

# Mild N–O Bond Cleavage Reactions of a Pyramidalized Nitrosyl Ligand Bridging a Dimolybdenum Center.

M. Angeles Alvarez, M. Esther García, Daniel García-Vivó, Miguel A. Ruiz,\* and Adrián Toyos.

Departamento de Química Orgánica e Inorgánica / IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain.

Supporting Information Placeholder

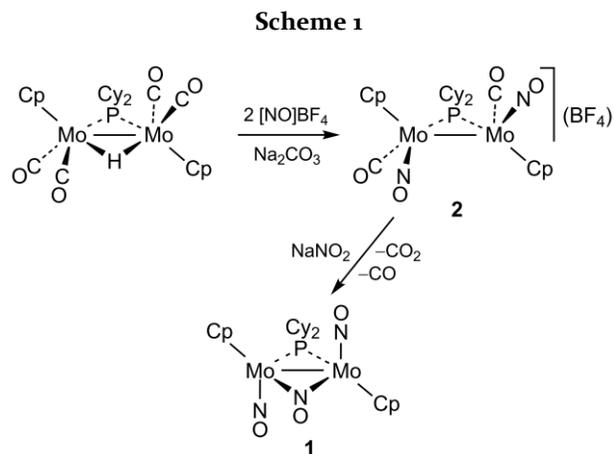
Complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-NO})(\text{NO})_2]$  (**1**) was prepared by reacting  $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_4]$  with 2 equiv of  $[\text{NO}]\text{BF}_4$ , then treating the resulting product  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{NO})_2](\text{BF}_4)$  with  $\text{NaNO}_2$  at 323 K, and it was shown to display a bridging nitrosyl ligand with significant pyramidalization at the N atom, a circumstance related to an unusual behavior concerning degradation of the bridging nitrosyl. Indeed, complex **1** reacts with  $\text{HBF}_4 \cdot \text{OEt}_2$  to give the nitroxyl-bridged derivative  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-}\kappa^1\text{-}\eta^2\text{-HNO})(\text{NO})_2](\text{BF}_4)$ , is reduced by  $\text{Zn}(\text{Hg})$  in the presence of trace  $\text{H}_2\text{O}$  to give the amido complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-NH}_2)(\text{NO})_2]$ , and reacts with excess  $\text{P}(\text{OPh})_3$  to give the phosphoraninato-bridged derivative  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)\{\mu\text{-NP}(\text{OPh})_3\}(\text{NO})_2]$ .

The chemistry of metal nitrosyl complexes is a subject of interest not only because of the great versatility of the NO molecule as a ligand,<sup>1</sup> but also because the latter molecule has relevant activity in living organisms associated to its interaction with different metal centers,<sup>1,2</sup> while being at the same time a major atmospheric pollutant requiring catalytic abatement, a process also relying on the interaction of NO with metal atoms.<sup>1,3,4</sup> The latter has been much studied over the last decades, mostly on heterogeneous systems that typically catalyze the reduction (with CO,  $\text{NH}_3$ , hydrocarbons, etc) or decomposition of nitric oxide. Yet, the quest for more efficient, cheaper and durable catalysts continues.<sup>4</sup> In this context, finding new ways of activation and cleavage of the strong N–O bond of the nitric oxide molecule when bound to metal centers remains a target worthy of attention.

Recently, we isolated and characterized spectroscopically the trinitrosyl complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-NO})(\text{NO})_2]$  (**1**), a side product (9%) formed in the reaction of the unsaturated compound  $[\text{Mo}_2\text{Cp}_2(\mu\text{-CH}_2\text{Ph})(\mu\text{-PCy}_2)(\text{CO})_3]$  with  $\text{NO}$ .<sup>5</sup> Compound **1** is a 34-electron complex for which a single metal–metal bond should be formulated, and is devoid of any particularly chromogenic ligand; therefore, it would be expected to display a color in the red to yellow range, as it is the case of the isoelectronic dinitrosyl complexes  $[\text{W}_2\text{Cp}_2(\mu\text{-PPh}_2)_2(\text{NO})_2]$ ,<sup>6</sup> and related molecules.<sup>7</sup> Surprisingly, however, compound **1** turned to be a dark blue material both in solution and in the solid state. We wondered whether such unexpected color could be originated from any unanticipated structural feature, and whether this circumstance in turn could lead to unexpected chemical properties. Thus we

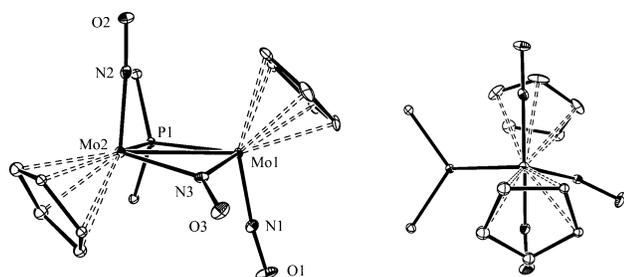
sought for a high-yield route to this trinitrosyl complex, so we could explore in more detail its structure and reactivity. As shown below, compound **1** displays a bridging nitrosyl ligand with significant pyramidalization at the N atom, a circumstance that seems to be related with an unusual chemical behavior involving, *inter alia*, easy activation and cleavage of its N–O bond under mild conditions, with this in turn providing access to complexes having new ligands or new coordination modes of nitrosyl-derived ligands.

Compound **1** can be conveniently prepared *via* a two-step procedure first involving reaction of complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_4]$ <sup>8</sup> with 2 equiv of  $[\text{NO}]\text{BF}_4$  in  $\text{CH}_2\text{Cl}_2$ , in the presence of  $\text{Na}_2\text{CO}_3$  to remove the hydride ligand. This gives the cationic dinitrosyl  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{NO})_2](\text{BF}_4)$  (**2**), which is then decarbonylated upon reaction with  $\text{NaNO}_2$  in warm tetrahydrofuran (323 K), to render the trinitrosyl **1** with 63% overall yield (Scheme 1).<sup>9</sup>



Dark blue crystals of **1**·1/2 $\text{CH}_2\text{Cl}_2$  were grown from  $\text{CH}_2\text{Cl}_2$  solutions of the complex. As anticipated from spectroscopic data, the molecule of **1** is built from two  $\text{MoCp}(\text{NO})$  moieties arranged in a transoid disposition and connected through a single metal–metal bond (2.8935(3) Å), and bridging  $\text{PCy}_2$  and nitrosyl ligands (Figure 1). The latter groups define a somewhat puckered  $\text{Mo}_2\text{PN}$  central skeleton (P–Mo–Mo–N ca.  $164^\circ$ ) so the terminal nitrosyls are not strictly antiparallel. However, the salient feature in this structure concerns the bridging nitrosyl ligand, which exhibits significant pyramidalization at the N atom (average Mo–Mo–N–O ca.  $163.5^\circ$ ), instead of the expected trigonal planar environment. A search at the Cambridge Structural Database revealed that only a few other complexes have been found previously with

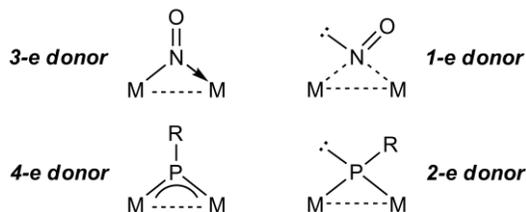
such a distortion (5 examples with av. M–M–N–O < 165°),<sup>10</sup> but no attention seems to have been paid to it.



**Figure 1.** ORTEP diagram (30% probability) of compound **1** (left) with H atoms and Cy groups (except their C<sup>1</sup> atoms) omitted, and its projection along the Mo–Mo bond (right). Selected bond lengths (Å) and angles (°): Mo1–Mo2 = 2.8935(3); Mo1–N1 = 1.784(2); Mo1–N3 = 2.031(2); Mo2–N2 = 1.798(2); Mo2–N3 = 2.018(2); N–O = 1.227(3). Mo1–Mo2–N2 = 88.9(1); Mo2–Mo1–N1 = 105.4(1).

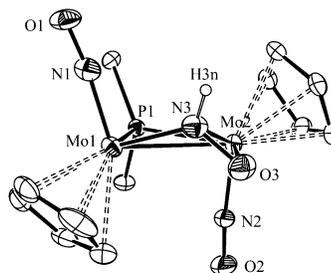
To rule out crystal forces as a possible origin of the distorted geometry of **1** we carried out DFT calculations on the isolated molecule,<sup>11</sup> and found a geometry very similar to the one in the crystal (Mo–Mo–N–O = 170.6° for the bridging NO). Interestingly, a structure with a bridging nitrosyl forced to a planar environment around the N atom (**1F**) was computed to have a nearly flat Mo<sub>2</sub>PN central skeleton and to be some 12 kJ/mol less stable (see the SI). Since the structures of several isoelectronic derivatives of **1** to be discussed below display flat Mo<sub>2</sub>PN central skeletons, we conclude that the structural distortion in **1** has an electronic (rather than steric) origin. An analysis of the atomic charges indicates that the distorted structure concentrates a slightly higher negative charge at the pyramidalized N atom, when compared to the undistorted structure **1F**. Thus, we might view the nitrosyl distortion of **1** as one dissipating some electron density from a relatively electron-rich dimetal center. Taken to its extreme, such a distortion should end up with a N atom bearing a lone electron pair and effectively contributing with two less electrons to the dimetal center. This sort of ambivalence, well known for terminal nitrosyl ligands,<sup>10,12</sup> seems to be unreported for bridging nitrosyls, but is well established in the chemistry of bridging phosphinidene ligands (Chart 1).

**Chart 1**



The chemical behavior of **1** reveals considerable nucleophilicity at the N atom of the bridging NO. Indeed, **1** is readily protonated at this site upon reaction with HBF<sub>4</sub>·OEt<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution, to give the nitroxyl-bridged derivative [Mo<sub>2</sub>Cp<sub>2</sub>(μ-PCy<sub>2</sub>)(μ-κ<sup>1</sup>:η<sup>2</sup>-HNO)(NO)<sub>2</sub>](BF<sub>4</sub>) (**3**),<sup>9</sup> instead of the hydroximido complex that would have been expected from protonation at the O site.<sup>10,13</sup> An X-ray study of **3** confirmed the presence in the cation of a nitroxyl ligand bridging two metal atoms in an alkenyl-like, κ<sup>1</sup>:η<sup>2</sup> fashion (Figure

2), this resulting in a substantial weakening of the N–O bond, as judged from the corresponding length of 1.348(6) Å, significantly longer than the values of ca. 1.20 Å found in mononuclear complexes bearing this ligand N-bound to a single metal atom.<sup>14</sup> We note that no nitroxyl-bridged complexes have been characterized previously.



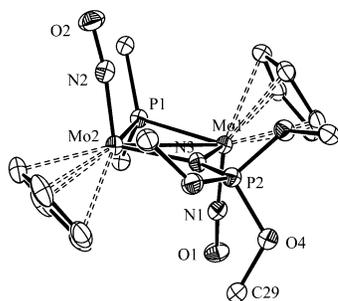
**Figure 2.** ORTEP diagram (30% probability) of the cation in compound **3** with most H atoms and Cy groups (except their C<sup>1</sup> atoms) omitted. Mo1–Mo2 = 2.9995(5); Mo1–N3 = 2.007(4); Mo2–N3 = 2.193(5); Mo2–O3 = 2.092(4); N3–O3 = 1.348(6).

Surprisingly, the electron-rich complex **1** is easily reduced in a number of ways, all of them involving the cleavage of the N–O bond of the bridging nitrosyl. For instance, reaction with Zn(Hg) proceeds smoothly at 293 K in tetrahydrofuran to give the amido derivative [Mo<sub>2</sub>Cp<sub>2</sub>(μ-PCy<sub>2</sub>)(μ-NH<sub>2</sub>)(NO)<sub>2</sub>] (**4**).<sup>9</sup> Although **4** is isoelectronic with **1**, it displays a bright yellow color (rather than blue), so a significant structural difference between these two molecules must exist. Indeed, an X-ray study revealed that the molecule of **4** is made up from two transoid MoCp(NO) fragments bridged by PCy<sub>2</sub> and NH<sub>2</sub> ligands that now define an almost planar Mo<sub>2</sub>PN central core (P–Mo–Mo–N = 177.3°, Figure S1). As a result, the terminal nitrosyls are now antiparallel and the intermetallic length is a bit shorter (2.8654(8) Å).

The N-bound H atoms in **4** likely come from trace water present in the solvent, since on-purpose addition of H<sub>2</sub>O to the reaction solvent increases the yield of **4**.<sup>9</sup> A related NO to NH<sub>2</sub> transformation has been previously reported for the dichromium complex [Cr<sub>2</sub>Cp<sub>2</sub>(μ-NO)<sub>2</sub>(NO)<sub>2</sub>], but this required the use of strong hydride donors and was of poor selectivity.<sup>15</sup> More interestingly, we found that **4** also was formed slowly as the unique organometallic product upon reaction of **1** with CO (40 atm) in toluene at 353 K, thus suggesting that even very mild reducing agents might trigger an N–O cleavage at the bridging nitrosyl. Prompted by this observation, we then examined reactions with P donors and found that **1** is reactive towards several phosphites. For instance, its reaction with a 10-fold excess of P(OPh)<sub>3</sub> in refluxing toluene was completed in 6 h to give the phosphoraniminato-bridged derivative [Mo<sub>2</sub>Cp<sub>2</sub>(μ-PCy<sub>2</sub>)(μ-NP(OPh)<sub>3</sub>)(NO)<sub>2</sub>] (**5**) as major product,<sup>9</sup> along with smaller amounts of **4**, the latter obviously arising from a side-reaction with trace water in the medium. Indeed, on-purpose addition of water to the solvent increased the relative amount of **4**, although did not suppress the formation of **5**. Since water alone did not react with **1** in refluxing toluene, it has to be concluded that the phosphite acts as an oxygen acceptor in this reaction (indeed P(O)(OPh)<sub>3</sub> is present in the final reaction mixture), to give an undetected nitrido-bridged intermediate that would add a second phosphite molecule to build the phosphoraniminato complex **5**. To our

knowledge, related nitrosyl transformations have been only described so far in reactions of mononuclear complexes with phosphines.<sup>1a</sup>

An X-ray study of **5** (Figure 3) confirmed the presence of a phosphoraniminato ligand (P–N = 1.515(3) Å) symmetrically bridging the dimetal center through its N atom and defining a nearly flat Mo<sub>2</sub>PN core comparable to the one found in the amido complex **4**. We should remark that **5** seems to be the first isolated complex with a X<sub>3</sub>P=N<sup>−</sup> ligand bearing alkoxy substituents. Recently, a mononuclear iron(IV) nitride complex was reported to react with phosphites to give the corresponding phosphoraniminato derivatives, although these products were not actually isolated.<sup>16</sup>



**Figure 3.** ORTEP diagram (30% probability) of compound **5** with H atoms and Cy and Ph groups (except their C<sup>1</sup> atoms) omitted. Mo1–Mo2 = 2.8778(4); Mo1–N3 = 2.131(3); Mo2–N3 = 2.104(3); N3–P2 = 1.515(3). Mo1–Mo2–N2 = 101.9(1); Mo2–Mo1–N1 = 96.0(1).

In summary, we have shown that compound **1** displays a bridging nitrosyl ligand with substantial pyramidalization at the N atom, likely to drain electron density away from the dimetal center, and this increases the basicity of this ligand at the N site and its ability to transfer its oxygen atom to even mild reducing reagents, whereby unusual transformations of the bridging nitrosyl take place under mild conditions. Further work to explore in more detail the chemistry of **1**, as well as that of electron-richer related complexes, is now in progress.

## ASSOCIATED CONTENT

### Supporting Information

A PDF file containing preparative and spectroscopic data for new compounds, and details of DFT calculations. CCDC 1429198–1429201 contain the crystallographic data for compounds **1**, **3**, **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\* E-mail: [mara@uniovi.es](mailto:mara@uniovi.es).

### Notes

The authors declare no competing financial interests.

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## SYNOPSIS TOC

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