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The reaction of rhenium nitrosyl with a sterically hindered NHC-carbene†‡

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In this article, we present the serendipitous synthesis of the unknown Re(I) complex [(OPPh₃)Re(NO)₂Cl₃] (**3**) that we obtained reacting the Re(V) complex *trans*-[(PPh₃)₂ReOCl₃] (**1**) with NO gas in presence of CH₃COOH. We found that **3** reacts with 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IMes) to yield a stable oximate–Re(III) complex [(OPPh₃)Re(NO)(ON=IMes)Cl₃] (**4**). We speculate that the IMes reacts with a bent NO, because the DFT calculations excluded the formation of both dimeric and η²-NO complexes in solution. The reactivity of the NO toward the carbene is probably due to an internal fluxional process in which the NO passes from linear to bent, triggered by the π-electrons given by the three chlorides to the Re through the mesomeric effect.

Introduction

Nitric oxide (NO) is an intriguing molecule that holds many roles, both in Biochemistry (as a bio regulator)^{1,2} and Organometallic Chemistry (as non-innocent ligand).³ It may possess a character of: cation (nitrosyl or nitrosonium, NO⁺: isoelectronic with CO and N₂, hybridized sp, linear, 10 electrons, 1 electron donor), radical (nitric oxide, NO[•], hybridized sp, linear, 11 electrons, 2 electrons donor) or anion (nitroxyl HNO, with its conjugate base NO⁻: isoelectronic with O₂, hybridized sp², bent, 12 electrons, 3 electrons donor). Depending on the conditions in which it is synthesized, the radical species can be oxidized to NO⁺ or reduced to NO⁻ or it may simply react as a radical (NO[•]). It is actually possible to have another form of NO[•], *i.e.*, the dimeric one (NO)₂²⁻. The latter dianion has been isolated for the first time by Evans and co-workers and it has a linear structure with a double bond between the two N [(ON=NO)²⁻].⁴ The ligands of the metal and its oxidation state dictate the binding mode of the NO. For instance, Keilwerth and Meyer presented a series of complexes in which Fe is bound to the tris-NHCs ligand tris[2-(3-mesitylimidazol-2-ylidene)ethyl]-amine (TIMEN^{Mes}).⁵ With the help of TIMEN^{Mes} the Fe centre can be stable in different oxidation

states and the authors exploited this characteristic to synthesize, among others, a Fe(III) complex [(TIMEN^{Mes})Fe(NO)(CH₃CN)]³⁺. The latter was reduced with a Cs electride to afford the complex [Cs(crypt-222)] [(TIMEN^{Mes})Fe(NO)], that presented a metalacyclic [Fe–(NO–NHC)³⁻] nitrosoalkane unit in which the NO was bridging between the metal centre and the C1 carbon of one of the carbene ligands. An aspect that must be taken into account in presence of a metal–NO bond (M–NO), is its bonding nature. The binding modes with which NO can coordinate a metal centre are four: linear M–NO, bent M–NO, isonitrosyl M–ON and as a η²-nitrosyl.^{6–8} Because of these characteristics, NO has been particularly important for the chemistry of many metals⁹ including Re,¹⁰ imparting catalytic activity to the complexes of which it is part. In the present article, we will present and discuss, with the help of DFT calculations, the synthesis of the unknown Re(I) dinitrosyl complex [(OPPh₃)Re(NO)₂Cl₃] (**3**) and of its reaction with a bulky carbene [1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene] (IMes free carbene) yielding the hitherto unknown complex [(OPPh₃)Re(NO)(ON=IMes)Cl₃] (**4**), in which the IMes binds the N of the NO, forming an oximate-like ligand.

Results and discussion

Re nitrosyls showed extremely good catalytic activity^{11–20} and, as entry point to access the Re–NO complexes, we focused our attention on the well-known Re(V) *trans*-[(PPh₃)₂ReOCl₃] (**1**),^{21–23} complex that has shown to react with NO in benzene to give the paramagnetic complex Re(II) [(OPPh₃)₂Re(NO)Cl₃] (**2**).²⁴ When we attempted the synthesis of complex **2** following a procedure similar to the one reported by Dzięgielewski and

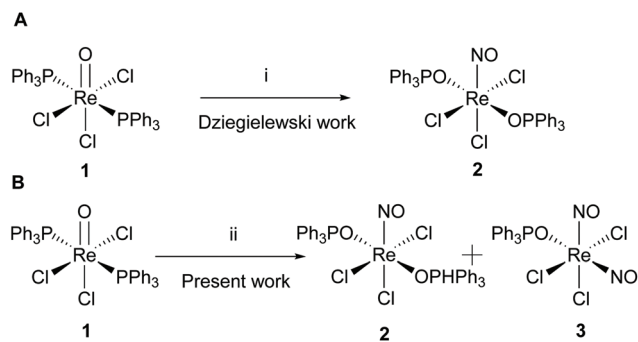
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Scheme 1 The synthesis made by Dziegielewski and co-workers²⁴ yielded the complex **2** (A) while using similar conditions we got the mixture of **2** and **3** (B): (i) benzene, NO(g), 5–6 hours reflux. (ii) Toluene, NO(g), 80 °C, 3 hours.

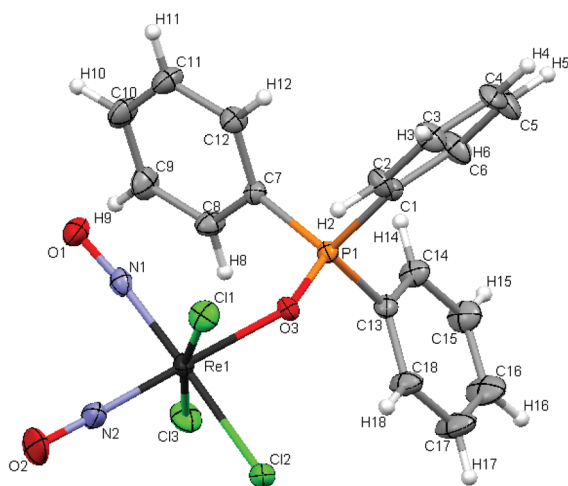


Fig. 1 The structure of the complex **3** in solid state. The solvate molecules are omitted for clarity. The displacement ellipsoids are drawn at the 30% probability. Selected bond lengths (Å) and angles (°): N1–O1 1.155(4), N2–O2 1.150(4), Re1–O3 2.027(2), O3–P1 1.529(2), Re1–Cl2 2.3641(9), Re1–Cl1 2.3826(10), Re1–Cl3 2.3812(10), Cl1–Re1–Cl2 87.43(4), Cl2–Re1–Cl3 86.66(4), P1–O3–Re1 143.85(14), N2–Re1–N1 87.44(14), O1–N1–Re1 174.5(3), O2–N2–Re1 177.8(4).

co-workers (Scheme 1A),²⁴ we did get the wanted product **2** but together with the new dinitrosyl Re(i) diamagnetic complex $[(\text{OPPh}_3)_2\text{Re}(\text{NO})_2\text{Cl}_3]$ (**3**) (Scheme 1B) as confirmed by: FTIR (ESI, Tables S1 and S5[†]), crystal structure (Fig. 1) and HR-ESI MS analysis (S19, ESI[†]). The assignments of the NO of the FTIR will be discussed later in the paper.

In literature are present examples in which the reaction of **1** with gaseous NO gave different results than those obtained by the group of Dziegielewski. For instance, Abram and co-workers reacted **1** with NO in a mixture of CH_2Cl_2 and EtOH, and obtained the following three different Re(II) complexes with a $5d^5$ low-spin configuration: $[(\text{PPh}_3)_2\text{Re}(\text{NO})\text{Cl}_2(\text{OPPh}_3)(\text{OREO}_3)]$, $[(\text{OPPh}_3)_2\text{Re}(\text{NO})\text{Cl}_2(\text{OREO}_3)]$, $[(\text{OPPh}_3)_3\text{Re}(\text{NO})\text{Cl}_2][\text{ReO}_4]^{25}$ With shorter reaction times where even isolated further complexes of formula: $[(\text{PPh}_3)_2\text{Re}(\text{NO})\text{Cl}_3]$, $[(\text{PPh}_3)\text{Re}(\text{NO})\text{Cl}_3(\text{OPPh}_3)]$ and

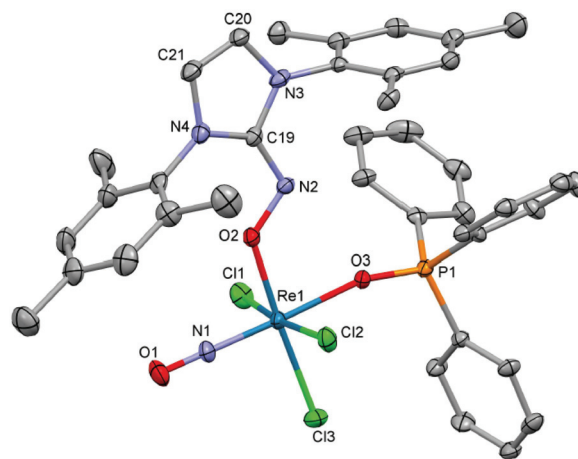
$[(\text{PPh}_3)_2\text{ReCl}_4]$. All these different results could rise from one or more different factors as: type of solvent, amount of solvent used, amount of NO reacted, temperature, reaction time and presence of compounds able to react with NO giving rise even to more effective nitrosating agents. For instance, it is known that the solubility of the NO depends strongly from the type of solvent used in the reaction. We schematized below the differences in the reactions described above (Table 1). Furthermore, in the procedure followed by Abram, after that the flux of NO was stopped, it was added absolute EtOH and the solution was left overnight in contact with air. Neither in our synthesis (under N_2) nor in the case of the synthesis of Dziegielewski (under Ar) the contact with O_2 took place.²⁴ It is important to point out that NO reacts with O_2 yielding other two reactive species, *i.e.*, the radical nitrogen dioxide ($\cdot\text{NO}_2$) and the dinitrogen trioxide (N_2O_3). The latter has a structure similar to the Angeli's salt ($\text{Na}_2\text{N}_2\text{O}_3$) (Scheme 2).²⁶

The presence of all these different nitrosating agents together with O_2 , may explain why the complex $[(\text{PPh}_3)_2\text{ReOCl}_3]$ gave rise to many different products, including some that had as a counter ion an oxidized form of Re ($[\text{ReO}_4]^-$). Finally, we found that residual CH_3COOH , present in the synthesis of **1**, was responsible for the formation of **3**. In

Table 1 Comparison between different reaction conditions applied in former works and in the present one

Reference	Solvent	Time (min)	Substr./ Solvent (mg mL^{-1})	NO solubility ^a
Dziegielewski ²⁴	Benzene	300–360	21.3	9.07
Abram ²⁵	CH_2Cl_2 ^b	>180	4.2	7.42 ^c
Present work	Toluene	180	5.0	8.33

^a $K_{\text{H}}/10^7 \text{ N m}^{-2}$, the solubility of NO in various solvents at 25 °C expressed as the Henry's law coefficient K_{H} . ^b EtOH was added after the flux of NO was stopped. ^c We used the value that refers to Cl_4 .

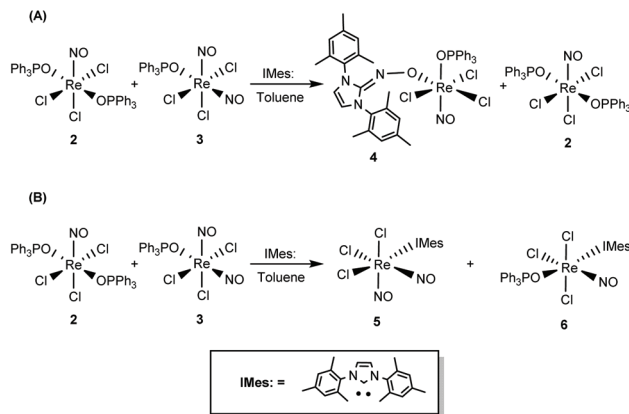


Scheme 2 Reaction of O_2 and NO. The O_2 present in the air reacts with NO giving both dinitrogen trioxide (N_2O_3) and nitrogen dioxide ($\cdot\text{NO}_2$).



fact, it is known that CH_3COOH is able to form nitrosyl carboxylate reacting with derivatives of the NO as the nitrosyl chloride (ClNO).²⁷ We tried to figure out the mechanisms of the formation of both the complexes **2** (Scheme 3A) and **3** (Scheme 3B), assuming that CH_3COOH is present just in the reaction that yields **3**. It is worth noting that the CH_3COOH is needed in catalytic amount since during the reaction is not consumed. To confirm our findings, we synthesized a new batch of **1** without CH_3COOH , and we obtained just **2**. However, with 100 μL of CH_3COOH for 40 mL of toluene and 0.85 g of the freshly synthesized **1** we obtained the mixture of **2** and **3**, in less than 60 minutes at 80 °C. We did try to improve the yield of the synthesis of **3** varying the amount of NO employed and the conditions of the reaction, but without success. The reaction always yielded a mixture of mono- and di-nitrosylated complexes and in some cases more than two products (ESI, S25[†]). Then, we reacted **3** with 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IMes free carbene), to try to substitute the TPPO present in both **2** and **3**.

The IMes reacted just with **3**, but instead of replacing the TPPO as we expected, it reacted with one of the NOs coordinated to the Re yielding **4** (Scheme 4A). The latter possesses a carbene-oxime like ligand as proven by the crystal structure (Fig. 2). Instead, **2** is unreactive toward the carbene used in the reported conditions. We have drawn the complexes **5** and **6** that should have formed theoretically (Scheme 4B). To our best knowledge the only example reported of a triplet carbene that reacted with NO is the one reported by Forrester and Sadd that used NO to convert the carbene into an iminoxyl radical to observe the latter by E.S.R. spectroscopy.²⁸ Something similar was made by Cuesta and co-workers that synthesized the complexes $[\text{Re}(\text{ONCMe}_2)(\text{CO})_3(\text{bipy})]$ and $[\text{Re}(\text{ONCMe}_2)(\text{CO})_3(\text{phen})]$ reacting the oxime salt KONCMe_2 with



Scheme 4 Reaction of the IMes with the mixture of complexes **2** and **3**. The theoretical reaction in which the carbene replaces the OPPh_3 (path B) to produce the theoretical complexes **5** and **6** and the reaction that instead took place (path A). In the latter, the carbene attacked the N of a NO yielding **4**.

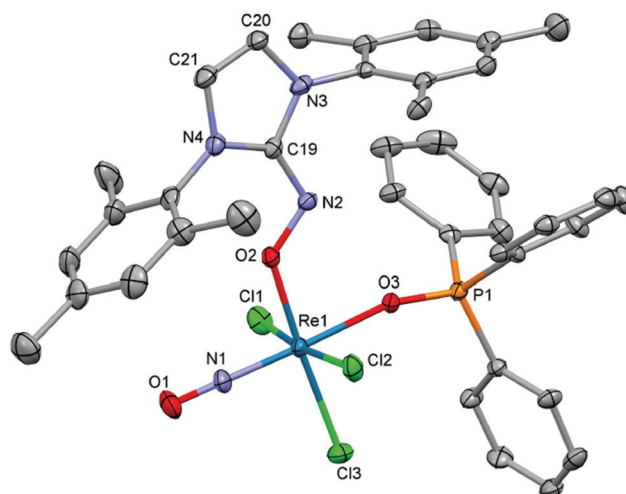
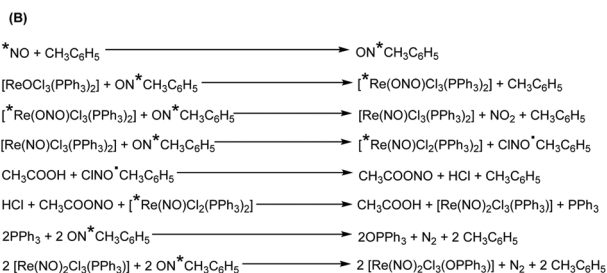
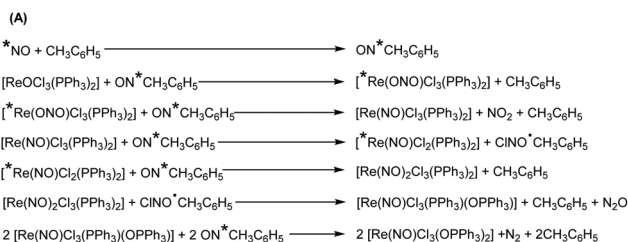


Fig. 2 The crystal structure of the complex **4** in solid state. The solvate molecule and the H atoms are omitted for clarity. The displacement ellipsoids are drawn at the 30% probability. Selected bond lengths (Å) and angles (°): N1–O1 1.176(10), Re1–N1 1.737(7), Re1–Cl1 2.381(3), Re1–Cl2 2.394(3), Re1–Cl3 2.375(3), Re1–O2 1.952(6), O2–N2 1.325(9), N2–C19 1.373(10), C19–N2–O2 109.0(7), N2–O2–Re1 123.7(5), O1–N1–Re1 179.1(9).



Scheme 3 The formation of **2** (A) and **3** (B) is explained step by step. The star (*) indicates the radical species while the dot (·) indicates a charge transfer complex. CH_3COOH is present just in the mechanism B.

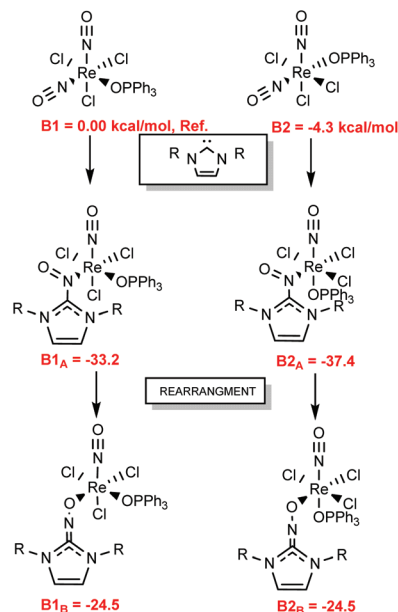
the complex $[(\text{N}-\text{N})\text{Re}(\text{OTf})(\text{CO})_3]$ (N–N = bipy, phen).²⁹ However, in the latter case, the oxime group was introduced at once at the Re centre and it was not formed, as in our case, after the reaction of a NO with a carbene. We can say that our is the first example of this kind, nevertheless, why the carbene reacted with the N of the NO? Probably, the IMes acted as electrophile toward the N of a bent NO, during an ongoing equilibrium in which the NO passes from linear to bent. However, the carbene reacted in that way probably because of the presence of a NO in *trans* to the TPPO. The NO preferred to keep the latter instead of having the most *trans* labilizing carbene.



For instance, the work of Yang and co-workers can be an example of this strong *trans* labilizing effect of bulky carbenes.³⁰ We tried to obtain the corresponding labelled versions of the complexes **2** and **3** using ¹⁵NO gas, reacting the latter with **1** in toluene in the presence of CH₃COOH. The procedure for the evolution of ¹⁵NO implied the use of both H₂SO₄ and FeSO₄ which we mixed in a separate reaction vessel together with Na¹⁵NO₂, following the procedure described by Dzięgielewski (Scheme 3).²⁴ Once ¹⁵NO was evolved, it was transferred inside the reaction vessel containing **1** using vacuum. The experiment yielded the wanted labelled [(OPPh₃)Re(¹⁵NO)₂Cl₃] (**7**) and [(OPPh₃)Re(¹⁵NO)Cl₃] (**8**), as we can see comparing the FTIR spectrum of the above mentioned complexes with the one of the non-labelled ones (ESI, S7†). It is worth noting that in the spectrum of the complexes **2** and **3** (ESI, S6†) there are three signals attributable to the NO (1881, 1792, 1762 cm⁻¹) that we cannot find in the spectrum of the complex **7** and **8** (ESI, S5†) because in the latter the peak at 1841 cm⁻¹ is so broad to hide the second ¹⁵NO band. The broadness of the aforementioned signals is due to the higher mass of the ¹⁵NO compared with ¹⁴NO. This difference in size is responsible as well for the fact that the peaks corresponding to the ¹⁵NOs are at lower frequencies in contrast with those of the ¹⁴NOs.

DFT calculations

Theoretical calculations have been carried out with the help of the Gaussian 16 program package³¹ using the B3LYP functional³² in conjunction with the Stuttgart/Dresden (SDD) effective core potential³³ for the metal centre and the standard 6-31+G(d) basis set³⁴ for the remaining atoms to investigate the possibility of the appearance of dimeric species formed from **3** after the loss of a TPPO in solution. Furthermore, other calculations were carried out to gain insight into the reaction between the carbene and one of the NOs of **3**. The geometries were optimized starting from the structure of **3** determined by X-ray crystallography (Fig. 1). Through these calculations, we were able to exclude the formation of both η²-NO and dimeric structures, into which **3** could transform once in solution, after loss of the TPPO by dimerization (Schemes S23 and S24, ESI†). Once we understood, which structure **3** could have in solution, we investigated the thermodynamics of the reaction between the IMes free carbene and **B1** (Scheme 5). We assumed that the IMes attacked the N_{NO} atom directly after the NO bent and after this attack, the NO-IMes intermediate rearranged giving rise to **4**. The calculations revealed that an alternative isomeric structure of **3**, in which both NOs are in *trans* position to the Cl, could be involved (Scheme 5, **B1**). This isomer has a calculated energy that is slightly higher (+4.9 kcal mol⁻¹) than the structure of **3** that is present in solid state. However, the attack of the IMes carbene can occur on the NO *trans* to the Cl, which again would give rise to an oximate-like ligand structure and this would lead to the formation of an isomer of **4** with the same calculated energy. The NO that



Scheme 5 Energies of the postulated two-step mechanism transforming **3** by nucleophilic attack of IMes to the NO of a coordinated Re–NO moiety (R = H, for the DFT calculations).

reacts with the IMes, gets destabilized by the π-donor Cl. For instance, similar conclusions were drawn by Fomitchev and Coppens studying Ru(II) NO complexes with the NO in *trans* positions to ligands, such as: OH⁻, NH₃, Cl⁻, SCN⁻, Br⁻, I⁻ with different π-donor abilities.³⁵ They found that the higher is the π-donation of the ligand in *trans* to the NO, the weaker is the binding of the NO toward the metal. The order: OH⁻ < NH₃ < Cl⁻ < SCN⁻ < Br⁻ < I⁻ of increasing donor ability was found. The OH⁻ is an exception probably because of a strong σ (inductive) interaction that overcomes the π (mesomeric) one.³⁷ We can also see that the intermediate **B2A** has a lower energy (−4.2 kcal mol⁻¹) when compared with the intermediate **B1A**, that would form from the isomer **B1**. However, at room temperature the pathway including **B2** is the favoured one.

Intramolecular redox equilibrium of the complex *mer*-[(OPPh₃)Re(NO)₂Cl₃]

As we can see from the FTIR of the mixture of the complexes **2** and **3** (Table 1), there are two strong peaks at 1391 and 1378 cm⁻¹. We assigned these two peaks to the NO belonging to **3**. We did it because: the FTIR of **2** alone does not contain such peaks, the FTIR of the labelled complexes **7** and **8** contains the same peaks. The latter disappears after the reaction of the mixture of **2** and **3** with the IMes (ESI, S3–S5 and S16†). We believe that these two peaks are the result of a fluxional process that involves the uneven distribution of the π* orbital between N and O of the NO. In fact, the behaviour of the NO depends on the amount of charge that lies on these atoms.



Usually, the π^* orbital is localized as 60% on the N and 40% on the O and the localization of such orbital influences the geometries (M–NO, M–ON, M– η^2 –NO, ...) of the M–NO complexes.³⁶ Moreover, the π^* orbital works as an acceptor orbital that NO can exploit to accept electronic charge from the metal. In our case the distribution of the π^* orbital of the NOs of **3** probably is such to create, for the M–NO bond of both NOs, an internal equilibrium between a Re–nitrosonium NO^+ and a Re–nitroxyl NO^- . This equilibrium would account for both the multiple signals in the ^{15}N NMR (ESI, S10†) and for the peaks at 1391 and 1398 cm^{-1} found in the FTIR of **3** and **8** (ESI, S5 and S6†). Examples of complexes containing both NO^+ and NO^- are for instance $[\text{Fe}(\text{NO})_4]$ and $[\text{Ni}(\text{NO})_2(\text{PPh}_3)_2]$. Indeed, both signals at 1391 and 1398 cm^{-1} are quite low to be non-bridging NOs, but in literature are present examples of complexes as $\text{K}_3[\text{Co}(\text{NO})(\text{CN})_5]$ ($\nu_{\text{NO}} = 1125 \text{ cm}^{-1}$) for which the NO stretching frequency is really lower than usual (1100–1200 cm^{-1}).³⁷ However, it must be taken in the due account that in literature were reported cases in which a mono NO complex was able to give two bands assignable both to a single NO. For instance, Booth and Chatt synthesized the mononitrosyl Co complexes $[(\text{PEt}_3)_2\text{Co}(\text{NO})\text{X}_2]$ (X = Br, I) that showed two clear ν_{NO} bands in the IR analysis in the 1650–1750 cm^{-1} region.³⁸ The authors speculated that different types of Co–NO bonding were in equilibrium, generating in that way two different ν_{NO} bands. It is possible as well to have a dinitrosyl complex with both linear and bent coordinated NO groups present at the same time.^{39–42} Considering the existing literature, we believe that the complex *mer*- $[(\text{OPPh}_3)\text{Re}(\text{NO})_2\text{Cl}_3]$ probably possesses an internal fluxional process that is responsible for the reactivity of its NOs and for all the signals present in the ^{15}N NMR (ESI, S9†). We excluded the presence of signals belonging to paramagnetic species in the ^{15}N NMR that we have run, since the number of scans (less than 3000) and the condition used ($T_1 > 30 \text{ s}$) for the NMR analysis would not have allowed us to observe such complexes. Furthermore, after the ^{15}N NMR was run, we run the ^{31}P NMR that showed a single signal. We supposed that there was a fast internal interconversion between $\text{Re}(\text{I})[(\text{OPPh}_3)\text{Re}(\text{NO})_2(\text{Cl})_3]$ and $\text{Re}(\text{III})[(\text{OPPh}_3)\text{Re}(\text{NO})(\text{NO}^-)(\text{Cl})_3]$ in which the switch between NO linear and NO bent brought to a modification of the oxidation state of the metal. This mechanism could have been triggered by the three Cl bound to the Re that donated electron density to the latter through their lone-pair electrons that interacted with the d orbitals of the metal.⁴³ In the complex **3** all the d orbitals $d_{x^2-y^2}$ and d_{z^2} available for a bond were already full and there were no other free orbitals with proper geometry that could have been used to accommodate the π -electrons. Then, the presence of these π -electrons created a destabilization named “filled–filled” interaction. The two NOs bound to the Re, being π -acid ligands, helped the metal reducing the filled–filled interaction through a push–pull mechanism. The NOs did that accepting the electrons coming from the d_{xz} metal orbital in their π^* -orbital.⁴⁴ As anticipated above, we believe that in our case the extent of the electron-transfer was such that the NO got a nega-

tive charge forming species as for instance the $\text{Re}(\text{III})[(\text{OPPh}_3)\text{Re}(\text{NO}^+)(\text{NO}^-)(\text{Cl})_3]$ that are in a fluxional equilibrium with the $\text{Re}(\text{I})[(\text{OPPh}_3)\text{Re}(\text{NO})_2(\text{Cl})_3]$. The reactivity of the N holding the negative charge toward the IMes was then higher than in a linear NO. This particularly would account for the unique reaction pattern that the NO and the IMes followed and that yielded **4**.

Conclusions

In this paper, we presented the reaction of **1** with NO gas that in the presence of CH_3COOH brings to the serendipitous synthesis of the unknown complex **3** together with the expected complex **2**. Then, we found that **3** reacts with a bulky carbene (IMes) to yield the stable oximate– $\text{Re}(\text{III})$ complex **4**, while **2** is inert toward the carbene in the same reaction conditions. Since the DFT calculations excluded the formation in solution of both dimeric NO complexes and η^2 NO complexes, we concluded that the IMes reacted with a bent NO. The reactivity of the NO toward the IMes is probably due to an internal fluxional process in which the NO passes continuously from linear to bent, triggered by the π -electrons given by the three Cl to the Re through the mesomeric effect.

Author contributions

OB performed the X-ray diffraction analyses, the structure determinations and run the DFT calculations. GG conceived the project, synthesized all the complexes cited in this work and crystalized them, performed all the experiments, wrote the original draft, reviewed and edited it.

Conflicts of interest

There are no conflicts to declare.

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