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Mild N−O Bond Cleavage Reactions of a Pyramidalized Nitrosyl Ligand Bridging a Dimolybdenum Center

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Supporting Information

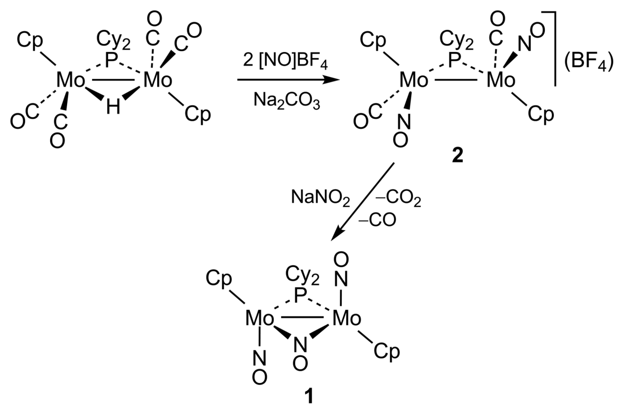
ABSTRACT: Complex $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$ (**1**) was prepared by reacting $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ with 2 equiv of $[NO]BF_4$ and then treating the resulting product $[Mo_2Cp_2(\mu\text{-}PCy_2)(CO)_2(NO)_2](BF_4)$ with $NaNO_2$ at 323 K, and it 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 $HBF_4{\cdot}OEt_2$ to give the nitroxyl-bridged derivative $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}\kappa^1{:}\eta^2\text{-}HNO)(NO)_2](BF_4)$, is reduced by Zn(Hg) in the presence of trace H_2O to give the amido complex $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NH_2)(NO)_2]$, and reacts with excess $P(OPh)_3$ to give the phosphoraniminato-bridged derivative $[Mo_2Cp_2(\mu\text{-}PCy_2)\{\mu\text{-}NP(OPh)_3\}(NO)_2]$.

The chemistry of metal nitrosyl complexes is a subject of interest not only because of the great versatility of the nitric oxide (NO) molecule as a ligand[1] but also because the latter molecule has relevant activity in living organisms associated with its interaction with different metal centers,[1,2] while at the same time being a major atmospheric pollutant requiring catalytic abatement, a process also relying on the interaction of NO with metal atoms.[1,3,4] The latter has been much studied over the last decades, mostly on heterogeneous systems that typically catalyze the reduction (with CO, NH_3, hydrocarbons, etc.) or decomposition of NO. Yet, the quest for more efficient, cheaper, and durable catalysts continues.[4] In this context, finding new ways of activation and cleavage of the strong N−O bond of the NO molecule when bound to metal centers remains a target worthy of attention.

Recently, we isolated and characterized spectroscopically the trinitrosyl complex $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$ (**1**), a side product (9%) formed in the reaction of the unsaturated compound $[Mo_2Cp_2(\mu\text{-}CH_2Ph)(\mu\text{-}PCy_2)(CO)_2]$ with NO.[5] 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 is expected to display a color in the red-to-yellow range, as is the case of the isoelectronic dinitrosyl complexes $[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$[6] and related molecules.[7] Surprisingly, however, compound **1** is dark blue both in solution and in the solid state. We wondered whether such an unexpected color originated from an unanticipated structural feature and whether this circumstance, in turn, could lead to unexpected chemical properties. Thus, we sought 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 to 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 involving the reaction of complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$[8] with 2 equiv of $[NO]BF_4$ in CH_2Cl_2, in the presence of Na_2CO_3 to remove the hydride ligand. This gives the cationic dinitrosyl $[Mo_2Cp_2(\mu\text{-}PCy_2)(CO)_2(NO)_2](BF_4)$ (**2**), which is then decarbonylated upon reaction with $NaNO_2$ in warm tetrahydrofuran (THF; 323 K), to render the trinitrosyl **1** with 63% overall yield (Scheme 1).[9]

Scheme 1



Dark-blue crystals of $\mathbf{1}{\cdot}{}^1/_2CH_2Cl_2$ were grown from CH_2Cl_2 solutions of the complex. As anticipated from spectroscopic data, the molecule of **1** is built from two MoCp(NO) moieties arranged in a transoid disposition, connected through a single metal−metal bond [2.8935(3) Å], and bridging PCy_2 and nitrosyl ligands (Figure 1). The latter groups define a somewhat puckered Mo_2PN central skeleton (P−Mo−Mo−N ca. 164°) so the terminal nitrosyls are not strictly antiparalell. 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°), instead of the expected

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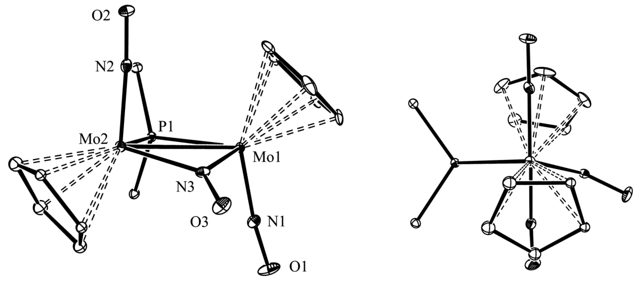
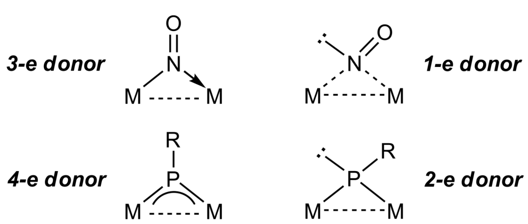


Figure 1. ORTEP diagram (30% probability) of compound **1** (left) with H atoms and Cy groups (except their C[1] atoms) omitted and its projection along the Mo−Mo bond (right). Selected bond lengths (Å) and angles (deg): Mo1−Mo2 = 2.8935(3); Mo1−N1 = 1.784(2); Mo1−N3 = 2.031(2); Mo2−N2 = 1.798(2); Mo2−N3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

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 (five examples with average M−M−N−O < 165°),[10] but no attention seems to have been paid to it.

To rule out crystal forces as a possible origin of the distorted geometry of **1**, we carried out density functional theory (DFT) calculations on the isolated molecule[11] 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 into a planar environment around the N atom (**1F**) was computed to have a nearly flat Mo_2PN central skeleton and to be some 12 kJ/mol less stable (see the Supporting Information). Because the structures of several isoelectronic derivatives of **1** to be discussed below display flat Mo_2PN central skeletons, we conclude that the structural distortion in **1** has an electronic (rather than steric) origin. Analysis of the atomic charges indicates that the distorted structure concentrates a slightly higher negative charge at the pyramidalized N atom 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,[1a,12] 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 $HBF_4 \cdot OEt_2$ in CH_2Cl_2 solution to give the nitroxyl-bridged derivative $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}\kappa^1{:}\eta^2\text{-HNO})(NO)_2](BF_4)$ (**3**),[9] instead of the hydroximido complex that would have been expected from protonation at the O site.[1a,13] An X-ray study of **3** confirmed the presence in the cation of a nitroxyl ligand bridging two metal atoms in an alkenyl-like, $\kappa^1{:}\eta^2$ fashion (Figure 2), resulting in a substantial

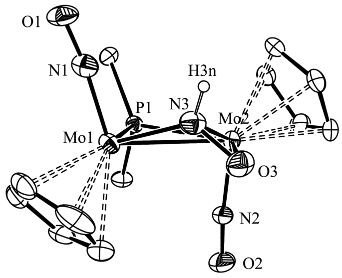


Figure 2. ORTEP diagram (30% probability) of the cation in compound **3** with most H atoms and Cy groups (except their C[1] atoms) omitted. Selected bond lengths (Å) and angles (deg): Mo1−Mo2 = 2.9995(5); Mo1−N3 = 2.007(4); Mo2−N3 = 2.193(5); Mo2−O3 = 2.092(4); N3−O3 = 1.348(6).

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.[14] We note that no nitroxyl-bridged complexes have been characterized previously.

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 THF to give the amido derivative $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NH_2)(NO)_2]$ (**4**).[9] 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_2 and NH_2 ligands that now define an almost planar Mo_2PN 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 because the on-purpose addition of H_2O to the reaction solvent increases the yield of **4**.[9] A related NO-to-NH_2 transformation has been previously reported for the dichromium complex $[Cr_2Cp_2(\mu\text{-}NO)_2(NO)_2]$, but this required the use of strong hydride donors and was of poor selectivity.[15] 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 toward several phosphites. For instance, its reaction with a 10-fold excess of $P(OPh)_3$ in refluxing toluene was completed in 6 h to give the phosphoraniminato-bridged derivative $[Mo_2Cp_2(\mu\text{-}PCy_2)\{\mu\text{-}NP(OPh)_3\}(NO)_2]$ (**5**) as a major product,[9] along with smaller amounts of **4**, the latter obviously arising from a side reaction with trace water in the medium. Indeed, the on-purpose addition of water to the solvent increased the relative amount of **4**, although it did not suppress the formation of **5**. Because 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 $P(O)(OPh)_3$ 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

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Inorg. Chem. XXXX, XXX, XXX−XXX

nitrosyl transformations have only been described so far in reactions of mononuclear complexes with phosphines.[1a]

An X-ray study of **5** (Figure 3) confirmed the presence of a phosphoraniminato ligand [P−N = 1.515(3) Å] symmetrically

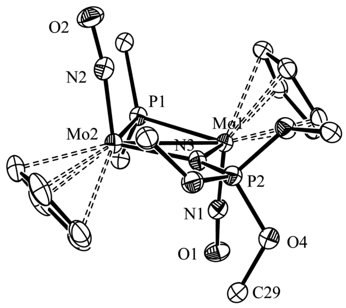

Figure 3. ORTEP diagram (30% probability) of compound **5** with H atoms and Cy and Ph groups (except their C^1 atoms) omitted. Selected bond lengths (Å) and angles (deg): Mo1−Mo2 = 2.8778(4); Mo1−N3 = 2.131(3); Mo2−N3 = 2.104(3); N3−P2 = 1.515(3); Mo1−Mo2−N2 = 101.9(1); Mo2−Mo1−N1 = 96.0(1).

bridging the dimetal center through its N atom and defining a nearly flat Mo_2PN 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 $X_3P{=}N^-$ 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.[16]

In summary, we have shown that compound **1** displays a bridging nitrosyl ligand with substantial pyramidalization at the N atom, likely to drain some 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 O 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02292.

Preparative and spectroscopic data for new compounds and details of DFT calculations (PDF)

CCDC 1429198−1429201 containing crystallographic data for compounds **1** and **3**−**5** (CIF)

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Notes

The authors declare no competing financial interest.

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(9) The Supporting Information (SI) contains details of the synthesis, analytical, spectroscopic, and crystallographic data of complexes **1**−**5**.

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