

Table II

Approx description of mode	Freq, cm ⁻¹		
	(C ₂ H ₄)Pd	(C ₂ H ₄ ads)Pd ⁹	Δ
ν(CH ₂)	2952	2980	28
ν(C=C)	1502	1510	8
δ(CH ₂)	1223	Not obsd	
ρ _w (CH ₂)	913	Not obsd	

The small "blue" frequency shift on passing from (C₂H₄)Pd to (C₂H₄ads)Pd implies a slight strengthening of the C—H and C=C bonds of the coordinated ethylene moiety on going from a single Pd atom site to a Pd atom in the metal surface. This might be taken to imply that the extent of Pd → C₂H₄ charge transfer is marginally less from a Pd surface atom site than from an isolated Pd atom. Such a change in electron transfer between metal-ethylene and metal-metal bonds might be taken as evidence in support of photoelectron emission studies¹⁵ which show that alkenes are net electron acceptors from Pt(0) in complexes such as (Ph₃P)₂Pt(C₂H₄) yet net electron donors to surface Pt atoms.¹⁶

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Registry No. (C₂H₄)Pd, 60595-00-8.

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Electron Transfer in Diazonium Complexes of Ruthenium

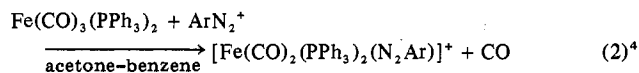
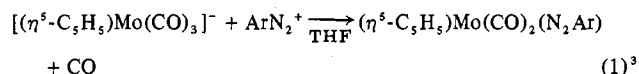
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William F. Little, and Thomas J. Meyer*

Received August 30, 1976

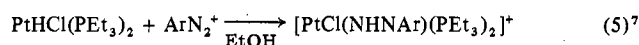
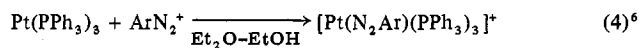
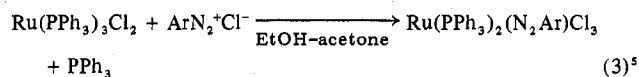
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Although of recent origin the synthetic chemistry leading to the aryldiazonium-metal (aryldiazonato¹ or aryldiazenido²) linkage (M—NNAr) has proven to be extensive and analogies with related metal nitrosyl complexes can be drawn.¹ The

synthetic chemistry involved has relied mainly on reactions between diazonium salts and appropriate transition metal complexes. In the net sense the reactions which have been used include substitution (eq 1 and 2), addition or oxidative addition

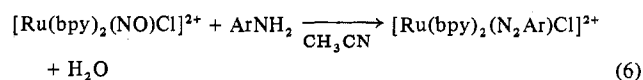


(eq 3 and 4), and insertion into a metal-hydride bond (eq 5).



Diazonium ions are moderately strong oxidants⁸ and net electron-transfer reactions from metal to ArN₂⁺ might in certain cases be expected to compete with the synthetically useful reactions mentioned above or to provide pathways for decomposition of M—N₂Ar complexes once formed. As an example of the first kind, (C₆Me₆)Cr(CO)₂PPh₃ is known to be oxidized to the monocation by diazonium ions.⁹

We have described the preparations of a series of diazonium complexes of ruthenium by a route not involving diazonium salts. The reactions involve diazotization of primary aromatic amines using a bound nitrosyl group (eq 6).¹⁰ As in metal



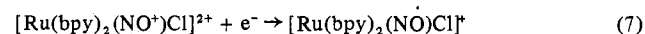
nitrosyls, attempts to describe the electronic structure of the M—NNAr group can lead to certain ambiguities as evidenced by the limiting valence bond structures for the Ru—bpy complexes: Ru^{II}—NN⁺Ar and Ru^{IV}—NN⁻Ar. However, the complexes [Ru(bpy)₂(N₂Ar)Cl]²⁺ have high ν(NN) stretching frequencies (>1980 cm⁻¹ in CH₃CN) and chemical reactivity properties similar to those of free ArN₂⁺ ions indicating a considerable diazonium ion-ruthenium(II) character in the RuN₂Ar linkage.¹⁰

From attempts to prepare Ru—bpy—diazonium complexes by direct reactions with ArN₂⁺ ions and from the chemical properties of the actual complexes prepared by reaction 6, it is apparent that simple one-electron-transfer processes play an important role in the underlying chemistry. We report here our observations on such processes in some detail since they appear to give general insight into the importance of electron transfer in the formation and stability of metal-diazonium complexes.

Results and Discussion

Electron-Transfer Properties of the Diazonium Complexes.

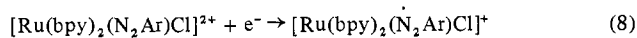
The series of nitrosyl complexes [Ru(bpy)₂(NO)L]ⁿ⁺ (n = 2, L = N₃, Cl, NO₂; n = 3, L = NH₃, py, CH₃CN) are known to undergo reversible one-electron reductions where the oxidizing site in the complex is localized largely at the nitrosyl group (eq 7). E_{1/2} values for the reduction processes, e.g.,



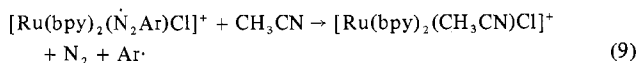
eq 7, fall into the range 0.18–0.56 V in 0.1 M [N(n-C₄H₉)₄](PF₆)-acetonitrile at 22 ± 2 °C vs. the saturated sodium chloride calomel electrode (SSCE).¹² A close similarity has been noted previously between the properties of nitrosyl and related diazonium complexes.^{10,13} From their chemical and physical properties, there is clearly considerable

NO^+ and ArN_2^+ character in the RuNO and RuN_2Ar groups, respectively.

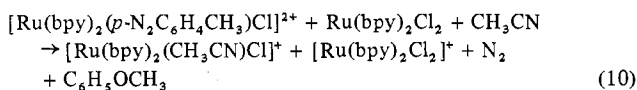
Under the same conditions used for the nitrosyl complexes, a cyclic voltammogram of the complex $[\text{Ru}(\text{bpy})_2(p\text{-N}_2\text{C}_6\text{H}_4\text{CH}_3)\text{Cl}]^{2+}$ has a single irreversible reduction wave at $E_p = 0.08$ V vs. the SSCE. Coulometry on the diffusion plateau of the reduction wave gave $n \approx 1.0$ with noticeable gas evolution (N_2). The ruthenium product of the one-electron reduction was $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$ as shown by spectrophotometry ($\lambda_{\text{max}} 480$ nm, $\epsilon 6740$) and by cyclic voltammetry ($E_{1/2} = 0.86$ V).¹⁴ By analogy with the nitrosyl complexes the reduction probably occurs at a level largely $\pi^*(\text{NNAr})$ in character (eq 8). Cyclic voltammetry even at



scan rates up to 20 V/s gave no evidence for a reverse oxidation wave so that the reduced complex once formed undergoes rapid decomposition on the cyclic voltammetry time scale (eq 9).

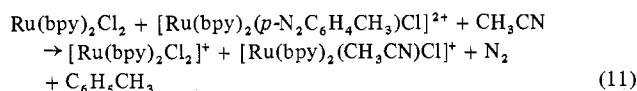


The diazonium complexes are also reduced chemically. A spectrophotometric titration of the reaction between $[\text{Ru}(\text{bpy})_2(p\text{-N}_2\text{C}_6\text{H}_4\text{OCH}_3)\text{Cl}]^{2+}$ and the chemical reductant $\text{Ru}(\text{bpy})_2\text{Cl}_2$ ($\lambda_{\text{max}} 553$, $\epsilon 9100$)¹⁴ showed that a reaction occurred with a 1:1 stoichiometry and that the ruthenium products were $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$ and $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^+$ ($\lambda_{\text{max}} 380$ nm, $\epsilon 5650$). GLC analysis of the solution at the end of the reaction showed that anisole was also formed as a product. The overall stoichiometry of the reaction is as given in eq 10. Presumably anisole appears as a product via the

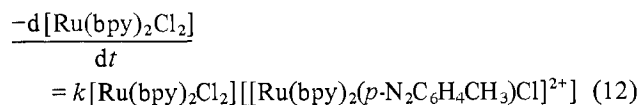


intermediate radical $\text{C}_6\text{H}_4\text{OCH}_3$ (eq 9) which abstracts a hydrogen atom from the solvent.

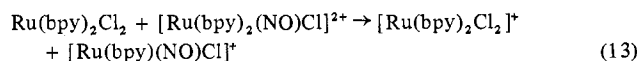
The kinetics of the reaction between $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and $[\text{Ru}(\text{bpy})_2(p\text{-N}_2\text{C}_6\text{H}_4\text{CH}_3)\text{Cl}]^{2+}$ (eq 11) were followed using



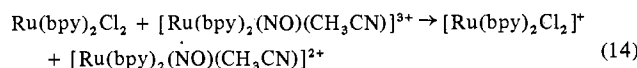
a stopped-flow spectrometer under pseudo-first-order conditions with the diazonium complex in excess. The reactions were followed in regions of high absorbance change, e.g., at λ_{max} for $\text{Ru}(\text{bpy})_2\text{Cl}_2$ at 553 nm. The rate law for the reaction was found to be first order in $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ and first order in diazonium complex (eq 12). At 25.0 + 0.1 °C in ace-



tonitrile, $k = (2.0 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ where k is the average value of 11 kinetic runs. The rate of the analogous reaction between $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ and the nitrosyl complex (eq 13),



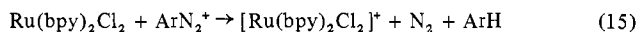
which is thermodynamically unfavorable ($\Delta\mathcal{G}^\circ = 0.10$ V), has not been determined. $E_{1/2}$ for the $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^{+0}$ couple is 0.30 V.¹⁴ However, for purposes of comparison, k for reaction 14 (for which $\Delta\mathcal{G}^\circ = 0.26$ V) has been measured under the same conditions and found to be $>10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C.¹²



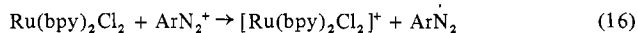
In summary, the diazonium complexes have been found to undergo relatively facile one-electron reduction processes. By analogy with the electron-transfer chemistry of the corresponding nitrosyl complexes, the site of reduction is probably at π^* levels largely diazonium in character. In contrast to the nitrosyl chemistry, reduction at coordinated diazonium leads to unstable intermediates which have low-energy pathways for decomposition via N_2 and aryl radicals. In both cases competitive back-bonding to bpy leads to considerable NO^+ and ArN_2^+ character. It is probably this feature which accounts for their ability as oxidants. For both the nitrosyl and diazonium complexes, the observed chemical reactivity and associated physical properties (e.g., high $\nu(\text{NO})$ and $\nu(\text{NN})$ stretching frequencies) represent nearly limiting cases for NO^+ and ArN_2^+ -type behavior.

Reactions with Diazonium Ions. Early synthetic attempts to prepare diazonium complexes by direct reactions between complexes like $\text{Ru}(\text{bpy})_2\text{Cl}_2$ or $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{COCH}_3)\text{Cl}]^+$ and diazonium salts were unsuccessful.¹³ In acetone, nitrobenzene, or acetonitrile, N_2 evolution was observed and $\text{Ru}(\text{III})$ complexes were obtained as products.

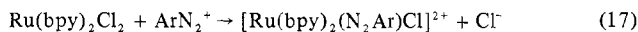
A spectrophotometric titration of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ by $(p\text{-N}_2\text{C}_6\text{H}_4\text{NO}_2)(\text{BF}_4)$ in acetonitrile showed that the reaction stoichiometry was 1:1 and that the ruthenium product was $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^+$ (eq 15). Clearly, in this case simple out-



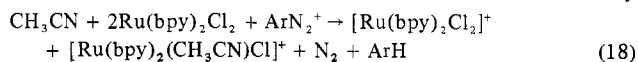
er-sphere electron transfer (eq 16) is more rapid than sub-



stitution at ruthenium and the reaction products are controlled by redox processes. If substitution at ruthenium were competitive (eq 17), $[\text{Ru}(\text{bpy})_2(p\text{-N}_2\text{C}_6\text{H}_4\text{NO}_2)\text{Cl}]^{2+}$ would have



been the initial product. If reduction of the diazonium complex by $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (eq 11) were in turn more rapid than substitution, the net reaction would be (18) and the stoichiometry



2:1.

The chemistry summarized in eq 15 is instructive from the synthetic point of view. The diazonium complexes once prepared are stable for extended periods (several hours) in polar organic solvents or in water. Even though the diazonium complexes are kinetically stable, their direct preparation using methods which have proven successful in other systems is not accessible because of competitive electron transfer, and they must be prepared by the diazotization route (eq 6).

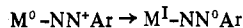
Electron-transfer reactions may also limit the usefulness of the diazotization reaction (eq 6). For example, attempts to diazotize ferrocenylamine were unsuccessful.¹³ The nitrosyl complexes undergo facile electron transfer and if the organic amine is a sufficiently strong reductant, preferential outer-sphere electron transfer may occur to give reduced nitrosyl (e.g., $[\text{Ru}(\text{bpy})_2(\text{NO})\text{Cl}]^+$) and oxidized amine ($[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{NH}_2)]^+$).

Implications for Synthesis in Metal Diazonium Chemistry.

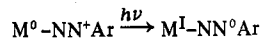
Diazonium ions are moderately strong oxidants and even for relatively weakly reducing metal centers, simple outer-sphere electron transfer can be an interfering factor in preparations based on direct reactions between ArN_2^+ salts and metal complexes. This is expected to be especially important in cases like $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and $(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_2\text{PPh}_3$ ⁹ where it is known or predicted that thermal substitution processes are relatively slow. The substitutional chemistry in such cases presumably involves relatively high-energy, lower or higher coordinate intermediates. However, for labile ions (e.g.,

$[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$)¹⁵ or for cases where the reactions can proceed by low free energy pathways involving addition of ArN_2^+ to an electron-rich metal center (eq 1-4), outer-sphere electron transfer may not be an important competing process.

Electron transfer may play an important role in $\text{M}-\text{N}_2\text{Ar}$ chemistry in other ways. Either thermal or photochemical decomposition may occur based on initial electron transfer from metal to ligand



or



followed by the production of Ar and either $\text{M}^{\text{I}}\text{N}_2$ or $\text{M}^{\text{I}} + \text{N}_2$ (eq 9, 14, 15). The importance of this decomposition pathway should be sensitive to the electronic structure in the $\text{M}-\text{N}_2\text{Ar}$ group and may be important for cases where the $\nu(\text{NN})$ stretching frequency is relatively high.

The failure to observe stable diazonium complexes may also be attributable to net electron-transfer processes in certain cases. For example, reactions between $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ and ArN_2^+ give dinitrogen complexes¹⁵ and between ArN_2^+ and organometallic anions like $\text{Co}(\text{CO})_4^-$ give highly colored species at -70°C which decompose on warming.¹⁶ In both cases the reactions may involve initial diazonium complex formation followed by reduction of the coordinated ligand.

Experimental Section

Electronic spectra were obtained using Cary 16, Bausch and Lomb 210, and Unicam SP800 spectrophotometers. Spectrograde acetonitrile was used as solvent in the experiments described. The preparations of the diazonium salts $[\text{Ru}(\text{bpy})_2(p\text{-N}_2\text{C}_6\text{H}_4\text{-Y})\text{Cl}](\text{PF}_6)_2$ ($\text{Y} = \text{OCH}_3, \text{CH}_3, \text{H}$) have been described.¹⁰ The diazonium salt $(p\text{-N}_2\text{C}_6\text{H}_4\text{NO}_2)(\text{BF}_4)$ was prepared using a standard literature procedure. Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode at $22 \pm 2^\circ\text{C}$ and are uncorrected for junction potential effects. The measurements were made using a PAR Model 173 potentiostat for potential control and a PAR Model 175 universal programmer as sweep generator for cyclic voltammetry experiments.

Spectrophotometric Titrations. In a typical experiment 15 mg of the salt $[\text{Ru}(\text{bpy})_2(p\text{-N}_2\text{C}_6\text{H}_4\text{CH}_3)\text{Cl}](\text{PF}_6)_2$ was dissolved in acetonitrile. The complex $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (18.6 mg) was dissolved in 100 ml of acetonitrile, aliquots of this solution were added to the solution containing the diazonium complex, and the spectrum of the resulting solution was recorded from 700 to 350 nm after each addition. The spectra contained absorption bands characteristic of $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$ ($\lambda_{\text{max}} 480 \text{ nm}$) and $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^+$ ($\lambda_{\text{max}} 380 \text{ nm}$) which grew in intensity as the amount of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ added was increased. The diazonium complex absorbs only weakly above 350 nm.¹⁰ When the amount of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ added exceeded a 1:1 ratio based on the diazonium complex present initially, an absorption band characteristic of unreacted $\text{Ru}(\text{bpy})_2\text{Cl}_2$ appeared in the spectrum at 553 nm. Plots of the OD changes at 550 and 375 nm vs. the equivalents of $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ added gave inflection points at $n = 1$ showing that the stoichiometry of the reaction was 1:1.

A similar experiment was carried out using the diazonium salt $p\text{-nitrobenzenediazonium tetrafluoroborate}$ in place of the diazonium complex. Once more plots of the OD changes at 550 and 375 nm vs. n showed that $n = 1$ and that the ruthenium product of the reaction was $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^+$.

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Registry No. $[\text{Ru}(\text{bpy})_2(p\text{-N}_2\text{C}_6\text{H}_4\text{CH}_3)\text{Cl}](\text{PF}_6)_2$, 42756-26-3; $\text{Ru}(\text{bpy})_2\text{Cl}_2$, 19542-80-4; $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$, 31847-85-5; $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^+$, 47514-47-6; $(p\text{-N}_2\text{C}_6\text{H}_4\text{NO}_2)(\text{BF}_4)$, 456-27-9.

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A Two-Step Synthesis of B_2D_6 Requiring No Metal Deuterides

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A need for quantities of deuterioborane derivatives had led us to study methods for preparing diborane- d_6 without resorting to known methods¹ employing expensive metal deuterides. We wish to report here the results of that investigation.

Previous studies^{2,3} of the hydrogen-exchange characteristics of trimethylamine-borane afforded a solution to the basic problem of how to achieve the B-H to B-D conversion without employing deuterides. Those studies showed that trimethylamine-borane undergoes reasonably facile D-H exchange on the borane group (eq 1) upon treatment with



acidified D_2O .

Although we were not able to precisely duplicate the literature results,² small modifications of the reported procedure afforded acceptable yields of trimethylamine-borane- d_6 . In a typical synthesis 1.00 g (13.7 mmol) of $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$ (Callery Chemical Corp.) in 50 ml of anhydrous diethyl ether was stirred with 20 ml of 1.2 N DCl (99%) in D_2O (99.7%) for 5 h. The ether layer was separated and dried over barium oxide, and the solution was fractionated using a trap held at -20°C to stop $(\text{CH}_3)_3\text{N}\cdot\text{BD}_3$. The solid was sublimed giving an isolated yield of 0.73 g (70%) and the extent of B-deuteration was estimated by IR methods to be at least 90%. Longer reaction times resulted in lower isolated yields due to the slow hydrolysis of trimethylamine-borane,⁴ but no noticeable increase in the percent of deuteration could be achieved by this approach. The earlier investigators² reported a 95% yield of $(\text{CH}_3)_3\text{N}\cdot\text{BD}_3$ which was 98% deuterated, but others³ found a 60-65% yield with no deuterium content given.

Samples of $(\text{CH}_3)_3\text{N}\cdot\text{BD}_3$ with greater deuterium content were produced by carrying out two sequential exchange reactions. In a typical synthesis 1.50 g (20.5 mmol) of $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$ in 80 ml of anhydrous ether was stirred in succession with two 30-ml portions of 1.2 N DCl in D_2O for 5 h each time. The ether was dried and stripped off as described previously and the residue was sublimed to give 9.35 g (60%) of $(\text{CH}_3)_3\text{N}\cdot\text{BD}_3$ which showed no appreciable B-H stretch in the IR region. This product was used later for the