Performing Organic Chemistry with Inorganic Compounds: Electrophilic Reactivity of Selected Nitrosyl Complexes

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ABSTRACT
The inorganic nitrosyl (NO^+) complexes $[Fe(CN)_5NO]^{2-}$, $[Ru(bpy)_2(NO)Cl]^{2+}$, and $[IrCl_5(NO)]^-$ are useful reagents for the nitrosation of a variety of organic compounds, ranging from amines to the relatively inert alkenes. Regarding $[IrCl_5(NO)]^-$, its high electrophilicity and inertness define it as a unique reagent and provide a powerful synthetic route for the isolation and stabilization of coordinated nitroso compounds that are unstable in free form, such as *S*-nitrosothiols and primary nitrosamines. Related to the high electrophilicity of $[IrCl_5(NO)]^-$, an unusual behavior is described for its PPh_4^+ salt in the solid state, showing an electronic distribution represented by $Ir^{IV}–NO^\bullet$ instead of $Ir^{III}–NO^+$ (as for the K^+ and Na^+ salts).

Introduction

Metal nitrosyls have attracted considerable attention since the discovery of endogenous NO as a biomolecule.[1] In later years it has been recognized that the chemistry of nitrosyl complexes is frequently different from that exhibited by the isoelectronic CO analogues.[2] Nevertheless, electrophilic reactions of coordinated nitrosyls have been studied in a relatively small number of cases, most of them involving $[Fe(CN)_5NO]^{2-}$ (pentacyanonitrosylferrate(II) or nitroprusside) in aqueous solutions.[3]

One of the objectives of our group has been to utilize the addition of nucleophiles to the nitrosyl ligand as a tool for the facile obtention of coordinated RXNO species (X = NH, S, CHR and R = alkyl, aryl) unstable in free form. Some of these species are interesting in relation to biological studies: *S*-nitrosothiols (RSNOs) are suggested to be the principal stores of nitric oxide; they are the source of thiyl radicals and are involved in some regulatory

processes. Others could be useful for synthetic purposes: primary nitrosamines and its tautomeric diazoic acids (RN(H)NO and RN=NOH) are precursors of diazonium salts, which are starting materials for a number of organic derivatives. However, RSNOs as well as diazonium salts (especially the aliphatic ones) are unstable in free form.

For the purpose of obtaining coordinated RXNO species, a compromise situation arises at the time of the selection of the reacting complex: if metal donation ability is poor, back-donation to the coordinated RXNO formed in the reaction will be negligible, 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 insufficient and it will not be capable of reacting with even the most potent nucleophile. A large π^* NO orbital population would be reflected in a weak NO bond and hence in a low NO stretching frequency.

There is a loose correlation between the NO stretching frequency in metal–nitrosyl complexes and the reactivity of the coordinated nitrosyl:[4] metal nitrosyl compounds having $\nu(NO)$s 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).[5] The $\nu(NO)$s in acetonitrile solution for the complexes utilized by our group: $[Fe(CN)_5NO]^{2-}$ (**1**; counterion: tetrabutylammonium), $[Ru(bpy)_2(NO)Cl]^{2+}$ (**2**; counterion: hexafluorophosphate), and $[IrCl_5(NO)]^-$ (pentachloronitrosyliridate(III) **3**; counterions: K^+, tetraphenylarsonium, or tetraphenylphosphonium), are 1886, 1931, and 1952 cm^{-1}, respectively. All three complexes are formally NO^+ species and therefore are able to function as nitrosating agents. Consistent with their $\nu(NO)$s, the reactions of **1** with aliphatic amines at room temperature in acetonitrile solution take several hours,[6,7] whereas **2** takes a few minutes[7,8] and **3** reacts within a few seconds.[9] While the last two react with aromatic amines,[7,10] $[Fe(CN)_5NO]^{2-}$ does not. It is interesting to note that in aqueous solvents the reactivity of $[Fe(CN)_5NO]^{2-}$ is higher, the NO stretching frequency being 1938 cm^{-1} (larger than the one corresponding to the ruthenium complex **2**). This is due to acceptor–donor interactions of the coordinated cyanides with solvating water molecules.[11,12] The reactivity is then related to the electronic density transferred to the metal by the coligands, which in some cases is strongly influenced by the solvent.

The reduction potential for the $NO^+/NO^\bullet$ couple has been shown to correlate with the nitrosyl electrophilicity better than $\nu(NO)$. A plot of ln k for the nucleophilic addition of OH^- or RSH^- vs $E_{NO^+/NO^\bullet}$ for different NO complexes gives a straight line (Figure 1).[13] The plot is a linear free energy relation, as frequently found in the correlation of kinetic vs thermodynamic parameters for a set of reactions governed by the same mechanism, being

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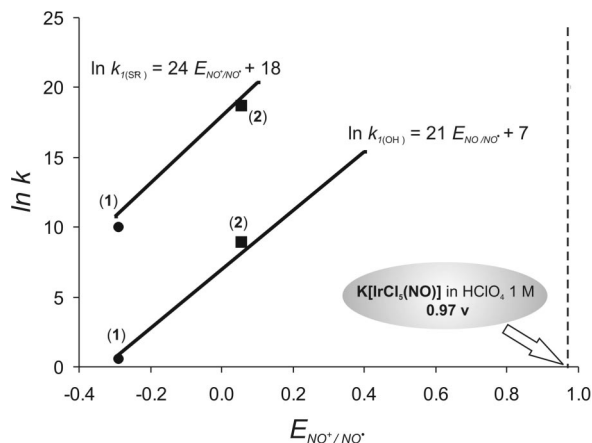
FIGURE 1. Linear free energy relationship plot of ln k against $E_{NO^+}/NO^{\bullet}$ for the reactions of a series of $\{MX_5NO\}^n$ complexes with RS^- (k_{RS^-}) and OH^- (k_{OH^-}). Values corresponding to complexes **1**, **2**, and **3** are indicated (rate constants have not been measured for complex **3**). Adapted from ref 13.

in this case nucleophilic addition of OH^- and RS^- to NO^+. In the case of the complexes **1**, **2**, and **3**, $E_{NO^+}/NO^{\bullet}$(Ag/AgCl) = −0.29, 0.05, and 0.97 V,[14] respectively, in aqueous solution, and $[IrCl_5(NO)]^-$ falls in the diffusional rate zone (see Figure 1). We will see that this high reactivity and the inertness of the iridium metal center characterize $K[IrCl_5(NO)]$ as a useful synthetic reagent. Not only that, the anion $[IrCl_5(NO)]^-$ shows a peculiar electronic behavior, as described in the next section.

Electronic Perturbation of $[IrCl_5(NO)]^-$ in the Solid State

Among electron-poor nitrosyls ("NO^+") the nitrosyl in $K[IrCl_5(NO)]$ is probably the most electrophilic known to date. This fact is reflected by the extremely high IR frequency in solid state (2006 cm^{-1}),[15] its electrochemical behavior (see Figure 1 and refs 14 and 16) and remarkable reactivity[9,17,18] observed in solution. This hexacoordinated $\{MNO\}^6$ reports a crystal structure which comprises an octahedral anion with a practically linear Ir–NO moiety (the Ir–N–O angle is 174.3°).[19]

As expected, the crystal structure of $Na[IrCl_5(NO)]$ obtained by our group is almost coincident with the above-mentioned structure of $K[IrCl_5(NO)]$ and with the DFT-optimized structure of the isolated ion (see Table 1).[20] It is interesting to note that the crystal packing is dependent on the counterion: while in the K^+ and Na^+ solids the anions are stacked one over the other in a "side by side" arrangement (Figure 2A), in the cases of the bulky cations PPh_4^+ and $AsPh_4^+$,[21] the $[IrCl_5(NO)]^-$ units are forced to be organized in a perfectly linear wirelike
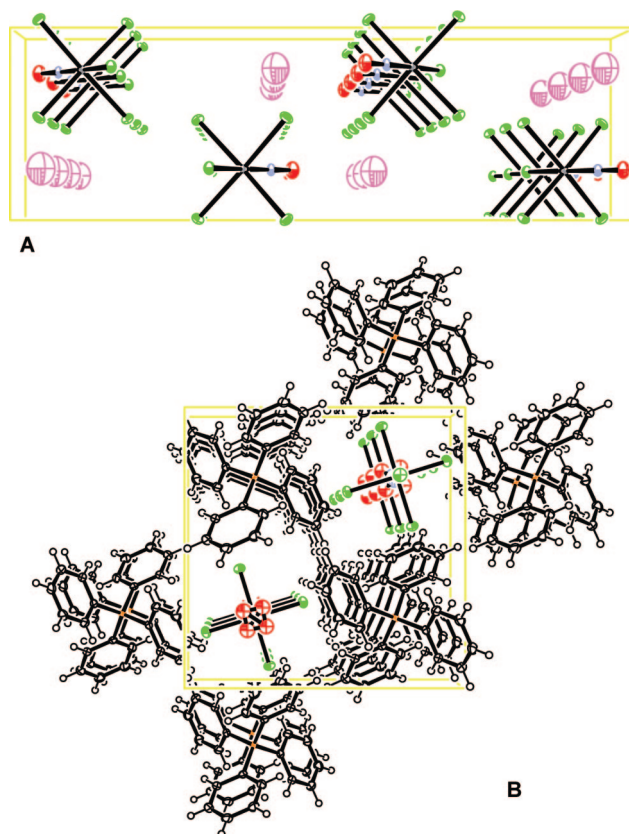
FIGURE 2. X-ray crystal structure of $Na[IrCl_5(NO)]$ (A) and $PPh_4[IrCl_5(NO)]$ (B). Unit cells are shown in yellow, O red, Cl green, N blue, C and H black, Ir gray, and Na pink.

arrangement. Therefore, a close O–Cl distance (2.8 Å) between the N–O moiety of one anion and the trans-chloride of the nearby upper one is observed. Moreover, the phenyl rings are perfectly stacked one over the other, determining the lattice structure (Figure 2B). The consequence of this peculiar layout is an unprecedented electronic distribution represented by Ir^{IV}–$NO^{\bullet}$ for the PPh_4^+ complex instead of Ir^{III}–NO^+ (as for the K^+ and Na^+ ones). This electronic perturbation could be produced by π–π stacking interactions among the phenyl rings in the crystal, which are in the range of the energy difference among both above-mentioned electronic distributions in vacuo (14 kcal mol^{-1}).[22,23]

Strong experimental evidence supporting the Ir^{IV}–$NO^{\bullet}$ configuration in $PPh_4[IrCl_5(NO)]$ was provided by X-ray absorption near edge structure (XANES) measurements in the solid state at the Ir L$_3$ edge, verifying that the oxidation state for $PPh_4[IrCl_5(NO)]$ is +4 as compared to +3 for $K[IrCl_5(NO)]$.[20] The area of the absorption peak in the XANES spectra at the Ir L$_3$ edge for $PPh_4[IrCl_5(NO)]$ is notably larger than the one for $K[IrCl_5(NO)]$, indicating a

Table 1. FTIR NO Stretching Frequencies and Selected Structural Parameters for $[IrCl_5(NO)]^-$ and Related Species[20]

$PPh_4[IrCl_5(NO)]$	ν_{NO} (cm^{-1})	$\angle$(MNO) (deg)	d(N–O) (Å)	d(M–N) (Å)
$K[IrCl_5(NO)]^a$	2006	174.3	1.124	1.760
$Na[IrCl_5(NO)]^a$	1986	172.9	1.140	1.760
$PPh_4[IrCl_5(NO)]$	1952^b	166.9^c	1.17^c	1.77^d

^{a} Experimental data from KBr pellet and X-ray crystallography. ^{b} Experimental data from KBr pellet. ^{c} DFT optimization in the solid state. ^{d} EXAFS data.
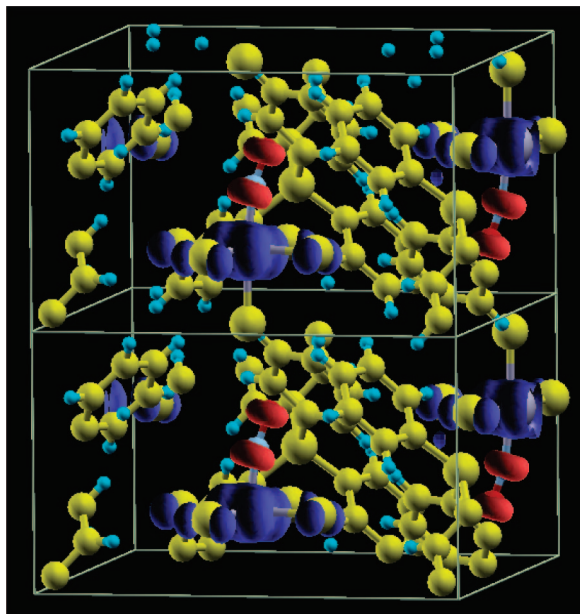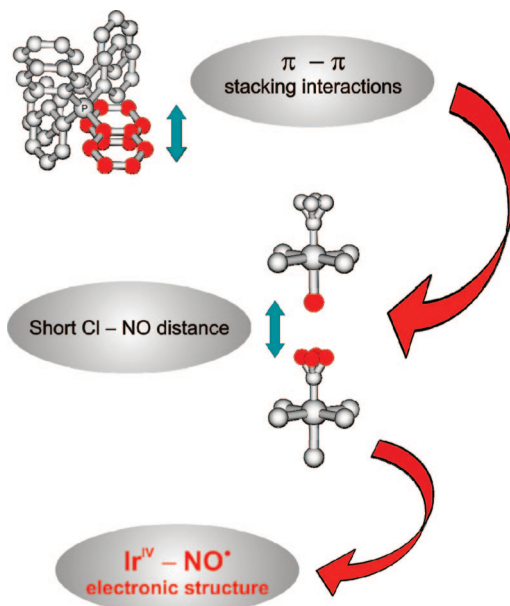
FIGURE 3. Electronic spin density for PPh$_4$[IrCl$_5$(NO)], calculated by DFT in the solid state (d(Ir–Ir) = 7.8 Å). Blue and red lobes represent unpaired electron density of opposite spin.

FIGURE 4. Summary of the factors governing the electronic perturbation exhibited by PPh$_4$[IrCl$_5$(NO)].

higher density of unoccupied states, i.e., a higher oxidation state for Ir in the first compound. The increment of the Ir L$_3$ white line intensity with its oxidation state was verified by performing XANES measurements for different Ir reference compounds. The white line area was determined and plotted versus the oxidation state for the references, finding a linear tendency. From the white line area of K[IrCl$_5$(NO)] and PPh$_4$[IrCl$_5$(NO)], the iridium oxidation state for the latter was determined to be almost 1 unit higher than for K[IrCl$_5$(NO)].

Since PPh$_4$[IrCl$_5$(NO)] is diamagnetic, the expected situation is an open-shell singlet (OSS), Ir↑–NO↓, with a d^5 low-spin Ir^{IV} center ($S = +^1/_2$) antiferromagnetically coupled to NO$^\bullet$ ($S = -^1/_2$). DFT calculations performed in the solid state on the structure of PPh$_4$[IrCl$_5$(NO)] show an OSS with half of the spin density localized on a metal-centered orbital and slightly spread onto the equatorial chlorides and the other half on an NO-based orbital (Figure 3). For the same compound, the d^6 CSS (closed-shell singlet) is higher in energy than the OSS. When the PPh$_4$$^+$ counterions are removed from the crystal cell, leaving isolated molecular [IrCl$_5$(NO)]$^-$ nanowires, an OSS is also obtained as the ground state, indicating that there are no important electronic effects derived from the presence of the counterions. Interestingly, when the DFT calculations are carried out with the Ir centers located as completely isolated units (21 Å apart, instead of 7.8 Å as in the crystal structure), the ground state is represented by a CSS. It is evident from the above that the proximity between the anions and their singular "nanowire-like" arrangement are responsible for the stabilization of the OSS.

In summary (see Figure 4), this is an interesting case of electronic perturbation in a third-row transition-metal complex in the ground state. The high sensitivity of the M–N–O moiety toward the environment, its high elec-
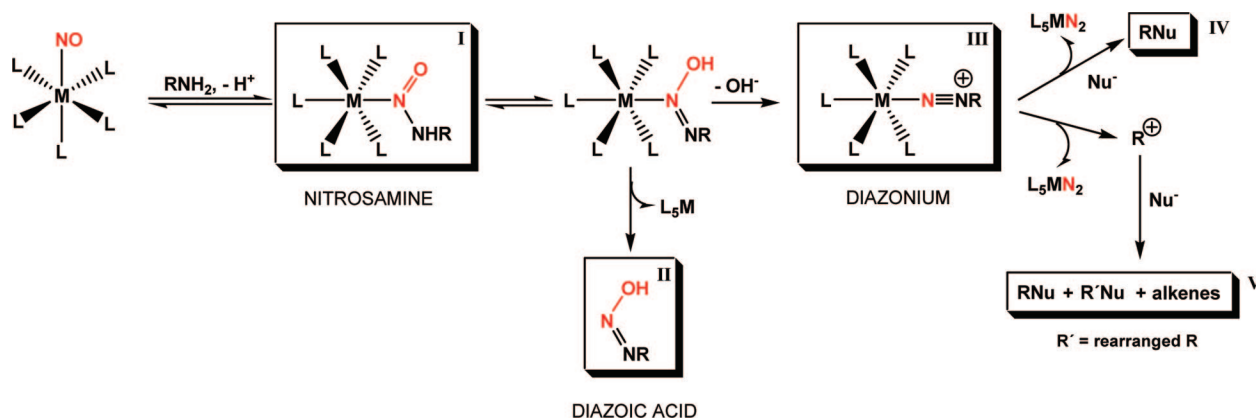
trophilicity, and, related to this, its interaction with the nearby chloride ligand in this singular "wirelike" [IrCl$_5$(NO)]$^-$ arrangement seem to be the impelling forces for the unique structural and electronic behavior of pentachloronitrosyliridate in the solid state.

Electrophilic Reactivity of [IrCl$_5$(NO)]$^-$, [Fe(CN)$_5$NO]$^{2-}$, and [Ru(bpy)$_2$(NO)Cl]$^{2-}$

Primary Amines. Primary nitrosamines (RN(H)N=O) and their tautomeric isomers, diazoic acids (RN=NOH), are important intermediates in the deamination of DNA bases[24] and in the formation of diazonium salts.[25] In acidic or neutral medium, these compounds rapidly produce unstable diazonium salts by loss of hydroxide ion.[26]

During the past few years, our group has studied the possibility of obtaining stabilized coordinated diazoates or diazonium salts—synthetic precursors for a variety of organic compounds—by reaction of nitrosyl complexes with aromatic and aliphatic primary amines.[6–9] This route was previously explored by Meyer et al., who obtained coordinated aromatic diazonium salts.[10] A general mechanism depicting nitrosamine formation by nucleophilic addition to MNO and its reactivity is shown in Scheme 1 (inside boxes are shown the species that have been isolated and characterized). In the first addition step, a coordinated primary nitrosamine is formed, in equilibrium with its tautomeric diazoic acid. Depending on the basicity of the amine, in most cases the reaction stops in this step for [IrCl$_5$(NO)]$^-$, since the coordinated nitrosamine is stable and precipitates out (Scheme 1, box I).[9] In the case of [M(CN)$_5$NO]$^{2-}$ (M = Fe, Ru, Os) in highly basic media (reaction with RNH$^-$) the diazoate salt is labilized (Scheme 1, box II).[27] For [Fe(CN)$_5$NO]$^{2-}$ or [Ru(bpy)$_2$(NO)Cl]$^{2+}$ in slightly basic medium, a coordinated diazonium ion might be formed by loss of wa-

Scheme 1. Proposed Reaction Pathways for the Electrophilic Addition of Primary Amines to Nitrosyl Complexes

Table 2. Yields of Secondary Amines Obtained by Reaction of Pentacyanonitrosylferrate(II) with Primary Amines[6]

reactant(s)	product (yield)
benzylamine	dibenzylamine (30%)[a]
n-butylamine	dibutylamine (81%)
1,4-diaminobutane	pyrrolidine (50%)[b]
butylamine/benzylamine (1:3)	butyl(benzyl)amine (58%)[c]

[a] Other products: N-benzylphenylmethanimine (66%), 1,2-diphenylethane (8%), toluene (8%). [b] Other product: N-nitrosopyrrolidine. [c] Other products: N-benzylphenylmethanimine (25%), 1,2-diphenylethane (7%), dibutylamine (24%).

ter. For the latter complex and an aromatic R group in RNH_2, the diazonium ion is stable enough as to be isolated (Scheme 1, box III).[10] If R is aliphatic and $L_5M = [Fe(CN)_5]^{3-}$, the diazonium ion lives enough time as to be attacked by a nucleophile before its decomposition takes place (Scheme 1, box IV).[6,7] In the case of $[Ru(bpy)_2(NO)Cl]^{2+}$ the aliphatic diazonium is unstable and besides products from nucleophilic attack, a carbocation that gives place to rearrangement or elimination products is also generated (Scheme 1, boxes IV and V).[7,8]
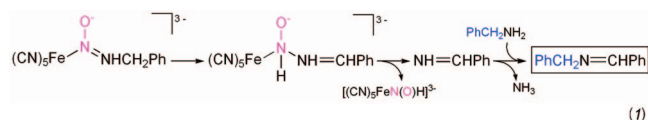
$[Fe(CN)_5NO]^{2-}$. Until a few years ago, reactions of pentacyanonitrosylferrate(II) involving primary[28,29] and secondary amines[30] as well as amino acids[31] had only been studied in aqueous media, where enormous amounts of nucleophiles are present in the form of hydroxide ions or water molecules. Our group has focused on reactions conducted in nonaqueous (organic) solvents, in an attempt to get more insight into the chemistry of coordinated diazonium ions and also to elucidate the possible role of pentacyanonitrosylferrate(II) as a nitrosating agent in lipophilic media.

The main organic product derived from the reaction of pentacyanonitrosylferrate(II) with aliphatic amines is, in most cases, the corresponding diamine (Table 2, also see Scheme 1, box IV; $Nu^- = RNH_2$).[6] Other products such as imines and triamines are also obtained in variable amounts, depending on the starting amine. The absence of rearranged products in these reactions indicates that the initially produced diazonium ion (Scheme 1, box III) is stabilized by coordination to iron.[6,7] This result was supported by DFT calculations.[7a] Nevertheless, when the reaction with n-butylamine is carried out in formamide, more than 50% of butenes—rearrangement products
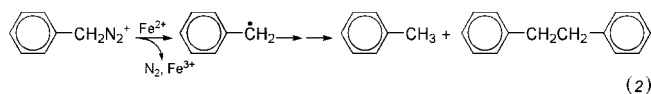
derived from the carbocation—are produced (Scheme 1, box V).

The interaction of the coordinated cyanides with the solvent changes significantly the electron-releasing capacity of the cyanides. In that sense, it is interesting to look at Gutmann's acceptor numbers (AN) for the intervening solvents (Gutmann's AN scale provides a numerical ranking of the relative strengths of Lewis acids).[32] If the reaction is carried out in a solvent—such as formamide—which has the possibility of accepting charge from the cyanides through hydrogen bonding, the electron-releasing capacity of the ligands decreases and, with that, the electron density on the nitrosyl.[6] While AN = 19 for acetonitrile, AN = 40 for formamide. Therefore, back-donation is diminished as compared to the acetonitrile case, and as a consequence of this the stabilization of the diazonium ligand drops down.

In the case of benzylamine, the main organic product from nitrosation is N-benzylphenylmethanimine, probably formed by isomerization of the diazoate favored by the presence of the phenyl ring (eq 1).[7b] The whole process could be viewed as a redox reaction involving the amine/imine and NO^+/NO^- couples.

(1)

Apart from the usual nucleophilic substitution products (dibenzylamine and benzyl alcohol, see Scheme 1, box IV), products originated from benzyl radical were also detected: toluene and 1,2-diphenylethane. The radical is probably produced by Fe(II) reduction of the diazonium ion (eq 2). Consistent with this, arenediazonium salts have been shown to undergo outer-sphere one-electron reduction by ferrocyanide.[33] In the case of the benzyldiazonium ion, this reduction is expected to be much more favorable, and, moreover, it probably occurs via an inner-sphere electron transfer while the diazonium is still coordinated.
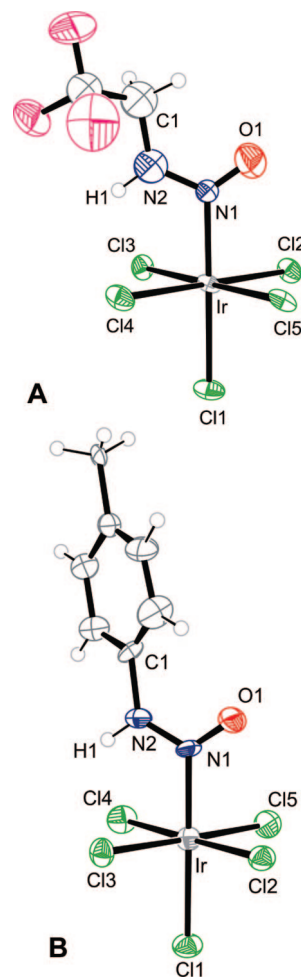
(2)

Trying to find evidences for the formation of diazoic acid, $[Fe(CN)_5NO]^{2-}$ was allowed to react with lithium *n*-butylamide (BuNHLi). In this highly basic medium, the intermediate diazoic acid was expected to deprotonate before loss of hydroxide would produce the diazonium salt. Free (*E*)-*n*-butyldiazoate was found as the only product (eq 3, see also Scheme 1, box II). It was not possible to find appropriate reaction conditions to isolate the diazoate complex before labilization, even by using the inert $[Os(CN)_5NO]^{2-}$ as starting complex.[27]

$$[(CN)_5M-NO]^{2-} + BuNH^- \longrightarrow (CN)_5M \overset{OH}{\underset{}{\overset{N}{\underset{N}{\parallel}}}} NBu \longrightarrow \boxed{BuN=NO^-} \quad (3)$$

$$M = Fe, Ru, Os \qquad H^+, [(CN)_5M]^{3-}$$

$[Ru(bpy)_2Cl(NO)]^{2+}$. In this case, the reactions are much faster due to the increased electrophilicity of the nitrosyl. Its reactivity toward different amines was studied: *n*-butylamine, benzylamine, 2,2,2-trifluoroethylamine. In the first case ca. 20% of the characteristic R′Nu products derived from free carbocations were obtained (alkenes, rearranged alcohols, and chlorides), apart from the organic products (RNu) derived from nucleophilic attack to the aliphatic diazonium ion or the carbocation (Scheme 1, boxes IV and V). This fact suggests that the $[Fe(CN)_5]^{3-}$ moiety is more successful in stabilizing the intermediate diazonium ion through back-donation, as supported by DFT calculations.[7]

The reaction with benzylamine rendered nucleophilic substitution products along with oxidation and radical products, whose origin can be explained as for $[Fe(CN)_5NO]^{2-}$.[7] However, the organic products obtained by reaction with 2,2,2-trifluoroethylamine were only unrearranged (RNu).[8] Although the main decomposition product is expected to be trifluorodiazoethane (by rapid proton loss), we found no evidence for its formation. We believe that the complete absence of this or other rearrangement products in this case is mainly due to the higher stability and electrophilicity of the intermediate diazonium ion derived from trifluoroethylamine, as compared to the one derived from *n*-butylamine, in agreement with computational results. Both factors would tend to favor the reaction of the postulated diazonium ion with hydroxide ion or chloride ion before decomposition takes place.

$[IrCl_5(NO)]^-$. In this case all reactions with amines are fast at room temperature. Although examples of primary nitrosamines as ligands are scarce, when *p*-toluidine, *n*-butylamine, benzylamine, or 2,2,2-trifluoroethylamine was added to an acetonitrile solution of $K[IrCl_5(NO)]$, immediate formation of the corresponding coordinated nitrosamine was observed in high yield, according to Scheme 1 (box I). This was the first direct evidence for the formation of coordinated primary nitrosamines by nucleophilic attack of primary amines to a transition metal nitrosyl. For these amines, loss of water or hydroxide to produce a diazonium ion did not occur due to, on one hand, the stabilization of the nitrosamine form and, on the other hand, to the increased acidity (see below), both effects being produced by the $[IrCl_5]^{2-}$ moiety.[9] On the contrary, when a more basic amine, such as *p*-phenylenediamine, was employed, the coordinated diazonium ion was observed.

FIGURE 5. X-ray crystal structure and atom numbering for $[IrCl_5(N\text{-}nitroso\text{-}2,2,2\text{-}trifluoroethylamine})]^{2-}$ (A) and $[IrCl_5(N\text{-}nitroso\text{-}p\text{-}toluidine)]^{2-}$ (B).

The X-ray structures (Figure 5) correspond to *syn* compounds with respect to the R- and O-substituents, while all known free diazoates are more stable when in *E* conformation.[34] Moreover, these coordinated nitrosamines bond to the metal through the NO moiety, while all known nitrosamines acting as non chelating ligands bond to the metal center through the NH moiety.

Probably the high acidity of the coordinated nitrosamines favor their stability, as compared with the corresponding free nitrosamines (or diazoic acids).[9] Free *Z*-diazoic acids tend to lose hydroxide rather easily in neutral and acidic solutions, while these coordinated nitrosamines are stable in aqueous neutral solutions and even in the presence of acids.[26]

In conclusion, the factors contributing to the stabilization of the products can be summarized as follows: regarding the coordination sphere in these complexes, a decreasing back-donation increases the diazoic acid acid-
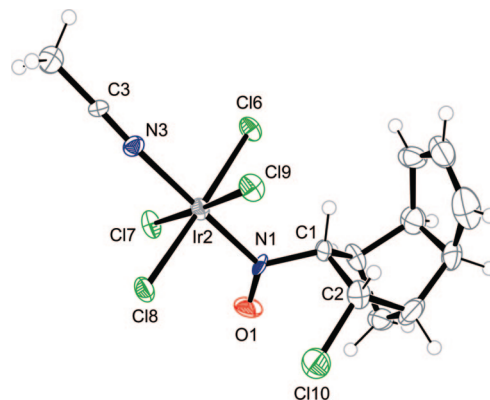
FIGURE 6. Summary of the organic products obtained by reaction of $[Fe(CN)_5NO]^{2-}$, $[Ru(bpy)_2(NO)Cl]^{2-}$, and $[IrCl_5(NO)]^-$ with Primary Amines. $RN\equiv N^+$, $RNH-N=O$, and RNu as depicted in Scheme 1. R''(OX) represents oxidized products (imines and free radical derived products).

FIGURE 7. X-ray crystal structure and atom numbering for *syn*-$[IrCl_4(CH_3CN)(1\text{-nitroso-2-chlorodicyclopentadiene})]^-$.

Scheme 2. Formation of
***syn*-$[IrCl_4(CH_3CN)(1\text{-nitroso-2-chlorodicyclopentadiene})]^-$ by**
Nucleophilic Attack of Dicyclopentadiene to $[IrCl_5NO]^-$

ity and a consequent stabilization of the diazoate due to negative charge delocalization. On the other hand, the diazonium ion stability is diminished due to the predominance of N–N triple-bond character (Figure 6). Regarding the amines, the formation of diazonium ions is favored by their increasing basicity, which on one hand helps to stabilize their electron defficiency and on the other hand diminishes the acidity of the diazoic acid form, favoring the loss of hydroxide. In the case of the aromatic amines, this fact is clearly illustrated for $[IrCl_5(NO)]^-$ (Figure 6). While its reaction with *p*-toluidine produces the corresponding coordinated nitrosamine, *p*-phenylenediamine— more electron-releasing due to the presence of the *para* amino group—forms the coordinated diazonium salt. Finally, regarding aliphatic diazonium ions, because of the absence of resonance stabilization, they are unstable and so far could not be isolated in any case. Quantitative analysis of the products allows an estimation of their relative stability through the rearranged/unrearranged product ratio.

Formation of Coordinated *C*-Nitroso by Reaction with Alkenes. There is an increasing interest on nitrosoalkanes ($RN=O$; R = alkyl) and nitrosarenes ($ArN=O$; Ar = aryl) due to the discovery of the important role of these compounds in a variety of metabolic processes.[35] Taking into account this renovated interest, in the past two decades their synthetic routes have been improved or new ones have been developed.[36]
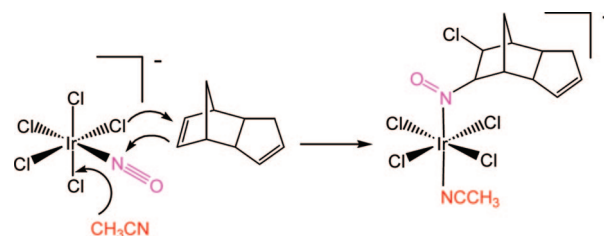
Reactions of olefins with NO^+ to produce *C*-nitroso compounds have been studied. The addition of nitrosyl chloride to dicyclopentadiene yields the dimeric nitroso chloride,[37] while addition to norbornadiene produces only the *cis exo* unrearranged isomer.[38] Only one reaction has been described between a ruthenium nitrosyl and an alkyne.[39] There are a few examples of reactions of Co–NO complexes with alkenes, which produce cobalt dinitrosoalkanes.[40] Relatively few examples of *C*-nitrosoalkane complexes have been previously crystallized.[41]

Our group has obtained stable coordinated nitrosoalkanes by reaction of pentachloronitrosyliridate(III) with alkenes.[18] When dicyclopentadiene is added to an aceto-

nitrile solution of $K[IrCl_5(NO)]$, immediate formation of the corresponding coordinated *C*-nitroso compound is observed as a green precipitate (Figure 7).

The isomer observed, as described in the literature,[38] is the unrearranged molecule in which the C–Cl and C–N bonds are in a *syn* arrangement. Initial nucleophilic attack by the alkene is probably followed by immediate or simultaneous *syn* addition of chloride. The chloride located *trans* to NO is labilized and replaced by an acetonitrile molecule (Scheme 2). Other alkenes, substituted by attracting groups such us cyanides or carboxylic acids, did not react under the conditions described for dicyclopentadiene, but simple ones such as cyclohexene and *cis*-cyclooctene, originate analogous *C*-nitroso products.

Stable *S*-Nitrosothiol Complexes. *S*-Nitrosothiols (RSNOs) have been known from the middle of the 19th century, but the first intentional synthesis and identification were described in 1909 by Tasker and Jones.[42] Because of their low stability, RSNOs did not attract much attention until their physiological role, related to NO transport, was suggested.[43] We have recently reported an investigation of the reaction between *S*-nitroso-L-cysteine ethyl ester and L-cysteine ethyl ester as a model of physiologically relevant transnitrosation processes (i.e., NO exchange from one moiety to another).[44]

Several mechanistic studies[45] report that in the presence of a thiolate anion a great variety of nitrosyl complexes of general formula type $\{(X)_5MNO\}^n$, with X comprising ligands of different donor–acceptor abilities, and M = Fe, Ru, and Os, are transformed into the *S*-nitrosothiolato-*N* complex via nucleophilic attack of the thiolate on the NO ligand.[46] In most cases, the $[M(X)_5N(O)SR]^{n-}$ complexes are unstable and decompose
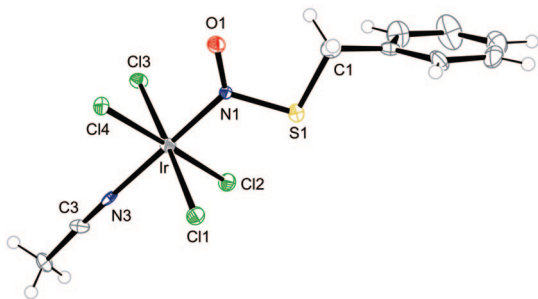
FIGURE 8. X-ray crystal structure and atom numbering for $[IrCl_4(CH_3CN)N(O)SCH_2Ph]^-$.

spontaneously to metal complexes and disulfides, the lifetimes depending strongly on the thiol structure.[47] Olabe et al. have reported the rate constants for reactions of several metal nitrosyls with cysteine in aqueous solution.[13] Ashby et al. have described time-resolved IR spectra in solution for the first time, for the transient "red products", the widely postulated adducts that are formed when pentacyanonitrosylferrate(II) reacts with thiols in aqueous media.[48] Although these products are red the same as free RSNOs, their molar absorbances in the 500 nm range are much larger, usually 20–30-fold.

Our group has obtained for the first time the X-ray structure of a coordinated *S*-nitrosothiol: *trans*-$K[IrCl_4(CH_3CN)N(O)SCH_2Ph]$.[17] This surprisingly stable compound could be isolated in high yield and fully characterized. When benzylmercaptan is added to an acetonitrile solution of $K[IrCl_5(NO)]$, immediate formation of the corresponding coordinated RSNO is observed (eq 4, Figure 8).
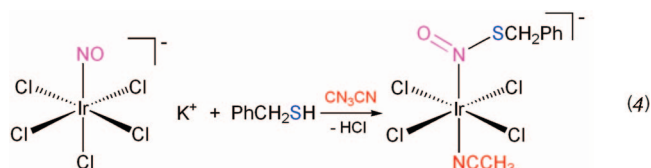
Looking at the structure, acetonitrile is coordinated to the *trans* position due to labilization of the *trans* chloride after electrophilic attack of the thiolate. The conformational preference for the C–S–N=O moiety is *syn*, in agreement with the results reported for free RSNOs.[49] In

contrast with free RSNOs and other metal-coordinated ones, the iridium complex is very stable in aqueous solution. Previous works indicate that when synthesized in situ in oxygen-free CH_3CN, $PhCH_2SNO$ decomposes to give mainly the disulfide. On standing under air, the decomposition is observed within 2 h at room temperature.[50] The Ir–nitrosothiol complex is stable in CH_3CN and in water, even in the presence of air over a period of weeks. As shown by DFT calculations, the N–O bond distances in the Ir complex are longer than the corresponding distances in $PhCH_2SN=O$ (1.21 Å vs 1.19 Å), while the S–N bond distance is shorter than the same distance in $PhCH_2S$–NO (1.86 Å vs 1.90 Å). Consistent with this, the $\nu(NO)$ stretching vibration becomes 70–100 cm^{-1} lower upon coordination (1431 cm^{-1} vs 1500–1530 cm^{-1} for the free RSNO).[51] These facts are probably due to the electrophilicity of the Ir center, as has been also shown by DFT calculations.[49]

Other relevant thiols such as L-cysteine ethyl ester, mercaptosuccinic acid, and phenylthiol also react with $K[IrCl_5(NO)]$ in an analogous manner and exhibit similar stability as the above complex.

Conclusions

Inorganic nitrosyl complexes dissolved in organic solvents are useful reagents for the nitrosation of a variety of compounds, ranging from the nucleophilic amines to the relatively inert alkenes. The electrophilicity of the nitrosyl ligand can be modulated by the oxidation state of the metal and the coligands present in the coordination sphere.

Considering the three complexes discussed in the present review, with regard to the nitrosation reactions of amines, $[Fe(CN)_5NO]^{2-}$ results to be synthetically useful for the obtention of aliphatic diamines, while $[Ru(bpy)_2(NO)Cl]^{2+}$ produces stabilized aromatic diazonium salts. On the other hand, the most interesting complex for synthetic purposes is undoubtedly $[IrCl_5-(NO)]^-$, which rapidly produces coordinated nitroso compounds by using the appropriate nucleophile (amines, alkenes, or thiols). By coordination to $[IrCl_5]^{2-}$, compounds such as primary aliphatic nitrosamines, highly unstable in free form, can be stabilized and easily isolated

Table 3. Relevant X-ray Crystallographic Data for $[Cl_4(L)IrN(O)XR]^{2-}$ Complexes (X = NH, S, CH; L = Cl^- or CH_3CN)

	nitrosamines			
	toluidyne[a]	trifluoroethylamine[b]	nitrosothiol[c]	*C*-nitroso compound[d]
distances (Å)				
$d(N1-X)$	1.309	1.323	1.738	1.494
$d(N1-O1)$	1.225	1.139	1.218	1.216
$d(X-C1)$	1.455	1.466	1.815	1.387/1.390
$d(N1-Ir)$	1.992	2.020	1.959	1.948
$d(X-Ir)$	2.832	2.851	3.180	3.011
angles (deg)				
$\angle(XN1O1)$	118.4	120.0	117.1	117.3
$\angle(IrN1O1)$	124.9	124.7	124.1	123.2
$\angle(XN1Ir)$	116.7	115.4	118.8	122.8

[a] X-ray crystallographic data for $(PPh_4)_2[Cl_5Ir(N$-nitroso-2,2,2-trifluoroethylamine)], ref 9. [b] X-ray crystallographic data for $(PPh_4)_2[Cl_5Ir(N$-nitroso-*p*-toluidyne)], ref 9. [c] X-ray crystallographic data for $PPh_4[Cl_4(CH_3CN)Ir(S$-nitrosobenzylhiol)], ref 18. [d] X-ray crystallographic data for *trans*-$K[Cl_4Ir(CH_3CN)$ (syn-1-chloro-2-nitroso-1,2-dihydrodicyclopentadiene)], ref 18.

with excellent yields by precipitation from the reaction mixtures. Relevant X-ray crystallographic parameters for these products are shown in Table 3. Moreover, we have preliminary results showing that $[IrCl_5]^{2-}$ is an excellent candidate for the isolation of coordinated aliphatic diazonium ions. These compounds could have powerful synthetic applications such as in C–C bond formation reactions.

The facile formation of stable *S*-nitrosothiol complexes as well as primary nitrosamines and *C*-nitroso compounds, all of them which remain stabilized by coordination and can be easily crystallized, occurs thanks to the high electrophilicity and inertness of $[IrCl_5]^{2-}$. While the first characteristic is probably a result of a very weak backbonding, the second one could be attributed to the presence of the third-row metal center. However, both features are aided by the 3+ oxidation state on iridium. These two qualities, high electrophilicity and inertness, generally not compatible, define the anion $[IrCl_5(NO)]^-$ as a rather unique reagent and provide a powerful synthetic route for the obtention of coordinated nitroso compounds.

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