Iron–molybdenum-oxo complexes as initiators for olefin autoxidation with $O_2$†‡

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The reaction between [(TPA)Fe(MeCN)$_2$(OTf)$_2$] and [nBu$_4$N](Cp*MoO$_3$) yields the novel tetranuclear complex [(TPA)Fe$_4$·Cp*MoO$_3$]$_2$(OTf)$_2$. 1, with a rectangular [Mo–O–Fe–O–]$_2$ core containing high-spin iron(ii) centres. 1 proved to be an efficient initiator/(pre)catalyst for the autooxidation of cis-cyclooctene with $O_2$ to give cyclooctene epoxide. To test, which features of 1 are essential in this regard, analogues with zincco(i) and cobalt(i) central atoms, namely [(TPA)Zn(Cp*MoO$_3$)](OTf), 3, and [(TPA)Co(Cp*MoO$_3$)](OTf), 4, were prepared, which proved to be inactive. The precursor compounds of 1, [(TPA)Fe(MeCN)$_2$](OTf)$_2$ and [nBu$_4$N](Cp*MoO$_3$) as well as Cp$_2$*Mo$_2$O$_5$, were found to be inactive, too. Reactivity studies in the absence of cyclooctene revealed that 1 reacts both with O$_2$ and PhIO via loss of the Cp* ligands to give the triflate salt 2 of the known cation [(TPA)FeO(μ-O)(μ-MoO$_4$)$_2$]$^2+$. The cobalt analogue 4 reacts with O$_2$ in a different way yielding [(TPA)Co$_2$(μ-MoO$_4$)](OTf)$_2$, 5, featuring a Mo$_2$O$_5^-$ structural unit which is novel in coordination chemistry. The compound [(TPA)Fe$_4$(μ-MoO$_4$)$_2$], 6, being related to 1, but lacking Cp* ligands failed to trigger autoxidation of cyclooctene. However, initiation of autoxidation by Cp* radicals was excluded via experiments including thermal dissociation of Cp$_2$*.

1. Introduction

Epoxides are important synthons for commodity and fine chemicals, and hence their synthesis from olefins via oxygenation is an important issue in academic and industrial laboratories. Elegant routes have been developed where the oxidation step is catalysed by metals employing, for instance, alkyl hydroperoxides, hypochloride or iodosylbenzene as the oxidants. 1–3 Obviously, from an environmental and economical point of view dioxygen would represent a much more favourable oxidant, as it does not produce any waste products and is rather cheap.

An important class of aerobic oxidation processes consists of autoxidation reactions. Due to the presence of several different strong oxidants in autoxidation reactions and the multitude of different possible reaction pathways and products, usually autoxidation is considered as a process that has to be suppressed. However, autoxidation reactions may also be utilised on purpose for the aerobic epoxidation of olefins. Even industry pursues corresponding approaches, although the selectivity that can be reached is clearly determined by the substrate. Important industrial scale processes include the oxidation of p-xylene to terephthalic acid (44 Mt·a⁻¹), the oxidation of cyclohexane to cyclohexanol and cyclohexanone (6 Mt·a⁻¹) and the production of ethylbenzene hydroperoxide (6 Mt·a⁻¹). 3 Generally the autooxidation of hydrocarbons is assumed to proceed via a branched radical chain reaction 4 while the chain mechanism has been deeply explored in the past, the processes by which the chain reactions may be initiated still receive attention. 5–7 Autoxidation initiation by direct reaction of unactivated hydrocarbons with molecular dioxygen (reactions 1 and 2) is both thermodynamically and kinetically unfavourable 2 and therefore rarely observed. 8

\[ \text{R–H + O}_2 \rightarrow \text{R}^* + \text{HOO}^* \quad (1) \]

\[ \text{R–H + O}_2 + \text{H–R} \rightarrow \text{R}^* + \text{HOOH} + \text{R}^* \quad (2) \]

This is usually circumvented by the use of initiators, typically aliphatic azo compounds, dialkyl peroxides or samples of the corresponding hydroperoxides. 1,2 Once initial peroxyl or alkyl radicals have been formed (reactions 1 and 2), the chain
reactions propagate through trapping of molecular dioxygen by the latter (see reaction 3), while the former can abstract a hydrogen atom from an unactivated hydrocarbon to give an alkyl hydroperoxide and an alkyl radical (reaction 4). Decomposition (reaction 5) generates new radicals which cause branching of the chain reaction.

\[ R' + O_2 \rightarrow ROO' \] (3)  
\[ R-H + ROO' \rightarrow R' + ROOH \] (4)  
\[ ROOH(ROOR) \rightarrow RO' + HO'(RO') \] (5)

In olefin autoxidations there are additional possibilites for chain reaction propagation: alkyl peroxide species can either abstract hydrogen atoms from the α-allylic position of olefins (reaction 6) or add to double bonds leading to the formation of epoxides (reactions 7 and 8) or polyperoxides (reaction 9).2

\[ ROO' + HCR_2=CR_2 \rightarrow RO_2H + \cdot CR_2=CR_2 \] (6)  
\[ ROO' + C=CR_2 \rightarrow RO_2CR_2=CR_2' \] (7)  
\[ RO_2CR_2=CR_2' \rightarrow RO' + epoxide \] (8)  
\[ RO_2CR_2=CR_2' + O_2 \rightarrow RO_2CR_2=CR_2'OO' \] (9)

Typical autoxidation “catalysts” enhance the rate of radical generation by formation of metal–alkyl hydroperoxide complexes, which subsequently undergo homolytic unimolecular decomposition to generate alkylperoxo (reaction 11) and alkoxy radicals (reaction 10) initiating radical chain reactions in the process.2,9

\[ ROOH + M^{(n-1)+} \rightarrow RO' + M^{n+} + OH^- \] (10)  
\[ ROOH + M^{n+} \rightarrow ROO' + M^{(n-1)+} + H^+ \] (11)

This contribution focuses on radical chain initiation with O₂: we report an iron–molybdenum-oxo complex which triggers autoxidation of cyclooctene, as an exemplary hydrocarbon, by initial activation of O₂ and thus complements the few systems reported in this context so far.13-15

2. Results and discussion

In recent years, we have been interested in molecular heterobimetallic oxo compounds that can mimic certain structural units proposed to occur on the surfaces of corresponding heterogeneous catalysts composed of two metal oxide components.16-22 The fact that MoO₃/Fe₂O₃ catalysts are employed for the oxidation of methanol to formaldehyde in the so-called FORMOX process has spurred us to investigate Fe–O–Mo compounds. While some purely inorganic polyoxometal aggregates23-30 and coordination polymers30-37 featuring Fe–O–Mo entities have been published, so far only five structurally characterised molecular coordination compounds have been reported, where molybdate units are bridging ligated iron ions.27,38-43 Since the replacement of purely inorganic molybdate by a monovalent organomolybdate, namely Cp*MoO₃⁻ [Cp* = η⁵-C₅Me₅], has already served us for the preparation of model compounds in the past,16-18 we were interested in an investigation on [L]Fe^{II}/Cp*MoO₃⁻ (L = ligand molecule) systems.

Hence, [TPA][Fe]OTf₂ [TPA = tris(2-pyridylmethyl)-amine, OTf = trifluoromethanesulfonate] was reacted with [Bu₄N][Cp*MoO₃] in acetonitrile (Scheme 1) resulting in an immediate colour change from yellow to red-brown. After reduction of the volume, layering of the solution with diethyl ether led to red-brown crystals of [TPA][Fe(µ-Cp*MoO₃)]₂(OTf)₂(MeCN)₂ (1-{MeCN})₂, Fig. 1), which were suitable for structure determination by single crystal X-ray crystallography.

1-{MeCN}₂ crystallises with two independent molecules in the asymmetric unit. In the molecular structure of 1-{MeCN}₂, two [[TPA][Fe]²⁺ fragments are bridged by two bidentate Cp*MoO₃⁻ ligands, resulting in an eight-membered macrocyclic structure, in which alternating iron-oxo and molybdenum-oxo units [Mo=O–Fe–O]₂ form a bent rectangle (torsion angles as measured for Fe1, Mo1, Mo2, Fe2 = 143.17(2)/-145.45(2)°).

The iron centres are coordinated by TPA, Mo=O⁻Fe–O(2,4,7,9) 2.120(4)-2.153(4) Å and Mo–O⁻Fe–O(1,3,8,10) 1.962(4)-1.968(4) Å functional groups in a distorted octahedral manner. The corresponding N–Fe–N angles are considerably smaller than those of the precursor [TPA][Fe(MeCN)₂]OTf₂ 34 as the latter is a low-spin complex, where the iron(II) ion has a smaller radius than the high-spin iron(II) centre in 1. Compared to the typical lengths of molybdenum-oxygen double bonds of 1.69(2) Å, like in Cp₂*MoO₃ 45 all Mo=O bonds are significantly lengthened, extending to 1.725(4)-1.731(4) Å for the non-coordinating Mo=O groups and to 1.749(4)-1.757(4) Å for the molybdenum oxido units, whose oxygen atoms are additionally coordinated to an iron
The peak assignment was deduced from peak integration, observed line widths and $T_1$ relaxation measurements.\cite{47,48,52} based on the strong paramagnetic shift, its integral and relative broadness, the signal at the lowest field with a shift of 141.1 ppm ($\Delta\nu_{1/2} = 1550$ Hz) was assigned to the pyridyl $\alpha$ protons. These are closest to the high-spin metal ion (3.24 Å) and, consistently the $T_1$ ($T_1$ measurements at 500.1 MHz and 296 K, Table S2†) determined, was 0.2 ms. The intense broad signal at 55.7 ppm ($\Delta\nu_{1/2} = 1200$ Hz) also shows a very fast $T_1$ relaxation (0.4 ms) which again is due to the close proximity of the respective protons to the metal centre and thus points to an assignment to the methylene groups. Relatively sharp features at 47.1 ($\Delta\nu_{1/2} = 125$ Hz, $T_1 = 3.0$ ms), 44.8 ($\Delta\nu_{1/2} = 90$ Hz, $T_1 = 4.2$ ms) and 25.5 ($\Delta\nu_{1/2} = 65$ Hz, $T_1 = 10.4$ ms) are observed for more distant $\beta$ (5.03 Å), $\beta$ (5.20 Å) and $\gamma$ (5.88 Å) protons; the signal with the smallest chemical shift at 8.7 ppm ($\Delta\nu_{1/2} = 120$ Hz, $T_1 = 3.7$ ms) stems from the Cp*-methyl groups. These experimentally determined $T_1$ values favourably agree with those predicted using the Solomon equation.\cite{51-53} Due to the large Fe···Fe distance in 1, calculations considering the effect of the distant paramagnetic iron centre do not show a significant effect on the longitudinal relaxation time. However, the typical pattern of downfield shifts attenuating in the order $\alpha$, $\beta$, $\gamma$-H observed here has been linked to a predominant $\sigma$ delocalization mechanism of unpaired spin density\cite{54} and thus a distorted octahedral coordination sphere around the metal centre hinting at a structure of 1 in solution that corresponds to the one in Fig. 1.\cite{44,49,50,52}

Unlike the parent complex $[[\text{TPA}]\text{Fe(MeCN)}_2][\text{OTf}]_2$, 1 proved to be reactive towards dioxygen in solution, which led us to investigate whether 1 could be employed in the selective oxygenation of model substrates, most notably cis-cyclooctene. The results showed that the (yet unidentified) primary product of the reaction between 1 and O₂ initiates autoxidation of cyclooctene.

cis-Cyclooctene autoxidation

Typically olefin autoxidation experiments are conducted with high concentrations or even a neat substrate as the solvent.\cite{1,2} To study subtle effects, here low concentrations were favoured that concomitantly decrease reaction rates and yields. In a typical experiment a solution of a certain amount of 1, cis-cyclooctene, and an internal standard in acetonitrile were heated to 80 °C and the atmosphere was replaced by approximately 1.2 bar of pure dioxygen. Samples were collected periodically, freed from metal ions by means of chelex complexation, filtrated over celite and subjected to GC-FID analysis. This proved selective oxidation of cyclooctene to give cyclooctene epoxide (COE, Fig. 2, see Fig. S2† for a GC chart). Investigating the kinetics of this reaction, several aspects of the observed behaviour were not explicable under the assumption of a classical metal-catalysed oxidation reaction. All of the conducted experiments of cyclooctene epoxidation showed S-shaped yield vs. time curves hinting towards an initial reaction step forming the active oxidant and/or catalyst in solution. Also, the initial reaction rate did not show a linear correlation...
Interestingly, the rate of AIBN driven autoxidation drops to a rate similar to that observed with 0.07 μmol 1, which stresses the efficiency of 1 as a radical chain initiator and also suggests that beyond that it also acts as a (pre)catalyst. Referring to the beginning of this section it should be emphasized at this point that rate and yield can be enhanced dramatically by increasing the substrate concentration (for a demonstration of the effect of adding twice the amount of substrate see Fig. S1†), while the selectivity of the reaction is essentially unaffected (Fig. S2†).

In order to find out how far the potential to initiate autoxidation is a special property of 1, we have compared the reactivity of the precursors used for the synthesis of 1, of related Cp₂*Mo₂O₅ and related high-spin iron(n) complexes (TPA)-FeCl₂,⁵⁵ and (TPH₃Me)FeCl (TP = trispyrazolylborato).¹² However, no chain initiation was observed employing [(TPA)Fe(MeCN)₂](OTf)₂, (TPA)FeCl₂, [(TPH₃Me)FeCl], or [nBu₄N] (+)MoO₃, whereas using Cp₂*Mo₂O₅ the observed activity was negligible, so that neither ligated iron(n) nor molybdenum entities featuring terminal or bridging oxido ligands can be solely responsible for the observed behaviour.

Therefore we became interested in the nature of the initiating species formed from 1. Low temperature UV/VIS experiments conducted in acetonitrile (−40 °C), dichloromethane or propionitrile (−80 °C) solutions did not reveal any labile intermediates and thus did not provide any evidence regarding the nature of the initial 1/O₂ product.

To evaluate the importance of the iron centres in 1, we have also reacted [(TPA)Zn](OTf)₂ and [(TPA)Co](OTf)₂ with [nBu₄N]−(Cp₂*MoO₃), analogous to the synthesis of 1. This led to the isolation of [(TPA)Zn(Cp₂*MoO₃)](OTf) (3) and [(TPA)Co(Cp₂*MoO₃)](OTf) (4) (Scheme 2). Prolonged drying in high vacuum led to the loss of co-crystallised solvent molecules and afforded the analytically pure compounds. In contrast to the molecular structure of 1 within the single crystal, in the molecular structures of both 3(MeCN)₂ and 4(Et₃O)₃.₅(MeCN)₅ the coordination of only one Cp₂*MoO₅⁻ unit per 3d-metal centre is observed, leading to slightly distorted trigonal bipyramidal coordination spheres at the central atoms. Both structures are largely similar (Fig. 4 shows the structure of 4(Et₃O)₃.₅(MeCN)₅; for the molecular structure of 3(MeCN)₂ see Fig. S4†), with only minor differences around the Co/Zn and molybdenum centres. The ¹H NMR spectrum of 4 in acetonitrile-d₃ features a set of signals that is in good agreement with a diamagnetic complex exhibiting a three-fold symmetry in solution. In contrast, the proton NMR spectrum of 4 in the same solvent at 300.1 MHz and 295 K displays a set of broad paramagnetically shifted signals in the region from 144.5 to −0.8 ppm again indicative of a three-fold symmetry for dissolved 4 on the NMR time scale (Fig. S8, S9†). Integrals, linewidth data and T₁ relaxation times were considered to assign the signals to the groups of equivalent protons in 4. Correct longitudinal relaxation times can be predicted for methylene, α and one of the β proton groups using the Solomon equation (eqn S1−S4, Table S3†), while in contrast to 1 the measured values of the second group of β protons and the γ protons are
much larger than calculated. Hence, the paramagnetic relaxation mechanism does not seem to be dominant in this case. Moreover, due to the smaller line broadening compared to 1 a standard 2D COSY-DQF experiment could be used to identify scalar couplings and thus to establish bond connectivities between the pyridylic $\beta/\beta'$ and $\gamma$ protons (Fig. S10). The characteristic upfield shift of the pyridyl $\gamma$-H in metal-TPA complexes has been observed before and interpreted as the effect of a $\pi$ mechanism superimposed on a dominant $\sigma$ delocalisation mechanism of unpaired spin density. Since this is only possible in a trigonal pyramidal geometry around the metal centre, NMR indicates that the molecular structure of 4 in the solid state is retained in solution.

Fig. 4 Molecular structure of the cation of $\text{[TPA}Co(Cp^*\text{MoO}_3)](\text{OTf})$ (4). Hydrogen atoms, triflate anions and co-crystallised solvent molecules have been omitted for clarity. Selected bond lengths (in Å) and angles (in °): Co1–O1 1.924(6), O1–Mo1 1.809(6), Mo1–O2 1.728(6), Mo1–O3 1.730(6), Mo1–Cp 2.116(4), Co1–O1–Mo1 147.1(3), O1–Mo1–O2 106.2(3), O2–Mo1–O3 105.7(3), O3–Mo1–O1 105.4(3).

Cyclooctene epoxidation studies conducted for 3 and 4 showed that, under the same conditions as those employed in the case of 1, neither of these compounds proved to be an initiator for the autoxidation reaction: 4 reacts with dioxygen, but no main oxidation product could be identified. Not surprisingly, 3 does not react at all. Contemplating the functioning of 1 as a radical chain initiator one mechanistic possibility is the initial binding and activation of $O_2$ between its two iron centres, finally leading to a high valent Fe$^{IV}═O$ species, which triggers radical reactions via $H$ atom abstraction or addition to the $\pi$ bond. The Fe⋯Fe distance of 5.23 Å should allow to accommodate a peroxide ligand between the iron centres (a simultaneous dissociation of one pyridyl arm should be expected). Hence the independent generation of such Fe$^{IV}═O$ species was pursued in the next step employing iodosobenzene (PhIO) as the oxygen atom transfer reagent. For comparison the same reaction was studied for 4.

1 reacts with iodosobenzene (Scheme 1), formally, losing Cp$_2^*^+$ and MoO$_3$ to give the known diiron(m) cation $\text{[TPA}Fe)_2(\mu-MoO_4)(\mu-O)]^{2+}$ (2, Fig. S3). In the presence of cyclooctene no chain initiation was observed. According to HR-ESI investigations, $\text{[TPA}Fe)_2(\mu-MoO_4)(\mu-O)]^{2+}$ is also the major final product of the reaction of 1 with $O_2$. This is further corroborated by molybdenum K-edge XAS measurements for acetonitrile solutions of 1 prior to and after exposition to dioxygen under conditions suitable for cyclooctene autoxidation. For 1, the Mo K-edge shape, EXAFS spectrum and respective simulation parameters were in agreement with the crystal structure (chapter S4, Table S4 and Fig. S11), albeit with the typical deviations in bond lengths and angles that occur comparing the molecular structure in solution and in the solid state. They reveal one Mo⋯O bond (1.74 Å), two Mo⋯O bonds (1.77 Å), two Mo⋯Fe distances at 3.45 Å, and pronounced contributions to the spectrum by Mo⋯C interactions due to the Cp$^*$ ring. For 1/O$_2$, the K-edge revealed an increased pre-edge feature (at 20 010 eV), which suggested an increased number of Mo⋯O bonds. In the EXAFS spectrum, Mo–C$^{\sigma\Pi}$ contributions were not observed any more and its simulation revealed a first-sphere coordination of the Mo with likely four Mo⋯O bonds ($2 \times 1.70$ Å and $2 \times 1.93$ Å). The presence of two molybdenum–oxygen distances differing by 0.2 Å explained the diminished FT amplitude of 1/O$_2$ compared to 1, which is due to interference effects. The Mo⋯Fe distances in 1/O$_2$ appear to be slightly shorter compared to 1. All these observations are in agreement with the formation of 2 as the final product after O$_2$ treatment of 1 dissolved in acetonitrile. It is stable in air and can thus not account for autoxidation. An intermediate between 1 and 2 formed in situ will thus be responsible. The reaction of 4 with PhIO (Scheme 2) proceeds differently from

![Scheme 2](image-url)
the one of 1: it affords the novel compound \([([\text{TPA})\text{Co}])_2\mu_2\text{Mo}_2\text{O}_5\text{O}_4\text{O}_2\text{OTf}_2\] (5, Fig. 5) that features two \([([\text{TPA})\text{Co}])\] units, bridged by a \(\text{Mo}_2\text{O}_8\) unit, which is hitherto unprecedented as a building block of heterometallic coordination compounds. So far it has only been observed bound by additional molybdenum atoms in larger aggregates.\(^{61-64}\) The \(\tau\)-value calculated for the coordination spheres of the symmetry equivalent molybdenum atoms is effectively zero indicating perfectly square pyramidal coordination environments.\(^{65}\) Consequently, the reactions of both 1 and 4 with oxidants led to a loss of the \(\text{Cp}^*\) ligands, probably in the form of \(\text{Cp}^*\) radicals. Indeed, after the reaction of 4 with \(\text{PhIO}\), decamethylbis(cyclopentadienyl) \(\text{Cp}^*\) was isolated as a byproduct in yields up to 20%, indicating the intermediate formation and recombination of \(\text{Cp}^*\) radicals. This raised the idea that \(\text{Cp}^*\), which is known to trap dioxygen leading to peroxyl radicals,\(^{66}\) might play a role in the initiation of autoxidation. To test the hypothesis that \(\text{Cp}^*\) radicals are relevant, a further experiment was carried out employing independently synthesised \(\text{Cp}_2\text{Fe}^+\) radicals, which was then subjected to thermal dissociation under reaction conditions. However, no chain initiation was observed thus ruling out the involvement of these radicals.\(^{67-69}\) In this context \([([\text{TPA})\text{Fe})_2\mu_2\text{Mo}_2\text{O}_5\text{O}_4\text{O}_2\text{OTf}_2\] (6, Fig. S5†) was also synthesised and subjected to test reactions. Over 7 h at 80 °C this did not reveal observable activity, perhaps not surprisingly as 6 is rather similar to 2. However, from these results it is clear that although \(\text{Cp}^*\) radicals are not directly responsible for the autoxidation initiation, \(\text{Cp}^*\) nevertheless plays an important role as a spectator ligand governing the initial reactivity of the system.

3. Conclusions

From the gathered results we conclude the following:

- \(1/\text{O}_2\) represents an efficient system for initiating autoxidation.
- \(1\) is unique with respect to its dioxygen reactivity as compared to the complex metal fragments it was constructed from and also with respect to related iron/molybdenum compounds.
- The presence of iron(II) ions is important as their replacement deactivates the system.
- It follows that dioxygen is activated at one or both of the iron centres within 1. However, the ultimately formed oxidant is different from the one produced via treatment with \(\text{PhIO}\), as the latter cannot be used to achieve autoxidation.
- We propose that the oxidizing species formed triggers autoxidation of cyclooctene by H-atom abstraction or \(\pi\) bond addition.

In our future work we will extend these studies to other types of ligands at the iron centres with the aim of gathering further information on the active species and the influence of the organomolybdate on its formation.

4. Experimental details

4.1 General procedures

All manipulations were carried out in a glovebox, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. Microanalyses were performed using a Hekatech Euro EA 3000 elemental analyser. Infrared (IR) spectra were recorded using samples prepared as KBr pellets using a Shimadzu FTIR-8400S spectrometer. HR-ESI-MS spectra were collected using samples prepared as KBr pellets using a Time-of-Flight LC-MS instrument.

4.1.1 NMR spectroscopy. The NMR spectra were recorded using Bruker DPX 300, Avance III 300 \((^1\text{H} 300.1 \text{MHz})\) or Avance III 500 \((^1\text{H} 500.1 \text{MHz})\) NMR spectrometers. Chemical shifts are reported in ppm, relative to residual proton signals of the deuterated solvent (dichloromethane-d$_2$ at 5.32 ppm, acetonitrile-d$_3$ at 1.94 ppm, benzene-d$_6$ at 7.16 ppm), respectively. Measurements to obtain non-selective proton longitudinal relaxation times \((T_1)\) were performed using a standard inversion recovery experiment with a 180°–\(\tau\)--90°-AQ pulse sequence. To ensure the validity of the results, for each sample multiple experiments with different transmitter frequency offsets were carried out. The Bruker Topspin $T_1/T_2$ module was used to obtain $T_1$ values in a non-linear fitting procedure.

4.1.2 Crystal structure determination. All data were collected at 100 K with a STOE IPDS 2T diffractometer. The
crystals were mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the diffractometer. In all cases Mo-Kα radiation (λ = 0.71073 Å) was used; the radiation source was a sealed tube generator with a graphite monochromator. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares procedures based on F² with all measured reflections (SHELXL-97). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their idealized positions and refined as riding. A multi-scan absorption correction was applied for complex 1, and numerical absorption correction was used for the other complexes (Table 1).

4.1.3 GC-FID analysis. All autoxidation yields were determined using a Varian 3800-GC equipped with FID and Varian 4000 MS detectors. The samples were injected automatically employing split injectors. The capillary columns used were Varian factor FOUR VF-5 ms or VF-WAXms 30 mm × 0.25 mm i.d. Gas chromatograms were recorded on a Varian 3800-GC equipped with FID and Varian 8453A diode-array spectrometer using quartz capillaries equipped with a Unisoku, Japan Unispeks USP-203-A Cryostat providing a controlled temperature environment during measurements.

4.1.7 Materials. TPA,75 LiCp*,76 Fe(MeCN)₂[OTf]₃,77 [(TpPh₂Me)Fe]Cl₁,2 [(TPA)FeCl₃],78 [nBu₄N][CP*MoO₄]₇9 Cp₂*Mo₂O₅,46 [(Cp*Me)CrCl],10 [(Cp*)CrCl₂],10 [(TPA)Mo₂O₆],46 10 [nBu₄N][Cp*MoO₄]₇9 Cp₂*Mo₂O₅,46 [nBu₄N][MoO₄]₈0 and iodosobenzene81 were prepared according to the literature procedures. CuCl₂ was purchased from Acros Organics, Belgium. Zn[OTf]₂ (98%) was purchased from Sigma-Aldrich. Dioxygen N₄8 was obtained from Air Liquide. Solvents were purified, dried, degassed, and stored over molecular sieves (3 Å) prior to use.

4.1.7.1 Synthesis of 1,1′,2′,2″,3′,4′,4″,5′-decamethyl-bis(cyclopentadienyl) (Cp₂*). Cp₂* was synthesised by a modified literature procedure.69 To a suspension of 0.98 g (10 mmol) CuCl₂ in 40 mL of MeCN at −78 °C a suspension of 1.42 g LiCp* (10 mmol) in 25 mL of MeCN was added. The mixture was stirred at that temperature and allowed to slowly warm to r.t. overnight. The reaction mixture was filtered off and the volume of the filtrate was reduced. The residual oil was extracted three times with 7 mL of n-hexane. All volatiles were then removed under reduced pressure to give a slightly yellow oil. Addition of

Table 1 Crystal data and experimental parameters for the crystal structure analysis

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<th>Compound</th>
<th>Formula</th>
<th>Fw/g mol⁻¹</th>
<th>Fw/(g mol⁻¹)</th>
<th>Fw/(g mol⁻¹)</th>
<th>Fw/(g mol⁻¹)</th>
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<td>1-MeCN₄</td>
<td>C₆₄H₇₉Co₂Fe₂Mo₂N₁₀O₁₃S₂</td>
<td>1670.22</td>
<td>Monoclinic</td>
<td>10.62(1)</td>
<td>1.595</td>
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<tr>
<td>2-MeCN₄</td>
<td>C₆₄H₇₉Co₂Fe₂Mo₂N₁₀O₁₃S₂</td>
<td>1670.22</td>
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<td>10.62(1)</td>
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<tr>
<td>3-MeCN₄</td>
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<td>10.62(1)</td>
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<tr>
<td>4-MeCN₄</td>
<td>C₆₄H₇₉Co₂Fe₂Mo₂N₁₀O₁₃S₂</td>
<td>1670.22</td>
<td>Monoclinic</td>
<td>10.62(1)</td>
<td>1.792</td>
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</table>

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3 mL of *n*-hexane and storing the resulting solution at −80 °C for several days resulted in the formation of slightly yellow crystals, which were isolated by filtration, while cold, to give 840 mg (3.11 mmol, 62%) of Cp*Fe. 1H NMR, δ in ppm, CD6D6: 1.77 (s, 12H), 1.68 (s, 12H), 1.16 (s, 6H).

4.2 Synthesis of [(TPA)Fe(μ-Cp*MoO3)](OTf)2 (1)
1.000 g (1.37 mmol) of [(TPA)Fe(MeCN)2](OTf)2 was dissolved in 30 mL of acetonitrile resulting in an orange solution. 0.720 mg (1.37 mmol) of [nBu4N][Cp*MoO3] were then added to this mixture. This was accompanied by an immediate colour change to give a brown solution, which was then concentrated under reduced pressure to about one-third of the original volume. Layering with diethyl ether resulted in the formation of green crystals which were suitable for analysis by single crystal X-ray-diffraction. Drying overnight in high vacuum resulted in the loss of the co-crystallised solvent molecules to give 0.227 mg (0.290 mmol, 84%) of 3 as a yellow powder.

4.3 Synthesis of [(TPA)Fe(μ-O)(μ-MoO3)](OTf)2 (2)
0.164 g (0.745 mmol, 2.1 eq.) of iodosobenzene was added resulting in the formation of green crystals which were suitable for analysis by single crystal X-ray-diffraction. Drying overnight in high vacuum resulted in the loss of the co-crystallised solvent molecules to give 0.227 mg (0.290 mmol, 84%) of 3 as a yellow powder. Elemental analysis, calcd for C29H33F3MoN4O6SCo: C 44.80, H 4.28, N 7.21, S 4.09, found: C 44.74, H 4.29, N 7.22, S 4.01%. IR (KBr) 3110 vw, 3071 vw, 3035 vw, 2961 w, 2915 w, 2857 vw, 1610 s, 1573 s, 1437 m, 1377 w, 1319 w, 1267 vs, 1223 m, 1183 m, 1159 s, 1152 s, 1138 s, 1107 w, 1095 vw, 1053 w, 1031 vs, 985 w, 962 w, 883 vs, 856 vs, 805 m, 790 vs, 776 m, 753 w, 732 m, 637 vs, 629 w, 571 vw, 517 m, 505 w. 1H NMR, δ in ppm, CD3CN 9.04 (dq, 3H, J = 5.4 Hz, J = 0.8 Hz), 8.05 (dt, 3H, J = 7.8 Hz, J = 1.7 Hz), 7.62 (ddd, 3H, J = 7.6 Hz, J = 5.5 Hz, J = 0.8 Hz), 7.52 (dt, 3H, J = 7.9 Hz), 4.14 (6H, s, CH3), 2.05 (s, 15H, CH3).

4.4 Synthesis of [(TPA)Zn(Cp*MoO3)](OTf)3 (3)
0.100 g (0.34 mmol) of TPA were dissolved in 20 mL of acetonitrile and 0.125 g (0.34 mmol) of Zn(OTf)2 were then added. The suspension was stirred until all solid was dissolved resulting in a clear colourless solution (30 min). Upon addition of 0.179 g (0.34 mmol) [nBu4N][Cp*MoO3] the solution immediately became yellow in colour. The solution was stirred at r.t. overnight, concentrated to 2 mL under reduced pressure and layered with diethyl ether. After a few days 3 was isolated as yellow crystals which were suitable for analysis by single crystal X-ray-diffraction. Prolonged drying in high vacuum resulted in the loss of the co-crystallised solvent molecules to give 0.227 mg (0.290 mmol, 84%) of 3 as a yellow powder.

4.5 Synthesis of [(TPA)Co(Cp*MoO3)](OTf) (4)
1.000 g (3.44 mmol) TPA were dissolved in 100 mL acetonitrile and 1.229 g (3.44 mmol) Co(OTf)2 were then added. The suspension was stirred for 30 min to give a solution which was deep purple in colour. 1.794 g (3.44 mmol) of solid [nBu4N]([Cp*MoO3]) were added resulting in a deep green solution which was stirred overnight at r.t. The solution was concentrated to 20 mL. The product was crashed by addition of 100 mL of diethyl ether and the mixture was filtered off using a stainless steel filter cannula. The green solid was redisolved in 20 mL of acetonitrile and layered with diethyl ether which resulted in the formation of green crystals of 4 as a green powder. Elemental analysis, calcd for C29H33F3MoO6N5Co: C 44.80, H 4.28, N 7.21, S 4.09, found: C 44.74, H 4.29, N 7.22, S 4.01%. IR (KBr) 3108 vw, 3067 vw, 3035 vw, 2948 vw, 2915 w, 1609 s, 1573 w, 1485 w, 1435 m, 1377 w, 1314 w, 1267 vs, 1223 m, 1183 m, 1151 s, 1151 s, 1139 w, 1053 w, 1032 vs, 985 w, 962 w, 883 vs, 856 vs, 805 m, 790 vs, 776 m, 753 w, 732 m, 637 vs, 629 w, 571 vw, 517 m, 505 w. 1H NMR, δ in ppm, CD3CN 9.04 (dq, 3H, J = 5.4 Hz, J = 0.8 Hz), 8.05 (dt, 3H, J = 7.8 Hz, J = 1.7 Hz), 7.62 (ddd, 3H, J = 7.6 Hz, J = 5.5 Hz, J = 0.8 Hz), 7.52 (dt, 3H, J = 7.9 Hz), 4.14 (6H, s, CH3), 2.05 (s, 15H, CH3).

4.6 Synthesis of [[(TPA)Co2(μ-Mo2O8)]](OTf)2 (5)
0.0283 g (0.129 mmol) of iodosobenzene was added to a stirred deeply green solution of 0.100 g (0.129 mmol) 4 in 10 mL of acetonitrile. The resulting suspension was stirred...
overnight and within several hours the colour changed to light purple. The mixture was filtered and the filtrate was dried. The purple coloured solid residue was then redissolved in 4 mL of acetonitrile and layered with diethyl ether to give 5-(MeCN)$_4$ as purple crystals. Drying in high vacuum afforded 49 mg (0.037 mmol, 58%) of 5 as a purple solid. Crystals, which are suitable for analysis by single crystal X-ray diffraction can be grown directly from the reaction mixture by ultrasonication of a suspension of 13.7 mg (0.018 mmol) of iodosobenzene in 0.6 mL acetonitrile in a sealed NMR tube followed by storage of respective tube in a horizontal position overnight. Elemental analysis, calcd for C$_{36}$H$_{36}$Fe$_2$Mo$_2$N$_8$O$_{8}$: C 35.10, H 3.10, N 8.12, S 4.26%. IR (KBr) $\tilde{\nu}$ cm$^{-1}$: 3074 vv, 3039 vv, 2961 vv, 2942 vv, 1609 m, 1487 w, 1465 w, 1447 w, 1437 w, 1383 vv, 1276 vs, 1272 vs, 1261 vs, 1224 m, 1158 m, 1113 vs, 1092 vv, 1056 vv, 1030 vs, 997 vv, 923 w, 890 m, 836 w, 821 m, 776 m, 757 w, 740 w, 667 m, 660 w, 636 s, 573 w, 518 w, 506 w. $^1$H NMR, δ in ppm, CD$_3$CN 8.54 (ps-d, 1H, J = 5.9 Hz), 8.51 (ps-d, 2H, J = 5.7 Hz), 7.91 (td, 2H, J = 7.8 Hz, J = 1.5 Hz), 7.72 (td, 1H, J = 15.5 Hz, J = 1.5 Hz), 7.55 (d, 2H, J = 7.9 Hz), 7.40 (ps-t, 1H, J = 6.1 Hz), 7.29 (ps-t, 2H, J = 6.4 Hz), 7.08 (ps-d, 1H, J = 7.9 Hz), 5.50 (d, 2H, J = 15.9 Hz), 4.78 (s, 2H), 4.69 [d, 2H, J = 16.1 Hz].

4.7 Synthesis of [(TPA)Fe(μ-MoO$_4$)$_2$] (6)

To a solution of 290.4 mg (1.00 mmol) of TPA in 10 mL of acetonitrile, 436.1 mg (1.00 mmol) of [Fe(MeCN)$_2$](OTf)$_2$ were added. The brown solution was stirred for 15 min at r.t. 644.9 mg (1.00 mmol) of [nBu$_3$N]$_2$(MoO$_4$) were then added causing immediate precipitation of a brown solid. 90 mL of acetonitrile were subsequently added, and the resulting suspension was stirred overnight. After the addition of 100 mL of diethyl ether, the mixture was filtered and the solid residue was dried under high vacuum overnight to afford 388 mg (0.383 mmol, 77%) of 6 as a brown solid. Red crystals of 6-[MeCN)$_2$ suitable for single crystal X-ray-diffraction analysis were grown by slow diffusion of a solution of 35.5 mg (0.055 mmol) [nBu$_3$N]$_2$(MoO$_4$) in 4 mL acetonitrile into a solution of 20.0 mg (0.028 mmol) [(TPA)Fe(MeCN)$_2$](OTf)$_2$ in 8 mL acetonitrile. Elemental analysis, calcd for C$_{38}$H$_{38}$Fe$_2$Mo$_2$N$_8$O$_{8}$: C 42.71, H 3.58, N 11.07, found C 42.49, H 3.53, N 10.95%. IR (KBr) $\tilde{\nu}$ cm$^{-1}$: 3059 vv, 3055 vv, 3016 vv, 2922 vv, 2917 vv, 1601 m, 1570 w, 1478 w, 1456 w, 1441 m, 1391 vv, 1369 vv, 1349 vv, 1311 vv, 1289 vv, 1263 vv, 1152 vv, 1116 vv, 1097 w, 1049 vv, 1015 vv, 996 vv, 979 vv, 903 w, 860 vs, 847 vs, 781 s, 769 s, 660 vv, 636 vv, 621 vv.

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