The Nickel-Substituted Quasi-Wells – Dawson-Type Polyfluoroxometalate, $[Ni^{II}(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$, as a Uniquely Active Nickel-Based Catalyst for the Activation of Hydrogen Peroxide and the Epoxidation of Alkenes and Alkenols

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Abstract: A series of transition metal substituted polyfluorooxometalates (PFOM) $[M(L)H_2F_6NaW_{17}O_{55}]^{q-}$, M = Zn^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, Ru^{2+}, Ni^{2+} and V^{5+} and L = H_2O, O^{2-}, of quasi-Wells – Dawson structure, was synthesized. In the series prepared, only the nickel-substituted polyfluorooxometalate was capable of catalytic activation of hydrogen peroxide in biphasic reaction media, the reaction leading mainly to the selective epoxidation of alkenes and alkenols. The manganese-, cobalt-, ruthenium-, iron-, vanadium-, and zinc-substituted polyfluorooxometalates were catalytically inactive, although, except for the zinc polyfluorooxometalate, very significant catalase activity was observed. Oxidation of thianthrene showed that sulfoxides were oxidized more easily than sulfides. Kinetic profiles of cyclooctene epoxidation showed that the reaction was zero order in both cyclooctene and hydrogen peroxide. Hydrogen peroxide was consumed at a rate 40% higher than the rate of epoxidation of cyclooctene. The reaction appears to proceed through an intermediate peroxo/hydroperoxo species that was observed in the IR spectrum. Atomic absorption, IR and ^{19}F NMR spectroscopy indicated that the $[Ni(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ compound was stable under reaction conditions.

Keywords: homogeneous catalysis · hydrocarbons · hydrogen peroxide · oxidations · polyoxometalates

Introduction

The activation of hydrogen peroxide towards epoxidation of alkenes and alkenols remains an important research activity in the quest for "green" oxidation techniques. Some catalysts (not an exhaustive listing) recently shown to be highly active and perhaps of industrial potential in such reactions include methyl rhenium trioxide,[1] titanium silicalites,[2] manganese triazacyclononane,[3] and peroxophosphotungstates.[4] We are interested in oxidation catalyzed by low-valent transition metal substituted polyoxometalates. In this context, various types of transition metal substituted polyoxometalates in combination with various oxidants or oxygen donors such as iodosobenzene,[5] *N*-oxides,[6] periodate,[7] ozone,[8] *tert*-butylhydroperoxide,[9] molecular oxygen[10–12]and hydrogen peroxide[13] have been shown to be effective for alkene and alkane oxidation. Three major polyoxometalate structure types have been used in this research. They are the more common Keggin and Wells – Dawson compounds[5, 7, 9, 10, 11, 13g] and also the so-called "sandwich" compounds.[6, 8, 12, 13a–f,h] Transition metal substituted polyoxometalates that have been found to be active upon insertion of the transition metal into the polyoxometalate environment include those containing manganese, iron, cobalt, copper, and noble metals.

Catalytic oxidation catalyzed by nickel-based complexes is comparatively rare. From a historical perspective, nickel peroxide[14] is a long-known *stoichiometric* oxidant, which, however, is inactive for epoxidation of alkenes. More recently, Burrows and her group[15] published a series of reports showing that saturated macrocyclic compounds such as cyclam coordinate nickel(II), and can be used in conjunction with two-electron oxygen donors such as hypochlorite and iodosobenzene for catalytic oxidation. Nickel(IV) – oxo species have been postulated as the active species. Some nickel-based catalysts have also been reported to be active in Mukaiyama-type oxidation reactions (molecular oxygen in the presence of aldehydes as cooxidants).[16] To our knowledge, there are no reports that nickel-coordinated complexes and hydrogen peroxide as terminal oxidant are catalytically active in the epoxidation of alkenes. In published reports on oxidation with a series of transition metal substituted polyoxometalates, the nickel-based compounds were also described as inactive (or similar in activity to noncatalytic control systems) compared

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to isostructural complexes with other transition metals such as manganese, iron, cobalt, and so forth.

Upon preparing a new series of polyoxometalates containing transition metals, we were therefore somewhat surprised to find that the nickel-containing analogue was the most active one for the activation of hydrogen peroxide towards epoxidation of alkenes. The transition metal substituted polyoxometalates prepared in this series differ from more common polyoxometalates in that oxygen has been substituted by fluorine in parts of the polyoxometalate framework. These compounds are termed polyfluorooxometalates (PFOMs). Recently a few compounds of this type have been prepared, although they have not been examined as catalysts. In one type of PFOMs, the structure is analogous to the Keggin structure, with partial substitution of one to four atoms of oxygen by fluorine.[17] In a second group of PFOMs, compounds of an elliptical egg shape akin to Wells–Dawson-type polyoxometalates (herein termed quasi-Wells–Dawson structures; Figure 1) were prepared. Both nonsubstituted (all tungsten)[18] and cobalt- and iron[19]-substituted compounds have been reported. A zinc-substituted compound has also been well-characterized in a doctoral thesis.[20]

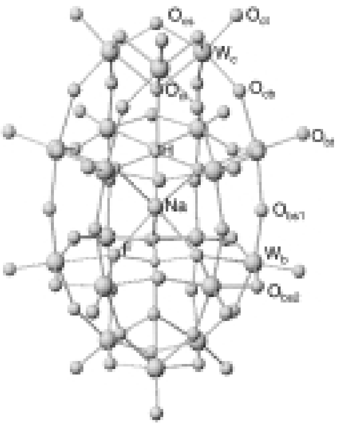

Figure 1. Structure of the $[M(L)H_2F_6NaW_{17}O_{55}]^{q-}$ polyfluorooxometalate family.

This paper describes the preparation and characterization of a series of quasi-Wells–Dawson PFOMs of general formula $[M(L)H_2F_6NaW_{17}O_{55}]^{q-}$, where $M = Zn^{2+}$, Co^{2+}, Mn^{2+}, Fe^{2+}, Ru^{2+}, Ni^{2+} and V^{5+}; $L = H_2O$, O^{2-}. First, the zinc analogue, $[Zn^{II}(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$, was prepared. The remaining PFOMs were then prepared by metathetical exchange with appropriate transition metal salts. Catalytic activity towards epoxidation of alkenes and alkenols with hydrogen peroxide was then measured.

Results and Discussion

Synthesis and characterization: The zinc-substituted PFOM,[20] $[Zn(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ was prepared in satisfactory yield from a sodium tungstate solution brought to pH 4.5 by addition of HF. The precipitate of unknown composition was filtered off, and zinc acetate was added to the filtrate, which presumably contained the lacunary PFOM, $[H_2F_6NaW_{17}O_{55}]^{11-}$; this yielded the $[Zn(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ compound, which was collected as the potassium salt after addition of KCl. Although some other isostructural PFOMs, $M = Co^{2+}$, Fe^{2+}, Mn^{2+} and Ni^{2+}, were reported to have been synthesized[19, 20] in low yields by addition of other salts to the lacunary $[H_2F_6NaW_{17}O_{55}]^{11-}$, our attempts to convincingly repeat these reported syntheses were unsuccessful, especially for $M = Fe^{2+}$, Mn^{2+} and Ni^{2+}. Therefore, we chose to change the synthetic strategy and to prepare the further transition metal substituted PFOMs, $[M(L)H_2F_6NaW_{17}O_{55}]^{q-}$, where $M = Co^{2+}$, Mn^{2+}, Fe^{2+}, Ru^{2+}, Ni^{2+} and V^{5+} and $L = H_2O$, O^{2-}, by metathetical exchange of the zinc atom by the other transition metals. Such a strategy was very successful and reliable in the past for the synthesis of transition metal substituted "sandwich" compounds.[21] In this case, yields for the metathetical exchange reaction were in the range of 50–65%.

Single crystals for X-ray diffraction analysis were grown for the vanadium-substituted $K_8[V(O)H_2F_6NaW_{17}O_{55}] \cdot 17\,H_2O$, the ruthenium-substituted $K_9[Ru(H_2O)H_2F_6NaW_{17}O_{55}] \cdot 15\,H_2O$, and the nickel-substituted $K_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}] \cdot 15\,H_2O$ analogues. From the crystallographic data (Table 1) it was clear that the transition metal substituted PFOMs were of the same structure, and that they were completely isostructural to the previously reported $[H_2F_6NaW_{17}O_{56}]^{7-}$ anion.[18] The vanadium-substituted sample gave the best data. A sodium heteroatom in the center is surrounded by six fluorine atoms (Na–F, 2.24(2) Å) in a trigonal prism coordination. There are two different types of tungsten atoms (the substituted transition metal, M), with 12 atoms in a "belt" position, W_b, and six atoms in a "capped" position, W_c.[22] The belt tungsten atoms (M) are coordinated as distorted octahedrons (bond lengths to the bridging oxygen positions: W_b–O_{bs1} 1.91(4) Å, W_b–O_{bs2} 1.91(2) Å, W_b–O_{cb} 1.90(3) Å; bond length to the terminal oxygen position: W_b–O_{bt} 1.70(4) Å; longer W_b–F bonds, 2.21(5) Å). The atoms in the capped position have very similar tetragonal coordination (bond lengths to the bridging oxygen positions: W_c–O_{cs} 1.95(4) Å and W_c–O_{cb} 1.91(7) Å, bond lengths to the terminal oxygen positions: W_c–O_{ct} 1.71(3) Å, and longer, W_c–O_{ci} bonds, 2.25(5) Å). In the refinement procedure, placement of the substituted metal in

Table 1. Crystallographic data for $K_8[V(O)H_2F_6NaW_{17}O_{55}] \cdot 17\,H_2O$ $K_9[Ru(H_2O)H_2F_6NaW_{17}O_{55}] \cdot 15\,H_2O$, and $K_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}] \cdot 15\,H_2O$.

	Vanadium	Ruthenium	Nickel
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a [Å]	22.736 (3)	22.591 (3)	22.701 (3)
b [Å]	12.335 (2)	12.310 (2)	12.324 (2)
c [Å]	29.504 (5)	27.870 (4)	29.310 (5)
β [°]	92.15 (2)	98.79 (2)	93.62 (3)
V [Å^3]	8269 (2)	7659 (2)	7886 (2)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	3.83	4.04	3.89
$\mu(Mo_{K\alpha})$ [cm^{-1}]	239.92	264.93	247.43
no. of unique reflections	7648	6980	7112
no. of reflections $I \geq 3\sigma_I$	4775	4423	4539
R (R_w)	0.050 (0.069)	0.155 (0.220)	0.851 (0.108)

either the belt or capped position gave similar *R* values. The position of the substituted metal can therefore not be determined by the X-ray data, and the substituted metal is assumed to be in both positions.

Credence to the assumption that the substituted metal is located in both belt and capped positions was gained from two NMR experiments. The first is the ^{51}V NMR spectrum of $K_8[V(O)H_2F_6NaW_{17}O_{55}]^{8-}$ in D_2O (Figure 2) and the second is its ^1H NMR spectrum in CD_3CN. For metal substitution in both the belt and capped position, two peaks are expected and were observed. $VOCl_3$ was used as external standard, and two peaks at $\Delta\ -502$ ($\Delta\nu_{1/2} = 490$ Hz) and -516 ($\Delta\nu_{1/2} = 270$ Hz) were observed, with an area ratio of approximately 1:1.75. The peaks were shifted slightly downfield relative to those of other monovanadotungstates.[23] Statistical and isomorphous substitution of one vanadium atom each from the belt and capped positions would be expected to give, approximately, the observed peak areas. Additionally, since proximate fluorine substitution in the belt position would be expected to give an upfield shift in the ^{51}V NMR, the relative shifts of the peaks are logical. For example, for VO_4^{3-}, $\delta = -540$, for $VO_2F_2^-$, $\delta = -595$ and for VOF_4^{1-}, $\delta = -797$.[24] The relative peak areas (capped and belt) correlate with the chemical shift.

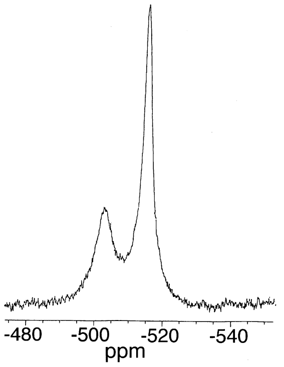

Figure 2. ^{51}V NMR spectrum of $K_8[V(O)H_2F_6NaW_{17}O_{55}]$ in D_2O.

The position of the hydrogen atoms was not resolved in the X-ray structure, but is surmised to be between the O_{ci} oxygen and the neighboring fluorine atoms, together forming HF_3O tetrahedra.[18–20] $[M(L)H_2F_6NaW_{17}O_{55}]^{q-}$ isomers with M in the belt or capped position are nonsymmetric, and two quartets in the coupled $^1H\{^{51}F\}$ NMR spectrum are to be expected. Therefore, four quartets are ideally to be expected for an isomeric mixture. Indeed, this was observed for the series of $[M(L)H_2F_6NaW_{17}O_{55}]^{q-}$ compounds measured in CD_3CN to avoid interference from HOD, but most clearly, for $^4Q_8[V(O)H_2F_6NaW_{17}O_{55}]$ where $^4Q = (n\text{-}C_4H_9)_4N^+$ (Figure 3). Four quartets at $\delta = 5.09$, 4.97, 4.91, and 4.77 are clearly observable, with an area ratio of 1.6:1.6:1.1:1.0 measured from the decoupled ^1H NMR spectrum. The peaks at $\delta = 5.09$ and 4.77 are clearer after Gaussian apodization (inserts). The additional peak (singlet) at $\delta = 4.84$ is associated with an impurity (2.5 % by integration) and there are two additional impurities, not shown, <1 % each, at $\delta = 5.41$ (triplet) and 4.62 (singlet). The coupling constants $^1J_{H,F}$ of the four quartets are 10.7, 9.5, 10.4, and 10.8 Hz, respectively. Based on statistical probabilities, and similar to the ^{51}V NMR spectrum, the area ratios seem to indicate that the peaks at $\delta = 4.91$ and 4.77 are associated with metal substitution in the capped location, while the peaks at $\delta = 5.09$ and 4.97 are associated with belt substitution. The poorer resolution of the quartets at $\delta = 5.09$ and 4.77 versus the quartets at $\delta = 4.97$ and 4.91 is associated with the proximity of ^{51}V ($I = 7/2$), which would distort the peaks, to the HF_3O tetrahedra. The more resolved quartets are related to the distal (from vanadium) HF_3O tetrahedra. It is important to additionally note that ^{183}W ($I = 1/2$) is not expected to cause significant peak broadening, whereas paramagnetic centers, for example Ni^{2+}, significantly shift and broaden peaks.

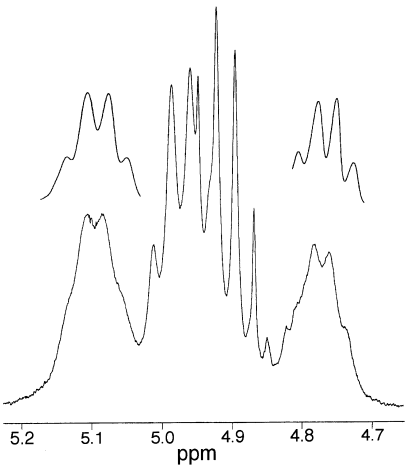

Figure 3. $^1H\{^{19}F\}$ NMR spectrum of $^4Q_8[V(O)H_2F_6NaW_{17}O_{55}]$ in CD_3CN.

Further characterization of the $[M(L)H_2F_6NaW_{17}O_{55}]^{q-}$ compounds was by ^{19}F NMR and ^{183}W NMR spectroscopy. It is important to note that for the series of PFOMs, the spectra were essentially the same, regardless of the substituted transition metal. In the $^{19}F\{^1H\}$ NMR spectra (Figure 4) of $[Ni(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ dissolved in D_2O, five peaks were observed at $\delta = -140.1$, -160.0, -162.3, -165.8 and -168.50. The relative intensities vary somewhat, depending on the substituted metal, but are approximately 1:1:1:2.5:1.2. Two further comments are worthwhile making. First, the peaks appeared as singlets and were not affected by the adjoining hydrogen atoms. Second, as is common for transition metal substituted polyoxometalates, fast exchange on

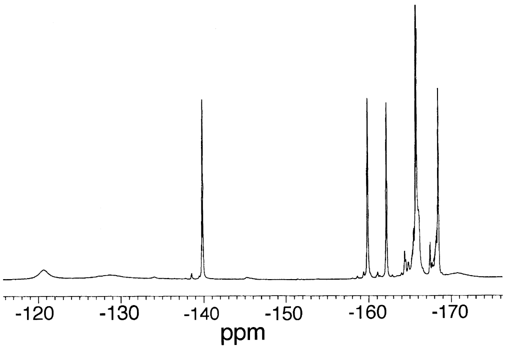

Figure 4. ^{19}F NMR spectrum of $K_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ in D_2O.

the NMR time scale of the substituted transition metal prevents the resolution of all the theoretically expected peaks.[25] Theoretically, the belt-substituted isomer is expected to yield six peaks of equal intensity in the ^{19}F NMR spectrum. The capped-substituted isomer is expected to yield an additional six lines, if non-NMR equivalence of the three fluorine atoms distal to the substituted metal is assumed; if these three fluorine atoms are regarded to be NMR equivalent, then four lines of a 1:1:1:3 intensity ratio are expected. Considering the statistical 2:1 ratio of belt versus capped positions, all in all, either 12 or 10 lines are expected, with an area ratio of 2:2:2:2:2:2:1:1:1:1:1:1 or 2:2:2:2:2:2:1:1:1:3, respectively.

The ^{183}W NMR spectrum of the nonsubstituted parent compound,[18] $[H_2F_6NaW_{17}O_{56}]^{7-}$, is simple. There is a doublet due to coupling with fluorine associated to the belt tungsten atoms and a singlet from the tungsten atom in the capped position. The inclusion of a transition metal very significantly changes the ^{183}W{^{19}F} NMR spectrum (measured as the lithium salt for maximum solubility) (Figure 5), because of the reduction in symmetry. As was observed for ^{19}F NMR, the substituted transition metal did not affect the ^{183}W NMR spectra. Lacking a W–F decoupler, needed to reliably sort out W–F connectivities, we have so far not been able to further analyze the spectra.

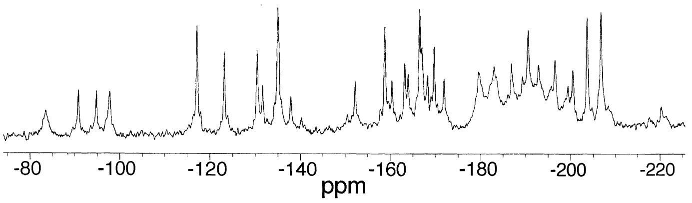

Figure 5. ^{183}W NMR spectrum of $Li_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$in D_2O.

Catalytic activation of hydrogen peroxide: We began our survey of the catalytic activity of the series $[M(L)H_2F_6NaW_{17}O_{55}]^{q-}$, $M = Zn^{2+}$, Co^{2+}, Mn^{2+}, Fe^{2+}, Ru^{2+}, Ni^{2+} and V^{5+}, by testing the compounds for activity in the epoxidation of cyclooctene with 35 % aqueous hydrogen peroxide. At room temperature, cyclooctene (1 mmol), $Q_q[M(L)H_2F_6NaW_{17}O_{55}]$ (Q = tricaprylmethyammonium) (0.001 mmol), 1,2-dichloroethane (1 mL) and H_2O_2 (35 %, 3 mmol) were stirred 24 h. Analysis showed that *only* the nickel-substituted compound, $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$, resulted in significant conversion, 24.6 %, with nearly 100 % selectivity to cyclooctene oxide. For all the other PFOMs, the conversion of cyclooctene was <2 %, although considerable hydrogen peroxide dismutation to oxygen and water was observed. The dismutation reaction was quantified by measurement of the amount of oxygen formed at room temperature. Thus, solutions of $K_q[M(L)H_2F_6NaW_{17}O_{55}]$ (1 μmol) and hydrogen peroxide (35 %, 1 mmol) in acetate buffer (1 mL) were mixed and oxygen evolution was measured with a gas burette. The zero-order rates in hydrogen peroxide were $0.2 < 0.8 < 2.2 < 3.2 < 8.7 < 13.9$ mol hydrogen peroxide decomposed per mol PFOM per minute for the zinc- < vanadium- < iron- < ruthenium- < cobalt- < manganese-substituted compounds, respectively.

The activity of the nickel-substituted PFOM was further investigated on a series of simple alkenes (Table 2). $[Ni(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ was rather successful at catalyzing the epoxidation reaction (catalyst/substrate ratio 1:100), even in the case of difficult-to-epoxidize terminal alkenes (1-octene). Interestingly, cyclohexene, which is very sensitive towards formation of allylic oxidation products by metal-catalyzed autooxidation, showed high yields of epoxide and temperature-independent selectivity. Styrene oxide was unstable under the reaction conditions, yielding both the rearranged product phenylacetaldehyde, and a subsequent oxidation product $PhCOCH_2OH$, in addition to the carbon–carbon bond-cleavage product, benzaldehyde. Interestingly, these nickel-substituted PFOM-catalyzed reactions significantly contrast with the previously studied epoxidation catalyzed by manganese-substituted "sandwich" polyoxometalates.[13b,c] Here, turnover numbers for an active substrate such as cyclooctene are lower, but the active intermediate is a more potent oxidant, as yields for epoxidation of a relatively inert alkene, 1-octene, are higher. In addition, the reaction here is much less sensitive to temperature compared to the manganese "sandwich" case, where, at 60 °C, cyclohexene gave predominantly allylic oxidation products while yielding epoxide only at approximately 0 °C. The $[Ni(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$-catalyzed epoxidation of primary alkenols was also studied (Table 3). The reactivity is significantly higher for the allylic alcohols (catalyst/substrate ratio 1/1000) than for

Table 2. Epoxidation of representative alkenes catalyzed by $[Ni(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$.[a]

Substrate	Conversion [mol %]		Selectivity [mol %]	
	25 °C	60 °C	25 °C	60 °C
cis-cyclooctene	78.3	> 99	98	> 99
1-octene	25.2	46.3	88	97
trans-2-octene	43.2	61.5	89	94
cyclohexene	42.9	74.6	75[b]	74[b]
styrene	33.6		[c]	

[a] Reaction conditions: substrate (1 mmol), catalyst (0.01 mmol), 1,2-dichloroethane (1 mL), 35 % H_2O_2 (3 mmol), 24 h. The selectivity is given as mol epoxide per mol total products. The other products were allylic oxidation products. [b] The remaining products were mostly 2-cyclohexenol and 2-cyclohexenone. [c] the products were 42 % benzaldehyde, 16 % phenylacetaldehyde and 42 % $PhCOCH_2OH$ (GC-MS).

Table 3. Epoxidation of representative alkenols catalyzed by $[Ni(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$.[a]

Substrate	Conversion [mol %]	Selectivity [mol %]
cis-2-hexen-1-ol	88.3	96
trans-2-hexen-1-ol	72.5	97
cis-3-hexen-1-ol	27.3	94
trans-3-hexen-1-ol	5.1	92

[a] Reaction conditions: substrate (1 mmol), catalyst (0.001 mmol), 1,2-dichloroethane (1 mL), 35 % H_2O_2 (1 mmol), 25 °C, 24 h. The selectivity is given as mol epoxide per mol total products. The other products were allylic oxidation products. *trans*-2-octene gave 4.8 mol % conversion under reaction conditions.

alkenes, although the homoallylic alcohols are significantly less reactive. *cis*-Alkenols are more reactive than *trans*-alkenols. Selectivity for the epoxide is high in all cases.

Where the activity of a new catalysts is described, an important factor determining the practicality of the catalyst for a specific use is its stability. The use of polyoxometalates for the activation of hydrogen peroxide has shown that Keggin-type polyoxometalates are not stable under the typical reaction conditions,[26] whereas "sandwich"-type polyoxometalates are very stable.[13b,c,h] Also important in the activation of hydrogen peroxide is, of course, the identity of the active intermediate and the reaction yield in hydrogen peroxide. In this research, we have used four independent methods to study the question of catalyst stability and performance.

First, the reaction profile for the epoxidation of cyclooctene as a model alkene was measured (Figure 6). The reaction profile shows that the reaction is zero-order in cyclooctene and hydrogen peroxide, as is expected, since the catalyst is the limiting species. However, more importantly, the reaction profiles give additional important insights: a) There appears to be no induction period; an induction period would be indicative of the time-dependent formation of an active species. b) There is no apparent reaction deceleration as a function of time; such a deceleration would point to significant catalyst deactivation. c) Hydrogen peroxide reacts only 40% more rapidly than cyclooctene; this indicates minimal nonproductive hydrogen peroxide consumption.

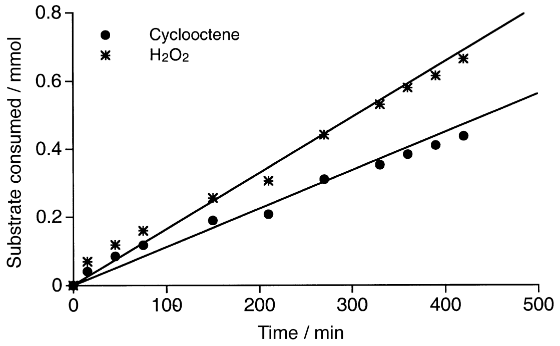

Figure 6. Reaction profile for the oxidation of cyclooctene. Reaction conditions: substrate (1 mmol), catalyst (0.01 mmol), 1,2-dichloroethane (1 mL), 35% H_2O_2 (3 mmol), $T = 60\,^{\circ}C$. Cyclooctene consumption was determined by GC, H_2O_2 consumption was determined from the amount used to form cyclooctene oxide and the amount of oxygen formed (gas burette). $k_{co} = 1.16$ mmol min^{-1}, $k_{H_2O_2} = 1.64$ mmol min^{-1}.

Second, the IR spectra of $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ were measured before and after addition of hydrogen peroxide (Figure 7). The original compound, bottom spectrum, is typical of the quasi-Wells–Dawson polyoxometalate; peaks were at 949, 882, 783, and 720 cm^{-1}. After addition of a 100-fold excess of hydrogen peroxide to $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ in 1,2-dichloroethane, at 60 °C for six hours, followed by phase separation and evaporation of the organic solvent, the original peaks remained and were essentially unchanged in position. In addition, a new peak was detected at 816 cm^{-1}. Our interpretation of these spectra is that the addition of hydrogen peroxide to $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ does not affect the overall structure of the latter, but that a peroxo or hydroperoxo moiety, which typically absorb at 800–840 cm^{-1}, is now bound to the PFOM, forming the active intermediate "$[Ni(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$–$H_2O_2$".

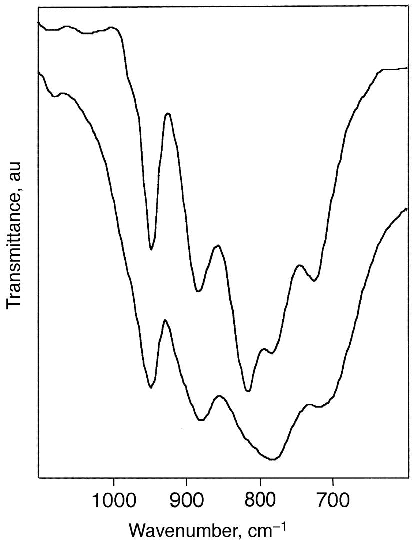

Figure 7. IR spectrum of $[Ni^{II}(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$. Bottom trace: before addition of H_2O_2; top trace: after addition of H_2O_2 (6 h at 60 °C).

Third, after $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ was heated in 1,2-dichloroethane with a 1000-fold excess of 35% H_2O_2, at 60 °C for 6 h, the aqueous phase was separated and tested for the presence of dissolved nickel by AAS. There was no indication of nickel down to a 10 ppm level of detection. Finally, the ^{19}F NMR spectrum of $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ was measured after addition of hydrogen peroxide. For this, $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ (0.02 mmol) was dissolved in $CDCl_3$ (2 mL), and H_2O_2 (35%, 6 mmol) was added. The stirred mixture was kept at 25 °C and the ^{19}F NMR spectra were measured before addition of H_2O_2, after 3 h, after 6 h and after 24 h (Figure 8). The ^{19}F NMR spectrum of $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ in CD_3CN was qualitatively different from the spectrum of $K_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ in D_2O (Figure 4). Six major peaks were resolved at $\delta = -163.4$, -164.4, -164.8, -165.0, -165.2, and -167.1, and an addi-

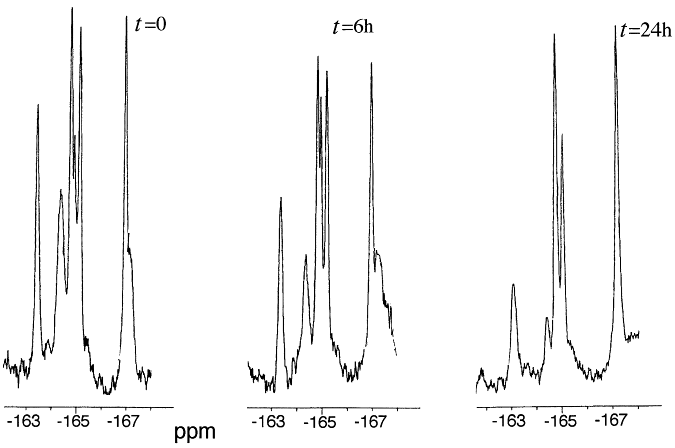

Figure 8. Changes in the ^{19}F NMR spectrum of $[Ni^{II}(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ with time after addition of H_2O_2.

tional shoulder was observed at $\delta = -167.2$. Relative peak intensities differed significantly from those of the sample in water. None of the peaks is attributable to F–H coupling, as the spectrum was unchanged by ^{1}H decoupling. That the peak downfield from the one at $\delta = -140$ found in D_2O was not detected in CD_3CN could quite conceivably mean that that peak is associated with a lacunary species. As noted above, we believe that the ^{19}F NMR spectrum is not completely resolved. Upon addition of H_2O_2 at room temperature, the ^{19}F NMR spectrum is essentially unchanged after 6 h. In this time period, significant catalytic activity, Tables 2 and 3, was observed. After a total period of 24 h, the ^{19}F NMR spectrum is slightly changed. The peak at $\delta -165$ is no longer observed. This same slight change is discernable after 6 h at 60 °C but there is no further change after longer time periods. Furthermore, no ^{19}F NMR peaks associated with free F^- ions that would be formed in the collapse or decomposition (fluorine in surface positions are quickly exchanged by oxygen) of the quasi-Wells–Dawson structure were detected in either the aqueous or organic phase. Our interpretation of the ^{19}F NMR data after 24 h at 25 °C or 6 h at 60 °C is that the quasi-Wells–Dawson structure is retained in the presence of H_2O_2. The slight loss of resolution is associated with the formation of a peroxo/hydoperoxo intermediate.

Conclusion

A partially new series of transition metal substituted polyfluorooxometalates with quasi-Wells–Dawson structure was prepared and characterized. Characterization by ^{51}V and ^{1}H{^{19}F} NMR spectroscopy show that the transition metal is substituted in both the belt and capped positions. The nickel-substituted compound was the only one active in the activation of hydrogen peroxide towards the selective epoxidation of alkenes and alkenols. Yields based on hydrogen peroxide were high. An intermediate peroxo/hydroperoxo compound was detected by IR spectrometry. Use of IR, AAS, and ^{19}F NMR indicates that the nickel-substituted polyfluorooxometalate structure is stable under reaction conditions of aqueous hydrogen peroxide at 60 °C.

Experimental Section

General: Reactants and solvents were all from commercial sources and were used without additional purification. Water was determined by thermogravimetric analysis (Mettler 50). ^{19}F NMR and ^{1}H NMR spectra were measured on a Bruker 400 DRX instrument at 376.499 MHz and 400.132 MHz in D_2O or CD_3CN, with neat CF_3COOH as external standard. ^{51}V NMR and ^{183}W NMR spectra were measured on a Bruker 300 AMX spectrometer at 78.86 MHz and 12.505 MHz in D_2O, with $VOCl_3$ and $NaWO_4$ as external standards. IR spectra were measured on a Nicolet 510M FT spectrometer; atomic absorption measurements were done on a GBC 921 spectrometer. Oxidation reaction products were characterized with the aid of reference compounds, when available, by GLC (Hewlett-Packard 5890 gas chromatograph) with a flame ionization detector and a 15 m × 0.32 mm 5 % phenylmethylsilicone (0.25 μm coating) capillary column and helium carrier gas. Products with uncertain initial identity were unambiguously identified with a gas chromatograph equipped with a mass-selective detector (GC-MS Hewlett-Packard GCD) and the same column described above. IR spectra were measured on samples on NaCl plates, obtained by evaporation of a solution of $Q_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$ dissolved in 1,2-dichloroethane. The lithium salt, $^{Li_9}[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$, for the ^{183}W NMR measurement was obtained after the potassium salt, $^{K_9}[Ni(H_2O)H_2F_6NaW_{17}O_{55}]$, was passed through a lithium-substituted Dowex 50 ion-exchange column. The solution was concentrated to approximately 1 M for the ^{183}W NMR measurement.

Synthesis

$[Zn(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$: The zinc-substituted PFOM, $[Zn(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ was prepared according to a previously reported method,[20] by which $NaWO_4 \cdot 2H_2O$ (44 g) was dissolved in water (100 mL) in a teflon beaker. The solution was heated to 80 °C and 49 % HF was added dropwise until the pH reached 4.5. The white precipitate was filtered off and the filtrate was reheated to 80 °C. Zinc acetate (7 g) dissolved in water (5 mL) was added slowly, while the pH was kept at 4.5. The solution was stirred an additional hour at 80 °C, cooled, and then KCl (3 g) was added. The white precipitate was filtered and recrystallized twice from water. Yield: 9.6 g. ^{19}F NMR (in H_2O, neat CF_3COOH as standard, relative intensities given in parentheses) $\delta = -140.3(1), -160.1(1), -162.5(1), -165.8(2.5), -168.7(1)$.

$K_8[V(O)H_2F_6NaW_{17}O_{55}] \cdot 17H_2O$: The other transition metal substituted PFOMs were prepared from $[Zn(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ PFOM as starting material. For example, $K_8[V(O)H_2F_6NaW_{17}O_{55}] \cdot 17H_2O$ was prepared as follows: $VOSO_4$ (0.326 g, 2 mmol), dissolved in 5 mL of an acetate buffer (pH = 5), was added over 5 min to a solution of $[Zn(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ (4.8 g, 1 mmol) in an acetate buffer ($pH = 5$) (40 mL) at 50 °C. The solution turned purple immediately. After being stirred for 30 min, the solution was cooled and filtered. A saturated KCl solution was added to the filtrate, and the precipitate formed was filtered. The precipitate (3.0 g) was dissolved in water (15 mL) and heated to 90 °C, followed by addition of $K_2S_2O_8$ (750 mg). Upon addition of the oxidant, the color of the solution turned from deep purple-brown to yellow in 20 min. Upon being cooled, the solution yielded only yellow needle-like crystals, yield 2.4 g, which were recrystallized from water. Elemental analysis calcd (%)for $K_8[V(O)H_2F_6NaW_{17}O_{55}] \cdot 17H_2O$: K 6.48, Na 0.48, V 1.05, W 64.70, H_2O 6.34, F 2.19; found: K 6.59, Na < 0.5 detected but precision limited due to sensitivity limitation, V 1.15, W 63.87, H_2O 6.29, F 2.36.

$K_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}] \cdot 15H_2O$: Nickel nitrate hexahydrate (0.4 g) dissolved in an acetate buffer (pH 5) (5 mL) was added slowly to a solution of $[Zn(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ (4.8 g) in an acetate buffer (pH 5) (40 mL) at 50 °C. The solution turned light green immediately. After being stirred for 30 min, the solution was cooled and filtered. To the filtrate, a saturated KCl solution was added, and the precipitate formed was filtered and recrystallized; yield 2.85 g. Elemental analysis calcd (%) for $K_9[Ni(H_2O)H_2F_6NaW_{17}O_{55}] \cdot 15H_2O$: K 7.27, Na 0.48, Ni 1.21, W 64.53, H_2O 5.95, F 2.35; found: K 7.11, Na < 0.5 detected, Ni 1.32, W 64.92, H_2O 5.91, F 2.12.

$K_9[Ru(H_2O)H_2F_6NaW_{17}O_{55}] \cdot 15H_2O$: $Ru(DMSO)_4Cl_2$ (0.43 g) dissolved in 50 mL of an acetate buffer (pH 5) was added slowly to a solution of $[Zn(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ (4.8 g) in an acetate buffer (pH 5) (40 mL) at 50 °C. The solution turned light brown immediately. After being stirred at 60 °C for 5 h, the solution was cooled and filtered. To the filtrate a saturated KCl solution was added and the precipitate formed was filtered and recrystallized; yield 2.7 g. Elemental analysis calcd (%) for $K_9[Ru(H_2O)H_2F_6NaW_{17}O_{55}] \cdot 12H_2O$: K 7.28, Na 0.48, Ru 2.09, W 64.69, H_2O 4.85, F 2.36; found: K 7.37, Na < 0.5 detected, Ru 1.91, W 64.01, H_2O 4.99, F 2.19.

Other substituted compounds: The other substituted compounds were prepared in an identical way, yielding a pale brown manganese compound, a black iron compound and a purple cobalt compound. We were unsuccessful in preparing the analogous copper and chromium compounds by this procedure. Quaternary ammonium salts of the various transition metal substituted PFOMs, $Q_9[M(H_2O)H_2F_6NaW_{17}O_{55}]$, where Q is the quaternary ammonium cation, were prepared by $[M(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$ (1 mmol) being dissolved in water (100 mL); to this, an equinormal amount quaternary ammonium salt, for example, tetrabutyl ammonium bromide or tricaprylmethyl ammonium chloride, dissolved in dichloromethane (75 mL), was added. The phases were mixed vigorously for 30 min. The organic phase was separated, dried with sodium sulfate and the solvent was evaporated. The yields were nearly quantitative.

X-ray crystallography: X-ray data were measured on a PW1100/20 Phillips four-circle diffractometer. $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cells were obtained by a least-squares fit of 24 centered reflections in the range of $10 \leq \theta \leq 15$. Intensity data were collected by the $\omega - 2\theta$ method to a maximum of 2θ of 50°. The scan width, $\Delta\omega$, for each reflection was $1.00 + 0.035 \tan\theta$ with a scan speed of 3.0° min^{-1}. Background measurements were made for a total of 10 s at both limits of each scan. Three standard reflections were measured every 60 min and no systematic variations were observed. Intensities were corrected for Lorentz, polarization and absorption effects. All non-hydrogen atoms were found from the results of the SHELXS-86 direct method analysis. The tungsten atoms were refined on the assumption of a random substitution of one substituted metal atom, and the electron densities were adjusted accordingly. Refinement proceeded to convergence after $\Sigma w\,|F_0|-|F_c|^2$ was minimized. A final difference Fourier synthesis map showed several peaks less than 2.3 e Å^{-3} scattered about the unit cell without significant feature. The discrepency indices are $R = \Sigma\,||F_0| - |F_c||/\Sigma\,|F_0|$ and $R_w = [\Sigma w\,|F_0| - |F_c|^2/\Sigma\,|F_0|^2]^{1/2}$. Further details of the crystal structure investigation may be obtained from the Fachinformationszenstrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-410811.

Catalytic epoxidation reactions: Typically, epoxidation reactions were carried out in 5-mL vials: the vial was loaded with catalyst (10 µmol) dissolved in 1,2-dichloroethane (1 mL) and substrate (1 mmol). Hydrogen peroxide (35 % aqueous, 3 mmol) was added after the reaction temperature was equilibrated. The reaction mixture was stirred magnetically and aliquots were removed at the appropriate time intervals for analysis by gas chromatography.

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[1] W. A. Herrmann, R. W. Fischer, M. U. Rauch, W. J Scherer, *Mol. Catal.* **1994**, *86*, 243.

[2] M. G. Clerici, G. Bellussi, U. Romano, *J. Catal.* **1991**, *129*, 159.

[3] D. E. De Vos, B. F. Sels, M. Reynaers, Y. V. S. Rao, P. A. Jacobs, *Tetrahedron Lett.* **1998**, *39*, 3221.

[4] C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem.* **1983**, *48*, 3831.

[5] a) C. L. Hill, R. B. Brown, *J. Am. Chem. Soc.* **1986**, *108*, 536; b) D. Mansuy, J.-F. Bartoli, P. Battioni, D. K. Lyon, R. G. Finke, *J. Am. Chem. Soc.*, **1991**, *113*, 7222; c) H. Weiner, Y. Hayashi, R. G. Finke, *Inorg. Chem.* **1999**, *38*, 2579.

[6] X. Zhang, K. Sasaki, C. L. Hill, *J. Am. Chem. Soc.* **1996**, *118,* 4809.

[7] a) R. Neumann, C. Abu-Gnim, *J. Chem. Soc. Chem. Commun.* **1989**, 1324; b) R. Neumann, C. Abu-Gnim, *J. Am. Chem. Soc.* **1990**, *112*, 6025; c) E. Steckhan, C. Kandzia, *Synlett* **1992**, 139; d) M. Bressan, A. Morvillo, G. J. Romanello,. *Mol. Catal*. **1992**, *77*, 283.

[8] R. Neumann, A. M. Khenkin, *Chem. Commun.* **1998**, 1967.

[9] a) M. Faraj, C. L. Hill, *J. Chem. Soc. Chem. Commun.* **1987**, 1487; b) R. Neumann, A. M. Khenkin, *Inorg. Chem.* **1995**, *34*, 5753.

[10] Autooxidation: a) J. E. Lyons, P. E. Ellis, V. A. Durante, *Stud. Surf. Sci. Catal.* **1991**, *67*, 99; b) N. Mizuno, T. Hirose, M. Tateishi, M. Iwamoto, *J. Mol. Catal*. **1994**, *88*, L125; c) N. Mizuno, M. Tateishi, T. Hirose, M. Iwamoto, *Chem. Lett.* **1993**, 2137; d) D. E. Katsoulis, M. T. Pope, *J. Chem. Soc. Dalton Trans.* **1989**, 1483; e) R. Neumann, M. Dahan, *J. Chem. Soc. Chem. Commun.* **1995**, 171; f) R. Neumann, M. Dahan, *Polyhedron* **1998**, *17*, 3557; g) H. Weiner, R. G. Finke, *J. Am. Chem. Soc.* **1999**, *121*, 9831.

[11] Autooxidation in presence of aldehydes: a) N. Mizuno, T. Hirose, M. Tateishi, M. Iwamoto, *Chem. Lett.* **1993**, 1839; b) N. Mizuno, M. Tateishi, T. Hirose, M. Iwamoto, *Chem. Lett.* **1993**, 1985; c) A. M. Khenkin, A. Rosenberger, R. Neumann, *J. Catal.* **1999**, *182*, 82.

[12] Dioxygenase: a) R. Neumann, A. M. Khenkin, M. Dahan, *Angew. Chem.*, **1995**, *107*, 1740; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1587; b) R. Neumann, M. Dahan, *Nature* **1997**, *388*, 353; c) R. Neumann, M. Dahan, *J. Am. Chem. Soc.* **1998**, *120*, 11969.

[13] a) A. M. Khenkin, C. L. Hill, *Mendeleev Commun.* **1993**, 140; b) R. Neumann, M. Gara, *J. Am. Chem. Soc.* **1994**, *116*, 5509; c) R. Neumann, M. Gara, *J. Am. Chem. Soc.* **1995**, *117*, 5066; d) R. Neumann, A. M. Khenkin, *J. Mol. Catal.* **1996**, *114*, 169; e) R. Neumann, D. Juwiler, *Tetrahedron* **1996**, *47*, 8781; f) R. Neumann, A. M. Khenkin, D. Juwiler, H. Miller, M. Gara, *J. Mol. Catal.* **1997**, *117*, 169; g) N. Mizuno, C. Nozaki, I. Kiyoto, M. Misono, *J. Am. Chem. Soc.* **1998**, *120*, 9267; h) Z. Zhang, Q. Chen, D. C. Duncan, R. J. Lachicotte, C. L. Hill, *Inorg. Chem.* **1997**, *36*, 4381.

[14] M. V. George in *Organic Syntheses by Oxidation with Metal Compounds* (Eds.: W. J. Mijs, C. R. H. I. de Jonge), Plenum, New York, **1986**, pp. 373–422.

[15] a) H. Yoon, C. J. Burrows, *J. Am. Chem. Soc.* **1988**, *110*, 4087; b) J. D. Koola, J. K. Kochi, *Inorg. Chem.* **1987**, *26*, 908; c) J. F. Kinneary, J. S. Albert, C. J. Burrows, *J. Am. Chem. Soc.* **1988**, *110*, 6124; d) J. F. Kinneary, T. R. Wagler, C. J. Burrows, *Tetrahedron Lett.* **1988**, *29*, 877; e) T. R. Wagler, Y. Fang, C. J. Burrows, *J. Org. Chem.* **1989**, *54*, 1584; f) H. Yoon, T. R. Wagler, K. J. O'Connor, C. J. Burrows, *J. Am. Chem. Soc.* **1990**, *112*, 4568; g) J. F. Kinneary, T. M. Roy, J. S. Albert, H. Yoon, T. R. Wagler, L. Shen, C. J. Burrows, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1989**, *7*, 155.

[16] a) T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, *Chem. Lett.* **1991**, 1; b) T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2109.

[17] a) S. H. Wasfi, W. L. Johnson, D. L. Martin, *Syn. React. Inorg. Met.* **1997**, 27, 401; b) S. H. Wasfi, J. C. Johnson, *Syn. React. Inorg. Met.* **1996**, *26*, 1073; c) S. H. Wasfi, J. C. Johnson, *Syn. React. Inorg. Met.* **1996**, *26*, 1339; d) S. H. Wasfi, J. C. Johnson, D. L. Martin, *Syn. React. Inorg. Met.* **1995**, *26*, 1061; e) S. H. Wasfi, W. L. Johnson, D. L. Martin, *Inorg. Chim. Acta* **1998**, *278*, 91; f) S. H. Wasfi, W. L. Johnson, D. L. Martin, *Syn. React. Inorg. Met.* **1997**, 27, 535; g) S. H. Wasfi, A. L. Rheingold, B. S. Haggerty, *Inorg. Chim. Acta* **1998**, *282*, 136.

[18] a) F. Chauveau, P. J. Souchay, *Inorg. Nucl. Chem.* **1974**, *36*, 1761; b) J.-P. Launay, M. Boyer, F. J. Chauveau, *Inorg. Nucl. Chem.* **1976**, *38*, 243; c) F. Chauveau, P. Doppelt, J. Lefebvre, *Inorg. Chem.* **1980**, *19*, 2803; d) T. L. Jorris, M. Kozik, L. C. W. Baker, *Inorg. Chem.* **1990**, *29*, 4584.

[19] S. H. Wasfi, C. E. Costello, A. L. Rheingold, B. S. Haggerty, *Inorg. Chem*. **1991**, *30*, 1788.

[20] T. L. Jorris, Ph. D. Thesis, Georgetown University, **1987**.

[21] C. M. Tourné, G. F. Tourné, F. Zonnevijlle, *J. Chem. Soc., Dalton Trans.* **1991**, 143.

[22] Full X-ray data will be given elsewhere, A. M. Khenkin, R. Neumann, *Inorg. Chem.* **2000**, in press.

[23] M. A. Leparulo-Loftus, M. T. Pope, *Inorg. Chem.* **1987**, *26*, 2112.

[24] R. C. Hibbert, *J. Chem. Soc. Dalton Trans.* **1986**, 751.

[25] a) R. Neumann, M. Levin, *J. Am. Chem. Soc.* **1992**, *114*, 7278; b) A. M. Khenkin, A. Rosenberger, R. Neumann, *J. Catal.* **1999**, *182*, 82.

[26] a) D. C. Duncan, R. C. Chambers, E. Hecht, C. L. Hill, *J. Am. Chem. Soc.* **1995**, *117*, 681; b) L. Salles, C. Aubry, R. Thouvenout, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J. M. Brégault, *Inorg. Chem.* **1994**, *33,* 871.

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