Oxygen activation and catalytic aerobic oxidation by Mo(IV)/(VI) complexes with functionalized iminophenolate ligands
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Niklas Zwettler, Martina E. Judmaier, Lara Strohmeier, Ferdinand Belaj and Nadia C. Mösch-Zanetti*

Synthesis of molybdenum(IV) dioxido complexes 1–3, coordinated by one or two functionalized iminophenolate ligands HL1 or HL2, bearing a donor atom side chain or a phenyl substituent, respectively, allowed for systematic investigation of the oxygen atom transfer (OAT) reactivity of such complexes towards phosphines. Depending on stoichiometry and employed phosphane (PMe3 or PPh3), different molybdenum(IV) and molybdenum(VI) complexes 4–7 were obtained. Whereas molybdenum(IV) complexes 4 and 5, bearing a terminal PMe3 ligand, readily reacted with molecular O2 to form oxido peroxido complexes 8 and 9, phoshane free µ-oxido bridged dinuclear molybdenum(IV) complexes 6 and 7 proved to be stable towards oxidation with molecular O2 under ambient conditions. Single-crystal X-ray diffraction analyses revealed different isomeric structures in the solid state for dioxido complexes 1 and 2 in comparison with oxido phosphane complex 5, dinuclear oxido µ-oxido complex 6 and oxido peroxido complexes 8 and 9, pointing towards an isomeric rearrangement during OAT. Compounds 1 and 2 were furthermore tested for their ability to catalyze the aerobic oxidation of PMe3 and PPh3. A significant difference in catalytic activity has been observed in the oxidation of PMe3, where complex 1 bearing donor atom functionalized ligands led to higher conversion and selectivity than complex 2 coordinated by phenyl iminophenolate ligands. In the oxidation of PPh3, complex 2 leads to higher conversion compared to 1. In a control experiment, phenyl-based dinuclear µ-oxido bridged molybdenum(V) complexes derived from complex 2, was found to be catalytically active, which suggests a lower energy barrier for disproportionation into [MoO–(L)2] and [MoO2(L)2] in comparison with methoxypropylene based compound 6, a prerequisite for subsequent reactivity toward molecular O2.

Introduction

The chemistry of molybdenum, as an abundant and biologically relevant transition metal, has been well established over the course of the past few decades. Especially in biomimetic chemistry, much effort has been made to elucidate and mimic the structure and function of various molybdoenzymes.1 An important class among these enzymes is represented by molybdenum oxotransferases such as DMSO reductase or xanthine oxidase, which contain a molybdenum(VI) metal center coordinated by an oxido ligand, as well as depending on the enzyme, one or two molybdopterin ligands.2 These oxotransferases catalyze oxygen atom transfer reactions via a molybdenum(IV)/molybdenum(VI) redox cycle.3 Whereas early modelling approaches for the corresponding active sites focused on sulfur rich dithiolene ligands, several other structurally diverse ligand systems have been explored.3,4 The ease of such molybdenum compounds to undergo oxygen atom transfer made them also interesting in industrial applications. Especially for the catalytic oxidation of alkenes to epoxides, several highly efficient systems exist nowadays.5

In general, these catalysts use H2O2 or organic peroxides such as tert-butyl hydroperoxide (TBHP) as terminal oxidants. In our group, Mo(VI) dioxido systems were investigated for their applicability in oxygen atom transfer (OAT) reactions as well as epoxidation catalysis.6–8,9 In that course, iminophenolate based complexes incorporating different functionalities were developed. While amides as internal hydrogen bond donors led to unprecedented C–C and C–N coupling behavior upon coordination,10 the introduction of donor atoms (ether or amine) led to Mo(VI) catalysts for highly selective oxidation of a broad scope of alkene substrates with TBHP.7

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† Electronic supplementary information (ESI) available. CCDC 1476035–1476040 and 1486756. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt01692h
Nevertheless, one of the major drawbacks of to date reported catalysts is the necessity of a terminal oxidant. To develop more sustainable catalytic processes it is of great interest to allow for the use of molecular oxygen and in further consequence air as a benign alternative to other oxidants. Not only is oxygen abundant, cheap and environmentally harmless, its use also reduces the formation of undesired side products.11 Whereas the activation of molecular oxygen has been described and thoroughly investigated for a variety of transition metals (e.g. iron, manganese),12 the number of molybdenum complexes that activate molecular oxygen is very limited. Only a few examples with full structural characterization have been disclosed,13,14 among them two examples are from our group.15,16 In general there are only a few examples of homogeneously catalyzed aerobic oxidation reactions using a Mo catalyst and these are severely hampered by disadvantages such as high catalyst loadings or the need of a co-catalyst.17

Since the number of molybdenum oxido peroxido compounds originating from oxygen activation is scarce, it is important to gain further insight into the electronic and structural parameters affecting the applicability of Mo(IV)/Mo(VI) systems for oxygen atom transfer as well as oxygen activation. Our group has thus an ongoing research interest in the OAT systems coordinated by functionalized iminophenolate ligands.15 Based on diatomic O2 viability, cheap and environmentally harmless, its use also reduces the formation of undesired side products.11 Whereas the activation of molecular oxygen has been described and thoroughly investigated for a variety of transition metals (e.g. iron, manganese),12 the number of molybdenum complexes that activate molecular oxygen is very limited. Only a few examples with full structural characterization have been disclosed,13,14 among them two examples are from our group.15,16 In general there are only a few examples of homogeneously catalyzed aerobic oxidation reactions using a Mo catalyst and these are severely hampered by disadvantages such as high catalyst loadings or the need of a co-catalyst.17

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Results and discussion

Ligand synthesis

Previously published ligands HL1 18 and HL2 19 were prepared using well established synthetic protocols. Briefly, 1.1 equiv. of a primary amine bearing the desired functionality were added to a methanolic solution of 3,5-di-tert-butyl-2-hydroxy-benzaldehyde and stirred overnight at reflux temperature. Whereas HL1 was obtained after evaporation of the solvent as a yellow oil, HL2 was recovered as an orange crystalline solid after filtration (Scheme 1). Their analytic data is in agreement with the literature.18,19

Synthesis of molybdenum dioxido complexes

For the synthesis of molybdenum(VI) complexes of the type [MoO2(L)2], synthetic procedures using [MoO2(acac)2],20 [MoO2Cl2] and [MoO2Cl2(DME)]21 (DME = dimethoxyethane) as metal sources were investigated. A reaction of two equiv. of HL1 and HL2, respectively, with the metal precursors [MoO2Cl2(DME)] and [MoO2Cl2] in the presence of excess NEt3 in toluene, led to the targeted [MoO2(L)2] complexes 1 and 2 in good yields (Scheme 2).

Generally, there are three possible isomers for molybdenum(VI) compounds with a cis dioxido arrangement coordinated by two iminophenolate ligands as depicted in Fig. 1. For complexes 1 and 2, 1H NMR data in CD3OD are consistent with the existence of two isomers in solution. One set of ligand resonances corresponds to isomer A as confirmed by single-crystal X-ray diffraction analysis. In principle also the O,O isomer B would feature one set of resonances but this would require a rotation of both ligands upon crystallization which seems highly unlikely. The non-equivalent ligand arrangement of the second isomer C in solution gives rise to two additional sets of ligand resonances. The ratio of the two isomeric forms is strongly dependent on...
the imine substituent. Whereas in the compound bearing the methoxypropylene-substituted ligands, the N,N form is predominant with a ratio of 3 : 1, in the complex with the phenyl-substituted ligand, the major isomer corresponds to the O,N form with a ratio of 2 : 3 (Scheme 2). In compound 1, the signals for the minor isomer are considerably broadened, as previously observed, whereas no significant broadening is observed in the $^1$H NMR spectrum of 2 at room temperature.

Dissolution of single crystals of 2 and immediate recording of $^1$H NMR spectra led to the same isomeric ratio in several attempts, suggesting a dynamic equilibrium in solution. Subsequent variable temperature $^1$H NMR spectroscopy of complex 2 in C$_6$D$_6$ ([Fig. S6†] showed a significant broadening of the O,N isomeric resonances upon heating accompanied by a slight change in the isomeric ratio [N,N : O,N approx. 2 : 3 at 9 °C to 5 : 6 at 30 °C]. Similar results have been reported previously for a complex closely related to 1 (R = methoxethylene). A more pronounced effect can be observed in the $^1$H NMR spectra of single crystals of 2 in different solvents (CD$_2$CN, CD$_2$Cl$_2$, [Fig. S7†]), where the isomeric N,N : O,N ratios are 1 : 1.2 (CD$_2$Cl$_2$) and 1.7 : 1 (CD$_2$CN), respectively, as recently observed for Re$^{III}$ iminophenolate complexes, further corroborating a dynamic equilibrium in solution.

Upon using [MoO$_2$(acac)$_2$] as a precursor, compound 1 was obtained in significant lower yield and compound 2 did not form. However, the monosubstituted complex [MoO$_2$(acac) (Lz)] (3) could be isolated in 34% yield which could not be improved with excess ligand (Scheme 3). NMR spectroscopy clearly features resonances for one iminophenolate and one acetylacetonate ligand.

The moisture sensitive complexes 1–3 are well soluble in most organic solvents including aliphatic hydrocarbons. Spectroscopic data ($^1$H, $^{13}$C NMR and FT-IR spectroscopy), elemental analyses as well as single-crystal X-ray diffraction analyses confirm their structures.

**OAT reactivity of complexes 1–3**

The reaction of Mo($^{VI}$) dioxido compounds 1 or 2 with excess PMe$_3$ (5 equiv.) led to phosphane coordinated Mo($^{VI}$) oxido compounds 4 and 5 in very good yields (Scheme 4). Similar to the $^1$H NMR resonances for 1 and 2, also for these oxido phosphane compounds two distinct species are observed in solution, reflected by two sets of resonances for non-equivalent arranged ligands each. For both isomers, the coordinated PMe$_3$ molecule gives rise to a distinct resonance in the decoupled $^{31}$P NMR spectra of 4 and 5.

The isomeric ratios for the oxido phosphane complexes are found to be 9 : 1 (4) and 3 : 1 (5), thus revealing a significant shift in the isomeric ratio for 4 in comparison with 1 (ratio 3 : 1), whereas the isomeric ratio for 5 is in a similar range than for 2 (ratio 3 : 2). As all possible isomers exhibit non-equivalent ligand surroundings, routine NMR spectroscopy does not allow for the determination of specific isomers. However, we were able to obtain single-crystals suitable for X-ray diffraction analysis of 5, which revealed it to be the O,O isomeric form (type B, [Fig. 1]) depicted in Scheme 4.

This is in contrast to the solid state structures of 1 and 2 which displayed the N,N isomeric form (type A, [Fig. 1]) and points towards an isomeric rearrangement during the transformation of 2 to 5. The rearrangement is likely caused by higher steric demand of the phosphane ligand, which is corroborated by the exclusive O,O isomeric structure of a previously reported system featuring ligands with high steric demand (R = tBu). Dissolution of single crystals and immediate recording of a $^1$H NMR spectrum showed an isomerically pure compound and allowed for the identification of the major isomer in solution as the O,O isomeric form. Interestingly, a $^1$H NMR spectrum of the same sample after 24 h still showed only resonances corresponding to the O,O isomer, accompanied by traces of oxidized complex 9. This suggests that the two isomers found for 5 are not in a dynamic equilibrium or equilibrate only slowly. Whereas similar unambiguous evidence via the solid state structure cannot be provided for compound 4, we assume that it exhibits similar properties, especially due to

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**Fig. 1** Possible isomers A–C for a cis molybdenum($^{VI}$) dioxido complex coordinated by two iminophenolate ligands, and atoms trans to oxido groups in brackets.

**Scheme 3** Synthesis of monosubstituted complex 3.

**Scheme 4** OAT reactions of complexes 1 and 2 with PMe$_3$ and PPh$_3$ with isomeric ratios for complexes 4 and 5. For clarity, only one possible isomer is depicted for all complexes.
the observation of the O\textsubscript{2}O structural motif in the molecular structure of both corresponding oxido peroxido compounds 8 and 9 \textit{(vide infra)}.

The reactions of dioxido compounds 1 and 2, respectively, with the more bulky PPh\textsubscript{3} or with stoichiometric amounts of PMe\textsubscript{3} led to species 6 and 7 in good yields (Scheme 4). Proton NMR spectroscopy reveals two sets of ligand resonances for 6 and 7 corresponding to a non-equivalent arrangement of the ligands, furthermore both compounds adopt a single isomer in solution. Neither 6 nor 7 shows any resonances in the \textsuperscript{31}P NMR spectra and both are thus phosphane free. Single-crystal X-ray diffraction analysis of 6 identified the compound as a µ-oxido bridged dinuclear oxidomolybdenum(v) complex as shown in Scheme 4, complex 7 being likely of a similar structure. The reaction of the monosubstituted complex 3 with PMe\textsubscript{3} or PPh\textsubscript{3}, respectively, led to the formation of several un-identified products.

Complexes 4 and 5 are very well and complexes 6 and 7 are well soluble in organic solvents including aliphatic hydrocarbons. Whereas 4 and 5 are highly sensitive towards air and moisture, 6 and 7 are stable towards air and traces of moisture. In solution, 4 and 5 tend to decompose within hours (4) to days (5). The compounds were characterized \textit{via} \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{31}P NMR and FT-IR spectroscopy as well as elemental analyses, confirming their structures. Complexes 5 and 6 have additionally been characterized \textit{via} single-crystal X-ray diffraction analysis (\textit{vide infra}).

**Activation of molecular dioxygen**

Complexes 4 and 5 cleanly reacted with molecular dioxygen, indicated by a quick color change from red-brown to orange-red, to form oxido peroxido compounds 8 and 9 in excellent yields (Scheme 5). Compound 8 is alternatively accessible in a one-pot reaction from 1 \textit{via} the addition of excess PMe\textsubscript{3} (1 M solution in toluene) and subsequent stirring overnight under an O\textsubscript{2} atmosphere, similar to a previously reported procedure.\textsuperscript{16} Compounds 6 and 7 were virtually non-reactive toward molecular oxygen under ambient conditions.

Exposure of 6 and 7 to molecular oxygen at 80 °C led to the formation of a mixture of dioxido and oxido peroxido complexes 1/8 and 2/9, respectively, accompanied by severe decomposition to free ligands and NMR inactive species. The reaction of 6 or 7 with O\textsubscript{2} requires a preceding disproportionation reaction forming Mo(ν)O (and Mo(ν)O\textsubscript{2}), which is corroborated by the necessity of high temperatures and the resulting product mixture.

Whereas, in contrast to complexes 1, 2, 4 and 5, compound 8 exists as single isomer in solution, as evidenced by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy, complex 9 also exists as a mixture of two isomers in solution in an approximate ratio of 4:1.

Similar to the solid state structure of 5, both oxido peroxido compounds were identified as the O,O isomer (type B, Fig. 1) \textit{via} single-crystal X-ray diffraction analysis. It is feasible to assign the O,O form to the structure of 8 also in solution because only a single isomer is observed. Dissolution of single crystals of 9 and immediate recording of a \textsuperscript{1}H NMR spectrum showed only resonances for one species, which we thus also assign to the O,O isomer. Interestingly, a \textsuperscript{1}H NMR spectrum of the same sample after 24 h revealed the initial isomeric ratio of 4:1 pointing towards a (slow) dynamic equilibrium as previously observed in molybdenum(vi) isocyanide complexes.\textsuperscript{23} Comparing the structure of the oxido peroxido compounds 8 and 9 with previously published \textit{cis} oxido peroxido complexes originating from O\textsubscript{2} activation, it is evident that the O,O isomeriform is the preferred conformation for such compounds in the solid state.\textsuperscript{6,15,16} Complexes 8 and 9 are well soluble in most organic solvents and soluble in aliphatic hydrocarbons. Both complexes are stable towards air but sensitive towards moisture.

**Catalytic oxidation of phosphanes**

Complexes 1 and 2 were tested for their ability to catalyze the aerobic oxidation of phosphanes, namely trimethyl phosphane and triphenyl phosphane, according to Scheme 6. The conditions used were 1 mol\% catalyst with an excess of dry O\textsubscript{2} gas (1.5 atm) in C\textsubscript{6}D\textsubscript{6} at room temperature. Blank experiments under identical conditions but without catalysts led to conversions of PMe\textsubscript{3} and PPh\textsubscript{3} to <5%. In the aerobic oxidation of PMe\textsubscript{3}, catalyst 1 was found to be significantly more active compared to 2 (65 vs. 35% conversion, Table 1) and more active than the previously described tert-butyl based system (19%).\textsuperscript{16} Catalyst 2 proved to be unselective as only 25% of OPMe\textsubscript{3} was formed together with 10% of one side product. NMR spec-

Scheme 5 Activation of molecular oxygen to form oxido peroxido compounds 8 and 9.
troscopy revealed it to be methyl dimethylphosphinate (OP(OMe)Me2) where an additional oxygen atom was inserted into one P–C bond (Fig. S37 and 38†). This is highly interesting as it demonstrates for the first time the transfer of two oxygen atoms from a molybdenum oxido peroxido species to one substrate molecule.

In contrast, PPh3 was oxidized selectively to OPPh3 by 2, but only 23% was converted. Interestingly, catalyst 1 was virtually non-reactive for the oxidation of PPh3 (8%). To our further understanding of this reactivity difference, we subsequently tested the dimeric complexes 6 and 7 in the catalytic oxidation of PPh3. Phenyl-based compound 7 led to a fourfold higher yield of OPPh3 (12% vs. 3%) in comparison with methoxypropylene based complex 6. This is in good agreement with the activity difference of 1 and 2 in the aerobic oxidation of PPh3 and suggests lower activation energy for the disproportionation of 7, a requirement for reactivity with O2, in comparison with 6. The temperature increase in the catalytic oxidation of PPh3 was tested but due to significant autoxidation at 50 °C, as observed in a blank experiment, no reliable results could be obtained. To confirm the participation of the [MoO(O2)L2] species in the catalytic oxidation, we reacted complex 9 with 2 equiv. of PMe3 in a control experiment. Proton NMR measurement after 6 h of reaction time showed a mixture of 9 and the phosphane complex 5 together with OPMe3 and residual PMe3 but no dioxido species 2 (Fig. S45†). These results confirm the oxidation capability of complex 9 and are in good agreement with previous observations.16

Molecular structures

The molecular structures of molybdenum(VI) dioxido complexes 1–3, molybdenum(IV) oxido phosphane complex 5, molybdenum(V) oxido µ-oxido complex 6 as well as molybdenum(VI) oxido peroxido complexes 8 and 9 were determined by single-crystal X-ray diffraction analysis. The molecular views of 1–3 are given in Fig. 2, those of 5 and 6 in Fig. 3, and those of 8 and 9 in Fig. 4. Selected bond lengths and angles for com-

Fig. 2 Molecular views (50% probability level) of 1 (top), 2 (middle) and 3 (bottom); hydrogen atoms as well as solvent molecules are omitted for clarity.

Fig. 3 Molecular views (50% probability level) of 5 (top), and 6 (bottom); hydrogen atoms as well as solvent molecules are omitted for clarity, and tert-butyl substituents are depicted as a wireframe. For disordered fragments, only atoms with the higher site occupation factors are depicted. In complex 6, only atoms in the asymmetric unit are labelled.

Table 1 Yield of phosphane oxide after 24 h in the aerobic oxidation of phosphanes catalyzed by 1 or 2

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<thead>
<tr>
<th>Phosphane</th>
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<tr>
<td>PMe3</td>
<td>65</td>
<td>25&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>PPh3</td>
<td>8 (3)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>23 (12)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Conditions: 1 mol% catalyst, rt, C6D6. <sup>a</sup>35% conversion of PMe3. <sup>b</sup>Values in brackets correspond to dimeric molybdenum(V) µ-oxido complexes 6 and 7 as catalysts.
plexes 1–3, 5, 6, 8 and 9 are provided in Table 2, and full crystallographic details such as structure refinement as well as experimental details are provided in the ESI.†

In complexes 1–3, the molybdenum atoms are coordinated in a distorted octahedral fashion by two bidentate ligands and two terminal oxido ligands. In complexes 1 and 2, which are coordinated by two iminophenolate ligands, the ligand arrangement corresponds to the N,N isomer (type A, Fig. 1) whereas in monosubstituted compound 3 one imine nitrogen as well as one acetylacetonate oxygen is trans to the oxido ligands. The molybdenum oxido bond lengths observed in 1–3 are within the expected ranges (Table 2).²⁴

Compound 5, which is obtained via OAT from 2 to PMe₃, is coordinated by two bidentate iminophenolate ligands, one terminal phosphane and one terminal oxido ligand in a distorted octahedral fashion. Interestingly, the arrangement of the iminophenolate ligands differs from the parent compound. In 5, the phenolato oxygens are trans to the phosphane and oxido ligands, respectively, which correspond to the O,O isomer (type B, Fig. 1). The Mo–O bond length is 1.7037(13) Å and the Mo–P bond length is 2.5289(6) Å, thus both are rather long but comparable to previously structurally characterized molybdenum(iv) oxido phosphane complexes (Table 2).⁸,²⁵

Compound 6, obtained via OAT from 1 to PPh₃, displays a μ-oxido bridged dimeric structure with two molybdenum(vi) oxido metal centers each coordinated by two bidentate ligands, a terminal oxido ligand as well as the μ-oxido ligand in a distorted octahedral fashion. The complex is symmetric around the bridging oxido ligand with a Mo1–O2–Mo1' angle of 157.2(5)° as well as twisted about the Mo1•••Mo1' connecting line (O1•••Mo1•••O1' = 31.1(3)°, N1•••Mo1•••N2' = 42.8(3)°), rendering the two terminal oxido ligands in a gauche-like conformation in the solid state. The arrangement of the ligands around the metal centers resemble the O,O isomer (Fig. 1) with the phenolato oxygens trans to the oxido and μ-oxido ligands, respectively. The Mo=O and Mo–(μ-μ) oxido bond lengths are within the expected ranges (Table 2).²⁴,²⁶

Compounds 8 and 9 are coordinated by two bidentate iminophenolate ligands, a terminal oxido ligand and a η¹ side-on coordinated peroxido ligand in a distorted octahedral fashion. Both compounds adopt the O,O isomeric form in the solid state, with the phenolato oxygen atoms trans to the oxido and peroxido ligands, respectively. Whereas the Mo=O bond lengths for 8 and 9 as well as the Mo–O (peroxido) bond lengths in 9 are similar to previously reported Mo(vi) oxido peroxido compounds, the Mo–O (peroxido) distances in 8 are

$$\text{Table 2} \quad \text{Selected bond lengths [Å] and angles [°] for complexes 1–3, 5, 6, 8 and 9}$$

<table>
<thead>
<tr>
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<th>1</th>
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* Bond length and angle range given due to four distinct molecules in the unit cell. † O2 = μ-oxido.

Fig. 4 Molecular views (50% probability level) of 8 (left) and 9 (right); hydrogen atoms as well as solvent molecules are omitted for clarity, and tertbutyl substituents are depicted as a wireframe. For disordered fragments, only atoms with the higher site occupation factors are depicted.
metal center has a more significant impact on the metal
meric arrangement compared to the oxidation state of the
trans 
show a comparable but opposite trend, for example. A comparison of the Mo–O (phenolate) bond lengths in
these complexes shows a comparable but opposite trend, i.e. an elongation of the Mo–O (phenolate) bonds in the molecular structures of 5, 6 and 9, again likely caused by the oxido
trans influence. It can be thus further reasoned that the iso-
meric arrangement compared to the oxidation state of the
metal center has a more significant impact on the metal-
ligand bonding situation in these complexes.

Conclusions

The reaction of functionalized iminophenolate ligands with molybdenum(vi) metal precursors [MoO$_2$Cl$_2$] and [MoO$_2$Cl$_2$(DME)] yielded dissubstituted complexes 1 and 2, whereas the use of [MoO$_2$(acac)$_2$] as a metal source led to monosubstituted complex 3 coordinated by one iminopheno-
late and one acac$^-$ moiety. Subsequent oxygen atom transfer from 1 or 2 to phosphines gave rise to distinct molybdenum(v) and molybdenum(vi) complexes. The products obtained from the reactions of 1 and 2 were dependent on the nature of the phosphine (PMe$_3$ or PPh$_3$) as well as the employed stoichiometry. The use of excess of PMe$_3$ yielded molybdenum(v) oxide phosphine complexes 4 and 5. Upon the use of stoichiometric amounts of PMe$_3$ or PPh$_3$ molybdenum(v) μ-oxido complexes 6 and 7 were obtained. Compounds 4 and 5 readily reacted with molecular oxygen under ambient conditions to give oxide peroxydioxo complexes 8 and 9, while 6 and 7 did not show similar reactivity. Complexes 1, 2, 4, 5 and 9 exist as iso-
meric mixtures in solution, but for 8 only one isomer is observed.

Furthermore 1 and 2 adopt a different ligand arrangement than 5, 6, 8 and 9 in the solid state. A comparison of Mo–N and Mo–O bond lengths within the solid state structures of 1, 2, 5, 6, 8 and 9 reveals a significant impact of the oxido trans influence on the bonding situation in these complexes. Dioxo molybdenum(vi) complexes 1 and 2 have been found to catalyze the aerobic oxidation of PMe$_3$ and PPh$_3$ with noteworthy reactivity differences depending on the nature of the ligand. In the oxidation of PMe$_3$, compound 1 proved to be virtually unreactive whereas complex 2 gave significant yields of OPPh$_3$. In the case of PMe$_3$ oxidation, the active site is coordinated by a sub-
strate molecule. Thus, prior elimination of PMe$_3$ is necessary, occurring readily under O$_2$ which we have recently demonstrated. 16 This is not possible with the more bulky PPh$_3$ as evidenced by the formation of dinuclear μ-oxido bridged complexes in stoichiometric reactions. However catalysis experi-
ments using these dimeric compounds 6 and 7 as catalysts in the oxidation of PPh$_3$ showed the phenyl-based dinuclear compound 7 exhibiting catalytic activity whereas 6 was completely inactive. This indicates lower activation energy for the dis-
proportionation of 7, which is required for the reaction with molecular O$_2$, in comparison with compound 6. The results presented herein provide further understanding of the species involved in OAT reactions as well as oxygen activation with molybdenum(vi)/(vi) systems and also insight into the diverse effects of ligand functionalization on the reactivity of such systems.

Experimental section

General

Unless specified otherwise, experiments were performed under inert conditions using standard Schlenk equipment. Commer-
cially available chemicals were purchased from Sigma-Aldrich and used as received. No further purification or drying oper-
ations have been performed. The metal precursors [MoO$_2$(acac)$_2$] and [MoO$_2$Cl$_2$(DME)] were synthesized according to known procedures. Solvents were purified via a Pure-Solv MD-4-EN solvent purification system from Innovative Technology, Inc. Methanol was refluxed over activated mag-
nesium for at least 24 h and then distilled prior to use. The
$^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a Bruker Optics instrument at 300/75/121 MHz. The peaks are denoted as singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), triplet (t), pseudo-doublet (“dd”), pseudo-triplet (“t”) and multiplet (m). The used solvents and peak assignment are mentioned in the specific data sets. Resonances in $^{31}$P NMR were referenced to phosphoric acid as an external standard. Electron impact mass spectroscopy (EI-MS) measurements have been performed with an Agilent 5973 MSD mass spectrometer with a push rod. ESI-MS as well as HR-MS (ESI$^+$) measurements were performed at the University of Graz, Department of Analytical Chemistry. ESI measurements were performed using an Agilent 1100 Series LCMSD (SL type), HR-MS (ESI$^+$) measurements were performed using a Thermo Scientific Q-Exactive mass spectrometer in positive ion mode, and the used solvent was acetonitrile. The peaks are denoted as cationic mass peaks, and the unit is the according ion mass/charge ratio. Solid samples for infrared spectroscopy were measured on a Bruker Optics ALPHA FT-IR Spectrometer. Liquid samples were recorded in benzene on a Bruker FT-MIR matrix MF in situ spectrometer using a glass fiber optic probe.
The IR bands are reported with wavenumber (cm⁻¹) and intensities (s, strong; m, medium; w, weak). All elemental analyses were performed at the Technical University of Graz, Institute of Inorganic Chemistry using a Heraeus Vario Elma 1 automatic analyser.

X-ray diffraction analyses

Single-crystal X-ray diffraction analyses were performed on a BRUKER-AXS SMART APEX II diffractometer equipped with a CCD detector. All measurements were performed using monochromated Mo Kα radiation from an Incoatec microfocus sealed tube at 100 K (cf. Table S1†). Absorption corrections were performed semi-empirical from equivalents. The structures were solved by direct methods (SHELXS-97)²⁷ and refined by full-matrix least-squares techniques against F² (SHELXL-2014/6).²⁷ CCDC 1476035–1476040 and 1486756 contain the supplementary crystallographic data for this paper. Full experimental details for single-crystal X-ray diffraction analyses of all compounds are provided in the ESI.†

Ligand synthesis

All ligands are stable towards air and moderately stable towards moisture. They can be stored in a desiccator over P₂O₅ for several weeks without decomposition.

Synthesis of (E)-2,4-di-tert-butyl-6-((3-methoxypropylimino)methyl)phenol (HL₁).¹⁸ Ligand HL₁ was prepared following published procedures. In brief, 3-methoxy-1-propylamine (1.25 g, 14.0 mmol) was added to a solution of 3,5-di-tert-butyl-2-hydroxy-benzaldehyde (3.28 g, 14.0 mmol) in 50 mL of MeOH and the resulting yellow solution was stirred at reflux temperature overnight. The reaction solution was subsequently dried over MgSO₄ and the solvent was evaporated in vacuo to give HL₁ as a yellow oil (95%, 4.05 g). Analytical data is in compliance with the literature, and the ¹H NMR data is in compliance with the literature, and the ¹H NMR shifts in C₆D₆ as well as IR bands are given for the purpose of comparison.¹⁸ ¹H NMR (300 MHz, C₆D₆, 25 °C): δ: 14.14 (bs, 1H, OH), 7.91 (s, 1H, CH=N), 7.53 (d, 1H, ArH), 6.97 (d, 1H, ArH), 3.36 (t, 2H, CH₂), 1.62 (s, 9H, tBu), 1.32 (s, 9H, tBu) ppm; IR (ATR, cm⁻¹): 1628 (s), 1559 (w), 1460 (w), 1247 (s), 1108 (s), 1047 (w), 913 (m), 902 (s), 841 (s), 751 (s), 549 (s); EI-MS (70 eV) m/z: 738.6 [M]+; Anal. calcd for C₃₈H₆₀MoN₂O₆: C, 61.94; H, 8.21; N, 3.80; found: C, 61.62, H, 8.09; N, 3.78%.

Synthesis of [MoO₂(L₁)₂] (1). For the synthesis of 1, 2 equiv. of HL₁ (460 mg, 1.50 mmol) were dissolved in a small portion of dry toluene and slowly added to a solution of 1 equiv. [MoO₂Cl₂(DME)] (220 mg, 0.75 mmol) in the same solvent (5 mL). Subsequently 2.4 equiv. Et₃N (255 µl, 1.81 mmol) were added via syringe. The orange reaction mixture was stirred overnight and then filtered through a glass frit packed with Celite. The solvent was removed in vacuo to afford a waxy product which was thoroughly washed with cold dry pentane to obtain pure 1 as a bright yellow solid (81%, 450 mg). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via recrystallization from a concentrated THF solution layered with pentane at room temperature. ¹H NMR (300 MHz, C₆D₆, 25 °C, N,N isomer): δ: 7.00 (d, 2H, ArH), 7.09 (d, 2H, ArH), 3.63–3.58 (m, 4H, CH₂), 3.16–3.09 (m, 2H, CH₂), 3.03–2.99 (m, 2H, CH₂), 2.92 (s, 6H, OMe), 2.00–1.92 (m, 4H, CH₂), 1.29 (s, 18H, tBu), 1.27 (s, 18H, tBu) ppm; ¹³C NMR (75 MHz, C₆D₆, 25 °C, N,N isomer): δ: 160.04 (CH=N), 160.98 (Ar-O), 142.08, 139.58, 129.74, 128.19 (HSQC), 122.19 (Ar), 69.48 (CH₂), 58.11 (OMe), 57.36 (CH₂), 35.65, 34.38 (q-tBu), 31.60, 31.56 (tBu), 31.30 (CH₂) ppm; IR (ATR, cm⁻¹): 1628 (s), 1559 (w), 1460 (w), 1247 (s), 1108 (s), 1047 (w), 913 (m), 902 (s), 841 (s), 751 (s), 549 (s); EI-MS (70 eV) m/z: 738.6 [M]+; Anal. calcd for C₉₉H₆₄MoN₆O₈:C, 61.94; H, 8.21; N, 3.80; found: C, 61.62, H, 8.09; N, 3.78%.

Synthesis of [MoO₂(L₂)₂] (2). For the synthesis of 2, 2 equiv. of HL₂ (311 mg, 1.01 mmol) were dissolved in a small portion of dry toluene and slowly added to a suspension of 1 equiv. [MoO₂Cl₂(DME)] (100 mg, 0.51 mmol) in the same solvent (3 mL). Subsequently 2.4 equiv. Et₃N (168 µl, 1.21 mmol) were added via syringe. The dark red reaction mixture was stirred overnight whereupon a yellow solid was precipitated. The precipitate was washed twice with dry pentane, loaded onto a glass frit packed with Celite and eluted with dry Et₂O until the eluent turned colorless. The solution was evaporated and the residual waxy orange solid was recrystallized from dry MeCN at −35 °C to yield 2-MeCN as a dark yellow microcrystalline solid (65%, 389 mg). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via slow evaporation of a concentrated MeCN solution at −35 °C. ¹H NMR (300 MHz, C₆D₆, 25 °C, O, N isomer): δ: 7.68 (d, 1H, ArH), 7.66 (d, 1H, ArH), 7.56 (s, 1H, CH=N), 7.44–7.41 (m, 2H, ArH), 7.41 (s, 1H, CH=N), 7.20–7.16 (m, 1H, ArH), 7.09–7.00 (m, 1H, ArH), 6.90–6.75 (m, 7H, ArH), 6.44 (d, 1H, ArH), 1.70 (s, 9H, tBu), 1.49 (s, 9H, tBu), 1.26 (s, 9H, tBu), 1.23 (s, 9H, tBu); ¹³C NMR (300 MHz, C₆D₆, N, N isomer): δ: 7.88 (s, 2H, CH=N), 7.58 (d, 2H, ArH), 7.09–7.00 (m, 4H, ArH), 6.90–6.75 (m, 8H, ArH), 1.37 (s, 18H, tBu), 1.24 (s, 18H, tBu); ¹¹B NMR (HSQC 300/75 MHz, C₆D₆, 25 °C, O,N
isomer, q-C obscured) δ: 170.13, 165.54 (CH=N), 131.70, 129.59, 129.26, 128.97, 128.08, 127.95, 126.55, 126.00, 125.72, 125.67, 125.54, 123.26, 123.18, 123.06 (Ar), 31.21, 31.20, 29.85 (tBu); 13C NMR (HSQC 300/75 MHz, C6D6, 25 °C, N,N z-isomer, q-C obscured) δ: 169.00 (CH=N), 130.20, 128.91, 128.73, 128.58, 123.33, 123.18 (Ar), 31.21, 29.82 (tBu); IR (ATR, cm−1): δ: 2956 (s), 1611 (s), 1592 (m), 1559 (w), 1486 (w), 1437 (w), 1272 (m), 1253 (s), 1177 (s), 928 (w), 910 (s), 897 (s), 845 (m), 765 (m), 705 (w), 554 (w); El-MS (70 ev) m/z: 746.6 [M]+; Anal. calcld for C38H60MoN2O6·CH3CN: C, 67.25; H, 7.05; N, 5.35; found: C, 67.03, H, 7.01; N, 5.47%.

**Synthesis of [MoO2(acac)L2]** (3). For the synthesis of 3, 2 equiv. of H1L2 (380 mg, 1.23 mmol) were added to a suspension of [MoO2(acac)2] in dry MeCN (5 mL). The resulting orange reaction solution was then stirred at 80 °C overnight and subsequently evaporated in vacuo. The resulting oily product was treated with dry pentane (10 mL) and sonicated. The supernatant was removed via cannula filtration and the yellow residue was washed twice with 5 mL of dry pentane. Recrystallization of the residue from dry MeCN yielded 3 as bright yellow crystals (34%, 121 mg). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via slow evaporation of a concentrated MeCN solution at ~35 °C. H NMR (300 MHz, C6D6, 25 °C) δ: 7.71 (d, 1H, ArH), 7.65 (s, 1H, CH=N), 7.15–7.12 (m, 2H, ArH), 7.01–6.88 (m, 4H, ArH), 4.83 (s, 1H, CH), 1.65 (s, 9H, tBu), 1.44 (s, 3H, Me), 1.36 (s, 9H, tBu), 1.13 (s, 3H, Me) ppm; 13C NMR (300 MHz, C6D6, 25 °C) δ: 195.26, 185.83 (C=O), 166.81 (CH=N), 159.17 (Ar-O), 152.24, 142.66, 140.51, 130.47, 129.36, 128.45, 126.23, 123.91, 121.96 (Ar), 103.55 (CH=N), 35.75, 34.42 (q-tBu), 31.53, 30.09 (tBu), 27.27, 24.90 (Me) ppm; IR (ATR, cm−1): δ: 2962 (m), 1605 (m), 1518 (m), 1362 (m), 1275 (m), 1250 (m), 1177 (m), 928 (s), 901 (s), 848 (s), 794 (m), 762 (s), 695 (m), 568 (s), 450 (s); El-MS (70 ev) m/z: 573.3 [M]+; Anal. calcld for C26H35MoNO5: C, 58.32; H, 8.73; N, 3.52; found: C, 62.14; H, 8.76; N, 3.51%.

**Synthesis of [MoOP(Me)(L2)]2** (5). For the synthesis of 5, a solution of 1 equiv. 2 (100 mg, 0.13 mmol) in dry toluene was treated with 5 equiv. PMe3 (70 μl, 0.65 mmol) in toluene at room temperature. The dark red-brownish solution was stirred at room temperature overnight, whereupon the solvent was evaporated in vacuo. The crude residue was re-dissolved in little cold dry heptane and filtered through a glass frit packed with Celite. Evaporation of all volatiles gave 5 as a dark red-brownish solid material (81%, 93 mg). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via slow evaporation of a concentrated MeCN solution at ~35 °C. H NMR (300 MHz, C6D6, 25 °C, O,O isomer) δ: 8.11 (s, 1H, CH=N), 8.04 (s, 1H, CH=N), 7.84–7.81 (m, 2H, ArH), 7.69–7.66 (m, 2H, ArH), 7.58 (d, 1H, ArH), 7.42 (d, 1H, ArH), 7.23–7.18 (m, 3H, ArH), 7.11–7.05 (m, 3H, ArH), 6.95–6.90 (m, 2H, ArH), 1.42 (s, 9H, tBu), 1.34 (s, 18H, tBu), 1.33 (s, 9H, tBu), 0.45 (d, 9H, PMe3) ppm; 31P NMR (75 MHz, C6D6, 25 °C, O,O isomer) δ: 170.14 (CH=N), 166.47 (Ar-O), 163.63 (CH=N), 163.08 (Ar-O), 160.20, 157.97, 140.84, 138.73, 136.91, 136.67, 131.89, 131.16, 130.59, 129.28 (2×), 128.65, 128.03 (2×, HSQC), 126.57, 125.92, 124.85 (2×), 123.69 (2×), 121.44, 120.73 (Ar), 35.67, 35.53, 34.28, 34.04 (q-tBu), 31.82, 31.68, 30.15, 29.99 (tBu), 15.39 (d, PMe3) ppm; 31P NMR (121 MHz, C6D6, 25 °C) δ: −0.77 (O,O isomer, Mo-PMe3), −1.99 (putative ON isomer, Mo-PMe3) ppm; IR (ATR, cm−1): δ: 2949 (m), 1601 (m), 1587 (m), 1527 (m), 1485 (m), 1254 (m), 1165 (s), 953 (w), 927 (s), 866 (m), 764 (m), 704 (m), 694 (m), 637 (w), 523 (s), 448 (w); HR-MS (ESI) m/z: [M+] calculated for C45H61MoN2O3P: 806.3474; found: 806.3474; Anal. calculated for C45H61MoN2O3P: C, 67.15; H, 7.64; N, 3.48; found: C, 67.60; H, 7.43; N, 3.35%.

**Synthesis of [MoO(L1)][μ-O]** (6). For the synthesis of 6, a solution of 1 equiv. 1 (103 mg, 0.14 mmol) in dry toluene (3 mL) was treated with 2 equiv. of PMe3 (29 μl, 0.28 mmol). The addition resulted in a quick color change from orange to dark red. The solution was stirred for 1 h at room temperature, subsequently the solvent was removed in vacuo whereupon the crude product was re-dissolved in cold dry heptane (5 ml) and filtered through a glass frit packed with Celite. After concentration of the solution to ~2 mL, inert column chromatography on basic aluminum oxide with dry ether/pentane (1:1) as the eluent was performed and the first red band was collected. Evaporation of the solvent gave 6 as a dark red solid (68%, 69 mg). For elemental analyses, the complex was recrystallized from dry CH2Cl2. Alternatively, complex 6 is accessible by OAT from complex 1 (100 mg, 0.14 mmol, 1 equiv.) to PPH3 (37 mg, 0.14 mmol, 1 equiv.) in dry toluene (5 mL). After stirring for 24 h at room temperature, purification was followed the procedure described above. Residual traces of PPH3 were first eluted from the basic aluminum oxide column with pentane.
The use of polymer-bound PPh₃ led to insoluble by-products and thus a simplified work-up procedure. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of a concentrated MeCN solution at -35 °C. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ: 8.26 (s, 2H, CH=N), 8.10 (s, 2H, CH=CH=N), 7.57 (d, 2H, ArH), 7.46 (d, 2H, ArH), 7.02 (d, 2H, ArH), 6.84 (d, 2H, ArH), 5.04-4.97 (m, 2H, CH₂), 4.62-4.52 (m, 2H, CH₂), 4.39-4.30 (m, 2H, CH₂), 3.69-3.60 (m, 2H, CH₂), 3.42-3.24 (m, 4H, CH₂), 3.11-3.05 (m, 2H, CH₂), 3.02 (s, 6H, OMe), 2.92 (s, 6H, OMe), 2.78-2.47 (m, 8H, CH₂), 2.10-1.92 (m, 2H, CH₂), 1.41 (s, 18H, tBu), 1.31 (s, 18H, tBu), 1.22 (s, 18H, tBu), 1.19 (s, 18H, tBu) ppm; ¹³C NMR (75 MHz, C₆D₆, 25 °C) δ: 169.91, 166.01, 165.71 (Ar-O), 140.01, 139.28, 138.48, 137.47, 131.62, 129.66, 129.69, 128.85, 121.95, 121.87 (Ar), 70.26, 70.08, 61.30, 60.77 (CH₂), 58.35, 58.20 (OMe), 35.51, 35.23, 34.15, 33.99 (q-tBu), 33.25, 31.95 (CH₅), 31.32, 31.44, 29.81, 29.46 (tBu) ppm; IR (ATR, cm⁻¹) 8: 1611 (s), 1597 (s), 1256 (s), 1104 (br, s), 1014 (br, s), 928 (s), 798 (br, s), 529 (s); EI-MS (70 eV) m/z: 722.6 [MoO(L₁)]⁺; Anal. calcld for C₇₆H₁₂₄Mo₂N₄O₁₀·CH₂Cl₂: C, 59.80; H, 8.21; N, 3.62; found: C, 59.94; H, 8.40; N, 3.33%.

Synthesis of [MoO(LL₂)₂(μ-O)] (7). For the synthesis of 7, 1 equiv. of (200 mg, 0.13 mmol) and 1 equiv. of PPh₃ (34 mg, 0.13 mmol) were dissolved in dry MeCN (5 mL). The initially orange reaction solution was stirred at room temperature for 48 h whereupon it gradually darkened. The precipitate was subsequently filtered off, washed twice with little cold dry MeCN and dried in vacuo. After subsequent removal of the residual traces of PPh₃ and OPPh₃ via sublimation (110 °C, 2 × 10⁻⁵ atm), 7 was obtained as a dark purple solid (72%, 69 mg). The use of polymer-bound PPh₃ led to insoluble by-products and thus a simplified work-up procedure. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ: 8.14-8.12 (m, 4H, ArH), 8.02 (s, 2H, CH=N), 7.63 (d, 2H, ArH), 7.55 (d, 2H, ArH), 7.43 (s, 2H, CH=n), 7.41-7.36 (m, 6H, ArH), 7.09-6.99 (m, 10H, ArH), 6.88 (d, 2H, ArH), 6.55 (d, 2H, ArH), 1.36 (s, 18H, tBu), 1.26 “d”, 36H, tBu) ppm; ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ: 172.09, 169.54 (CH=N), 162.91, 161.76 (Ar-O), 157.25, 155.04, 140.88, 140.52, 139.39, 139.37, 131.00, 130.72, 130.43, 130.16, 128.09 (3×, HSQC), 127.97 (2×, HSQC), 126.82, 126.31 (2×), 126.05 (2×), 127.76, 127.69 (Ar), 126.60 (Ar), 35.70, 35.49, 34.27, 34.01 (q-tBu), 31.79, 31.50, 30.52, 30.11 (tBu) ppm; IR (ATR, cm⁻¹) 8: 1612 (s), 1256 (s), 1108 (br, s), 1089 (br, s), 914 (s), 839 (s), 800 (s), 779 (s), 748 (m), 539 (s); ESI-MS (100 V) m/z: 755.3 [M⁺]; Anal. calcld for C₃₁H₃₂MoO₅N₄O₄·0.2CH₂Cl₂: C, 59.60; H, 7.91; N, 3.64; found: C, 59.26; H, 7.99; N, 4.00%.

Synthesis of [MoO₂(O₂)₂(L₂)] (9). For the synthesis of 9, a solution of 5 (100 mg, 0.12 mmol) in dry toluene (3 mL) was treated with excess dry O₂ gas whereupon the initially red-brown solution quickly turned deep orange. The solution was stirred under an O₂ atmosphere (1.5 atm) overnight at room temperature. Subsequently all volatiles were removed in vacuo. The resulting waxy dark orange residue was dissolved in a minimum amount of cold dry heptane and the resulting suspension was filtered through a glass frit packed with Celite. Evaporation of all volatiles in vacuo and subsequent sublimation of residual OPMe₂, traces (60 °C, 2 × 10⁻⁵ atm) gave 7 as a dark orange solid (85%, 84 mg). ¹H NMR (300 MHz, C₆D₆, 25 °C, O,O isomer): δ: 8.11 (s, 1H, CH=N), 8.10 (s, 1H, CH=N), 7.89-7.85 (m, 2H, ArH), 7.70 (d, 1H, ArH), 7.61-7.56 (m, 2H, ArH), 7.54 (d, 1H, ArH), 7.24-7.18 (m, 2H, ArH), 7.13-6.99 (m, 4H, ArH), 6.90 (d, 1H, ArH), 6.86 (d, 1H, ArH), 1.37 (s, 9H, tBu), 1.26 (s, 9H, tBu), 1.25 (s, 9H, tBu), 1.23 (s, 9H, tBu) ppm; ¹³C NMR (HSQC) 300/75 MHz, C₆D₆, 25 °C, q-C obscured): δ: 169.10, 168.74 (CH=N), 133.20, 131.41, 130.24, 129.74, 128.81, 128.48, 126.48, 128.09, 127.15, 126.90, 125.44, 125.26 (Ar), 124.74 (2× Ar), 31.19, 30.99, 29.64, 29.54 (tBu); IR (ATR, cm⁻¹) 8: 2953 (m), 1611 (s), 1589 (s), 1540 (m), 1252 (s), 1172 (s), 927 (s), 838 (s), 765 (m), 704 (m), 692 (m), 538 (br s); HR-MS (ESI⁺) m/z: [M + Na⁺] calcld for C₄₂H₃₂MoN₄NaO₇: 785.2828, found: 785.2820; Anal. calcld for...
C$_{42}$H$_{32}$MoN$_{2}$O$_{5}$: C, 66.30; H, 6.89; N, 3.68; found: C, 65.81; H, 7.05; N, 3.66%.

Catalytic aerobic oxidation of phosphines

In a representative reaction, 5 mg of the respective catalyst (approx. 0.007 mmol) was dissolved in dry C$_6$D$_6$ under a N$_2$ atmosphere in a 50 mL Schlenk flask. Subsequently 100 equiv. of the respective phosphine (0.7 mmol PMe$_3$: 53 mg; PPh$_3$: 184 mg) were added to the solution. The Schlenk flask was then flushed with dry O$_2$ and placed under O$_2$ pressure (1.5 atm) whereupon the reaction solution was stirred for 24 h at room temperature. Subsequently the Schlenk flask was cooled to 0 °C and twice evacuated and backfilled with dry N$_2$. After addition of 0.2 mL of dry CD$_2$CN to ensure complete dissolution of all formed products, the reaction was monitored via $^1$H and $^{31}$P NMR spectroscopy, phosphate oxide yields were calculated via integration of the respective peak areas in the $^1$H NMR spectra, and conversion included the peak areas for the formed side product [OP(OMe)Me]$_2$: $^1$H NMR in C$_6$D$_6$: δ: 3.34 (d, 3H, OMe), 1.08 (d, 6H, 2× Me); $^{31}$P NMR in C$_6$D$_6$: δ: 49.93). Blank experiments without catalysts were included for both phosphines, where yields of <5% were observed for PMe$_3$ and PPh$_3$.

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References


