Oxygen activation and catalytic aerobic oxidation by Mo(IV)/(VI) complexes with functionalized iminophenolate ligands†

Niklas Zwettler, Martina E. Judmaier, Lara Strohmeier, Ferdinand Belaj and Nadia C. Mösch-Zanetti*

Synthesis of molybdenum(VI) 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 phosphanes. Depending on stoichiometry and employed phosphate (PMe3 or PPh3), different molybdenum(VI) and molybdenum(V) complexes 4–7 were obtained. Whereas molybdenum(VI) complexes 4 and 5, bearing a terminal PMe3 ligand, readily reacted with molecular O2 to form oxido peroxido complexes 8 and 9, phosphate free μ-oxido bridged dinuclear molybdenum(VI) 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 phosphate 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 complex 7, derived from complex 2, was found to be catalytically active, which suggests a lower energy barrier for disproportionation into [MoO2(L)2] and [MoO2(μ-O)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(VI)/molybdenum(V) 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.3

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

Institute of Chemistry, Inorganic Chemistry, University of Graz, Schubertstrasse 1, 8010 Graz, Austria. E-mail: nadia.moesch@uni-graz.at
†Electronic supplementary information (ESI) available. CCDC 1476035 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 peroxo 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 for oxygen atom transfer as well as oxygen activation. The chosen substituents are a methoxypropylene as well as a phenyl group. Whereas the donor functionality potentially acts as protection group for vacant coordination sites, the phenyl group was chosen as an electron withdrawing substituent with steric demand, allowing for the comparison with a previously published system.15,16 Two new molybdenum(IV) dioxido complexes employing these ligands were synthesized and investigated for their behavior in OAT reactions with the tertiary phosphines PMe₃ and PPh₃ and subsequent reactivity towards molecular oxygen. Structural characterization via single-crystal X-ray diffraction analyses allowed assessing the isomeric structures of the participating species. Furthermore, catalytic oxidation of the phosphines by molecular oxygen revealed significant reactivity differences depending on phosphines and catalysts employed. Both investigated systems surpassed the PMe₃ conversion obtained using a previously published system.16

Results and discussion

Ligand synthesis

Previously published ligands HL118 and HL219 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.16,19

Synthesis of molybdenum dioxido complexes

For the synthesis of molybdenum(VI) complexes of the type [MoO₂(μ-O)₂(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(μ-O)₂(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 2,1 H NMR data in C₆D₆ 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

Scheme 1 Synthesis of the iminophenolate ligands HL1 and HL2.

Scheme 2 Synthesis of molybdenum(VI) dioxido complexes 1 and 2 and their respective isomeric ratios (N,N : O,N).
the imine substituent. Whereas in the compound bearing the methoxypropylene-substituted ligands, the N,N form is predom-
inantly with a ratio of 3 : 1, in the complex with the phenyl-sub-
stituted 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. Sub-
sequent 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 50 °C). Similar results have been reported pre-
viously for a complex closely related to 1 (R = methoxymethy-
lene). 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(V) iminophenolate complexes, further corro-
boration of 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)
(L$_2$)] (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. Spectro-
toscopic data ($^1$H, $^{13}$C NMR and FT-IR spectroscopy), element-
al analyses as well as single-crystal X-ray diffraction analyses
confirm their structures.

**OAT reactivity of complexes 1–3**

The reaction of Mo(V) dioxido compounds 1 or 2 with excess
PMe$_3$ (5 equiv.) led to phosphane coordinated Mo(V) 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 phos-
phane compounds two distinct species are observed in solu-
tion, reflected by two sets of resonances for non-
equivalent arranged ligands each. For both isomers, the co-
ordinated 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 diffrac-
tion 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 trans-
formation of 2 to 5. The rearrangement is likely caused by
higher steric demand of the phosphane ligand, which is corro-
boration of 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 record-
ing of a $^1$H NMR spectrum showed an isomerically pure com-
 pound 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 reso-
nances 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 equi-
librate 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

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.
the observation of the O,O structural motif in the molecular structure of both corresponding oxido peroxido compounds 8 and 9 (*vide infra*).

The reactions of dioxo compounds 1 and 2, respectively, with the more bulky PPh₃ or with stoichiometric amounts of PMe₃ 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 ⁴¹P 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 oxomolybdenum(V) complex as shown in Scheme 4, complex 7 being likely of a similar structure. The reaction of the monosubstituted complex 3 with PMe₃ or PPh₃, 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 *via* ¹H, ¹³C, ⁴¹P NMR and FT-IR spectroscopy as well as elemental analyses, confirming their structures. Complexes 5 and 6 have additionally been characterized *via* single-crystal X-ray diffraction analysis (*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 *via* the addition of excess PMe₃ (1 M solution in toluene) and subsequent stirring overnight under an O₂ atmosphere, similar to a previously reported procedure.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 dioxo 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 O₂ requires a preceding disproportionation reaction forming Mo(ν)O (and Mo(ν)O₂), 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 ¹H and ¹³C 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) *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 ¹H NMR spectrum showed only resonances for one species, which we thus also assign to the O,O isomer. Interestingly, a ¹H 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(ν) isocyanide complexes.²³ Comparing the structure of the oxido peroxido compounds 8 and 9 with previously published cis oxido peroxido complexes originating from O₂ activation, it is evident that the O₂ isomeric form is the preferred conformation for such compounds in the solid state.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 O₂ gas (1.5 atm) in C₆D₆ at room temperature. Blank experiments under identical conditions but without catalyst led to conversions of PMe₃ and PPh₃ to <5%. In the aerobic oxidation of PMe₃, 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%).¹⁶ Catalyst 2 proved to be unselective as only 25% of OPMe₃ was formed together with 10% of one side product. NMR spec-

![Scheme 5](https://example.com/scheme5.png)

**Scheme 5** Activation of molecular oxygen to form oxido peroxido compounds 8 and 9.
Table 1  Yield of phosphane oxide after 24 h in the aerobic oxidation of phosphanes catalyzed by 1 or 2

|     | 1   | 2   |
|-----|-----|-----|
| PMe₃ | 65  | 25<sup>a</sup> |
| PPh₃ | 8 (3)<sup>b</sup> | 23 (12)<sup>b</sup> |

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.

...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 autooxidation at 50 °C, as observed in a blank experiment, no reliable results could be obtained. To confirm the participation of the [MoO(Ο₂)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-

---

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

<sup>Fig. 3</sup> 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.
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 phenolate 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 phosphate complexes (Table 2).6,25

Compound 6, obtained via OAT from 1 to PPh3, displays a μ-oxido bridged dimeric structure with two molybdenum(V) 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⋯Mo1#–O1# −31.1(5)°, N1–Mo1⋯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 phenolate oxygens trans to the oxido and μ-oxido ligands, respectively. The Mo=O and Mo–μ(μ)-O 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 phenolate 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(IV) oxido peroxido compounds, the Mo–O (peroxido) distances in 8 are

Table 2  Selected bond lengths [Å] and angles [°] for complexes 1–3, 5, 6, 8 and 9

|       | 1         | 2         | 3       | 5         | 6         | 8         | 9         |
|-------|-----------|-----------|---------|-----------|-----------|-----------|-----------|
| Mo1–O1| 1.7099(11)| 1.707(3)  | 1.7049(13)–1.7097(13)| 1.7037(13)| 1.694(6)  | 1.642(2)  | 1.6928(13) |
| Mo1–O2| 1.7099(11)| 1.706(3)  | 1.7028(13)–1.7109(13)| —         | 1.888(18)#| 1.981(2)  | 1.9581(13) |
| Mo1–O3| —         | —         | —       | —         | —         | —         | —         |
| Mo1–O11| 1.9729(11)| 1.946(3)  | 1.9243(12)–1.9304(13)| 2.0660(14)| 2.054(6)  | 2.0413(12)| 2.0166(12) |
| Mo1–O21| 1.9729(11)| 1.946(2)  | —       | 2.0816(11)| 2.063(5)  | 2.0262(12)| 2.0493(12) |
| Mo1–N1| 2.3319(12)| 2.373(3)  | 2.3974(15)–2.4021(15)| 2.1272(13)| 2.182(6)  | 2.1810(15)| 2.1237(15) |
| Mo1–N2| 2.3319(12)| 2.394(3)  | —       | 2.1769(13)| 2.155(6)  | 2.1852(15)| 2.1654(15) |
| O2–O3| —         | —         | —       | —         | —         | 1.430(3)  | 1.4425(18) |
| O1–Mo1–O2| 107.88(2)| 105.98(13)| 104.17(6)–104.51(7)| —         | 100.5(3)  | 99.53(9)  | 100.97(6)  |
| O1–Mo1–O3| —         | —         | —       | —         | —         | 100.03(9)| 104.14(6)  |
| O1–Mo1–O21| 161.05(6)| 152.33(11)| —       | 86.95(5)  | 79.9(2)   | 81.01(5)  | 77.09(5)   |
| N1–Mo1–N2| 75.13(6)  | 84.47(10)| —       | 164.99(5)| 174.3(3)  | 160.74(5)| 164.52(5)  |

a Bond length and angle range given due to four distinct molecules in the unit cell. b O2 = μ-oxido.
Dioxido molybdenum(VI) complexes influence on the bonding situation in these complexes. The metal center has a more significant impact on the metal dimeric arrangement compared to the oxidation state of the trans influence. It can be thus further reasoned that the isoergic structures of i.e. an elongation of the Mo–N bond lengths in the N,N isometric structure found in 2 which is likely caused by the trans influence of the oxido ligands. 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 isomeric 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(0) metal precursors [MoO2Cl2] and [MoO2Cl2(DME)] yielded disubstituted complexes 1 and 2, whereas the use of [MoO2(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(0) and molybdenum(0) complexes. The products obtained from the reactions of 1 and 2 were dependent on the nature of the phosphine (PMe3 or PPh3) as well as the employed stoichiometry. The use of excess of PMe3 yielded molybdenum(0) oxido phosphino complexes 4 and 5. Upon the use of stoichiometric amounts of PMe3 or PPh3 molybdenum(0) µ-oxido complexes 6 and 7 were obtained. Compounds 4 and 5 readily reacted with molecular oxygen under ambient conditions to give oxido peroxido complexes 8 and 9, while 6 and 7 did not show similar reactivity. Complexes 1, 2, 4, 5 and 9 exist as isomeric 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. Dioxido molybdenum(vi) complexes 1 and 2 have been found to catalyze the aerobic oxidation of PMe3 and PPh3 with noteworthy reactivity differences depending on the nature of the ligand. In the oxidation of PMe3 compound 1 was significantly more active and selective in comparison with 2, however 2 marked the first example of a catalyst capable of transferring both peroxido oxygen atoms to one substrate molecule and thus partially oxidizing trimethyl phosphate to methyl dimethylphosphinate (OP(OME)Me2). In the catalytic aerobic oxidation of PPh3, complex 1 proved to be virtually unreactive whereas complex 2 gave significant yields of OPPh3. In the case of PPh3 oxidation, the active site is coordinated by a substrate molecule. Thus, prior elimination of PPh3 is necessary, occurring readily under O2 which we have recently demonstrated. This is not possible with the more bulky PPh3 as evidenced by the formation of dinuclear µ-oxido bridged complexes in stoichiometric reactions. However catalysis experiments using these dimeric compounds 6 and 7 as catalysts in the oxidation of PPh3 showed the phenyl-based dinuclear compound 7 exhibiting catalytic activity whereas 6 was completely inactive. This indicates lower activation energy for the disproportionation of 7, which is required for the reaction with molecular O2, 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. Commercially available chemicals were purchased from Sigma-Aldrich and used as received. No further purification or drying operations have been performed. The metal precursors [MoO2(acac)2] and [MoO2Cl2(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 magnesium for at least 24 h and then distilled prior to use. The 1H, 13C and 31P 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 (“d”), pseudo-triplet (“t”) and multiplet (m). The used solvents and peak assignment are mentioned in the specific data sets. Resonances in 31P 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 LC/MSD (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 Elémentar automatic analyzer.

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-methoxypropyl)imino)methylphenol (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-hydroxybenzaldehyde (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 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), 3.17 (t, 2H, CH₂), 3.06 (s, 3H, OMe), 1.69 (m, 2H, CH₂), 1.62 (s, 9H, tBu), 1.32 (s, 9H, tBu) ppm; IR (ATR, cm⁻¹) ²: 1628 (s), 1559 (w), 1460 (w), 1504 (m), 1404 (s), 1332 (s), 1239 (s), 1190 (s), 1105 (m), 1047 (w), 913 (m), 841 (s), 751 (s), 549 (s); EI-MS (70 eV) m/z: 736.6 [M⁺]; Anal. calcd for C₂₁H₂₃O₄N: C, 78.0; H, 7.6; N, 5.5; found: C, 78.0; H, 7.5; N, 5.5.

Synthesis of (E)-2,4-di-tert-butyl-6-((phenylimino)methyl)phenol (HL2).¹⁹ Ligand HL2 was prepared following published procedures. In brief, aniline (0.92 mL, 10.0 mmol) was added to a solution of tert-butyl-2-hydroxy-benzaldehyde (2.34 g, 10.0 mmol) in 25 mL of MeOH and the resulting yellow solution was stirred at reflux temperature overnight. The reaction mixture was subsequently cooled to room temperature and filtered. The precipitate was washed with cold dry pentane to yield HL2 as an orange crystalline solid (89%, 2.75 g). Analytical 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.¹⁹ ¹H NMR (300 MHz, C₆D₆, 25 °C): δ: 14.14 (bs, 1H, OH), 8.08 (s, 1H, CH=N), 7.64 (d, 1H, ArH), 7.11–6.90 (m, 6H, ArH), 1.68 (s, 9H, tBu), 1.34 (s, 9H, tBu) ppm; IR (ATR, cm⁻¹) ²: 1605 (m), 1437 (m), 1361 (m), 929 (m), 878 (m), 794 (s), 568 (m), 448 (m).

Complex syntheses

All complexes are sensitive towards moisture; complexes 4 and 5 are additionally highly sensitive towards air. They can be stored in an N₂-filled glovebox for several weeks without decomposition.

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. Et₂N (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 wax 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.¹¹ ¹H NMR (300 MHz, C₂D₆, 25 °C, N,N isomer): δ: 7.99 (s, 2H, CH=N), 7.71 (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, C₂D₆, 25 °C, N,N isomer): δ: 168.04 (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) ²: 1628 (s), 1593 (w), 1460 (w), 1247 (s), 1108 (s), 1047 (w), 913 (m), 841 (s), 751 (s), 549 (s); EI-MS (70 eV) m/z: 736.6 [M⁺]; Anal. calcd for C₃₆H₇₆MoO₄N₂: 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] (100 mg, 0.51 mmol) in the same solvent (3 mL). Subsequently 2.4 equiv. Et₂N (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.¹¹ ¹H NMR (300 MHz, C₂D₆, 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, C₂D₆, 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); ¹³C NMR (300/75 MHz, C₂D₆, 25 °C, O, N, S, CH₂, CH₃, CH₄, CH₅): δ
isomer, q-CH obscured) δ: 170.13, 165.54 (CH=N), 131.70, 129.59, 129.26, 128.97, 128.08, 127.95, 126.50, 126.00, 125.72, 125.67, 125.54, 123.26, 123.18, 123.06 (Ar), 31.21, 31.20, 29.85, 29.69 (tBu); 13C NMR (HSQC 300/75 MHz, C6D6, 25 °C, N,N benzene, cm−1): 162.09 (CH=N), 145.60, 131.20, 129.96, 129.38, 127.45 (HSQC), 121.25, 121.17 (Ar), 71.06, 69.49, 68.81, 66.68, (CH3), 58.33 (2× OMe), 35.62, 35.45, 34.24, 33.99 (tBu), 33.30 (CH2), 31.86, 31.77 (tBu), 30.86 (CH3), 30.10, 29.91 (tBu), 16.53 (d, PMe3) ppm; 31P NMR (121 MHz, C6D6, 25 °C) δ: −3.17 (putative O,N isomer, Mo-PMe3), −3.48 (putative O,O isomer, Mo-PMe3) ppm; IR (FT-IR, benzene, cm−1): 1612 (s), 1435 (s), 1311 (m), 1256 (s), 1120 (s), 952 (m), 918 (s), 837 (s), 746 (m). ESI-MS (50 V) m/z: 722.3 [M − PMe3]; Anal. calcld for C45H69MoN2O5P: C, 61.79; H, 8.73; N, 3.52; found: C, 62.14; H, 8.76; N, 3.51%.

Synthesis of [MoO(PMe3)(L2)] (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 red-orange 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; 13C 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 O,N isomer, Mo-PMe3) ppm; IR (ATR, cm−1): ν: 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 C45H69MoN2O5P: 806.3474, found: 806.3474; Anal. calcld for C45H59MoN2O6P: 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 and filtered through a glass frit packed with Celite. Evaporation of all volatiles 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.

³¹H NMR (300 MHz, C₆D₆, 25 °C) δ: 8.26 (s, 2H, CH＝N), 8.10 (s, 2H, 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, 169.31 (CH＝N), 166.94, 162.57 (Ar＝O), 140.01, 139.28, 138.48, 137.47, 131.62, 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-Bu), 33.25, 31.95 (CH₂), 31.32, 31.44, 29.81, 29.46 (tBu) ppm; IR (ATR, cm⁻¹) ν: 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(L2)(µ-O)] (7).** For the synthesis of 7, 1 equiv. of 2 (100 mg, 0.13 mmol) and 1 equiv. of PPh₃ (34 mg, 0.13 mmol) were dissolved in dry MeCN (5 mL). The initially brown 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. ¹³¹H 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), 1.20 (“s”, 18H, 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×), 122.76, 120.69 (Ar), 35.70, 35.49, 34.37, 34.01 (q-Bu), 31.79, 31.50, 30.52, 30.11 (tBu) ppm; IR (ATR, cm⁻¹) ν: 1618 (m), 1434 (m), 1250 (s), 1168 (s), 928 (m), 835 (s), 703 (s), 693 (s), 532 (vs); HR-MS (ESI) m/z: [M]+ calcd for C₄₈H₁₅₀Mo₅O₅·0.2CH₂Cl₂: C, 59.60; H, 7.91; N, 3.64; found: C, 59.26; H, 7.99; N, 4.00%.

**Synthesis of [MoO₂(L2)] (9).** For the synthesis of 9, a solution of 4 (50 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 [(60 °C, 2 × 10⁻⁵ atm) gave 7 as a dark orange solid (85%, 84 mg)].³¹H 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), 131.39, 130.99, 29.64, 29.54 (tBu); IR (ATR, cm⁻¹) ν: 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]+ calcd for C₄₂H₂₅Mo₃N₄O₇: 785.2828; found: 785.2820; Anal. calcld for...
C₄₂H₅₂MoN₂O₅: C, 66.30; H, 6.89; N, 3.68; found: C, 65.81; H, 7.05; N, 3.66%.

Catalytic aerobic oxidation of phosphenes

In a representative reaction, 5 mg of the respective catalyst (approx. 0.007 mmol) was dissolved in dry C₆D₆ under a N₂ atmosphere in a 50 mL Schlenk flask. Subsequently 100 equiv. of the respective phosphane (0.7 mmol PMe₃; 53 mg; PPh₃; 184 mg) were added to the solution. The Schlenk flask was then flushed with dry O₂ and placed under O₂ pressure (1.5 atm) wherein 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 N₂. After addition of 0.2 mL of dry CD₂CN to ensure complete dissolution of all formed products, the reaction was monitored via ¹H and ³¹P NMR spectroscopy, phosphane oxide yields were calculated via integration of the respective peak areas in the ¹H NMR spectra, and conversion included the peak areas for the formed side product [OP(O)Me]Me₂. ¹H NMR in C₆D₆ δ: 3.34 (d, 3H, OMe), 1.08 (d, 6H, 2× Me); ³¹P NMR in C₆D₆ δ: 49.93. Blank experiments without catalysts were included for both phosphanes, where yields of <5% were observed for PMe₃ and PPh₃.

Acknowledgements

Financial support by the Austrian Science Fund (FWF) (grant number P26264) and NAWI Graz is gratefully acknowledged.

References

1 (a) C. G. Young, in Biomimetic Oxidations Catalyzed by Transition Metal Complexes, ed. B. Meunier, World Scientific, Singapore, 2000, pp. 415–459; (b) S. Groyzman and R. H. Holm, Biochemistry, 2009, 48, 2310–2320.
2 (a) F. J. Hine, A. J. Taylor and C. D. Garner, Coord. Chem. Rev., 2010, 254, 1570–1579; (b) P. Basu and S. J. Burgmayer, Coord. Chem. Rev., 2011, 255, 1016–1038; (c) R. Hille, J. Hall and P. Basu, Chem. Rev., 2014, 114, 3963–4038.
3 K. Heinze, Coord. Chem. Rev., 2015, 300, 121–141.
4 (a) R. H. Holm, E. I. Solomon, A. Majumdar and A. Tenderholt, Coord. Chem. Rev., 2011, 255, 993–1015; (b) A. Majumdar and S. Sarkar, Coord. Chem. Rev., 2011, 255, 1039–1054.
5 S. A. Hauser, M. Cokoja and F. E. Kühn, Catal. Sci. Technol., 2013, 3, 552–561.
6 G. Lyashenko, G. Saischek, M. E. Judmaier, M. Volpe, J. Baumgartner, F. Belaj, V. Jancik, R. Herbst-Irmer and N. C. Mösch-Zanetti, Dalton Trans., 2009, 5655–5665.
7 M. E. Judmaier, C. Holzer, M. Volpe and N. C. Mösch-Zanetti, Inorg. Chem., 2012, 51, 9956–9966.
8 M. Volpe and N. C. Mösch-Zanetti, Inorg. Chem., 2012, 51, 1440–1449.
9 (a) J. A. Schachner, P. Traar, C. Sala, M. Melcher, B. N. Harum, A. F. Sax, M. Volpe, F. Belaj and N. C. Mösch-Zanetti, Inorg. Chem., 2012, 51, 7642–7649; (b) M. E. Judmaier, C. H. Sala, F. Belaj, M. Volpe and N. C. Mösch-Zanetti, New J. Chem., 2013, 37, 2139; (c) A. Dupé, M. K. Hossain, J. A. Schachner, F. Belaj, A. Lehtonen, E. Nordlander and N. C. Mösch-Zanetti, Eur. J. Inorg. Chem., 2015, 3572–3579; (d) N. C. Mösch-Zanetti, D. Wurm, M. Volpe, G. Lyashenko, B. Harum, F. Belaj and J. Baumgartner, Inorg. Chem., 2010, 49, 8914–8921.
10 N. Zwettler, A. Dupé, J. A. Schachner, F. Belaj and N. C. Mösch-Zanetti, Inorg. Chem., 2015, 54, 11969–11976.
11 Modern Oxidation Methods, ed. J.-E. Bäckvall, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2010.
12 (a) C. E. MacBeth, A. P. Golombek, V. G. Young Jr., C. Yang, K. Kucsera, M. P. Hendrich and A. S. Borovik, Science, 2000, 289, 938–941; (b) R. L. Shook, S. M. Peterson, J. Greaves, C. Moore, A. L. Rheingold and A. S. Borovik, J. Am. Chem. Soc., 2011, 133, 5810–5817; (c) W. Nam, Acc. Chem. Res., 2015, 48, 2415–2423; (d) K. Ray, F. F. Pfaf, B. Wang and W. Nam, J. Am. Chem. Soc., 2014, 136, 13942–13958.
13 H. Arzoumanian, J. F. Petignani, M. Pierrot, F. Ridouane and J. Sanchez, Inorg. Chem., 1988, 27, 3377–3381.
14 (a) J. Tachibana, T. Imamura and Y. Sasaki, J. Chem. Soc., Chem. Commun., 1993, 1436–1438; (b) M. Minato, D.-Y. Zhou, K.-i. Sumiura, Y. Oshima, S. Mine, T. Ito, M. Kakeya, K. Hoshino, T. Asaeda, T. Nakada and K. Osakada, Organometallics, 2012, 31, 4941–4949.
15 G. Lyashenko, G. Saischek, A. Pal, R. Herbst-Irmer and N. C. Mösch-Zanetti, Chem. Commun., 2007, 701–703.
16 A. Dupé, M. E. Judmaier, F. Belaj, K. Zangger and N. C. Mösch-Zanetti, Dalton Trans., 2015, 44, 20514–20522.
17 (a) C. Y. Lorber, S. P. Smidt and J. A. Osborn, Eur. J. Inorg. Chem., 2000, 655–658; (b) S. N. Rao, N. Kathale, N. N. Rao and K. N. Munshi, Inorg. Chim. Acta, 2007, 360, 4010–4016; (c) M. A. Katkar, S. N. Rao and H. D. Juneja, RSC Adv., 2012, 2, 8071.
18 H. Audouin, R. Bellini, L. Magna, N. Mézailles and H. Olivier-Bourbigou, Eur. J. Inorg. Chem., 2015, 5272–5280.
19 G. Aless, M. Sanz, M. E. G. Mosquera and T. Cuenda, Eur. J. Inorg. Chem., 2008, 2008, 4638–4649.
20 H. Gehrke and J. Veal, Inorg. Chim. Acta, 1969, 3, 623–627.
21 T. Robin, F. Montilla, A. Galindo, C. Ruiz and J. Hartmann, Polyhedron, 1999, 18, 1485–1490.
22 N. Zwettler, J. A. Schachner, F. Belaj and N. C. Mösch-Zanetti, Inorg. Chem., 2016, 55, 5973–5982.
23 J. Leppin, C. Förster and K. Heinze, Inorg. Chem., 2014, 53, 1039–1047.
24 J. M. Mayer, Inorg. Chem., 1988, 27, 3899–3903.
25 (a) R. D. Rogers, E. Carmona, A. Galindo, J. L. Atwood and L. G. Canada, J. Organomet. Chem., 1984, 277, 403–415; (b) K. Most, J. Hoßbach, D. Vidović, J. Magull and...
N. C. Mösch-Zanetti, *Adv. Synth. Catal.*, 2005, **347**, 463–472;
(c) K. Hüttinger, C. Förster, T. Bund, D. Hinderberger and K. Heinze, *Inorg. Chem.*, 2012, **51**, 4180–4192.

26 (a) A. B. Blake, F. A. Cotton and J. S. Wood, *J. Am. Chem. Soc.*, 1964, **86**, 3024–3031; (b) B. Modec, M. Šala and R. Clérac, *Eur. J. Inorg. Chem.*, 2010, **2010**, 542–553;
(c) M. M. El-Essawi, F. Weller, K. Stahl, M. Kersting and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1986, **542**, 175–181;
(d) J. Leppin, C. Förster and K. Heinze, *Inorg. Chem.*, 2014, **53**, 12416–12427.

27 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.