

Aerobic Carbon–Carbon Bond Cleavage of Alkenes to Aldehydes Catalyzed by First-Row Transition-Metal-Substituted Polyoxometalates in the Presence of Nitrogen Dioxide

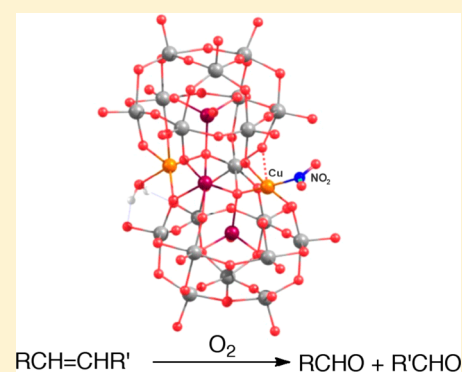
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Supporting Information

ABSTRACT: A new aerobic carbon–carbon bond cleavage reaction of linear di-substituted alkenes, to yield the corresponding aldehydes/ketones in high selectivity under mild reaction conditions, is described using copper(II)-substituted polyoxometalates, such as $\{\alpha_2\text{-Cu(L)P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ or $\{[(\text{Cu(L)})_2\text{WZn}(\text{ZnW}_9\text{O}_{34})_2]\}^{12-}$, as catalysts, where $\text{L} = \text{NO}_2$. A biorenewable-based substrate, methyl oleate, gave methyl 8-formyloctanoate and nonanal in >90% yield. Interestingly, cycloalkenes yield the corresponding epoxides as products. These catalysts either can be prepared by pretreatment of the aqua-coordinated polyoxometalates ($\text{L} = \text{H}_2\text{O}$) with NO_2 or are formed in situ when the reactions are carried with nitroalkanes (for example, nitroethane) as solvents or cosolvents. Nitroethane was shown to release NO_2 under reaction conditions. ^{31}P NMR shows that the Cu-NO_2 -substituted polyoxometalates act as oxygen donors to the C–C double bond, yielding a Cu-NO product that is reoxidized to Cu-NO_2 under reaction conditions to complete a catalytic cycle. Stoichiometric reactions and kinetic measurements using $\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ as oxidant and *trans*-stilbene derivatives as substrates point toward a reaction mechanism for C–C bond cleavage involving two molecules of $\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ and one molecule of *trans*-stilbene that is sufficiently stable at room temperature to be observed by ^{31}P NMR.



INTRODUCTION

In the research described herein, we were interested in the aerobic cleavage of carbon–carbon double bonds of alkenes, especially to aldehydes, which is a valuable transformation of synthetic importance.¹ The use of renewable resources such as unsaturated fatty acid derivatives as feedstock substrates for such reactions is also enticing. High yields of carboxylic acids from disubstituted alkenes can be obtained using reagents such as permanganate/periodic acid,² ruthenium tetroxide with hypochlorite or periodate,³ and hydrogen peroxide with peroxotungstate catalysts under acidic conditions through formation of epoxide and diol intermediates.⁴ The strong oxidizing conditions used in these reactions typically prevent the selective preparation of aldehydes from disubstituted alkenes. For such transformations a common procedure is to utilize the 1,3-dipolar addition of ozone to a double bond to yield an initial ozonide or 1,2,3-trioxolane, which is then decomposed to yield aldehydes under reducing conditions.⁵ The explosive nature of ozone often renders a multistep reaction cascade of epoxidation and hydrolysis to yield a glycol, which can then be cleaved by any number of procedures, as a more attractive alternative. Classically, periodic acid and lead acetate have often been used for the cleavage of glycols to aldehydes,⁶ but catalytic methods have also been disclosed including use of oxygen as oxidant.⁷

It would be advantageous to use molecular oxygen, O_2 , in a one-step oxidative cleavage of carbon–carbon bonds to yield aldehydes and/or ketones. Cerium ammonium nitrate on K10-montmorillonite has been reported as a catalyst in this context.⁸ Generally, however, the reaction of hydrocarbons with ground-state O_2 ubiquitously occurs via free radical autoxidation mechanisms typically initiated by the cleavage of a carbon–hydrogen bond and formation of a carbon-centered free radical, for example at the allylic position of an alkene.⁹ These mechanistically very complex autoxidation reactions, which involve the interplay of many reactions steps and multiple pathways, result in nonselective product formation, the bane of organic synthesis.

Paramagnetic nitrogen dioxide, NO_2 , is a known reagent for nitration, nitrosation, and the facilitation of halogenation reactions; it also has been used for oxidation.¹⁰ The most reported type of oxidation reactions has been that of thioethers and other sulfur-containing compounds.¹¹ Typically, NO_2 , a “weak” radical, is only active in hydrogen-atom-transfer reactions when the carbon–hydrogen bond is weak, as in alcohols,¹² although electron-transfer oxidation of reactive substrates such as anthracene and polyhydroxyarenes is also

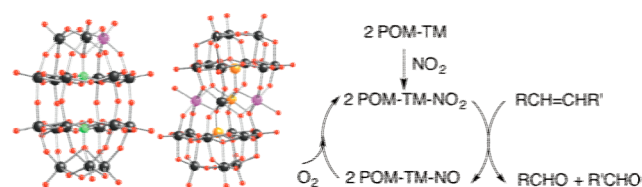
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known.¹³ As pertains to the reaction of NO₂ with alkenes, commonly addition to the double bond to yield nitroalkenes was observed.¹⁴ In certain cases, epoxidation has been observed such as with diadamantylidene and related hindered alkenes,¹⁵ and the reaction of phenylethenes with NO₂ has been reported to give some carbon–carbon bond cleavage products, albeit with low selectivity and yields.¹⁶

The working hypothesis behind this research, based on the results as will be shown below, is that the reaction of NO₂ with a transition-metal-substituted polyoxometalate would yield a metal–nitro intermediate that was surprisingly competent for the oxidative cleavage of alkenes with formation of metal nitrosyl intermediates. The latter could be reoxidized with O₂ to yield a catalytic cycle, as shown in Scheme 1.

Scheme 1. Proposed Aerobic Oxidative Cleavage of Alkenes Catalyzed by Transition-Metal Polyoxometalates Using the Wells–Dawson $\{\alpha_2\text{-M(L)P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ (Left) or the “Sandwich” $\{[(\text{M(L)})_2\text{WZn}(\text{ZnW}_9\text{O}_{34})_2]\}^{12-}$ (Right) Type Compounds^a



^aKey to colors: M, magenta; W, black; O, red; P, green; Zn, orange. M = Co²⁺, Cu²⁺.

To the best of our knowledge, the selective cleavage of carbon–carbon double or triple bonds with metal–nitro or metal–nitrito complexes has not been reported. In fact, metal–nitro and metal–nitrito compounds have been used only relatively rarely as oxygen donors.¹⁷ Thus, palladium–nitro-catalyzed oxidation of alkenes¹⁸ and iron heme and non-heme sulfoxidation of thioethers¹⁹ are the most reported transformations. Recently, nitrites have also been used as oxygen donors in the anti-Markovnikov palladium-catalyzed Wacker reaction.²⁰

RESULTS AND DISCUSSION

Characterization of $\{\alpha_2\text{-M}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$. The rationale behind the use of the Wells–Dawson-type polyoxometalate in the initial studies was that the two phosphorus atoms have different chemical environments, and this fact can effectively be utilized in ³¹P NMR studies for speciation in solution.²¹ Since NO₂ reacts quickly with water, the metal–NO₂ complexes were prepared in dichloromethane (DCM) from Q₈{ $\alpha_2\text{-M}^{\text{II}}(\text{H}_2\text{O})\text{P}_2\text{W}_{17}\text{O}_{61}\}$, where M = Cu, Co and Q = trioctylmethylammonium. The standard procedure was to evacuate the Q₈{ $\alpha_2\text{-M}^{\text{II}}(\text{H}_2\text{O})\text{P}_2\text{W}_{17}\text{O}_{61}\}$ solution, add an excess of gaseous NO₂, and then purge the excess NO₂ under a flow of Ar. Under these conditions, NO₂ reacted with (i) the quaternary ammonium cation and (ii) the Cu/Co site of the polyoxometalate. The former interaction was deduced from the thermogravimetric analysis (TGA, see Experimental Section). Separately, NO₂ was also reacted with the quaternary ammonium (C₈H₁₇)₃CH₃NCl salt (QCl) to yield a NO₂ adduct (Q'Cl = [(C₈H₁₇)₃CH₃N-NO₂]Cl) of indeterminate structure.²² The latter was deduced from ³¹P NMR spectra. In Figure 1, one may observe that the initial ³¹P NMR spectra of

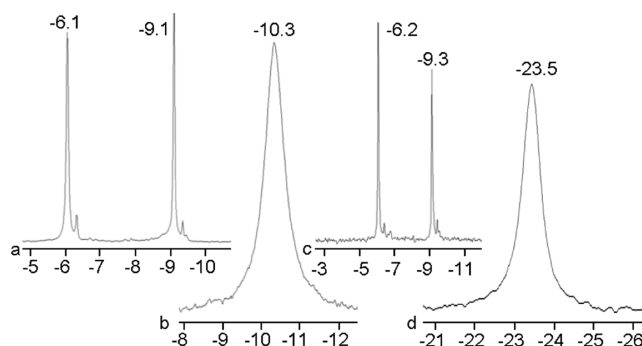


Figure 1. ³¹P NMR spectra of 48 mM $\{\alpha_2\text{-M(L)P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ in DCM/acetone-*d*₆ (80/20, vol%). (a) M = Cu; L = NO₂. (b) M = Cu; L = H₂O. (c) M = Co; L = NO₂. (d) M = Co; L = H₂O.

Q₈{ $\alpha_2\text{-M}^{\text{II}}(\text{H}_2\text{O})\text{P}_2\text{W}_{17}\text{O}_{61}\}$ show broad peaks at –23.5 (Co) and –10.3 (Cu) ppm, attributable to the phosphorus atoms distal to the M(II) site. The peaks attributable to the phosphorus atom vicinal to the M(II) are very broadened (not shown) and strongly shifted downfield. Upon addition of NO₂, new spectra are obtained with major sharp peaks at –6.2 and –9.3 ppm (Co) and –6.1 and –9.1 ppm (Cu), attributable to a M(III)-NO₂[–] diamagnetic species or anti-ferromagnetically coupled M(II)-NO₂[•] species. Density functional theory (DFT) calculations (see below) suggest an electronic formulation of Co(III)-NO₂[–] and Cu(II)-NO₂[•] species, respectively.

The $\{\alpha_2\text{-M}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ anions and the corresponding precursors, $\{\alpha_2\text{-M}(\text{H}_2\text{O})\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ anions, were also evaluated by mass spectrometry. Electrospray ionization did not yield any substantial data; however, matrix-assisted laser desorption/ionization did yield clean spectra (Figures S1 and S2). Clearly, ligation of NO₂ changed the spectra, most noticeably in the low *m/z* ranges; however, the high degree of fragmentation as well as the high charge did not allow unequivocal assignment of peaks. Evidence indicates the reaction of NO₂ with the polyoxometalates did not leach M(II) from the polyoxometalate: (i) The ³¹P NMR spectrum for the lacunary species, $\{\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\}^{10-}$, was not observed. (ii) The ¹H NMR spectrum showed no formation of HNO₃, which could form M(NO₃)₂ from trace amounts of water. (iii) Reactions (see below) using M(NO₃)₂ or M(NO₂)₂ in place of $\{\alpha_2\text{-M}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ showed no reactivity. It was not possible to gain any structural information on the nature of the M-NO₂ moiety through crystallization. Peaks in the IR spectra at 1328 and 1285 cm^{–1} for $\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$, attributable to $\nu_{\text{N-O(assym)}}$ and $\nu_{\text{N-O(sym)}}$, suggest a metal–nitro species rather than a metal–nitrito species.^{17b} Both the $\{\alpha_2\text{-M}^{\text{II}}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ compounds were EPR silent; trace amounts (~1% by double integration) of NO₂[•]-type species were observed as impurities. The IR spectrum of $\{\alpha_2\text{-Cu}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ is essentially the same as that of $\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$.

Computer-generated structures, as shown in Figure 2, were calculated for $\{\alpha_2\text{-M}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$. The exchange of the original aqua ligand by NO₂ is exergonic by 11.1 kcal·mol^{–1} (M = Co). Prior to commenting on these structures, it should be noted that the nitrito structures M–ONO were also calculated and found to be less stable by ~6 kcal·mol^{–1}, in agreement with the conclusion that nitro species are present from IR spectra. From the bond lengths for the cobalt versus copper complexes, one can observe that NO₂ is more tightly bound for cobalt than for Cu. Furthermore, the Cu atom is more weakly bonded to

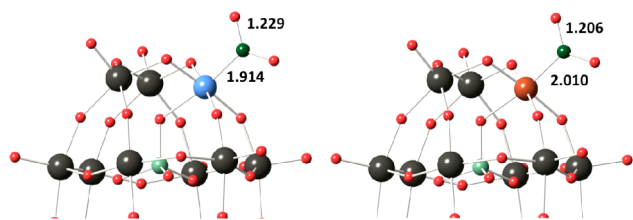


Figure 2. DFT structures for $\{\alpha_2\text{-M}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$. Left, $\text{M} = \text{Co}$; right, $\text{M} = \text{Cu}$. Key to colors: P, green; W, gray; O, red; N, dark blue; Co, light blue; Cu, orange. For $\text{M} = \text{Co}$, bond lengths around Co are $\text{Co}-\text{O}(\text{W}) = 1.911, 1.911, 1.913,$ and 1.915 \AA and $\text{Co}-\text{O}(\text{P}) = 2.025 \text{ \AA}$. For $\text{M} = \text{Cu}$, bond lengths around Cu are $\text{Cu}-\text{O}(\text{W}) = 1.905, 1.916, 2.218,$ and 2.326 \AA and $\text{Co}-\text{O}(\text{P}) = 2.010 \text{ \AA}$.

the polyoxometalate framework with two exceptionally long equatorial $\text{Cu}-\text{O}(\text{W})$ bonds, behavior that can be easily rationalized from the double occupation of the $d_{x^2-y^2}$ -like orbital when the metal is $\text{Cu}(\text{II})$. For the cobalt-substituted compound, the analysis of frontier molecular orbitals clearly suggests that substitution of the original aqua ligand induces an internal oxidation of the metal center from $\text{Co}(\text{II})$ to $\text{Co}(\text{III})$. In the $\text{Co}-\text{NO}_2$ Wells–Dawson anion, the t_{2g} -like orbitals of the transition metal are doubly occupied, while the $d_{x^2-y^2}$ -like orbital is unoccupied. Electron transfer from the cobalt to the NO_2 ligand is supported by atomic population analysis, where $-q(\text{NO}_2)$ is estimated to be $-0.32 e$ (Mulliken) and $-0.16 e$ (NBO), and by the polarization of the sigma bonding and antibonding $\text{Co}-\text{NO}_2$ orbitals (framed orbitals in Figure S3). Both support a formulation of the cobalt-substituted compound as $\{\alpha_2\text{-Co}^{\text{III}}(\text{NO}_2^-)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$. When the metal is Cu , population analyses do not assign electron transfer from the polyoxometalate to the ligand, and the corresponding bonding and antibonding $\text{Cu}-\text{NO}_2$ orbitals are less polarized, as expected for a metal of group 11. Consequently, we propose that the copper-substituted compound is better formulated as $\{\alpha_2\text{-Cu}^{\text{II}}(\text{NO}_2^\bullet)\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$, the ground state also being a singlet as in its homologous Co anion.

Stoichiometric Reactions of $\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}$ with Alkenes. The reactivity of $\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}$ was tested using *trans*-stilbene as a model substrate. Thus, a reaction of 0.156 M $\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}$ with 0.078 M *trans*-stilbene in 0.5 mL of $\text{DCM}/\text{acetone}$ ($80/20, \text{ vol\%}$) under Ar at 295 K yielded benzaldehyde as the sole product at 80% conversion by gas chromatographic (GC) analysis. In order to verify that $\text{Q}' = [(\text{C}_8\text{H}_{17})_3\text{CH}_2\text{N}-\text{NO}_2]^+$ was not involved in this oxidative cleavage reaction and that the $\text{Co}(\text{III})-\text{NO}_2$ moiety was responsible for the reaction observed, two control reactions were performed. The first was simply the reaction of *trans*-stilbene with $\text{Q}'\text{Cl}$, and the second involved the addition of 8 equiv of $\text{Q}'\text{Cl}$ to the $\text{Co}(\text{II})$ -aqua species, $\text{Q}_8\{\alpha_2\text{-Co}^{\text{II}}(\text{H}_2\text{O})\text{P}_2\text{W}_{17}\text{O}_{61}\}$, and then its reaction with *trans*-stilbene. In neither case was any formation of benzaldehyde observed. The oxidation of a series of phenyl-substituted alkene substrates by $\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}$ to yield the carbonyl product was shown to be general, as depicted in Figure 3. The order of reactivity, as determined by the relative rate of reaction, was $1,1$ -disubstituted alkenes $<$ $1,2$ -disubstituted alkenes $<$ $1,1,2$ -trisubstituted alkenes $<$ tetraphenylethene. *trans*-Stilbene was more reactive than the *cis*-isomer. All the reactions were entirely selective toward the aldehyde/ketone products. On the other hand, oxidation of a mono-substituted alkene such as styrene

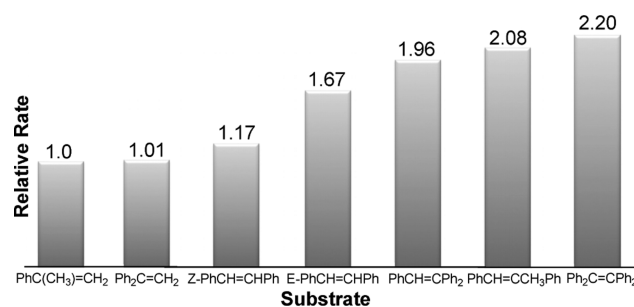


Figure 3. Relative rate of oxidation of phenyl-substituted alkene substrates by $\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}$. Reaction conditions: 62.5 mM substrate, 15.6 mM $\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}$ in $\text{DCM}/\text{acetone}$ ($80/20 \text{ vol\%}$), Ar , 295 K .

was slower and was much less selective ($\sim 40\%$) to benzaldehyde.

Kinetic analysis measured by ^{31}P NMR and by the method of initial rates using plots of the log rate versus $\log [\textit{trans}\text{-stilbene}]$ and $\log [\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}]$ (see Figures S4 and S5) showed that the reaction was first order in the polyoxometalate and 0.5 order for *trans*-stilbene when the rate is defined as $-\text{d}[\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}]/\text{d}t$, as shown in eq 1.

$$-\text{d}[\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}]/\text{d}t = k_{\text{obs}}[\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}]^1[\textit{trans}\text{-stilbene}]^{1/2} \quad (1)$$

Using various substituted *trans*-stilbene derivatives led to a Hammett plot that showed a change in the reaction mechanism from a positively charged transition state to a negatively charged one when going from electron-donating substituents ($\rho = -0.77$) to electron-withdrawing substituents ($\rho = 0.28$) on the $4,4'$ -positions of the phenyl rings (Figure 4). The low

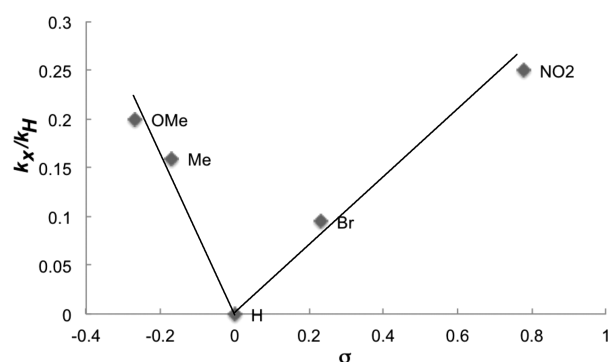


Figure 4. Hammett plot for oxidative cleavage of *trans*-stilbene derivatives (62.5 mM) by $\text{Q}'_8\{\alpha_2\text{-Co}(\text{NO}_2)\text{P}_2\text{W}_{17}\text{O}_{61}\}$ (15.6 mM). Reactions were carried out in $\text{DCM}/\text{acetone}-d_6$ ($80/20, \text{ vol\%}$) under Ar at 295 K .

absolute ρ values indicate only a partial charge at the transition state and, therefore, more than likely a homolytic bond cleavage reaction rather than a more ionic heterolytic bond cleavage step.

The temperature dependence of the oxidative cleavage reaction was surveyed for *trans*-stilbene and its $4,4'$ -OMe and $4,4'$ -NO₂ derivatives as substrates (Table 1). As can be seen, the activation parameters, ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger , extracted from the Eyring plots (Figures S6–S8), are very similar for all three

Table 1. Activation Parameters for the Reaction of *trans*-Stilbene Derivatives^a

substituent	$\Delta G_{298}^{\ddagger}$ ^b	$\Delta H_{298}^{\ddagger}$ ^b	$\Delta S_{298}^{\ddagger}$ ^c
4,4'-OMe	20.5	2.4	-60.5
H	20.7	3.1	-59.1
4,4'-NO ₂	20.4	2.3	-60.8

^aReaction conditions: *trans*-stilbene derivatives (62.5 mM) and $Q_8\{\alpha_2\text{-Co}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}$ (15.6 mM) in 0.5 mL of DCM/acetone-*d*₆ (80/20, vol%) under Ar at 233–298 K. ^bIn kcal·mol⁻¹. ^cIn cal·mol⁻¹·K⁻¹.

substrates. Most significantly, the reaction is entropy controlled, the large negative value of ΔS^{\ddagger} indicating a highly ordered transition state.

The fate of the $\{\alpha_2\text{-Co}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ anion during the oxidative cleavage reaction of the *trans*-stilbene derivatives was followed by ³¹P NMR (Figure 5). One may observe the

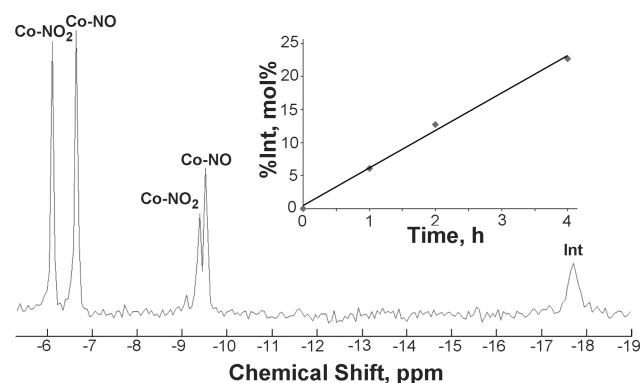


Figure 5. ³¹P NMR spectrum of a reaction mixture of $Q_8\{\alpha_2\text{-Co}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ and *trans*-stilbene. Inset: the amount of Int formed over time.

formation of the nitrosyl product, $\{\alpha_2\text{-Co}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$, which has a spectrum, $\delta = -6.7$ and -9.6 ppm, identical to that of a separately prepared compound (Figure S9). In addition, an intermediate species, Int, was observed that is assigned to a $\{\alpha_2\text{-Co}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ -*trans*-stilbene adduct that disappeared upon heating of the sample. The amount of Int increases as the reaction continues (Figure 5, inset). The peak width, the upfield chemical shift and position, and the absence of a complementary peak attributable to the phosphorus atom vicinal to the cobalt center argue for an intermediate in which it is reasonable that electron density is transferred from the double bond of the *trans*-stilbene to the polyoxometalate; that is, it is a Co(II) species. Further evidence for this assignment came from the integration of the combined $\{\alpha_2\text{-Co}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ and Int peaks, which showed a conversion commensurate with the conversion observed by GC analysis.

Aerobic Catalytic Oxidative Cleavage of Alkenes.

Once it was shown that $\{\alpha_2\text{-Co}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ was reactive for the oxidative cleavage of alkenes in stoichiometric reactions under anaerobic conditions, the subsequent objective was to carry out a catalytic reaction using O₂ as the terminal oxidant, as described in Scheme 1. Surveying the reactivity of nitrosyl-ligated compounds revealed that the copper-substituted compound, $Q_8\{\alpha_2\text{-Cu}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}$, did slowly react with O₂ at slightly elevated temperatures of 65 °C to yield $\{\alpha_2\text{-Cu}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}^{8-}$ with a ~10% conversion after 1.5 h (Figure S10), but the cobalt analogue did not. Increasing the

temperature showed that the polyoxometalate lost stability by demetallation of the Cu center and formation of the lacunary species $\{\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\}^{10-}$. Measurement of the kinetics of the reaction (Figures S11 and S12) of O₂ and $Q_8\{\alpha_2\text{-Cu}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}$ to give $Q_8\{\alpha_2\text{-Cu}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}$ showed that the reaction was second order in $Q_8\{\alpha_2\text{-Cu}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}$ and zero order in O₂, as shown in eq 2. This reaction order suggests

$$\begin{aligned}
 & -d[Q_8\{\alpha_2\text{-Cu}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}]/dt \\
 & = k_{\text{obs}}[Q_8\{\alpha_2\text{-Cu}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}]^2[\text{O}_2]^0
 \end{aligned}
 \quad (2)$$

that O₂, while obviously necessary, is not involved in the rate-determining step.²³ Thus, we surmise that two $Q_8\{\alpha_2\text{-Cu}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}$ molecules react in a rate-determining step to form a “Cu(NO)₂Cu” dimer species, for which there is precedent in the literature with various transition metals and typically bulky ligands.²⁴ Such a species probably reacts relatively quickly, in a stepwise manner, to yield a “Cu-NO-O₂-ON-Cu” intermediate that then rearranges to give the product, $Q_8\{\alpha_2\text{-Cu}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}$.

It should be stressed that $Q_8\{\alpha_2\text{-Cu}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}$ showed reactivity in stoichiometric reactions almost identical to that of $Q_8\{\alpha_2\text{-Co}(\text{NO}_2)_2\text{P}_2\text{W}_{17}\text{O}_{61}\}$.²⁵ However, since $Q_8\{\alpha_2\text{-Cu}(\text{NO}_x)\text{P}_2\text{W}_{17}\text{O}_{61}\}$ was insufficiently stable for efficient catalysis, the significantly more stable sandwich-type compounds,²⁶ $\{[(\text{M}(\text{L}))_2\text{WZn}(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, were used for the catalytic reactions. In this way, $Q_x\{[(\text{M}(\text{NO}_2)_2)_2\text{WZn}(\text{ZnW}_9\text{O}_{34})_2]\}$ was prepared for M = Cu, Mn, Ru, Fe, Co, and Ni and reacted with *trans*-stilbene in the presence of O₂.

The results show that the Cu-substituted compound was the most reactive catalyst, and thus it was used for the remaining studies (Figure 6). It should be noted that the Cu-NO₂

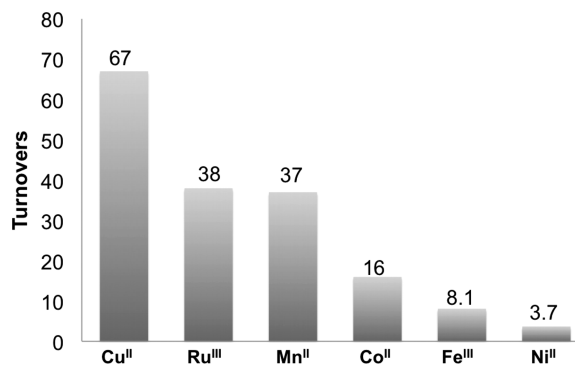
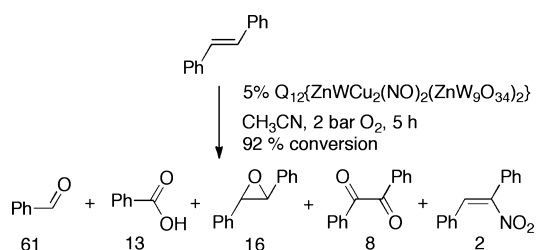


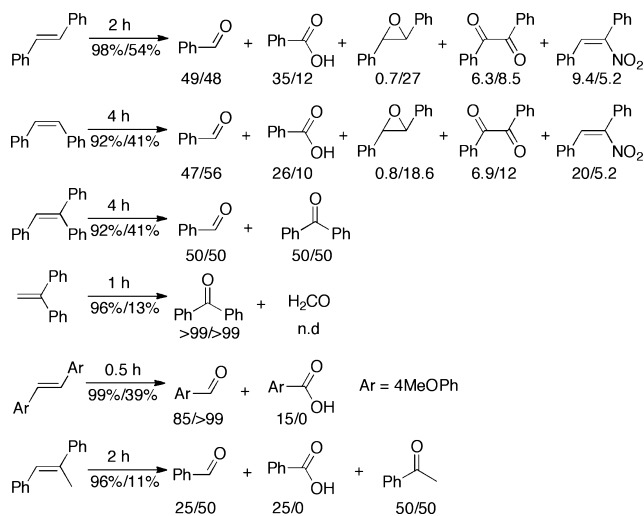
Figure 6. Turnovers after 1 h for the oxidation of 0.32 M *trans*-stilbene catalyzed by 0.32 mM $Q_x\{\text{ZnWM}_2(\text{NO}_2)_2(\text{ZnW}_9\text{O}_{34})_2\}$ in 9 mL of MeCN, 2 bar O₂, 85 °C.

structure in a model compound, $[\text{Cu}^{\text{II}}(\text{H}_2\text{O})\text{Cu}^{\text{II}}(\text{NO}_2)\text{WZn}(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, was found by calculation to be similar to the one discussed above for the analogous Wells–Dawson polyoxometalate (Figure S13). Furthermore, it is important to note that, under O₂ pressure at 85 °C, a control reaction with $Q'\text{Cl} = (\text{C}_8\text{H}_{17})_3\text{CH}_3\text{NCl-NO}_2$ showed no oxidation reaction. Similarly, the aqua complex, $Q_{12}\{\text{ZnWCu}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2\}$, was also inactive. However, although the nitrosyl compounds, $Q_8\{\alpha_2\text{-Cu}(\text{NO})\text{P}_2\text{W}_{17}\text{O}_{61}\}$ and $Q_{12}\{\text{ZnWCu}_2(\text{NO})_2(\text{ZnW}_9\text{O}_{34})_2\}$, did not lead to oxidation of *trans*-stilbene in the absence of O₂, a reaction in the presence of O₂ was efficient (Scheme 2).

Scheme 2. Oxidative Cleavage of (*E*)-Stilbene Catalyzed by $Q_{12}\{ZnWCu_2(NO)_2(ZnW_9O_{34})_2\}$


Finally, it is interesting to note that the addition of $Q'Cl$ to $Q_{12}\{ZnWCu_2(H_2O)_2(ZnW_9O_{34})_2\}$ did yield a catalytically active system at more elevated temperatures ($>70^\circ C$), although not at room temperature, as noted above in the analysis of the stoichiometric reactions. This raised the possibility that organic nitro compounds could be used as solvents/reagents in the oxidative cleavage reactions.

In Chart 1, a comparison is made between the reaction of aryl-substituted ethenes catalyzed by the nitro-ligated com-

Chart 1. Oxidative Cleavage of Aryl Ethenes^a


^aSystem A (values left of slash): 0.065 mmol of substrate, 5 mol% $Q_{12}\{ZnWCu_2(H_2O)_2(ZnW_9O_{34})_2\}$, 0.5 mL of $EtNO_2$, 2 bar O_2 , $85^\circ C$. System B (values right of slash): 0.065 mmol of substrate, 5 mol% $Q'_{12}\{ZnWCu_2(NO)_2(ZnW_9O_{34})_2\}$, 0.5 mL of $MeCN$, 2 bar O_2 , $85^\circ C$.

pound, $Q'_{12}\{ZnWCu_2(NO)_2(ZnW_9O_{34})_2\}$, carried out in acetonitrile and a reaction catalyzed by aqua compound $Q_{12}\{ZnWCu_2(H_2O)_2(ZnW_9O_{34})_2\}$ carried out in nitroethane. The reactions carried out in nitroethane gave significantly higher conversions, and thus aldehyde products tended to be further oxidized to benzoic acid derivatives. It should be noted, however, that increasing the pressure to 3 bar O_2 for reactions carried out using system B raised the conversions to $>90\%$, with little change in reaction selectivity. Only in the case of *cis*- and *trans*-stilbene was nitration at the double bond observed. *trans*-Stilbene oxide could be further oxidized to benzaldehyde, but the diketone benzil was not reactive. Therefore, the former may be an intermediate in the reaction, although in the stoichiometric reactions it was not observed. Importantly, O_2 was required when nitroethane was used as a solvent. Use of acetonitrile/nitroethane as solvents with $Q_{12}\{ZnWCu_2(H_2O)-$

$2(ZnW_9O_{34})_2\}$ as catalyst was also efficient; the kinetic profiles showed that reactions were dependent on nitroethane concentration (Figure S14).

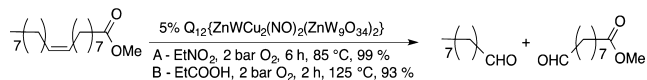
The reaction with nitroethane as solvent or reagent was especially intriguing and raised several questions: (i) Does $Q_{12}\{ZnWCu_2(H_2O)_2(ZnW_9O_{34})_2\}$ in the presence of O_2 catalyze the formation of NO_2 , which would then yield a $Cu-NO_2$ active species? (ii) What products are formed from the alkyl chain, and what can be learned from their identification? (iii) Is there a structure–activity relationship between the nitroalkane and the oxidative cleavage reaction? In order to investigate the in situ formation of NO_2 , a reliable probe for its presence needed to be developed. Since NO_2 reacts with the Cu -substituted polyoxometalate that is EPR silent, EPR was not an option. Therefore, a highly reactive arene, 1,3,5-trimethoxybenzene, was used that would react very quickly with even traces of NO_2 , either bound to a metal center or free in solution. Addition of an excess of NO_2 to a DCM solution of 1,3,5-trimethoxybenzene yielded a blue solution [UV–vis: λ_{max} nm (ϵ , $cm^{-1} M^{-1}$) 265 (2010), 391 (1080), 614 (1229). 1H NMR: δ 3.96 (6H), 4.15 (3H), 6.55 (2H)]. Low-temperature crystallization of the compound revealed that it was the bis-substituted 2,4,6-trimethoxybenzene nitrosium cation, with a nitrate anion (Figure S15). This same compound was obtained when $Q'_{12}\{ZnWCu_2(NO)_2(ZnW_9O_{34})_2\}$ was added to 1,3,5-trimethoxybenzene, but perhaps more significantly this compound was also obtained when nitroethane was heated to $85^\circ C$ in the presence of the aqua compound, $Q_{12}\{ZnWCu_2(H_2O)_2(ZnW_9O_{34})_2\}$, and O_2 . In addition, the UV–vis spectrum of $\{ZnWCu_2(NO)_2(ZnW_9O_{34})_2\}^{12-}$ shows upon addition of NO_2 a peak at 475 nm attributable to the $Cu-NO_2$ moiety. Such a peak is also observed when $\{ZnWCu_2(H_2O)_2(ZnW_9O_{34})_2\}^{12-}$ is heated in nitroethane under O_2 (Figure S16). One can conclude that NO_2 is formed from nitroethane under the aerobic reaction conditions noted in Chart 1.

A comparison of reactions with various nitroalkanes, RNO_2 , as solvent, where $R = Me, Et, i-Pr,$ and $t-Bu$ (5% $Q_{12}\{ZnWCu_2(H_2O)_2(ZnW_9O_{34})_2\}$, 0.065 mmol of *trans*-stilbene, 0.5 mL of $R-NO_2$, 3 bar O_2 , $85^\circ C$, 1 h) showed conversions of 88% (*Et*) \sim 85% (*Me*) $>$ 40% (*i-Pr*) $>$ \sim 1% (*t-Bu*). Calculations at the G4 level of the homolytic cleavage reaction of RNO_2 to R^\bullet and NO_2 showed $\Delta G_{r,298} = 49.98$ (*Me*), 48.46 (*Et*), 49.10 (*i-Pr*), and 48.60 (*t-Bu*) $kcal \cdot mol^{-1}$. These very endergonic values, which are also invariant as a function of R , clearly show that homolytic cleavage of RNO_2 is not the likely source of NO_2 . More reasonably, there is C–H bond activation of the acidic hydrogen atom by the polyoxometalate, which then reacts with O_2 , setting off a cascade of autoxidation reactions that release NO_2 . The need for O_2 to form NO_2 from nitroalkanes as well as the significant formation of acetic acid as byproduct in reactions with nitroethane strongly supports this scenario. Thus, under typical conditions noted in Chart 1, 0.06–0.1 mmol of acetic acid was formed, representing a 0.85–1.5% conversion of nitroethane to acetic acid; \sim 20–30 equiv of acetic acid was formed per polyoxometalate.

It was shown and noted above that NO_2 bound to a copper-substituted sandwich-type polyoxometalate efficiently catalyzed the oxidative cleavage of arylated ethenes when NO_2 was either used as a reagent or formed in situ by oxidation of a nitrosyl-substituted precursor or via decomposition of a nitroalkane under the reaction conditions. The scope of the reaction for further substrate types was investigated. One interesting

example is the oxidation of a biorenewable-based substrate, such as methyl oleate. Thus, the aerobic oxidative cleavage of methyl oleate to yield the aldehyde, methyl 8-formyl-octanoate, could be a very accessible pathway to 9-aminomethylnonanoate that could be used to make nylon 9. According to Scheme 3,

Scheme 3. Oxidative Cleavage of Methyl Oleate



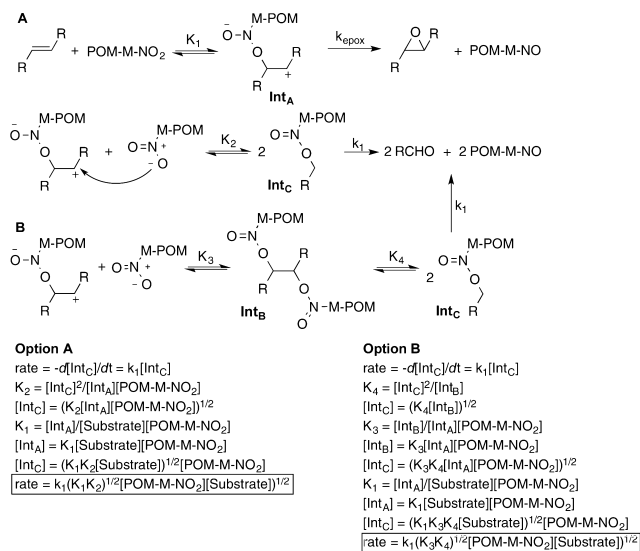
>90% yields of aldehyde products, nonanal and methyl 8-formyl-octanoate, were attainable using nitroethane as solvent at 85 °C, or using a minimal amount of NO₂ with propionic acid as solvent at 125 °C. There was only slight formation of epoxide and carboxylic acids, <3%, and no nitration products were seen.

Interestingly, cyclic alkenes such as *cis*-cyclooctene and a mixture of *cis*- and *trans*-cyclododecene gave only epoxides as products (>95% yield); no oxidative cleavage was observed.²⁷ Similarly, aryl-substituted alkynes PhC≡CR, where R = H, Me, and Ph, also reacted to yield benzoic acid as the major product in 67%, 95%, and 85% yield, respectively, with PhC(O)C(O)R as the remaining minor product.

Mechanistic Scenarios. From the reaction kinetics found for the stoichiometric reaction for *stilbene-type substrates*, eq 1, one can conclude that two molecules of the metal–nitro-substituted polyoxometalate, POM-M-NO₂, react with one molecule of substrate. Furthermore, this reaction led to the formation of an intermediate, Int, that can be observed by ³¹P NMR (Figure 5) prior to the formation of the carbon–carbon bond cleaved product, which is accompanied by oxygen transfer and formation of the metal–nitrosyl-substituted polyoxometalate, POM-M-NO. Thus, two possible general mechanistic scenarios are supported by the rate equation for C–C bond cleavage based on the following elementary steps and steady-state approximations (Scheme 4).²⁸

The first pathway, Option A, suggests the fast formation of an intermediate, Int_A, which then reacts with another POM-M-

Scheme 4. Possible Mechanistic Scenarios with *trans*-Stilbene as a Model Substrate



NO₂ molecule to give 2 equiv of the carbon–carbon-cleaved intermediates bound to the polyoxometalate, Int_C. Each equivalent of intermediate then forms the carbonyl product and the nitrosyl-substituted polyoxometalate in a *unimolecular* rate-determining step. Such a scenario would also explain the formation of epoxides when the substrates are cyclic alkenes and the observation of some epoxide in the catalytic oxidation of stilbene, which however was not observed in the stoichiometric reaction. The second pathway, Option B, suggests that Int_A reacts quickly with POM-M-NO₂ to yield stable intermediate, Int_B, which then undergoes carbon–carbon bond cleavage by unimolecular rearrangement to similarly yield intermediates bound to the polyoxometalate, Int_C. As in pathway A, the reaction is completed by the formation of the products in a rate-determining step. The formation of a stable intermediate, Int_C, in either case is supported by the observation that, although the intermediate is observable by ³¹P NMR, injection into the gas chromatograph shows a yield that is commensurate with the amount of intermediate and product combined. The observed reaction kinetics, eq 1, support the proposed mechanism as shown in Scheme 4.

The Eyring plots and observed activation parameters, ΔH^\ddagger and ΔS^\ddagger , support an entropy-controlled reaction with a highly ordered transition state (Table 1). Furthermore, the Hammett plot showed a change in the reaction mechanism from a positively charged transition state to a negatively charged one when going from electron-donating substituents ($\rho = -0.77$) to electron-withdrawing substituents ($\rho = 0.28$, Figure 4). An exemplary transition-state representation that could arise from the formation of product from Int_C is shown in Scheme 5. The low ρ values can be attributed to N–O bond cleavage that is possibly of a homolytic nature.

Scheme 5. Possible Transition States for the Rate-Determining Step



CONCLUSIONS

Catalytic aerobic cleavage of carbon–carbon double bonds, preferably of at least disubstituted alkenes, is demonstrated. High yields of carbonyl products are typically obtained with minimal further oxidation to the carboxylic acids from aldehydes. The oxidation of methyl oleate, a biorenewable-based substrate, to nonanal and methyl 8-formyloctanoate in high yields appears especially attractive. The reactions were shown to proceed via POM-M-NO₂ species, where NO₂ can be added initially as a gas, or they can be formed in situ from nitroalkanes in the presence of O₂. Nitrosyl species, POM-M-NO, are formed after oxygen transfer, and in the case of POM-Cu-NO species, POM-Cu-NO₂ can be regenerated to complete a catalytic cycle, as shown in Scheme 1. The kinetics of the C–C bond cleavage reactions under stoichiometric conditions at room temperature suggest mechanisms (Scheme 4) where POM-M-NO₂ reacts with a double bond to yield a POM-M-NO₂–substrate intermediate that can react with another molecule of POM-M-NO₂ to yield the products via a carbon–carbon cleavage reaction, followed by release of the

products. Alternatively, another intermediate, POM-M-NO₂-substrate-POM-M-NO₂, can be formed that then leads to product formation in a similar manner. The high negative entropy of activation derived from the Eyring plots indicates a highly ordered transition state in the rate-determining step, for example as shown in Scheme 5. Cycloalkenes apparently react via a pathway where a POM-M-NO₂-substrate intermediate reacts to yields an epoxide, which does not react further for reasons unknown at this time. Future research will be dedicated to the oxidation of terminal alkenes and more control of reaction selectivity, for example, epoxidation versus carbon-carbon bond cleavage.

EXPERIMENTAL SECTION

Polyoxometalate Synthesis. K₈{α₂-M(H₂O)P₂W₁₇O₆₁}, where M = Co^{II}, Cu^{II}, was prepared by the known literature method,²⁹ as were the Na_x{ZnWM₂(H₂O)₂(ZnW₉O₃₄)₂} compounds for M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Ru^{III}, and Cu^{II}.³⁰

Aqua-Ligated Polyoxometalates. Q₈{α₂-M(H₂O)P₂W₁₇O₆₁}, where Q = triethylmethylammonium, was prepared by dissolving 200 mg of K₈{α₂-M(H₂O)P₂W₁₇O₆₁} in 20 mL of H₂O at room temperature. Eight equivalents of triethylmethylammonium chloride (133 mg) dissolved in 20 mL of DCM was added, and the biphasic mixture was vigorously stirred. The solvent was removed by evacuation from the lower organic phase to dryness, affording brown (M = Co^{II}) or green (M = Cu^{II}) oil with yields of 95–100%. ³¹P NMR (85% H₃PO₄ external standard): for M = Co^{II}, -23.5 ppm; for M = Cu^{II}, -10.3 ppm. Visible spectra: λ_{max} nm (ε, cm⁻¹ M⁻¹) for M = Co^{II}, 552 (96); for M = Cu^{II}, 722 (48). TGA measurements for both Q₈{α₂-M(H₂O)P₂W₁₇O₆₁} compounds showed a ~41% mass loss at up to 400 °C, corresponding to 8 equiv of Q per polyoxometalate unit.

Nitro-Ligated Polyoxometalates. Q₈{α₂-M(NO₂)P₂W₁₇O₆₁}, where Q' = [(C₈H₁₇)₃CH₃N-NO₂]⁺, was prepared by dissolving 300 mg of Q₈{α₂-M(H₂O)P₂W₁₇O₆₁} in 1 mL of DCM in a 50 mL flask, which was evacuated from air by three freeze-pump-thaw cycles. Then, at 77 K, NO₂(g) (**Caution, very toxic!**) was introduced into the flask under vacuum for 1–2 s, producing initially a blue hue in the flask. After thawing to room temperature, an orange-brown gas lies above the colored solution. The flask was purged with Ar for 30 min after being swirled for a few seconds. A purple (M = Co) or turquoise (M = Cu) oil in quantitative yield was obtained and stored under Ar. ³¹P NMR (85% H₃PO₄ external standard): for M = Co, -6.2 and -9.3 ppm; for M = Cu, -6.1 and -9.1 ppm. Visible spectra: λ_{max} nm (ε, cm⁻¹ M⁻¹) for M = Co, 542 (81); for M = Cu, 783 (22). TGA measurements for both Q₈{α₂-M(NO₂)P₂W₁₇O₆₁} compounds showed a ~45% mass loss at up to 400 °C, corresponding to 8 equiv of Q and 9 equiv of NO₂ per polyoxometalate unit. Q'_x{[(M(NO₂)₂)₂WZn(ZnW₉O₃₄)₂]} compounds were prepared for M = Cu, Mn, Ru, Fe, Co, and Ni in an identical fashion. TGA measurements for all Q'_x{[(M(NO₂)₂)₂WZn(ZnW₉O₃₄)₂]} compounds showed a mass loss of ~51% at up to 400 °C, corresponding to 12 equiv of Q and 14 equiv of NO₂ per polyoxometalate unit.

Nitrosyl-Ligated Polyoxometalates. Q₈{α₂-M(NO)P₂W₁₇O₆₁} was prepared by dissolving 80 mg of Q₈{α₂-M(H₂O)P₂W₁₇O₆₁} in 1 mL of DCM in a 50 mL flask, which was evacuated from air by three freeze-pump-thaw cycles. In parallel, NO(g) (**Caution, very toxic!**) was prepared by adding 900 mg of NaNO₂ (97%) to 5 mL of glacial acetic acid. If some NO₂ was formed (brown color), it was removed by a gentle flow of Ar. By syringe, 20 mL of the NO gas was injected to the polyoxometalate solution, which was shaken manually for 5 min with an accompanying color change. The flask was purged with Ar for 30 min. After removal of the solvent, pale-blue (M = Co) or yellow (M = Cu) oils were obtained in quantitative yield and stored under Ar. ³¹P NMR (85% H₃PO₄ external standard): for M = Co, -6.7 and -9.6 ppm; for M = Cu, -6.6 and -9.9 ppm. Visible spectra: λ_{max} nm (ε, cm⁻¹ M⁻¹) for M = Co, 685 (108); for M = Cu, ~400 shoulder. TGA measurements for both Q₈{α₂-M(NO)P₂W₁₇O₆₁} compounds showed

a mass loss of ~41% at up to 400 °C, corresponding to 8 equiv of Q and 1 equiv of NO per polyoxometalate unit.

Oxidation Reactions. Catalytic oxidation reactions were carried out in 25 mL Ace Glass pressure tubes. The tubes were charged with the catalyst, substrate, and solvent in the specified amounts, air was purged, and then the tubes were pressurized with O₂ and heated in a temperature-controlled oil bath. At each relevant time period, a 50 μL aliquot was taken, dissolved in 0.2 mL of DCM, and then analyzed by GC/GC-MS. The separation was carried out using a 30 m long column, 0.32 mm i.d., 0.25 μm coating 5% phenylmethylsilicone, using He as eluent.

Computational Methods. DFT calculations were performed with the Gaussian09 package³¹ using the hybrid exchange-correlation B3LYP functional.³² For Co, Cu, and W atoms, the LANL2DZ basis set was used.³³ The 6-31G(d,p) basis set³⁴ was used for NO₂ and for the O atoms directly bound to Co or Cu. For the rest of atoms, we employed a 6-31G basis set. Solvent effects were included by means of PCM³⁵ model calculations as implemented in Gaussian09.

ASSOCIATED CONTENT

Supporting Information

Additional experimental information and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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