Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO^{3+} + C_6H_5N(CH_3)_2 \rightarrow Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)_2^{2+} + H^+ \quad (6)$$

A deeply purple-colored compound has been obtained from reaction 6. However, attempted purification by column chromatography using dichloromethane (which is essential for clean chromatographic separation) results in partial decomposition on the column giving the analogous chloro complex and free nitrosoarene as shown spectrally (eq 7).

$$Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)_2^{2+} \xrightarrow{CH_2Cl_2} Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)Cl^+ + N(O)C_6H_4N(CH_3)_2 \quad (7)$$

The decomposition reaction appears to go to completion in dichloromethane solution over a period of 48 hr.

The nitrosoarene complexes range in color from deep blue ($N(O)C_6H_4NRCH_3$) to red-brown ($N(O)C_6H_4NO_2$). The origin of the colors are metal → ligand (either nitrosoarene or 2,2′-bpy) $d\pi \rightarrow \pi^*$ charge transfer transitions. The spectral and redox properties of the complexes will be discussed in a subsequent paper.[27] In contrast to first-row transition metal-nitrosoarene complexes, the ruthenium complexes are stable in solution. The spectral properties of solutions of the complexes in acetonitrile are stable for at least 10 days, even though acetonitrile complexes of bis(2,2′-bipyridine)ruthenium(II) are well-known and quite stable.[17,28] Elemental analysis data on the salts prepared are given in Table I.

Infrared Spectra. The infrared spectra of the nitrosoarene complexes include bands characteristic of the bis(2,2′-pyridine)ruthenium(II) group, as well as, bands characteristic of the bound nitrosoarenes. The spectra of the salts $[Ru(bpy)_2(N(O)C_6H_4NHCH_3)Cl](PF_6)$ and $[Ru(bpy)_2(N(O)C_6H_4CH_3)Cl](PF_6)$ in KBr pellets are shown in Figure 1. Band positions cited below are known to ± 2 cm^{-1}. All of the nitrosoarene complexes have a characteristic, strong band in the region 1330-1383 cm^{-1}. In addition, the p-nitrosoaniline complexes have very strong bands at ~1600 and ~1120 cm^{-1}, and a somewhat weaker band at ~1220 cm^{-1}.

In several cases bands characteristic of the remote, para substituent were observed, which proved to be a useful indicator of the presence of the bound ligand. The p-nitronitrosobenzene complex has strong bands at 1523 and 1340 cm^{-1} attributable to the symmetric and asymmetric $\nu(-NO_2)$ stretching frequencies of the aromatic nitro group. The p-N-methylnitrosoaniline and p-nitrosophenol com-

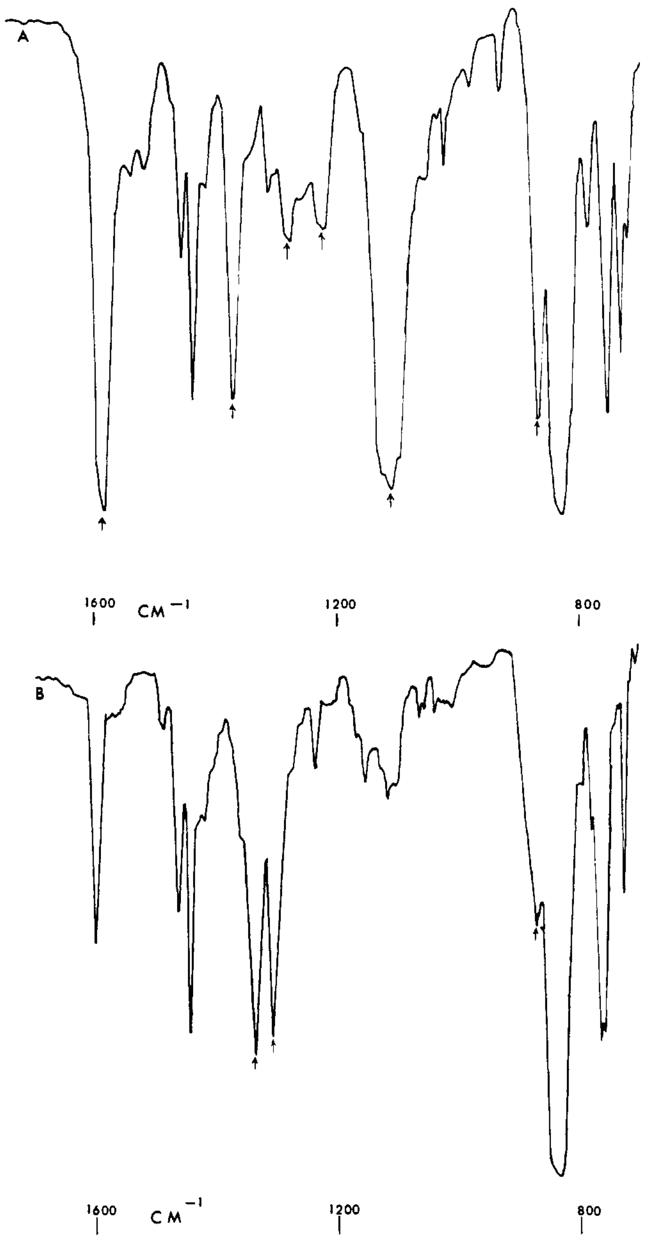


Figure 1. Infrared spectra of $[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)Cl]PF_6$ (A) and $[Ru(bpy)_2(N(O)C_6H_4CH_3)Cl](PF_6)$ (B) in a KBr pellet (±2 cm^{-1}). Characteristic 2,2′-bipyridine bands are at 1600, 1560, 1470, 1450, 1320, 1240, 1170, 1112, 1073, 1039, 1027, 765, and 724 cm^{-1}. Bands due to the bound nitrosoarene are indicated by arrows.

plexes have infrared bands which can be assigned to ν(N-H) (3420 cm^{-1}) and ν(O-H) (3250) stretching frequencies, respectively. The nitrite complexes, $Ru(bpy)_2(N(O)C_6H_4NRCH_3)NO_2^+$, have bands at 1348 and 1288 cm^{-1} (R = H) and at 1352 and 1293 cm^{-1} (R = CH_3) which can be assigned to the symmetric and asymmetric stretching frequencies for the N-bound nitrite group.[17] Upon conversion of the nitrite complex (R = CH_3) to the nitrosyl (eq 5), the $\nu(NO_2)$ bands disappear and are replaced by a strong ν(NO) band at 1931 cm^{-1}.

Perhaps the most interesting infrared band to consider is the expected ν(NO) stretching frequency for the bound nitrosoarene groups. The position of the ν(NO) stretching mode in the free ligands is a source of some controversy.[6,11,29,30] The ν(NO) vibration may, in fact, be strongly coupled with other molecular vibrations. In transition metal complexes, relatively high energy bands (>1450 cm^{-1}) have been observed, which shift upon coordination;[8,9] however, the assignment of a bound ν(NO) stretch is not clear, nor is it clear whether the complexes studied contain *O* or *N* bound nitrosoarene groups.

We have prepared the ^{15}N labeled complexes, $[Ru(bpy)_2(^{15}N(O)C_6H_4NRCH_3)Cl](PF_6)$ (R = H or CH_3), using eq 1 and the ^{15}N labeled nitrosyl complex prepared as shown in eq 8 and 9.[16]

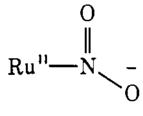
$$Ru(bpy)_2Cl_2(s) \xrightarrow[\Delta]{H_2O} Ru(bpy)_2(H_2O)Cl^+ + Cl^- \quad (8)$$

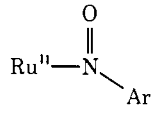
$$Ru(bpy)_2(H_2O)Cl^+ + {}^{15}NO_2^- + 2H^+ \longrightarrow Ru(bpy)_2(^{15}NO)Cl^{2+} + H_2O \quad (9)$$

A careful comparison between the spectra of the labeled and unlabeled products reveals the following shifts: for R = CH_3, 1286 cm^{-1}(^{14}N) → 1261 cm^{-1}(^{15}N), 875 cm^{-1}(^{14}N) → 866 cm^{-1}(^{15}N); for R = H, 1284 cm^{-1}(^{14}N) → 1268 cm^{-1}(^{15}N), 875 cm^{-1}(^{14}N) → 866 cm^{-1}(^{15}N). The magnitudes of the shifts in the higher energy bands are only approximate because of partial overlap with other, near-lying bands. However, the labeling experiment is informative. It shows that the ^{15}N is retained in the product. Further, only *one* relatively high energy band is shifted upon ^{15}N labeling, and that band (1284 cm^{-1} (R = H) and 1286 cm^{-1} (R = CH_3)) must be predominantly a bound ν(NO) stretching vibration.

In the complex $Ru(NH_3)_5(NOCH_2C(CH_3)_2OH)^{2+}$, bands at 1370 and 1365 cm^{-1} shift 10 cm^{-1} to lower energies in the ^{15}N complex.[26] Labeling studies were not carried out on the remaining nitrosoarene complexes, but they all have relatively strong bands in the range 1270-1340 cm^{-1} which can be assigned tentatively to the ν(NO) stretch. The nitrosobenzene, nitrosotoluene, and nitronitrosobenzene complexes have two strong bands in the region 1308-1350 cm^{-1}. The higher energy band is characteristic of the nitrosoarene group and the lower energy band (1308-1312 cm^{-1}) appears to be a combination of overlapped ν(NO) nitrosoarene and a characteristic, moderately strong 2,2′-bipyridine band at around 1310 cm^{-1}.

The ν(NO) frequencies fall in the same range as ν(NO) in trans nitrosoarene dimers[6,7] and as the symmetric and asymmetric stretching frequencies for a nitro group in bis(2,2′-bipyridine)ruthenium(II) complexes.[16] O-Bound, nitrito complexes of Ru(II) have a significantly different nitrite band pattern in the infrared.[17] The infrared data and the known N-bound structure of $Pd(N(O)C_6H_5)_2Cl_2$[12] suggest that the ruthenium complexes are also N bound, and that an analogy can be drawn between the nitrosoarene ligands and the bound nitrite ion. As will be discussed in a succeeding paper, spectral and electrochemical evidence shows clearly that significant back-bonding occurs between Ru(II) and the nitrosoarene ligands.[27] The strength of the back-bonding and its dependence on remote substituents in the aromatic ring also provide evidence that the ligand is N bound to Ru(II).


$$Ru^{II}-\overset{\overset{\displaystyle O}{\|}}{N}\!\!\diagdown_{O}^{-}$$


$$Ru^{II}-\overset{\overset{\displaystyle O}{\|}}{N}\!\!\diagdown_{Ar}$$

Nitro to Nitrosyl Interconversion. Addition of HPF_6 to a solution containing $Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2^+$ gave the nitrosyl complex, $Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO^{3+}$ (eq 5). The kinetics of the nitro → nitrosyl conversion were studied in 1.0 *M* aqueous NaCl solution at 25.2 ± 0.1°C at varying concentrations of added acid (HCl). The reactions were monitored at 590 nm where the nitrosyl complex absorbs negligibly and the nitro complex

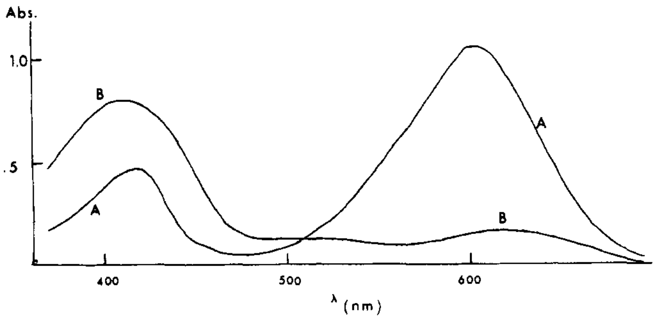


Figure 2. Uv-visible spectra of $Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2^+$ (A) and $Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO^{3+}$ (B) in 1 *M* aqueous NaCl solution (3.33×10^{-5} *M*), and in 1 *M* NaCl with added HCl, respectively; path length 1 cm.

has a λ_{max} (Figure 2). In the kinetic runs, an isosbestic point appears at 500 nm, which indicates that the nitrosyl and nitro complexes are the only absorbing species in the visible spectrum during the course of the reaction.

The disappearance of the nitro complex was followed in the presence of a large excess of added acid. Pseudo-first-order rate constants, k_{obsd}, were calculated from the slopes of plots of log $(A - A_\infty)$ vs. t (Table II). A plot of k_{obsd} vs. $[H^+]$ is linear, showing that the rate law for the reaction is first order in acid, as well as, first order in complex (eq 10).

$$\text{rate} = k[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2^+][H^+] \quad (10)$$

From the slope of the line in Figure 2, $k = 7.9 \pm 0.8 \times 10^{-2}$ M^{-1} sec^{-1}.

A related study has been carried out on the conversion of the nitro to the nitrosyl form of the nitroprusside ion (eq 11). Evidence was obtained which indicates that the rate determining step is loss of a water molecule from the protonated intermediate $Fe(CN)_5NO_2H^{3-}$ which is assisted by an additional proton.[31]

$$Fe(CN)_5NO_2^{4-} + 2H^+ \rightarrow Fe(CN)_5NO^{2-} + H_2O \quad (11)$$

The overall mechanism for the ruthenium reaction is probably similar (eq 12 and 13) where the slow step is k_1 because of a much lower affinity of the positively charged ruthenium complex for a proton.

$$Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2^+ + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2H^{2+} \quad (12)$$

$$Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2H^{2+} + H^+ \xrightarrow[\text{fast}]{} Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO^{3+} + H_2O \quad (13)$$

The isosbestic point in the kinetic runs shows that a single protonated intermediate does not build up appreciably during the course of the reaction. The same conclusion was reached in the conversion of $Ru(bpy)_2(NO)Cl^{2+}$ into the nitro complex by OH^- (eq 14). In that reaction no spectral evidence was found for the intermediate $Ru(bpy)_2(NO_2H)Cl^+$.[16]

$$Ru(bpy)_2(NO)Cl^{2+} + 2OH^- \rightarrow Ru(bpy)_2(NO_2)Cl + H_2O \quad (14)$$

As has been found for related nitrosyl complexes (eq 14), the nitrosoarene-nitrosyl complex can be converted into the nitro form quantitatively by base (eq 15), as shown spectrally.

$$Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO^{3+} + 2OH^- \rightarrow Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2^+ + H_2O \quad (15)$$

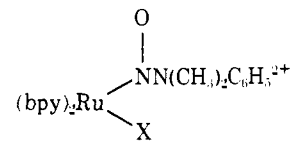
Table II. Rate Data for Nitro to Nitrosyl Conversion at 25.2 ± 0.1°C in Aqueous 1.0 *M* NaCl

k_{obsd}, sec^{-1}	$[H^+]$, *M*
3.19×10^{-3}	0.040
1.58×10^{-3}	0.020
9.16×10^{-4}	0.012
2.96×10^{-4}	0.004

Reactivity of the Nitrosyl Group. There is one noticeable difference in the reactivity patterns of the nitrosyl complexes and NO^+. For the nitrosyl complexes, the reactions with the tertiary $(C_6H_5N(CH_3)_2)$ and secondary $(C_6H_5NHCH_3)$ amines and with phenoxide ion give *p*-nitrosoarene complexes as isolable products. In the reaction between aqueous nitrous acid and $C_6H_5NHCH_3$, the initial product is the *N*-nitrosamine compound, $C_6H_5N(CH_3)NO$. The nitrosamine, once formed, undergoes the Fischer–Hepp rearrangement giving the nitrosarene, *p*-$N(O)C_6H_4NHCH_3$, but only under forcing conditions.

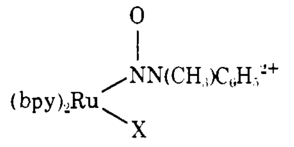
The details of the mechanism of nitrosation by the ruthenium complexes are unclear. The reactions may proceed via initial adduct or *N*-nitrosamine formation (eq 16 or 17), followed by metal-catalyzed Fischer–Hepp rearrangement. They may also occur by direct, electrophilic attack on the aromatic ring (eq 18).

$Ru(bpy)_2(NO)X^{2+} + C_6H_5N(CH_3)_2 \longrightarrow$



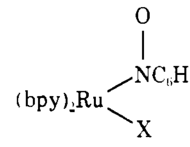
(16)

$Ru(bpy)_2(NO)X^{2+} + C_6H_5NHCH_3 \longrightarrow$



$+ H^+$ (17)

$Ru(bpy)_2(NO)X^{2+} + C_6H_5Y \longrightarrow$



$+ H^+$ (18)

Nitrosation occurs only for activated anilines, and the site of nitrosation is para to the activating group. The implied substituent effects argue both by reactivity and by orientation in favor of an electrophilic substitution reaction. We have obtained some experimental evidence for the existence of both adduct and *N*-nitrosamine complexes. However, it is not yet clear whether such complexes represent true intermediates along the reaction pathway to nitrosoarenes, or rather, by-products which deplete the active reagents in the overall nitrosation reaction.

As nitrosating agents for activated aromatic systems, the nitrosyl complexes appear to be competitive with the nitrosonium ion. The nitrosyl reactions are fairly rapid and nearly quantitative under mild conditions. In certain cases the nitrosyl complexes might prove useful as organic synthetic reagents; however, we have not yet investigated the ligand displacement chemistry necessary to give the free nitrosoarene products. It is also conceivable that nitrosation reactions with less strongly activated species may occur under more forcing experimental conditions or by using a more highly activated nitrosyl, e.g., $Ru(bpy)_2(NO)CH_3CN^{3+}$ (ν(NO) = 1970 cm^{-1} in CH_3CN).[32]

Experimental Section

Apparatus. Infrared spectra were taken with Perkin-Elmer 421 or Digilab-FTS spectrometers as KBr pellets. Uv-visible spectra were measured on Cary 14, Unicam SP800, or Bausch and Lomb 200 spectrophotometers. Commercially available reagent grade phenol, *N*-methylaniline, and *N,N*-dimethylaniline were used without further purification. Spectrograde acetonitrile was used for all reactions and solution spectra. Analyses were performed by Galbraith Laboratories. Nitrosobenzene, *p*-nitrosotoluene, *p*-nitronitrosobenzene, and *p*-nitrosodimethylaniline were obtained as gifts from Mr. K. W. Nordquest. The ruthenium nitrosyl complexes $[Ru(bpy)_2(NO)Cl](PF_6)_2$ and $[Ru(bpy)_2(NO)NO_2](PF_6)_2$ were prepared by the method of Meyer et al.[33,34]

Preparation of Nitrosoarene Complexes. Method I. Preparation of $[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)Cl]PF_6$, $[Ru(bpy)_2(N(O)C_6H_4NHCH_3)Cl]PF_6$, $[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2]PF_6$, and $[Ru(bpy)_2(N(O)C_6H_4NHCH_3)NO_2]PF_6$. The salts $[Ru(bpy)_2(NO)X](PF_6)_2$ (X = Cl, NO_2) (200 mg) were dissolved in 5 ml of CH_3CN and 1 ml of *N*-methylaniline or *N,N*-dimethylaniline was added. After being stirred for 4 hr the solution was added with stirring to 300 ml of ether. The solid product which precipitated was collected, air-dried, dissolved in a minimum amount of acetone, and allowed to dry on a small amount of Kieselguhr. The solid powder was chromatographed on a Kieselguhr column using mixtures of reagent grade benzene and dichloromethane. The solvent was removed by a rotary evaporator and the remaining solid product dissolved in dichloromethane and precipitated by adding to hexane or petroleum ether. Yields of 80%, based on ruthenium, were isolated after chromatography.

Method II. Preparation of $[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)Cl]PF_6$, $[Ru(bpy)_2(N(O)C_6H_4CH_3)Cl]PF_6$, $[Ru(bpy)_2(N(O)C_6H_5)Cl]PF_6$, and $[Ru(bpy)_2(N(O)C_6H_4(NO_2))Cl]PF_6$. The salt $[Ru(bpy)_2(NO)Cl](PF_6)_2$ (100 mg) was dissolved in acetone (25 ml) and NaN_3 (8.5 mg) was added. The solution was stirred for 2 hr and an excess of the nitrosoarene was added. The solution was stirred for 2 hr and precipitated with ether. The solid product was chromatographed as in method I.

Preparation of $[Ru(bpy)_2(N(O)C_6H_4OH)Cl]PF_6$. The salt $[Ru(bpy)_2(NO)Cl](PF_6)_2$ (200 mg) was dissolved in 10 ml of CH_3CN and about 50 mg of crystalline phenol was added along with a few grains of solid anhydrous K_2CO_3. The solution was stirred for 30 min, ether was added, and the solid product which precipitated was chromatographed as in method I.

$[Ru(bpy)_2(^{15}NO)Cl](PF_6)_2$. The compound $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (1.000 g) was dispersed in 150 ml of distilled water and heated at 100°C for 40 min. The resulting solution was filtered and 5 ml of 3 *M* HCl was added. The solution was then warmed to 45–50°C, and a solution of $Na^{15}NO_2$ (150 mg) was added with stirring over a period of 10 min. The solution was stirred for 15 min and a saturated solution of NH_4PF_6 in 5 ml of distilled water was added. The precipitate was collected and air-dried. The solid product was dissolved in 25 ml of a 50% methanol–50% acetonitrile solution and precipitated by adding to 400 ml of ether. Yields were similar to those reported previously for the ^{14}N complex.[33,34]

Preparation of $[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO](PF_6)_3$. The salt $Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2NO_2]PF_6$ (200 mg) was dissolved in 50 ml of CH_3CN, and 5 ml of concentrated HPF_6 was added. After 20 min, the product was precipitated by adding the solution to 400 ml of ether. The solid nitrosyl complex was dissolved in a minimum of acetone and precipitated by adding to 500 ml of CH_2Cl_2. The solid product was collected and air-dried. Yields of 80% were obtained, based on $[Ru(bpy)_2(NO)Cl](PF_6)_2$.

Kinetics of the Reaction between $[Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2]PF_6$ and Acid. The conversion of $Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO_2^+$ into $Ru(bpy)_2(N(O)C_6H_4N(CH_3)_2)NO^{3+}$ was monitored by following the changes in absorbance on a Unicam 800 spectrophotometer from 700 to 375 nm. Rate constants were calculated from the slope of first-order rate plots which were linear for at least three half-lives. The temperature was maintained at 25.2 ± 0.2°C in a thermostated cell compartment using Forma-Temp Model 2095 or 2220 constant temperature baths.

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