Stabilization of Aliphatic and Aromatic Diazonium Ions by Coordination: An Experimental and Theoretical Study

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The reaction of $[Ru(bpy)_2(NO)Cl]^{2+}$ and $[Fe(CN)_5NO]^{2-}$ with *n*-butylamine has been studied as a plausible route for obtaining aliphatic diazonium ions stabilized by coordination. These reactions yield a variety of products originating mainly by direct attack of nucleophiles on the intermediate carbocation (or diazonium ion) and by rearrangement of the carbocation or the diazonium ion. The ratio of unrearranged to rearranged products can be taken as an experimental measurement of the stabilization of the diazonium ions. DFT-computed results suggest that the stabilization by complexation of the diazonium ions is larger in the ironpentacyano complex, in agreement with the fact that no rearrangement products are observed in the reaction of this species with *n*-butylamine.

Introduction

Aromatic diazonium ions have been known for a long time. They show multiple applications in synthesis which are undoubtedly very useful and cover a large area in organic chemistry. On the contrary, the closely related diazonium ions attached to sp^3 carbons have been very elusive, except for a few examples observed at low temperature.[1,2] Stabilization of these ions by complexation would provide us a great opportunity to explore their rich chemistry and synthetic usefulness. So far there have been a few examples of methyldiazonium ions coordinated to tungsten.[3,4] These complexes were produced via diazomethane, and therefore this methodology is very limited from a synthetic standpoint since very few diazoalkanes are available. Our group is exploring the possibility of obtaining stabilized diazonium ions by diazotization of primary amines with coordinated nitrosyl ligands. This would provide an enormous number of possibilities, since a large number of amines are easily available.

This route was first pointed out by Meyer et al.,[5] who obtained aromatic diazonium salts stabilized by coordination to ruthenium through the reaction of $[Ru(bpy)_2(NO)Cl]^{2+}$ (bpy is 2,2′-bipyridyl) with aniline and other aromatic amines. Similar reactions involving aliphatic amines could provide insight into the chemistry of the extremely reactive aliphatic diazonium salts if coordination to the metal stabilizes them enough to reduce their reaction rates to a manageable time scale and if limited amounts of nucleophiles are present. If this strategy is to be followed, the coordinated nitrosyl has to be electrophilic enough as to react with amines. Reactions of $[Ru(bpy)_2(NO)Cl]^{2+}$ and $[Fe(CN)_5NO]^{2-}$ involving primary[6−8] and secondary amines[9] as well as amino acids[10] have been studied in the past only in aqueous media, where enormous amounts of nucleophile are present in the form of hydroxide or water molecules.

Regarding the selection of the reacting complex, a compromise situation arises: if metal donation ability is small, back-donation to the coordinated diazonium ion (named *diazenido* as a ligand) formed in the reaction will be small and the desired stabilization will not take place. On the other hand, if the nitrosyl ligand suffers a strong back-donation from the metal, its electrophilicity will be rather small and it will not be capable of reacting with even the most nucleophilic amine. A large π^* NO orbital population would be reflected in a weak NO bond and, hence, in a small NO stretching frequency. In fact, it has been shown that there is a good correlation between the NO stretching frequency in metal−nitrosyl complexes and the reactivity of the coordinated nitrosyl:[11] metal nitrosyl compounds having $\nu(NO)$ larger than about 1900 cm^{-1} will be susceptible to attack at the N atom by nucleophiles such as hydroxide, alkoxide, and ammonia (amines could be included in this last category). In this sense, the NO

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stretching frequency in the complex $[Ru(bpy)_2(NO)Cl]^{2+}$ is 1931 cm^{-1} in acetonitrile solution, while $[Fe(CN)_5NO]^{2-}$ shows a value of 1896 cm^{-1}. Consistent with this, the reaction of the ruthenium complex with butylamine is practically instantaneous at room temperature, whereas the iron complex takes several hours to react. This is due to the high electronic density transferred to the metal by the negatively charged cyanide ligands, as compared to the neutral bipyridyl ligand. It is interesting to note that in aqueous solvents the reactivity of the iron complex is higher, the NO stretching frequency being 1938 cm^{-1} (even larger than the one corresponding to the ruthenium complex!). This is due to electrostatic interactions of the coordinated cyanides with solvating water molecules.[12,13] All previous considerations have motivated us to select $[Ru(bpy)_2(NO)Cl]^{2+}$ as well as $[Fe(CN)_5NO]^{2-}$ as starting materials for reaction with *n*-butylamine. By characterizing the reaction products, information about reaction pathways and, in particular, about the postulated intermediate diazonium ions may be obtained.

The experimental information is complemented by the use of computational quantum chemistry tools. Among the most widely used techniques in modeling transition metal compounds, density functional theory (DFT) has proved to be a powerful and economical tool for the investigation of a variety of molecular properties.[14,15] Solvation effects can be readily incorporated into the formalism by using continuum[16] and/or discrete solvent models.[17] We have already employed this approach in the investigation of IR spectroscopy, structural properties, and reactivity of related Fe and Ru complexes.[12,13,18] In addition to the experimental study of the reaction pathways of $[Ru(bpy)_2(NO)Cl]^{2+}$ and $[Fe(CN)_5NO]^{2-}$ with amines, we investigated the structure and stability of coordinated and uncoordinated aliphatic and aromatic diazonium ions by using density functional theory (DFT) computations and continuum solvation models.

Computational Methodology

The calculations were performed using a Gaussian basis set implementation of density functional theory.[19] The Kohn−Sham self-consistent procedure was applied for obtaining the electronic density and energy through the determination of a set of one-electron orbitals.[20] Gaussian basis sets were used for the expansion of the one-electron orbitals and also for the additional auxiliary set used for expanding the electronic density. Matrix elements of the exchange−correlation potential were calculated by a numerical integration scheme.[21] The orbital and auxiliary basis sets optimized by Sim et al.[22] for DFT calculations were used for C, N, and H atoms. Basis sets for Fe and Ru were taken from refs 23 and 24, respectively. The contraction patterns were (5211/411/1) for C and N, (633321/53211/531) for Ru, (4333/431/41) for Fe, and (41/1) for H. The contraction patterns for the electronic density expansion sets are (1111111/111/1) for C and N, (1111111111/11111/11111) for Ru, (1111111111/111/111) for Fe, and (111111/1) for H. A more detailed description of the technical aspects of the program is given in ref 19.

Geometries were optimized for the isolated systems within the local density approximation (LDA) using the Vosko−Wilk−Nusair correlation functional.[25] It has been shown that LDA performs well in predicting bond distances and angles in Werner-type transition metal complexes.[26] Single-point calculations were performed at the LDA gas-phase optimized geometries using the GGA Becke and Perdew combination of functionals for exchange and correlation, respectively.[27,28] The GGA level of theory has been found to be necessary to obtain reliable metal−ligand bond dissociation energies. Specifically, in the case of Fe and Ru complexes, it has been shown that good agreement with gas-phase measurements is achieved at the GGA level for metal carbonyls.[29]

Solvent effects were modeled using two varieties of the self-consistent reaction field method (SCRF), namely, the Onsager's reaction field and the polarized continuum model (PCM) schemes. In the Onsager's model the solute is accommodated in a spherical cavity, while in the PCM scheme, the solute is placed in a cavity of realistic molecular shape. The Onsager's reaction field calculations have been performed using the methodology proposed by Frisch et al.[30,31] The PCM implementation given in ref 32, in which the self-consistency between the solute wave function and solvent polarization is achieved during the self-consistent field cycle, has been employed. PCM computations have been performed using the GAUSSIAN 98 software package.[33]

Experimental Section

General Comments. Unless otherwise noted all manipulations were performed with exclusion of oxygen and moisture

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Table 1. Selected Optimized Geometrical Parameters

	bond distances (Å)			angles (deg)	
	N1−N2	C1−N2	M−N1	M−N1−N2	C1−N2−N1
N_2	1.109				
$[BuN_2]^+$	1.113	1.415			176.0
$[PhN_2]^+$	1.111	1.358			179.9
$[Fe(CN)_5N_2]^{3-}$	1.134		1.817	179.5	
$[Fe(CN)_5N_2Ph]^{2-}$	1.181	1.354	1.638	164.6	148.9
$[Fe(CN)_5N_2Bu]^{2-}$	1.188	1.448	1.650	163.0	128.4
$[Ru(bpy)_2ClN_2]^+$	1.120		1.939	178.2	
$[Ru(bpy)_2Cl(N_2Ph)]^{2+}$	1.152	1.360	1.855	178.7	176.9
$[Ru(bpy)_2Cl(N_2Bu)]^{2+}$	1.142	1.410	1.849	173.5	167.8

using standard Schlenk procedures. Gas chromatograms were done on a Shimadzu GC-14A gas chromatograph. GC−mass spectra were recorded on a Shimadzu GC-17A gas chromatograph attached to a GCMS-QP5000S mass spectrometer. In both chromatographs a tandem consisting of two capillary Supelco SPB5 and SE54 columns was used (60 m × 0.32 mm each). Isoamyl alcohol or toluene was used as internal standard. All compounds were identified by comparison with authentic samples.

Reagents. Acetonitrile was distilled from CaH_2. *n*-Butylamine was purchased from Riedel de Haën and dried over 4 Å molecular sieves. $(NBu_4)I$ was purchased from ICN and used as received. $[RuCl_2(bpy)_2]$ and $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (sodium nitroprusside) were purchased from Aldrich and used as received. $(NBu_4)_2[Fe(CN)_5NO]$ was prepared by precipitation with $(NBu_4)I$ of a $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ solution and recrystallized from ethanol. $[Ru(bpy)_2Cl(NO)](PF_6)_2$ was prepared by known procedures.[34]

Reactions of *n*-Butylamine with Nitroprusside. a. Heterogeneous Reactions. *n*-Butylamine (0.10 mL, 1.0 mmol) was added to 75 mg (0.25 mmol) of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ and allowed to react at room temperature. The reaction was complete after 4 h, as jugded by measurement of the evolved nitrogen by means of a gas buret. After that time, the products were dissolved in a water/ethanol mixture and analyzed by GC and GC−MS after addition of 10 μL of standard.

b. Homogeneous Reactions. *n*-Butylamine (0.60 mL, 6.0 mmol for the 120:1 reaction or 75 μL, 0.75 mmol for the 15:1 reaction) was added to a solution of 35 mg (0.050 mmol) of $(NBu_4)_2[Fe(CN)_5NO]$ in 1.5 mL of acetonitrile and allowed to react at room temperature for 4−7 days. After that time, the products were analyzed by GC and GC−MS after addition of 10 μL of standard.

Reactions of *n*-Butylamine with $[Ru (bpy)_2Cl(NO)](PF_6)_2$. *n*-Butylamine (3 μL, 0.03 mmol for the 3:1 reaction or 15 μL, 0.15 mmol for the 15:1 reaction) was added to a solution of 7.7 mg (0.01 mmol) of $[Ru (bpy)_2Cl(NO)](PF_6)_2$ in 25 μL of acetonitrile and allowed to react at room temperature. The reaction was complete within 5−10 min, as judged by the color change of the solution from green to dark red and by FTIR measurements of the NO stretching signal of $[Ru(bpy)_2(NO)Cl]^{2+}$ at 1931 cm^{-1}. The products were analyzed by GC and GC−MS after addition of 10 μL of standard. For the reaction carried out in the presence of water, 18 μL of water was added to the acetonitrile solution just before the amine.

Results and Discussion

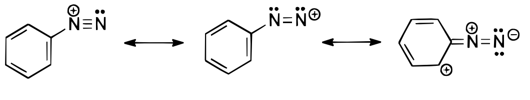
1. Stability of Uncoordinated Diazonium Ions.

Regarding the stability of diazonium salts, a fundamental question strikes immediately: why are aromatic diazonium salts much more stable than the ones attached to sp^3 carbons? The first explanation that comes to mind is the resonance interaction between the nitrogen atoms and the aromatic ring (eq 1):

Table 2. C1−N2 Bond Dissociation Energies (kcal/mol)

	LDA[a]	GGA[b]	GGA(Onsager)	GGA (PCM)
$[Fe(CN)_5N_2Ph]^{2-}$	308.8	294.3	104.6	70.6
$[Fe(CN)_5N_2Bu]^{2-}$	285.0	272.6	74.4	45.0
$[Ru(bpy)_2Cl(N_2Ph)]^{2+}$	35.2	18,2	51.3	47.3
$[Ru(bpy)_2Cl(N_2Bu)]^{2+}$	12.2	−4,5	23.1	19.6
$[Ph{-}N_2]^+$	59.6	44.1	41.0	43.8
$[Bu{-}N_2]^+$	36.1	19.3	14.1	19.6

[a] LDA: the local density approximation. [b] GGA: generalized gradient approximation.


(1)

The problem with this rationalization is that the resonance structure involving the aromatic π electrons does not seem to be very stable: it has too many charges. Our calculations (Table 1) indicate that the C−N bond is predominantly single, discarding an important contribution from this structure. The C−N bond is longer in $[N_2Bu]^+$ than in $[N_2Ph]^+$. This is consistent with the computed N−C bond dissociation energies, shown in Table 2. However, the N−N bond length is in both cases very close to typical values for triple bonds, as can be seen by comparing the computed values with results for isolated N_2. No other striking structural differences are observed between the benzenediazonium and the butyldiazonium ions. Additionally, bond distance measurements in benzenediazonium chloride show that the C−N distance is ∼1.38 Å and the N−N distance ∼1.10 Å,[35] values that fit more closely to a single and a triple bond than to two double bonds. Anyhow, it seems that simple ideas based on resonance schemes are not sufficient for explaining the behavior of these systems. What could then be the role of the aromatic ring? First, the π electrons provoke an inductive effect that stabilizes the positive charge on the nitrogen. But more important than this is the fact that the phenyl carbocation is less stable than an alkyl carbocation, therefore making the free energy for the dissociation reaction of the aromatic diazonium ion

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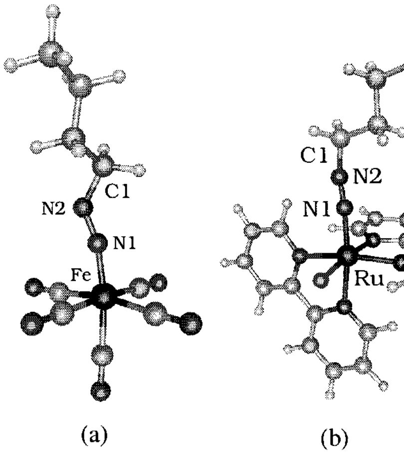


Figure 1. Structure of $[Fe(CN)_5N_2Bu]^{2-}$ and $[Ru(bpy)_2Cl(N_2Bu)]^{2+}$.

larger than that for its alkyl analogue (Table 2 and eq 2).

$$R-\overset{\oplus}{N}\equiv N \longrightarrow R^{\oplus} + N_2 \qquad (2)$$

As a conclusion, the greater stability of the aromatic diazonium salts with respect those attached to sp^3 carbons seems to be due more to instability of the phenyl carbocation than to stability of the diazonium ion itself. This can be confirmed by comparing the relative stabilities of the carbocations with respect to butane and benzene, respectively. At the GGA level, the butyl carbocation turns out to be 24 kcal/mol more stable than its aromatic analogue. Experimentally, the stability of carbocations can be compared by gas-phase measurements which determine the proton affinity of alkenes leading to carbocation formation. From these data, the hydride affinity of carbocations can be obtained, therefore providing a basis for comparison of their relative stability. The value of the hydride affinity for Et^+ is 274 kcal/mol,[36] while the value for Ph^+ is 298 kcal/mol[37] (Bu^+ is expected to be slightly more stable than Et^+). From these results it may be concluded that Et^+ is 24 kcal/mol more stable than Ph^+, consistently with the DFT computations.

2. Computed Coordination Geometries. The optimized structures of $[Fe(CN)_5N_2R]^{2-}$ and $[Ru(bpy)_2Cl(N_2R)]^{2+}$ with R a butyl or aryl group are shown in Figures 1 and 2, respectively. Relevant geometrical parameters are given in Table 1.

Since there are no X-ray results available for the investigated species, we have gauged the reliability of our DFT methodology (basis sets and functionals) by using experimental information of related species. For the iron complexes, we have taken $[Fe(CN)_5NO]^{2-}$ as an illustrative example. In this case, it can be seen that the agreement with experimental results[38] for $Na_2[Fe(CN)_5NO]_2(H_2O)$ is reasonably good at both the LDA and GGA levels. The rms deviation for the optimized bond distances is 0.027 and 0.028 Å for LDA and GGA computations, respectively. Bond angles agree well with experimental values at both levels of theory. This is consistent with DFT results reported for the same system in the literature.[15]

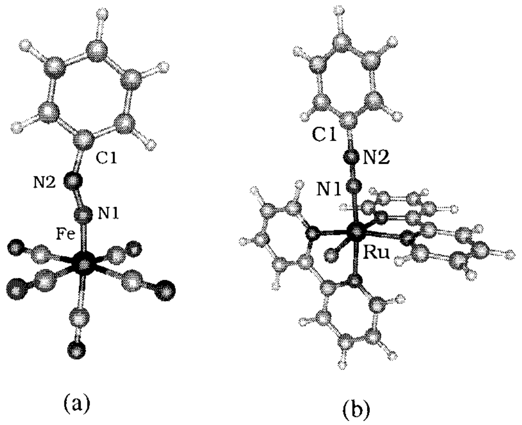
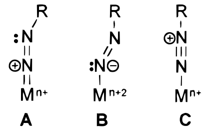


Figure 2. Structure of $[Fe(CN)_5N_2Ph]^{2-}$ and $[Ru(bpy)_2Cl(N_2Ph)]^{2+}$.

Regarding the reliability of our DFT scheme in predicting the geometries of Ru complexes, previous results for $[Ru(NH_3)_5Pz]^{2+}$ compared very well with experiment.[13] A comparison of our computed geometry for $[Ru(bpy)_2ClN_2]^+$ with experimental results[39] for $[Ru(bpy)_2Cl_2](H_2O)_5$ and $[Ru(bpy)_2Cl(CO)][ClO_4]$ has been made in order to gauge the quality of our results in bipyridyl complexes. The computed Ru−Cl bond distance is 2.440 Å, compared with the experimental results of 2.427 and 2.392 Å for $[Ru(bpy)_2Cl_2](H_2O)_5$ and $[Ru(bpy)_2Cl(CO)][ClO_4]$, respectively. The Ru−N distances range from 2.012 to 2.051 Å in our computed geometry and from 2.013 to 2.052 and 2.068 to 2.178 Å in $[Ru(bpy)_2Cl_2](H_2O)_5$ and $[Ru(bpy)_2Cl(CO)][ClO_4]$, respectively. Regarding bond angles, the N−Ru−N angle within the heterocyclic ring is 79.2° in $[Ru(bpy)_2Cl_2](H_2O)_5$, ranges from 76.8° to 78.7° in $[Ru(bpy)_2Cl(CO)][ClO_4]$, and from 78.3° to 79.6° in our optimized $[Ru(bpy)_2ClN_2]^+$ structure. It can be noted that the computed geometrical parameters compare very well with experimental data.

Coordination geometries in alkyl[40] and aryl[41] diazenido ligands have been explained in terms of the following resonance structures:



The relative weights of these resonance structures can be understood in terms of the degree of the metal-to-ligand electron donation. Slight back-donation from the metal into π^* orbitals of the diazenido moiety leaves the N−N bond essentially as a triple bond and the N2−N1−C1 angle close to 180°. Intermediate values of the angle might be ascribed to different relative importance of the

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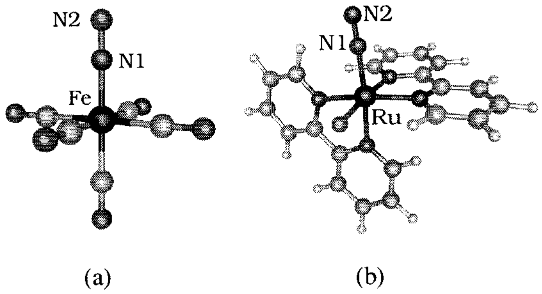


Figure 3. Structure of $[Fe(CN)_5N_2]^{3-}$ and $[Ru(bpy)_2Cl(N_2)]^+$.

linear and bent resonance structures or equivalently to different degrees of metal-to-ligand electron donation.

The computed structures of the butyl and aryl diazo ligands in the Fe complex assume a doubly bent geometry. The deviations from linearity are more pronounced in the butyl diazo species, in which the C1−N2−N1 and Fe−N1−N2 angles are 128.4° and 163.0°, respectively. The fact that the C1−N2−N1 angle is significantly closer to 120° than the Fe−N1−N2 angle may be related to the fact that both resonance structures A and B are relevant. The C1−N2−N1 and Fe−N1−N2 angles in the aryl case are 148.9° and 164.9°, respectively. The smaller deviations from linearity, compared to those observed in the butyl diazo complex, are consistent with a greater contribution of resonance structure C.

Regarding the Ru complex, the aryl species is practically linear, with Ru−N1−N2 and C1−N2−N1 angles of 178.7° and 176.9°, respectively. In the butyl complex there are larger deviations from linearity, with Ru−N1−N2 and C1−N2−N1 angles of 173.5° and 167.8°, respectively. This can be ascribed to the larger relevance of resonance structure C in the Ru complexes, which is consistent with the smaller increase in N1−N2 bond distance observed, compared to the uncoordinated ligand. A possible explanation for the smaller M−N1−N2 and C1−N2−N1 angles in the Fe complexes may be related to the larger electronic density available in these systems due to donation from the cyanides to the metal, which makes more favorable resonance structure B, in which a formal (−1) oxidation state is assigned to N1.

This back-donation is more pronounced in the diazenido iron complex than in $[Fe(CN)_5N_2]^{3-}$, as can be seen in the computed N1−N2 distances, (Table 1 and Figure 3) that are 1.181 and 1.188 Å in the aryl and butyl complexes, respectively, and 1.134 Å in $[Fe(CN)_5N_2]^{3-}$, reflecting a larger population in the π^* N_2 orbital. As can be expected by the larger electron availability in the iron pentacyano system, N1−N2 bond distances in the Ru complexes are smaller, reflecting a smaller degree of back-donation. In fact, the computed metal Mulliken populations in $[Fe(CN)_5N_2]^{3-}$ and $[Ru(bpy)_2N_2Cl]^+$ are $-0.96e$ and $0.33e$, respectively. Interestingly, the larger degree of back-donation in the diazenido complexes compared to the N_2 coordinated systems is also reflected in the M−N1 bonds, which are considerably shorter in the diazenido species, consistent with a stronger M−N bond.

3. Stabilization by Complexation: Computational Results. Meyer et al.[5] found that the aromatic diazonium salts produced by the reaction of $[Ru(bpy)_2(NO)Cl]^{2+}$ with aniline and other aromatic amines were strongly stabilized by complexation. Compared to free diazonium salts in aqueous solution, which decompose at temperatures higher than 5 °C, the salts of the type $[Ru(bpy)_2(N_2Ar)Cl]^{2+}$ are stable up to 60 °C. Calculations performed for the complexed benzenediazonium ion (Table 2) show that the ΔE for its decomposition reaction (eq 3) *in vacuo* is smaller than that for the free diazonium ion (eq 2; R = Ph), indicating that $[Ru(bpy)_2(N_2Ph)Cl]^{2+}$ is less stable than $(N_2Ph)^+$.

$$[Ru(bpy)_2(N_2Ph)Cl]^{2+} \rightarrow [Ru(bpy)_2(N_2)Cl]^+ + Ph^+ \qquad (3)$$

However, in the presence of a solvent (such as acetonitrile), this situation is turned upside-down and the complexed benzenediazonium ion is more stable than the free diazonium salt. While the value for the last one remains practically constant (at the same level of theory, GGA), the complex is slightly stabilized. This is mainly due to a charge stabilization effect: the dielectric more effectively stabilizes the doubly charged ruthenium complex than the singly charged products. In the case of the butyldiazonium ion, the stability of the coordinated form is similar to that *in vacuo* when solvation effects are taken into account.

Table 2 shows that the ΔE for the decomposition reaction of $[Fe(CN)_5(N_2R)]^{2-}$ (eq 4, R = Ph, Bu) is very large, which means that a hypothetical benzenediazenido complexed to the ironpentacyano moiety would be extremely stable. In this case, there is an important stabilization *in vacuo* due to complexation. This may be explained in simple electrostatic terms; in the ironpentacyano system the decomposition of the diazonium ion (eq 4) involves charge separation, while this is not the case for the ruthenium complex (eq 3). *In vacuo* the reaction energetic change for the decomposition reaction (eq 4) is huge, while in the presence of a solvent it is still rather large with both the Onsager and PCM solvation models. The effect of the solvent is again due to a charge stabilization effect: the dielectric stabilizes more effectively the triply charged iron complex $[Fe(CN)_5N_2]^{3-}$ than the doubly charged diazenido complex, therefore favoring the decomposition reaction. The large stabilization of the diazenido is mainly due to a strong back-donation from the metal to the ligand, induced by the electron-releasing cyanide ligands.

$$[Fe(CN)_5(N_2R)]^{2-} \rightarrow [Fe(CN)_5N_2]^{3-} + R^+ \qquad (4)$$

It is interesting to remark that even the simple Born−Onsager SCRF model is able to predict qualitatively the same trends as the more sophisticated PCM scheme. This is probably due to the fact that the main solvation effect is related to changes of the net charge upon dissociation, as discussed above, an effect that is taken into account in the Onsager's model. The larger differences between both models are observed in the iron complexes probably because of their higher net charges and smaller sizes, which affect solvation energies in such a way as to produce an increase in their values compared to the ruthenium complexes.

4. Stabilization by Complexation: Experimental Results. It could be supposed in principle that if the

Scheme 1. Reaction Pathways for Aliphatic Diazenido Complexes (charges for complexes not shown)

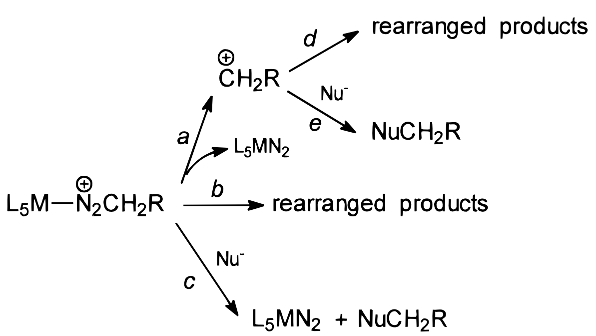


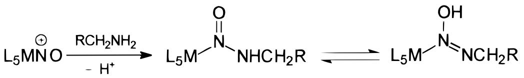
Table 3. Organic Products Obtained by the Reaction of $[Ru(bpy)_2(NO)Cl]^{2+}$ with *n*-Butylamine[a]

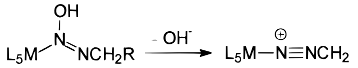
	expt 1	expt 2	expt 3
	2:**1** = 3:1	**2**:**1** = 15:1	H_2O:**2**:**1** = 100:3:1
1-butene	8.5	10	5.0
trans-2-butene	4.9	5.4	3.1
cis-2-butene	4.0	4.5	2.6
1-chlorobutane	5.6	8.3	8.7
2-chlorobutane	1.9	2.0	2.1
1-butanol	7.2	19	26
2-butanol	<1	7.5	<1
dibutylamine (**3**)	6.5	21	<1
N-butyl-1-butanimine (**5**)	2.0	6.6	<1
butyronitrile	21	23	9.1

[a] Results are expressed as moles of product per 100 mol of starting complex.

diazonium ion were stabilized by coordination, it would not have a tendency for rearrangement. This occurs through pathway *d* (Scheme 1), while pathways *c* and *e* should produce unrearranged products by nucleophilic attack. The free diazonium ion itself could also rearrange through pathway *b*, as has been previously suggested.[42] Since *a* and *c* are competing pathways, stabilization of the diazonium ion by complexation should lead to a decrease in the rate constant of pathway *a*, assuming that the activation energy of this pathway increases correspondingly with the increase in the energy gap between reactants and products. Therefore, stabilization would lead in the end to a higher ratio of unrearranged to rearranged products.

Table 3 shows the main organic products obtained by the reaction of $[Ru(bpy)_2(NO)Cl]^{2+}$ (**1**) with *n*-butylamine (**2**). Nucleophilic attack at coordinated NO in **1** by the amine and subsequent loss of hydroxide to produce a coordinated diazenido is proposed (eqs 5 and 6, R = propyl, charges for complexes not shown). An intermediate diazoate ($RCH_2N{=}N{-}O^-$) could be expected, since it has been shown that alkanediazoates are stable in basic, nonaqueous conditions.[43] ^1H and ^{13}C NMR data suggest the presence of diazoates in this reaction, which are persistent for a few minutes under the reaction conditions. Since alkanediazoates could in principle act as bidentate ligands, it is likely that coordination of the terminal oxygen to the metal catalyzes its decomposition. Butenes, 2-chlorobutane, and 2-butanol are produced by rearrangement (Scheme 1, pathways *b* and *d*). 1-Chlorobutane, *n*-butanol, and dibutylamine are produced by reaction of the carbocation or the diazonium salt with chloride ion, hydroxide, and *n*-butylamine, respectively (Scheme 1, pathways *c* and *e*). The chloride ion coordinated to the metal is labilized after the nitrosyl reacts, probably due to the absence of an NO^+ electron attracting effect, and in the end is replaced by another ligand, mainly *n*-butylamine. Hydroxide is produced by elimination from the initial adduct which gives place to the diazonium salt (butanol is produced even in anhydrous conditions). Butyronitrile is produced by oxidation of the coordinated amine. It has been demonstrated before[44] that butylamine is oxidized in the presence of ruthenium and oxygen to produce butyronitrile. However, the nitrile is formed even in the absence of oxygen, indicating that nitrosyl is also acting as an oxidizing agent. GC measurements of the gases from the reaction show that only 40% of nitrogen is produced, indicating that the rest of the nitrogen atoms could be in a more reduced state.


$$L_5M\overset{\oplus}{N}O \xrightarrow[-\ H^+]{RCH_2NH_2} L_5M{-}\overset{\overset{O}{\|}}{N}{-}NHCH_2R \rightleftharpoons L_5M{-}\overset{\overset{OH}{|}}{N}{=}NCH_2R \qquad (5)$$


$$L_5M{-}\overset{\overset{OH}{|}}{N}{=}NCH_2R \xrightarrow{-\ OH^-} L_5M{-}\overset{\oplus}{N}{\equiv}NCH_2 \qquad (6)$$

By comparing experiments 1 and 2 (Table 3) it can be observed that as expected, the amount of dibutylamine produced by the reaction increases with the ratio of *n*-butylamine to $[Ru(bpy)_2(NO)Cl]^{2+}$. The amount of butanol increases concomitantly, probably due to reaction with hydroxide liberated by the intermediate diazoate. In the absence of added water (expt 1) the ratio of rearranged products to unrearranged products is approximately 0.45. It decreases to 0.35 in the presence of an excess of *n*-butylamine (expt 2). When water is added the yield of *n*-butanol increases as expected, partly at the expense of the butenes (expt 3, Table 3). The yield of 1- and 2-chlorobutane also increases with respect to experiment 1, indicating that water replaces chloride in the ruthenium complex. The ratio of rearranged to unrearranged products drops to 0.29. However, even in the presence of this large amount of nucleophile rearranged products are present, indicating that the rupture of the diazonium ion to produce a free carbocation is a fast process.

Even if both the aromatic and aliphatic diazenido iron pentacyano complexes are predicted to be extremely stable, the aromatic diazenido complex cannot be prepared by the amine/nitrosyl route due to the low reactivity of pentacyanonitrosylferrate(II) toward nucleophiles in organic solvents: aromatic amines are not nucleophilic enough to react with the coordinated nitrosyl. However, aliphatic amines are able to react at a reasonable rate (the reaction takes several hours at room temperature). The reaction of pentacyanonitrosylferrate(II) with primary aliphatic amines in nonaqueous solvents has been recently studied by our group,[45] demonstrating that it is a potentially good route for the

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[42] Streitwieser, A., Jr. *J. Org. Chem.* **1957**, *22*, 861.

[43] Fishbein, J. C.; Ho, J. *J. Am. Chem. Soc.* **1994**, *116*, 6611.

[44] Tang, R.; Diamond, S. E.; Neary, N.; Mares, F. *J. Chem. Soc., Chem. Commun.* **1978**, 562.

[45] Doctorovich, F.; Trápani, C. *Tetrahedron Lett.* **1999**, *40* (25), 4635.

Table 4. Organic Products Obtained by the Reaction of Pentacyanonitrosylferrate(II) with *n*-Butylamine[a]

	expt 4[b]	expt 5[c]	expt 6[c]
$[Fe(CN)_5NO]^{2-}$:*n*-butylamine	1:4	1:15	1:120
dibutylamine (**3**)	82	70	95
tributylamine (**4**)	12	*d*	3
N-butyl-1-butanimine (**5**)	<1	<1	1
2-butylaminepentanenitrile (**6**)	2	2	5

[a] Results are expressed as moles of product per 100 mol of starting complex. [b] No solvent was added. Na^+ was present as counterion. [c] Acetonitrile was used as solvent. Tetrabutylammonium was present as counterion due to the insolubility of the sodium salt in acetonitrile. [d] Tributylamine could not be quantified since tetrabutylammonium ion decomposes in the GC to produce this same amine.

preparation of symmetrical, unsymmetrical, and cyclized secondary amines. In this reaction diazonium ions have been postulated as intermediates. The absence of rearranged products characteristic of carbocations indicates that the initially produced diazonium ion is strongly stabilized by coordination to iron. These results show that the aliphatic diazonium ions have, the same as their aromatic counterparts, the ability to act as π accepting ligands.

Table 4 shows the organic products obtained by the reaction of pentacyanonitrosylferrate(II) (**7**) with *n*-butylamine (**2**).[45] The main organic product is dibutylamine (**3**), while tributylamine (**4**), *N*-butyl-1-butanimine (**5**), and 2-butylaminepentanenitrile (**6**) were also detected as minor products. Nitrogen gas was produced in almost quantitative yield in all cases, as determined by GC and volumetrically. Approximately 4 mol of *n*-butylamine react per mol of **1** since 2 mol of amine are involved in the formation of dibutylamine, 1 mol is bound to iron in the butylaminepentacyanoferrate(II) complex, and the fourth is acting as counterion. The mechanistic pathways depicted in Scheme 1 and eqs 5 and 6 could also be applied here in a general sense.

The yields of dibutylamine in the reaction of pentacyanonitrosylferrate(II) are very high even in the presence of only stoichiometric amounts of *n*-butylamine (expt 4, Table 4). Rearranged products characteristic of carbocations are not observed, suggesting that pathways *a* and *b* of Scheme 1 are not operative. These results are largely in contrast with those obtained for the diazotization of butylamine by nitrous acid in water,[46] where only 30% of unrearranged products were obtained, and the rest corresponded to rearrangement and elimination products. Therefore, in agreement with computational results, we can conclude that the diazonium ion produced by diazotization of *n*-butylamine with pentacyanonitrosylferrate(II) is stabilized by coordination to the metal until it is attacked by a nucleophile according to pathway *c* in Scheme 1. If this nucleophile is *n*-butylamine, dibutylamine (**3**) is produced, while its reaction with dibutylamine produces tributylamine (**4**).

When the reaction is carried out in formamide ($[Fe(CN)_5NO]^{2-}$:*n*-butylamine = 1:4), 53% of butenes are produced. The interaction of the coordinated cyanides with the solvent gives rise to significant changes in the electron-releasing capacity of the cyanides. As depicted in the Introduction, if the reaction is carried out in a solvent —such as water—that has the ability to accept charge from the cyanides through hydrogen bonding, the electron-releasing capacity of the ligands will decrease and with that the electron density on the nitrosyl. In that sense, it is interesting to look at Gutmann's acceptor numbers (AN) for the intervening solvents.[47] While AN = 18.9 for acetonitrile, its value is 54.8 for water and 39.8 for formamide. The last one can form hydrogen bonds with the cyanide ligands, the same as water. Therefore back-donation is diminished in formamide as compared to acetonitrile, and the stabilization of the diazenido ligand drops concomitantly. This is consistent with the fact that Onsager continuum calculations predict a ΔE for the decomposition reaction of 48.8 kcal/mol, considerably smaller than in acetonitrile.

From experiments 4 and 6 (Table 4) it can be concluded that when the initial ratio **1**:**2** increases, some of the diazonium ion initially formed reacts with dibutylamine to produce tributylamine. However, dibutylamine is still the major product in experiment 4, indicating that the dibutylamine is less reactive than *n*-butylamine, probably due to steric hindrance produced by the coordinated cyanide groups. Experiments carried out independently have shown that, under the same conditions as those used for *n*-butylamine, dibutylamine does not react with pentacyanonitrosylferrate(II) either in acetonitrile solution or in the absence of solvent. When a 1:1 ratio of $[Fe(CN)_5NO]^{2-}$:*n*-butylamine is used, a small amount of tributylamine is produced as the only organic product. It is interesting to compare experiment 5 (Table 4) with experiment 2 (Table 3): under exactly the same conditions, no rearranged products are observed for the iron complex, while the ruthenium complex produces a good amount of butenes and 2-butanol.

Conclusions

Diazonium ions are important intermediates in many relevant reaction pathways in organic synthesis. In particular, we have chosen to investigate the reaction of nitrosyl transition metal complexes with *n*-butylamine as a plausible route for obtaining aliphatic diazonium ions stabilized by coordination. This reaction yields a variety of products originated mainly by direct attack of nucleophiles to the intermediate carbocation (or diazonium ion) and by rearrangement of the carbocation or the diazonium ions. The ratio of unrearranged to rearranged products can be taken as an experimental measurement of the stabilization of diazonium ions.

We have shown that it is possible to tune the relative importance of the possible reaction pathways by selecting adequately the complex. In particular, our DFT-computed results suggest that the stabilization by complexation of the diazonium ions is larger in the ironpentacyano complex, in agreement with the fact that no rearrangement products are observed in the reaction of this species with *n*-butylamine. Interestingly, carrying out the reaction in a different solvent can also have dramatic effects on the relative rates of the different pathways. This has been shown by performing the

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(46) Streitwieser, A., Jr.; Schaeffer, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 2888.

(47) Marcus, Y. *Chem. Soc. Rev.* **1993**, 409.

reaction of *n*-butylamine with $[Fe(CN)_5NO]^{2-}$ in acetonitrile and formamide. Our experimental results are consistent with the fact that the computed stabilization energy is much larger in acetonitrile than in formamide.

Our calculations indicate that the stability of free diazonium ions, either aliphatic or aromatic, is mainly supported by the instability of the carbocation produced by their decomposition. Moreover, our experimental and theoretical results have shown that a strong stabilization by coordination is possible even for aliphatic diazonium ions where back-donation was supposed to have a small contribution. The fact that this stabilization by coordination is feasible opens up an interesting future in the area of synthetic and mechanistic studies of aliphatic diazonium ions.

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