

## NO<sup>+</sup>, NO<sup>•</sup>, NO<sup>-</sup>! Nitrosyl siblings from [IrCl<sub>5</sub>(NO)]<sup>-</sup>

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### ARTICLE INFO

#### Article history:

Available online 10 March 2011

Dedicated to Professor W. Kaim

#### Keywords:

Nitrosyl  
Nitroxyl  
HNO/NO<sup>-</sup>  
NO<sup>•</sup>  
Iridium(III) complexes

### ABSTRACT

Pentachloronitrosyliridate(III) ([IrCl<sub>5</sub>(NO)]<sup>-</sup>), the most electrophilic NO<sup>+</sup> known to date, can be reduced chemically and/or electrochemically by one or two electrons to produce the NO<sup>•</sup> and HNO/NO<sup>-</sup> forms. The nitrosyl complex can be formed either by hydride attack to the NO<sup>+</sup> in organic solvent, or by decomposition of iridium-coordinated nitrosothiols in aqueous solutions, while NO<sup>•</sup> is produced electrochemically or by reduction of [IrCl<sub>5</sub>(NO)]<sup>-</sup> with H<sub>2</sub>O<sub>2</sub>. Both NO<sup>•</sup> and HNO/NO<sup>-</sup> complexes are stable under certain conditions but tend to labilize the *trans* chloride and even the *cis* ones after long periods of time. As expected, the NO<sup>+</sup> is practically linear, although the IrNO moiety is affected by the counterions due to dramatic changes in the solid state arrangement. The other two nitrosyl redox states comprise bent structures.

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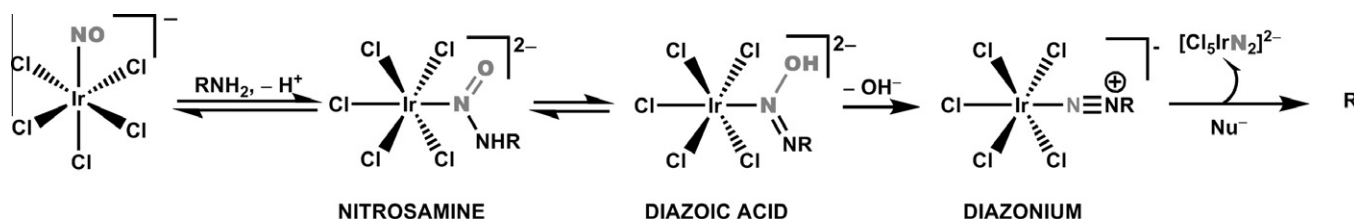
### 1. Introduction

For the last few years we have been studying the properties of [IrCl<sub>5</sub>(NO)]<sup>-</sup>, mainly the electrophilic reactivity of the coordinated nitrosyl. There is a certain correlation between the NO stretching frequency ( $\nu_{\text{NO}}$ ) in metal-nitrosyl complexes and the reactivity of the coordinated nitrosyl [1]: a higher frequency generally indicates an enhanced NO<sup>+</sup> character and electrophilicity. A large  $\pi^*$  NO orbital population would be reflected in a weak NO bond, and hence in a low NO stretching frequency. The nitrosyl in K[IrCl<sub>5</sub>(NO)] shows the highest NO stretching IR frequency known to date (2006 cm<sup>-1</sup>). On the other hand, the reduction potential for the NO<sup>+</sup>/NO<sup>•</sup> couple has been shown to correlate with the nitrosyl electrophilicity better than  $\nu_{\text{NO}}$ . A plot of  $\ln k$  for the nucleophilic addition of OH<sup>-</sup> or RSH<sup>-</sup> vs  $E_{\text{NO}^+/\text{NO}^\bullet}$  for different NO complexes gives a straight line with a positive slope [2]. In the case of K[IrCl<sub>5</sub>(NO)],  $E_{\text{NO}^+/\text{NO}^\bullet}$  (Ag/AgCl) = 0.97 V in aqueous (acidic) solution, being the highest reduction potential known to date for metal nitrosyls. This Ir complex falls in the diffusional rate zone for the abovementioned reactions [3]. Taking the above into account, we could say that K[IrCl<sub>5</sub>(NO)] is the most electrophilic nitrosyl known to date, very likely due to a very weak Ir–NO backbonding. However, the inertness of iridium, is such, that the Ir–N(O)X bonds are very strong in almost every studied. Therefore, the addition of nucleophiles to the nitrosyl ligand in [IrCl<sub>5</sub>(NO)]<sup>-</sup> is a potent tool for the facile obtaining of coordinated Ir–N(O)X species (X = NH, S, C and R = alkyl, aryl) that are unstable in free form.

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The reactions of pentachloronitrosyliridate(III) with amines are instantaneous; we were able to isolate and characterize a number of coordinated aliphatic and aromatic primary nitrosamines [4,5]. Although examples of primary nitrosamines as ligands are scarce, when *p*-toluidine or 2,2,2-trifluoroethylamine were added to an acetonitrile solution of K[IrCl<sub>5</sub>(NO)], immediate formation of the corresponding coordinated nitrosamine was observed in high yield. This was the first direct evidence for the formation of coordinated primary nitrosamines by nucleophilic attack of primary amines to a transition metal nitrosyl. Several intermediates have been isolated and characterized, allowing us to propose with reasonable certainty the mechanistic Scheme 1 [3]. Depending on the basicity of the amine, most of the times the reaction stops in the nitrosamine step, since the coordinated nitrosamine is stable and precipitates out. For these amines, the loss of water or hydroxide from the diazoic acid to produce a diazonium ion (R–N<sub>2</sub><sup>+</sup>) does not occur unless in highly acidic conditions. This is due to two facts, the stabilization of the nitrosamine form and the increased acidity; both effects are produced by the [IrCl<sub>5</sub>]<sup>2-</sup> moiety. A decreasing backdonation increases the diazoic acid acidity and consequently stabilizes the diazoate due to negative charge delocalization. The X-ray structures of the nitrosamines/diazoic acids correspond to *syn* compounds with respect to the R– and O– substituents. They are bonded to the metal through the NO moiety, while to our knowledge all known nitrosamines acting as non-chelating ligands are coordinated to the metal center through the NH moiety. Comparing with free diazoates, the ones having the same conformation than the Ir-coordinated ones (*Z*), tend to lose hydroxide rather easily in neutral and acidic solutions, while all known free diazoates are more stable when in *E* conformation [6]. Other amines were also tested showing in all cases the same behavior

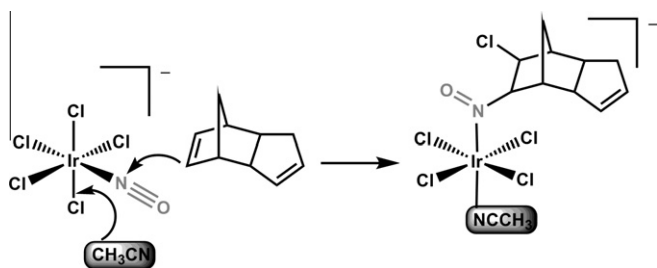


Scheme 1. Mechanistic pathway for the reaction of pentachloronitrosyliridate(III) with amines.

allowing isolation of the primary nitrosamine coordinated to  $[\text{IrCl}_5]^{2-}$  [5].

With regard to coordinated nitrosothiols, we were able to obtain for the first time the full characterization and X-ray structure of a coordinated *S*-nitrosothiol by reaction of benzylmercaptan with  $[\text{K}[\text{IrCl}_5(\text{NO})]]$ : *trans*- $[\text{K}[\text{IrCl}_4(\text{CH}_3\text{CN})\text{N}(\text{O})\text{-SCH}_2\text{Ph}]]$  [7]. Even in the case of free nitrosothiols, only a few X-ray structures have been obtained. This reaction was extended to a family of thiols [8]. Most of these complexes are easily obtained in excellent yields. In the majority of cases the chloride located *trans* to NO is labilized due to the increased electronic density on the NO moiety, and it is replaced by a solvent molecule ( $\text{CH}_3\text{CN}$ ). While in most cases, free *S*-nitrosothiols as well as  $[\text{M}(\text{X})_5\text{N}(\text{O})\text{SR}]^{n-}$  complexes ( $\text{M} = \text{Fe}, \text{Ru},$  and  $\text{Os}$ ) are unstable and decompose spontaneously to metal complexes and disulfides with lifetimes depending strongly on the thiol structure [9], the Ir complexes are quite stable in aqueous solution. Previous works indicate that when synthesized *in situ* in oxygen-free  $\text{CH}_3\text{CN}$ ,  $\text{PhCH}_2\text{SNO}$  decomposes over a period of 72 h to give mainly the disulfide. On standing under air, the decomposition is observed within 2 h at rt [10]. The complex *trans*- $[\text{K}[\text{IrCl}_4(\text{CH}_3\text{CN})\text{N}(\text{O})\text{-SCH}_2\text{Ph}]]$  is stable in  $\text{CH}_3\text{CN}$  and even in water over periods of days. The N–O bond distance in the Ir complex is longer than the corresponding distance in  $\text{PhCH}_2\text{-SNO}$ , and the S–N one is shorter than the same distance in  $\text{PhCH}_2\text{-SNO}$ . Consistent with this, the  $\nu(\text{NO})$  FTIR stretching vibration becomes 70–100  $\text{cm}^{-1}$  lower upon coordination. These facts are probably due to the electrophilicity of the Ir center, as has been shown by Density Functional Theory calculations (DFT).

Related to C–NO bond formation, coordinated nitrosoalkanes can be obtained by reaction of pentachloronitrosyliridate(III) and alkenes. Only a few examples of C-nitrosoalkane complexes have been previously crystallized, all of them containing an ethyl, *t*-butyl or *i*-propyl radical [11]. When *cis*-cyclooctene or dicyclopentadiene is added to an acetonitrile solution of  $[\text{K}[\text{IrCl}_5(\text{NO})]]$  at room temperature, immediate formation of the corresponding coordinated C-nitroso compound is observed as a green precipitate. Initial nucleophilic attack to the  $\text{NO}^+$  by the alkene is followed by immediate or simultaneous *syn* addition of chloride (from  $[\text{IrCl}_5(\text{NO})]^-$ ), forming a C–Cl bond (Scheme 2). Again, the chloride located *trans* to NO is labilized and replaced by an acetonitrile molecule.



Scheme 2. Reaction of pentachloronitrosyliridate(III) with dicyclopentadiene.

A summary of the abovementioned reactions is presented in Scheme 3. In the following sections we will describe another set of reactions involving  $[\text{IrCl}_5(\text{NO})]^-$ : the obtaining of the  $\text{NO}^+$  redox siblings  $\text{NO}^\cdot$  and  $\text{NO}^-$  from pentachloronitrosyliridate(III), by various chemical and electrochemical pathways.

## 2. Results and discussion

### 2.1. Electronic perturbation of $[\text{IrCl}_5(\text{NO})]^-$ in the solid state

As it was introduced, the high electrophilic anion  $[\text{IrCl}_5(\text{NO})]^-$  shows interesting structural aspects. According to the formalism of Enemark and Feltham [12], this hexacoordinated  $\{\text{MNO}\}^6$  with  $\text{K}^+$  or  $\text{Na}^+$  as counterions reports a crystal structure which comprises an octahedral anion with a practically linear Ir–NO moiety (for the  $\text{K}^+$  salt the Ir–N–O angle is  $174.3^\circ$ ) [13], almost coincident with the DFT optimized structure of the isolated ion (Fig. 1). However, the crystal packing is dependent on the counterion: while in the  $\text{K}^+$  and  $\text{Na}^+$  solids the anions are stacked one over the other in a “side by side” arrangement, in the cases of the bulky cations  $\text{PPh}_4^+$  and  $\text{AsPh}_4^+$  ( $\text{Ph} = \text{phenyl}$ ), the  $[\text{IrCl}_5(\text{NO})]^-$  units are forced to be organized in a perfectly linear wire-like arrangement. Moreover, the phenyl rings of the counterions are perfectly stacked one over the other, determining the lattice structure and giving place also to 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 (Fig. 2). The consequence of this peculiar layout is an unprecedented electronic distribution represented by  $\text{Ir}^{\text{IV}}\text{-NO}^\cdot$  for the  $\text{PPh}_4^+$  or  $\text{AsPh}_4^+$  salts, instead of  $\text{Ir}^{\text{III}}\text{-NO}^+$  (as for the  $\text{K}^+$  and  $\text{Na}^+$  ones) [14].

Strong experimental evidence supporting the  $\text{Ir}^{\text{IV}}\text{-NO}^\cdot$  configuration in  $\text{PPh}_4[\text{IrCl}_5(\text{NO})]$  was provided by X-ray absorption near edge structure (XANES) measurements in the solid state at the Ir L3 edge, verifying that the oxidation state for  $\text{PPh}_4[\text{IrCl}_5(\text{NO})]$  is +4 as compared to +3 for  $[\text{K}[\text{IrCl}_5(\text{NO})]]$  [14]. The increment of the Ir L3 white line intensity with its oxidation state was confirmed by performing XANES measurements for different Ir reference compounds and plotting such values versus the oxidation state, finding a linear tendency. From the white line area of  $[\text{K}[\text{IrCl}_5(\text{NO})]]$  and  $\text{PPh}_4[\text{IrCl}_5(\text{NO})]$ , the iridium oxidation state for the latter was determined to be almost 1 unit higher than for  $[\text{K}[\text{IrCl}_5(\text{NO})]]$ . Since  $\text{PPh}_4[\text{IrCl}_5(\text{NO})]$  is diamagnetic, the expected situation is an open-shell singlet (OSS),  $\text{Ir}^\uparrow\text{-NO}^\downarrow$ , with a  $d^5$  low-spin  $\text{Ir}^{\text{IV}}$  center ( $S = +1/2$ ) antiferromagnetically coupled to  $\text{NO}^\cdot$  ( $S = -1/2$ ). DFT calculations performed in the solid state on the structure of  $\text{PPh}_4[\text{IrCl}_5(\text{NO})]$  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. Calculations also demonstrate that the stabilization of such electronic configuration is supported by the presence of the counterions. For instance the  $\pi$ – $\pi$  interactions among the phenyl rings in the crystal, are in the range of the energy difference among both abovementioned electronic distributions *in vacuo* (14  $\text{kcal mol}^{-1}$ ) [15,16]. In summary, this is an interesting case of electronic perturbation in a third-row transition-metal complex in the ground state. The high

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