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Ruthenium nitrosyl complexes containing pyridine-functionalized carbenes – A theoretical insight

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ABSTRACT

The Ru–NO bonding situation in a set of ruthenium(II) nitrosyl complexes containing pyridine-functionalized carbenes as bidentate ligands is presented. Cheng's complex [(**L**)*Ru*(*NO*)Cl_3], where L = 3-tert-butyl-1-(2-pyridyl)imidazol-2-ylidene, **1a**, was used as a model structure and the effect of different families of pyridine-functionalized carbene ligands on the Ru–NO bond strength was explored, including imidazolylidenes, triazolylidenes, oxazolylidenes, thiazolylidenes, P-heterocyclic carbenes, imidazolidinone, triazolidinone, among others. The results reveal that the NO^+ group binds more strongly to the Ru(II), than carbene carbon or pyridine nitrogen atoms. The EDA-NOCV results show that the nature of the carbene has a direct influence on the lability of the Ru–NO, since it changes the electronic environment around the metallic centre. EDA-NOCV results point out that the nature of the $Ru{-}NO^+$ interactions (**1a**–**16b**) presents a very preponderant covalent character (circa 70%), while the electrostatic character covers circa 30% of the total interaction energy. The energy decomposition still reveals that $Ru{-}NO^+$ bonds are strengthen in complexes **1a**–**16a**, than in **1b**–**16c**. The weakest $Ru{-}NO^+$ interactions are observed for complexes containing P-heterocyclic ligands (PHCs), specially for complexes where the NO^+ is coordinated *trans* to the carbene carbon atoms. The metal→ ligand π-back-donation is more intense towards PHC than towards NO^+.

1. Introduction

The nitric oxide, NO, produced in a wide range of cells and tissues, has been associated with various physiological processes [1–3]. Nitric oxide acts in several important functions, such as the control of sleep, appetite, body temperature, neurotransmission, cardiovascular control and blood pressure [4–7]. The search for new systems, including iron and ruthenium nitrosyl complexes, able to storage and to release NO to desired targets, has increased considerably in the last years [8–12]. Particularly, ruthenium nitrosyl complexes have been extensively explored due to their properties such as thermal stability, low toxicity, water solubility, and the ability to release NO^0 through photochemical and chemical reduction, resulting in a considerable amount of experimental [13–19] and theoretical [8,10,12,20–24] studies. In this scenario, the adequate choice of ligands is considered as a convenient strategy for modelling the NO reactivity [25–28].

Since the first stable carbenes, initially prepared by Bertrand [29] in 1988 and later by Arduengo [30] in 1991, the chemistry of N-heterocyclic carbenes, NHCs, emerged from a simply phosphine mimic in organometallic chemistry to a well-established class of compounds [31], presenting applications in homogeneous catalysis as nucleophiles [32–36], and also as ligands with d-block metals and main-group elements [37–41]. NHCs are basically σ-donor with a relative poor π-acceptance [42,43], leading to a high *trans*-effect, favouring the dissociation of *trans* ligands. Ruthenium complexes containing NHCs were largely studied due their catalytic success in olefin metathesis, polymerization, isomerization, and also in miscellaneous reactions [44–52].

Six years ago, Cheng and co-workers synthesized and characterized by X-ray diffraction, IR, ^{1}H and ^{13}C NMR a series of ruthenium(II) carbonyl [53] and nitrosyl [54] complexes containing pyridine-functionalized NHCs. Complexes such as [(**L**)*Ru*(*NO*)Cl_3], where L = 3-tert-butyl-1-(2-pyridyl)imidazol-2-ylidene (**1a**); L = 3-n-butyl-1-(2-pyridyl)imidazol-2-ylidene, L = 3-tert-butyl-1-picolylimidazol-2-ylidene; L = 3-n-butyl-1-picolylimidazol-2-ylidene; and L = 3-benzyl-1-picolylimidazol-2-ylidene, were

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prepared by transmetalation from the corresponding silver carbene complexes. Significant shifts (25–40 cm^{-1}) in the NO^+ stretching frequency values relative to the starting material, $RuNOCl_3$ (1905 cm^{-1}), were reported, illustrating the charge outflow from pyridine-functionalized NHC groups into the π^* orbital of NO^+ through the metal center [54]. The X-ray diffraction results show that the structure of **1a** is a somewhat distorted octahedron with three chloride ions occupying *mer* configuration and the NO^+ group located *trans* to the pyridine nitrogen. The short $Ru{-}NO^+$ bond length (1.720(6)Å) suggests the presence of a strong π back-donation from ruthenium(II) d_π orbitals towards the π^* orbitals of NO^+ ligand. The presence of linear Ru–N–O arrangement confirms the nitrosonium character of the $Ru{-}NO^+$ core, which can be represented by Enemark-Feltham $\{RuNO\}^n$ notation (where n is the sum of d-electrons and π^* electrons of NO electrons) [55]. Formally, $Ru{-}NO^+$, $Ru{-}NO^o$, and $Ru{-}NO^-$ cores can be represented by $\{RuNO\}^6$, $\{RuNO\}^7$, and $\{RuNO\}^8$, respectively.

The ligands coordinated to $\{RuNO\}^6$ core have therefore a crucial role on the lability of Ru–NO bond. The replacement of ligands is a suitable strategy to adjust the NO reactivity [25–28]. We have already confirmed, by means of the energy decomposition analysis, the influence of different equatorial ligands, including tetraazamacrocycles [10] and tetraammines [12], on the electronic structure of the Ru–NO chemical bonding, and consequently on the lability of the Ru–NO bond. We have also investigated the Ru–NO bonding situation prior, $\{RuNO\}^6$, and after the monoelectronic reduction, $\{RuNO\}^7$, by considering different linkage isomers [8].

Considering the biological significance of NO chemistry and the enormous potential of the NHC ligands, we decided to employ the complex synthesized by Cheng [54], **1a**, as a prototype structure, which allows us to predict the effect that different types of carbenes have on the magnitude and physical nature of $\{Ru{-}NO\}^6$ bonds in ruthenium nitrosyl complexes bearing pyridine-functionalized carbenes, even before the synthesis of such complexes. It is important to emphasize that the number of different NHCs reported in the literature encompass a sheer number of different compounds either five-membered ring or ring-expanded analogues, and also analogues containing heteroatoms as P, S, and O, which were probed to have important effects on the stability and reactivity of carbenes and transition metal complexes bearing carbenes [56]. Therefore, the structures proposed for the carbenes in our manuscript are not merely hypothetical, but instead consciously based on already synthesized carbenes or transition metal complexes containing carbenes [56]. In the present manuscript, a theoretical study about the $Ru{-}NO^+$ bonding situation in a set of ruthenium(II) nitrosyl complexes containing pyridine-functionalized carbenes as bidentate ligands is presented (Fig. 1). The $Ru{-}NO^+$ lability achieved by substituting the pyridine-functionalized was investigated and therefore the chemical characteristic of the carbenes was systematically changed by including imidazolylidenes **1a**–**2a**, triazolylidenes **3a**–**4a**, oxazolylidenes **5a** and **8a**, thiazolylidenes **6a**, **9a**, P-heterocyclic carbenes, PHCs, **7a**, **10a**–**11a**, **16a**, imidazolidinone **12a**, triazolidinone **13a**, oxadiazolidinone **14a**, and thiadiazolidinone **15a** as ligands (Fig. 2). Since only the *mer* isomer with NO^+ *trans* to the pyridine nitrogen is reported [54], we decided to explore two other series of complexes, **1b**–**16b**, in which the chloride ions occupy the *fac* configuration, and **1c**–**16c**, in which the chloride ions occupy *mer* configuration and the NO^+ group is located *trans* to the carbene carbon (Figs. 1 and 2). The $Ru{-}NO^+$ bonding situation was studied with the energy decomposition analysis in combination with the natural orbital for chemical valence method (EDA-NOCV) [57] and natural bond orbitals (NBO) analysis [58,59].

2. Computational methods

The geometries of complexes **1a**–**16c** were optimized without constraints at the non-local DFT level of theory [60,61], by using the exchange functional of Becke [62] and the correlation functional of Perdew [63] in conjunction with the atom pairwise dispersion correction [64–66], BP86-D3, and all-electron relativistically recontracted basis sets derived from Ahlrichs def2-TZVP [67] basis set were employed. All geometry optimizations were performed with the ORCA package [68]. The EDA-NOCV method [57] was employed to characterize the ruthenium–nitrosyl interaction in $[(L)Ru(NO)Cl_3]$ complexes, **1a**–**16c**, by considering NO^+ and $[(L)Ru(Cl)_3]^-$ as interacting closed-shell fragments and by using BP86-D3 model. A triple-zeta STO basis set TZ2P+ [69], in conjunction with the zero-order regular approximation, ZORA, as implemented in ADF2013 software [70,71] was employed. The EDA-NOCV method combines the extended transition state method, ETS [72,73], with the natural orbitals for chemical valence scheme, NOCV [74–77]. Further details can be found at the supporting information material. In order to give support to the EDA-NOCV, the Natural bond orbital analysis, NBO [58,59], was also performed by using NBO 5.0 program implemented in GAMESS-US package [78]. The wave functions used in NBO analysis were obtained by employing BP86-D3/def2-TZVP as level of theory.

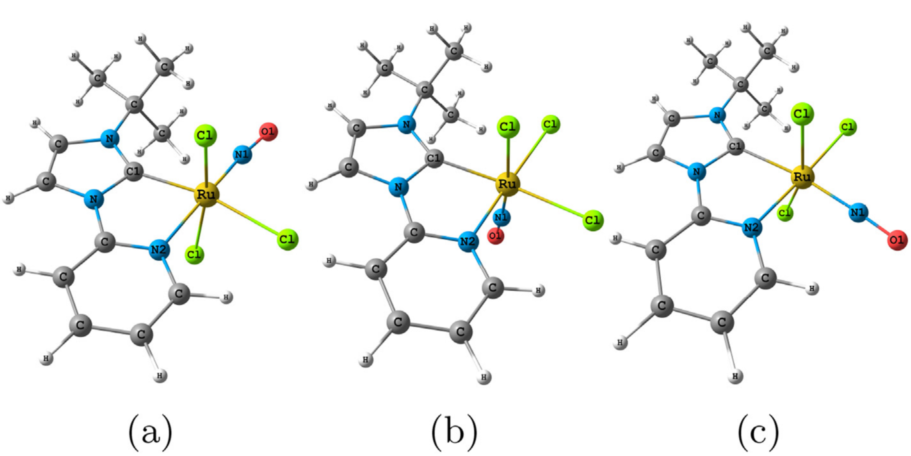

Fig. 1. Optimized structures (BP86-D3/def2-TZVP) of (a) **1a** *mer*-$[(L)Ru(NO)Cl_3]$, in which NO^+ is located *trans* to the pyridine nitrogen; (b) **1b** *fac*-$[(L)Ru(NO)Cl_3]$; and (c) **1c** *mer*-$[(L)Ru(NO)Cl_3]$, with NO^+ *trans* to the carbene carbon (L = 3-tert-butyl-1-(2-pyridyl)imidazol-2-ylidene).