Activation of Molecular Oxygen by a Molybdenum(IV) Imido Compound

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Supporting Information Placeholder

ABSTRACT: Activation of molecular dioxygen at a Mo(IV) imido compound led to the isolation and full characterization of a remarkably stable transition metal imido peroxydo complex.

The use of molecular oxygen as the primary oxidant in oxidation reactions is of fundamental interest in view of the urgent desire for the development of green chemical processes. At present, there is a growing interest in finding alternatives to precious metals, mainly for economic and environmental reasons. Molybdenum, being a non-precious, earth-abundant, non-toxic metal represents an ideal candidate for abovementioned task, as evident from the widespread use of Mo compounds in oxygenation chemistry. We have previously investigated high oxidation state molybdenum complexes with various O,N ligands for the catalytic oxidation of olefins. However, to date, the facilitation of molecular oxygen as oxidant remains elusive. Whereas the activation of molecular oxygen by molybdenum(IV) complexes has been established by our group and others, concomitant oxygen atom transfer is restricted to very few substrates.

All molybdenum complexes capable of activating molecular oxygen are of the general structure [MoO[Lα]2] and lead to the formation of [MoO(O)n][Lα] complexes, with Lα being either CN− or bidentate monoanionic ligands. The oxido ligand renders the metal center electron poor, thus leading to strong σ-bonds but simultaneously inhibiting any π-backbonding to the peroxido unit. In theory, such backbonding marks an important contribution to weaken the peroxide O-O bond. For this reason, we envisioned to exchange the “spectator” oxido ligand with an electron donating imido group to leave more electron density at the metal to increase π-backbonding, possibly enabling the transfer of the peroxido oxygen atoms.

In contrast to oxido peroxydo complexes, which are usually easily accessible via the reaction of MoO3 with H2O2 and appropriate ligand addition, the substance class of imido peroxydo complexes is so far only accessible via molecular oxygen activation and has not been described.

Generally, no transition metal complex bearing an imido and a peroxydo ligand has been disclosed to date. Herein, we present the synthesis of the first molybdenum(VI) imido peroxydo complex and the full characterization of all involved species by experimental and theoretical means. Furthermore first studies on the reactivity of this species are reported, obtaining valuable insight into the electronic influence on the bonding situation at the molybdenum center.

The oxido imido complexes [MoO(NtBu)(L1)], 1a and 1b, were prepared by reacting [MoO(NtBu)Cl(dme)]22–24 with the respective iminophenolate ligands H1L1 (R= Me) or H1L2 (R= tBu),26 as shown in Scheme 1.

NMR spectroscopic data of 1a and 1b reveals the presence of two isomers in solution (Scheme 1), reminiscent of previously reported dioxido molybdenum compounds. The N,N isomer (referring to the atoms in trans position to oxido and imido ligand) is typically the dominant form and the N,O isomer is primarily formed due to increasing steric congestion. Theoretical calculations reveal the N,N isomer being energetically favored by only 1.6 kcal/mol in the case of 1a, corroborating the isomeric equilibrium. Interestingly, single-crystal X-ray diffraction analysis reveals that the two compounds crystallized in different isomeric arrangements; in the case of 1a the putative minor isomer in solution crystallized (Figures S17 and S18, SI).

Scheme 1. Synthesis of molybdenum(VI) precursors 1a and 1b.
Two-electron reduction with PMe₃ generates the phosphane-coordinated molybdenum(IV) imido complexes [Mo(N₄Bu)(PMe₃)(L)]: (1a, R = Me and 2b, R = tBu), while no reaction was observed with the bulky phosphane PPh₃ (Scheme 2).

Proton NMR spectroscopy revealed the expected isomeric mixture for compound 2b (approx. 60:40), whereas only one isomer was observed for complex 2a. The isomerically pure complex 2a, equipped with the 2,6-dimethyl substituted phenolate ligands, subsequently reacted cleanly with molecular O₂ to form the desired molybdenum(VI) imido peroxido compound [Mo(N₄Bu)(1a)]₃. Although complex 2b was also reactive towards dioxygen, significant decomposition was observed during the reaction, which prevented a clean isolation of the respective peroxido species. For complex 3a, only one isomer was observed via NMR spectroscopy, and single-crystal X-ray diffraction analysis of the compound identified the isomeric form as the O,O arrangement. This is in good agreement with previously reported iminophenolate oxido peroxido compounds, where it has been observed that oxygen atom transfer is always concomitant to an isomeric rearrangement. Such a rearrangement is likely hampered by the additional sterically demanding tBu groups at the aromatic rings in 2b, thus preventing a clean reaction. Interestingly, the reduction of a pyrrol imine based oxido imido complex with PMe₃ cleanly led to an isomerically pure compound with retained stereochemistry during the OAT step.

IR spectroscopy reveals the Mo=O bands for 1a and 1b at 878 (calc.: 902, Figure S19, S1) and 890 cm⁻¹, respectively, which is 20-30 wavenumbers lower in energy compared to stretching frequencies observed for previously reported Mo oxido imido compounds. This corroborates a weakened Mo=O bond, as also observed by X-ray crystallography (vide infra). The ν(O=O) band in 3a is observed at 924 cm⁻¹ (calc.: 1007, Figure S20, S1), comparable to other weakly activated (O-O) bonds in transition metal peroxides. The ν(O=O) band for the related oxido peroxido complex [MoO(O⁻-O)(L)₂], is assigned at 927 cm⁻¹, in agreement with the virtually identical stretching frequencies computed for 3a and 3a’ (calc. for 3a’: 1005 cm⁻¹, Figure S21, S1), suggesting that the donating nature of the imido ligand does not lead to the envisioned n-backbonding.

Peroxido complex 3a reacts with PMe₃ as limiting reactant (0.25 equiv), slowly leading to a mixture of 1a and unreacted 3a (Scheme 3). This is in contrast to the related oxido peroxido compound where the higher reactivity of the dioxido compound prevented its observation during OAT. However, addition of a further equivalent of PMe₃ to the above mixture led to the expected mixture of 3a and [Mo(N₄Bu)(PMe₃)(L)]: 2a (Scheme 3).

This suggests a similar but generally lower reactivity of the imido peroxido system. Presumably for this reason, complexes 1a and 1b, [MoO(N₄Bu)(L)]: both were essentially inactive under catalytic conditions, which is in contrast to the dioxido analogue [MoO₂(L)₂]:. This may be attributed to the remarkable stability of the corresponding peroxides towards reduction. Furthermore, we did not observe a transfer of the imido group to the phosphane substrate for 1a, 1b or the peroxide 3a, suggesting that the imido transfer reaction is also energetically disfavoured.

Oxygen atom transfer to bulkier phosphanes or more challenging substrates as alkenes was not successful, the latter being in line with previous observations. Single-crystal X-ray diffraction analysis of 3a reveals similar geometric features to previously described dioxido and oxido peroxido complexes. In general, the more electron donating imido group leads to a slight elongation of Mo=O as well as Mo-(O-O) bonds in comparison to a second oxido ligand, reflecting weaker σ-bonds to the less electrophilic metal center (Table 1). The O-O bond lengths on the other hand are essentially identical (1.4399(17) in 3a vs. 1.4425(18) in 5), further corroborating an absent n-backbonding to the peroxido unit.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>1a</th>
<th>1b</th>
<th>3a</th>
<th>4′</th>
<th>5′</th>
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<tr>
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<td>1.7198(18)</td>
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<td>1.707(3), 1.706(3)</td>
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<tr>
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<td>1.739(2)</td>
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<tr>
<td>Mo-O-O</td>
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<td>-</td>
<td>1.9764(13), 1.9754(13)</td>
<td>1.9581(13), 1.9301(13)</td>
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<tr>
<td>O-O</td>
<td>-</td>
<td>-</td>
<td>1.4399(17), 1.4425(18)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 1. Molecular view (50% probability level) of imido peroxido species 3a; H atoms as well as solvent molecules are omitted for clarity reasons, bonds incorporated in the peroxido moiety are depicted in red.
Comparison of the molecular structures of the [MoO(NBu)L2] complexes 1a and 1b (Figures S17 and S18, SI) revealed a further interesting observation as their geometric arrangement in solid state is different, namely N,O in 1a and N,N in 1b. This corroborates previous postulations about the two isomeric forms of related molybdenum dioxide complexes.\textsuperscript{7,16}

The geometries and electronic structures of the imido complexes 1a and 3a were investigated by means of DFT/PBE0 calculations.\textsuperscript{32,33} For comparison reasons, such calculations were also executed for a corresponding oxido derivative 3a' of the structure [MoO(η²-O*)(L1)]. Theoretical details can be found in the supporting information. The optimized structures of complexes 1a (2 isomeric forms), 3a and 3a' as well as the corresponding frontier orbitals of 3a and 3a' are provided in Figures 2 and S22-S24 (SI), respectively. The pattern of the orbitals obtained is typical of Mo(VI) d\textsuperscript{5} complexes with a pseudo-octahedral geometry, i.e., all five d-orbitals are essentially empty. Comparison of the orbital geometries and energies of the two systems reveals that all d-orbitals other than the "z²" orbital, are lower in energy and thus more accessible in the oxido peroxido compound 3a'. Furthermore, in the imido complex 3a, only the "xy" orbital shows significant mixing with the peroxido ligand orbitals whereas in 3a' all orbitals except the "z²" orbital are partially localized at the peroxide (Figures 2, S23 and S24). Both observations are in good agreement with the pronounced stability of compound 3a towards reduction. With respect to the atomic charges (NPA population analysis)\textsuperscript{34–38} it is evident that the imido ligand in 3a is a significantly better electron donor, establishing a stronger coordination and providing an electron richer metal center compared to the oxido ligand in 3a' (Wiberg indices\textsuperscript{39} are 1.99 for the Mo=O(Imide) bond in 3a and 1.85 for the Mo=O bond in 3a'). This is also reflected by the metal charges which are 1.42 (3a) and 1.64 (3a'), as well as the corresponding ligand charges (-0.11 for the imido and -0.46 for the oxido ligand, respectively).

In conclusion, the first transition metal imido peroxydo complex is conveniently accessible via molecular oxygen activation at a molybdenum(IV) imido precursor. The complex has been fully characterized by spectroscopic means and theoretical considerations. Single crystal X-ray diffraction analysis as well as theoretical calculations both shows a larger electron donation by the imido ligand in comparison to an oxido moiety that leads to a less electrophilic metal center and thus weaker σ-bonds to the peroxy ligand.

However, the increased electron density is insufficient to facilitate π-backbonding to the peroxy unit in order to weaken the O-O bond. While it is possible that the low reactivity of the system is ultimately also a result of steric congestion, the observations presented herein clearly suggest that the weaker Mo-O σ-bonds do not have a positive effect on the ability to transfer the peroxy oxygen. The envisioned π-backbonding to the peroxy unit could not be realized by the larger electron density at the metal center, in contrary, the lower electrophilicity actually hampers the reduction step from Mo(VI) to Mo(IV) by raising the frontier orbital energies. A feasible method to enhance reactivity might be to make the metal center even more electropositive, e.g. by the incorporation of electron withdrawing groups in the ligands, a matter which is currently under investigation. The results presented herein provide for the first time very important information about the properties of imido supported peroxydo complexes and offer new directions for future ligand and complex design, also for the stabilization of notoriously unstable transition metal peroxides.

ASSOCIATED CONTENT
Supporting Information
Supporting Information (SI) available: Experimental, crystallographic and theoretical details. The Supporting Information is available free of charge on the ACS Publications website. CCDC 1560457-1560459 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes
The authors declare no competing financial interests.

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Figure 2. DFT/PBE0 calculated frontier orbital pattern for 3a and 3a', energy values in electron volts (left); calculated "x²-y²" orbitals of 3a and 3a' showing the different orbital localization at the peroxydo unit (right).
and PPh conditions but without catalysts led to conversions <5% for both PMe-atm) in C6 of 0.9536, according to literature.


**Synopsis.** Activation of molecular dioxygen at a Mo(IV) imido compound led to the isolation and full characterization of a remarkably stable transition metal imido peroxido complex.