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Noble Metal (Ru^{III}, Pd^{II}, Pt^{II}) Substituted "Sandwich" Type Polyoxometalates: Preparation, Characterization, and Catalytic Activity in Oxidations of Alkanes and Alkenes by Peroxides

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The polyoxometalates substituted with noble metals, Pd(II), Pt(II) and Ru(III), $K_{12}\{[WZnPd^{II}_2(H_2O)_2](ZnW_9O_{34})_2\}\cdot 38H_2O$, $K_{12}\{[WZnPt^{II}_2(H_2O)_2](ZnW_9O_{34})_2\}\cdot 36H_2O$, and $Na_{11}\{[WZnRu^{III}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot 42H_2O$, were prepared by exchange of labile zinc atoms with noble metal atoms from the isostructural starting material, $Na_{12}\{[WZn_3(H_2O)_2](ZnW_9O_{34})_2]\}\cdot 46H_2O$. The X-ray crystal structure of the ruthenium compound shows a structure compatible with a sandwich-type structure type with a WRuZnRu (Ru and W, Zn at opposing sides) ring between two B-XW_9O_{34} units. Magnetic susceptibility studies as a function of temperature provide convincing evidence of two ruthenium (III) centers with no magnetic interaction between them. The EPR spectrum is supportive of this formulation showing an anisotropic spectrum of a ruthenium (III) atom ($S = {}^1/_2$) in an octahedral field. The IR and UV−vis spectra of the ruthenium compound as well as of the diamagnetic palladium and platinum compounds are consistent with an isostructural series of compounds. The water soluble polyoxometalates may be extracted into an organic phase *e.g.* 1,2-dichloroethane by the addition of methyltricaprylammonium chloride to form their quaternary ammonium salts. The catalytic activity of these compounds was tested for the oxidation of alkenes and alkanes using aqueous 30% hydrogen peroxide and 70% *tert*-butyl hydroperoxide as oxidants. The alkene oxidation proceeded in high reactivity and moderate selectivity to the epoxide product using 30% H_2O_2. Kinetic profiles as well as UV−vis and IR spectra before, during and after the reaction indicate that the catalysts are stable throughout the reaction. Formation of epoxides rather than ketonization in the reaction of terminal alkenes as well as low reactivity with iodosobenzene indicates that the reaction is tungsten centered and not noble metal centered. Oxidation of alkenes with *tert*-butyl hydroperoxide gave mostly allylic oxidation and/or addition of *tert*-butyl alcohol to the double bond. Oxidation of cyclic alkanes such as cyclohexane and adamantane was successful with *tert*-butyl hydroperoxide with catalytic activity 10 times higher than previously found for transition metal substituted Keggin compounds. Ratios of hydroxylation of adamantane at tertiary *vs* secondary positions indicates different active species in the palladium-, platinum-, and ruthenium substituted-polyoxometalates.

Introduction

The development of new and effective catalytic systems for selective oxidation of hydrocarbons by simple and stable peroxides such as *tert*-butyl hydroperoxide and hydrogen peroxide continues to be the focus of many research efforts designed to develop new technologies for future industrial applications.[1−4] Often-used transition metal complexes coordinated with organic ligands such as metalloporphyrins, metals coordinated by Schiff bases, and many others often show high initial activity under mild conditions and high selectivities, *e.g.*, enantioselectivity. However, application remains a problem on a large scale due to irreversible deactivation of the catalytic species by self-oxidation of the organic ligand. In order to solve this problem of intrinsic instability to oxidation of metalloorganic catalysts, two approaches based on inorganic catalysts have been advanced. The first approach has been to site-selectively incorporate transition metal cations within molecular sieves or zeolites and to carry out reactions in a heterogeneous mode. The most significant results have been reported for titanium substituted ZSM-5 zeolites (TS-1)[5] although there are reports of use of other transition metals, and zeolites and aluminophosphates.[6] The second approach which is that discussed in this paper, involves incorporation of low-valent transition metals into lacunary polyoxometalates. This brings about formation of complexes that may be viewed as coordination of such transition metals by inorganic oxidatively stable ligands, the so called transition metal substituted polyoxometalates (TMSP). Research on the chemical activity of these TMSP complexes have shown the ability to coordinate[7] and activate dioxygen,[8−10] to form high valent metal−oxo intermediates,[11,12] and to catalyze oxidation of alcohols, alkenes, and alkanes with a variety of oxygen donors.[13−26] Generally, this approach has yielded compounds which are indeed oxidatively stable in

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(1) Sheldon, R. A. *CHEMTECH* **1991**, 566−576.

(2) Drago, R. S. *Coord. Chem. Rev.* **1992**, *117*, 185−213.

(3) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411−1456.

(4) Strukul, G. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*; Kluwer: Dordrecht, The Netherlands, 1992.

(5) Martens, J. A.; Buskens, Ph.; Jacobs, P. A.; van der Pol, A.; van Hooff, J. H. C.; Ferrini, C.; Kouwenhoven, H. W.; Kooyman, P. J.; van Bekkum, H. *Appl. Catal. A*, **1993**, *99*, 71.

(6) Chen, J. D.; Dakka, J.; Neeleman, E.; Sheldon, R. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1379−1380.

(7) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106* 2737−2738.

(8) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1989**, 1483−1488.

(9) Neumann, R.; Levin, M. *Stud. Surf. Sci. Catal.* **1991**, *66*, 121−128.

(10) Neumann, R.; Dahan, M. *J. Chem. Soc., Chem. Commun.* **1995**, 171−173.

(11) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1186−1188.

(12) Khenkin, A. M.; Hill, C. L. *J. Am. Chem. Soc.* **1993**, *115*, 8178−8186.

(13) Hill, C. L.; Brown Jr., R. B. *J. Am. Chem. Soc.* **1986**, *108*, 536−538.

(14) Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487−1489.

(15) Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932−2938.

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reactions with oxidants such as iodosobenzene or sodium periodate, but in many cases use of the environmentally and economically favored peroxide oxidants H_2O_2, *t*-BuOOH, and $KHSO_5$, especially in the presence of water, has shown that the originally used transition metal substituted Keggin and Dawson–Wells type polyoxometalates are solvolytically unstable.[27] These polyoxometalates generally degrade often yielding catalytic species *e.g.* $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, which are, however, not transition metal substituted. Recently, it has been found that poly transition metal substituted polyoxometalates of the "sandwich" type, the tetranuclear iron, $[(Fe^{II}_4)(PW_9O_{34})_2]^{10-}$,[24] and dinuclear manganese polyoxometalate, $[(WZnMn^{II}_2)(ZnW_9O_{34})_2]^{12-}$,[25,26,28] Figure 1, are of much higher solvolytic stability and in the latter case also highly active and chemoselective catalysts in oxidations of alkenes with hydrogen peroxide as oxidant. In this paper, we extend the scope of oxidation reactions with peroxide oxidants using dinuclear noble metal (Ru^{III}, Pd^{II}, Pt^{II}) substituted compounds of the general structure as defined in Figure 1.

The syntheses of $[(WZnPd^{II}_2)(ZnW_9O_{34})_2]^{12-}$ and $[(WZnPt^{II}_2)(ZnW_9O_{34})_2]^{12-}$ compounds was reported a few years ago,[29] but there was no in depth characterization or investigation into their catalytic activity. The preparation and use in alkane oxidation with molecular oxygen of the ruthenium compound, $[(WZnRu^{III}_2)(ZnW_9O_{34})_2]^{11-}$ was just recently communicated.[30] This article fully discusses the synthesis and characterization by single crystal X-ray crystallography of $[(WZnRu^{III}_2)(ZnW_9O_{34})_2]^{11-}$. In addition, the three noble metal substituted compounds are characterized by their IR, UV–vis and ESR spectra; the electrochemistry has been investigated by cyclic voltammetry, and for the ruthenium compound the magnetic interaction of the two ruthenium centers has been studied. Using hydrogen peroxide as oxidant, oxidations of alkenes have shown high activity and selectivity to formation epoxides for the Pd and Pt analogs (similar to the previously reported manganese polyoxometalate) and significantly poorer results for the ruthenium compound. In the oxidation of alkanes there was only very slight catalytic activity. On the other hand, with *tert*-butyl hydroperoxide as oxidant, reaction with alkenes were not selective with the predominant reactions being formation of mixed dialkyl peroxides by attack of *t*-butyl peroxide at the allylic carbon and formation of *t*-butyl ethers by addition of *t*-butyl alcohol to the carbon–carbon double bond. Oxidations of alkanes were, however, much more selective, and high activities (turnovers) could be obtained. Interestingly, in this case the ruthenium polyoxometalate was more reactive than the palladium and platinum analogs with the former being more

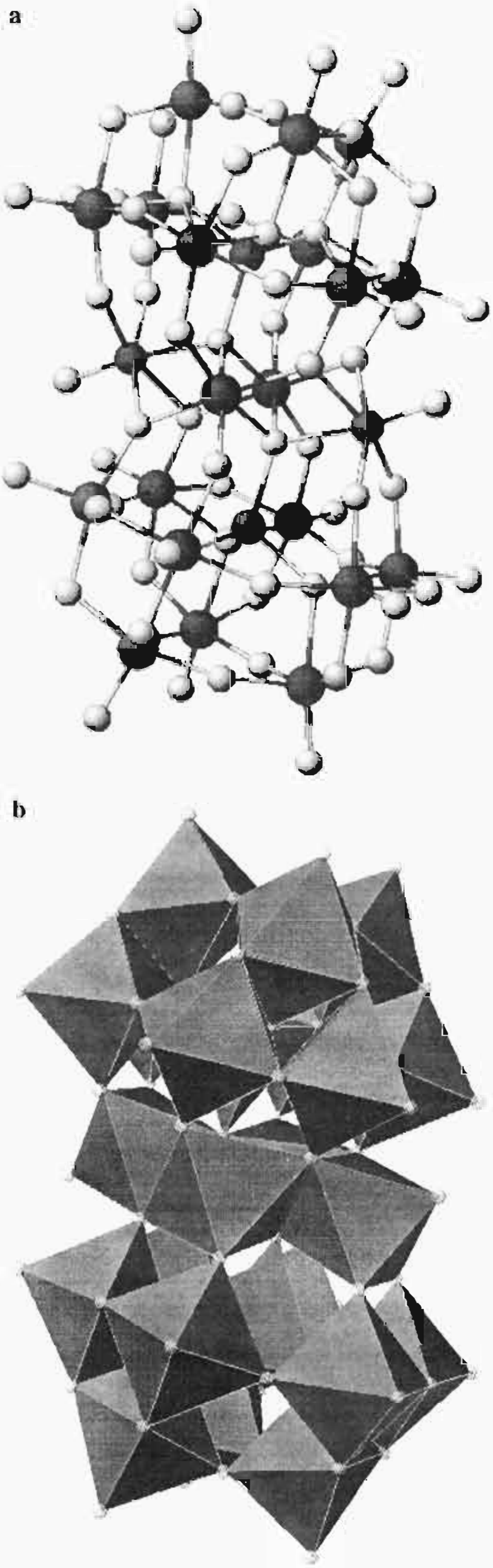

Figure 1. Ball and stick (a) and polyhedral (b) models of the "sandwich" type polyoxometalates.

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(16) Neumann, R.; Abu-Gnim, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1324–1325.

(17) Neumann, R.; Abu-Gnim, C. *J. Am. Chem. Soc.* **1990**, *112*, 6025–6031.

(18) Ellis, P. E.; Lyons, J. E. *Coord. Chem. Rev.* **1990**, *105*, 181–193.

(19) Mansuy, D.; Bartoli, J.-F.; Battioni, P.; Lyon, D. K.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7222–7226.

(20) Mizuno, N.; Tateishi, M.; Hirose, T.; Iwamoto, M. *Chem. Lett.* **1993**, 2137–2140.

(21) Kuznetsova, N. I.; Detusheva, L. G.; Kuznetsova, L. I.; Fedetov, M.; Licholobov, V. A. *Kinet. Katal.* **1992**, *33*, 516–523.

(22) Hill, C. L. *Activation and Functionalization of Alkenes;* Hill, C. L., Ed.; Wiley: New York, 1989; pp 243–279.

(23) Hill, C. L.; Weeks, M. S.; Khenkin, A. M.; Hou, Y. *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1992**, 1093–1097.

(24) Khenkin, A. M.; Hill, C. L. *Mendeleev Commun.* **1993**, 140–141.

(25) Neumann, R.; Gara, M. *J. Am. Chem. Soc.* **1994**, *116*, 5509–5510.

(26) Neumann, R.; Gara, M. *J. Am. Chem. Soc.* **1995**, *117*, 5066–5074.

(27) Duncan, D. C.; Chambers, R. C.; Hecht, E.; Hill, C. L. *J. Am. Chem. Soc.* **1995**, *117*, 681–691.

(28) When polyoxometalates are described as anions only, the terminal ligand (water, hydroxy) of the substituted transition metal is noted as included in the molecular formula because the identity of these ligands are functions of the cation and the solvent *e.g.* ref 7.

(29) Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. *J. Chem. Soc., Dalton Trans.* **1991**, 143–155.

(30) Neumann, R.; Khenkin, A. M.; Dahan, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1740–1742.

selective to reaction at the tertiary position. UV−vis and IR spectroscopic analysis of the polyoxometalates, before, during, and after the reactions with peroxides show these polyoxometalates to be stable under reaction conditions, thus making these noble metal substituted polyoxometalates promising candidates for epoxidation of alkenes with hydrogen peroxide and oxidation of alkanes with *tert*-butyl hydroperoxide.

Experimental Section

Materials. Sodium 5-zinc-19-tungstate, $Na_{12}\{[WZn_3(H_2O)_2](ZnW_9O_{34})_2]\}\cdot46H_2O$,[29] and the ruthenium(II) salt $Ru[(CH_3)_2SO]_4Cl_2$[31] were prepared by the literature methods. The noble metal derivative compounds of Pd(II) and Pt(II), $K_{12}\{[WZnPd^{II}_2(H_2O)_2](ZnW_9O_{34})_2\}\cdot38H_2O$ and $K_{12}\{[WZnPt^{II}_2(H_2O)_2](ZnW_9O_{34})_2\}\cdot36H_2O$, were likewise synthesized by the reported literature procedure.[29] The ruthenium-substituted compound, $Na_{11}\{[WZnRu^{III}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot42H_2O$, was prepared as described below. The methyltricaprylammonium salts of noble metal substituted polyoxometalates were prepared by mixing stoichiometric amounts of methyltricaprylammonium chloride with the potassium salt of the polyoxometalate, followed by extraction of the organically soluble salt into 1,2-dichoroethane and drying over Na_2SO_4. Solvents were of analytical grade purity (Frutarom) and used without further purification. Alkanes and alkenes used as substrates in oxidation reaction were reagent grade from Fluka and Aldrich and had purities >99% by gas chromatography (GC). Alkenes were purified over an alumina column prior to use. Aqueous 30% hydrogen peroxide (Merck), 70% *tert*-butyl hydroperoxide (Fluka), and other oxidants (Aldrich) were of reagent grade and used as is.

Preparation of Sodium Nanodecatungstotrizincodiruthenate(III), $Na_{11}\{[(WZnRu^{III}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot42H_2O$. To a solution of 23 g (3.9 mmol) of $Na_{12}\{[WZn_3(H_2O)_2](ZnW_9O_{34})_2]\}\cdot46H_2O$ in 10 mL of water at 90 °C under argon was added 4.0 g (12.2 mmol) of $Ru[(CH_3)_2SO]_4Cl_2$. The solution was stirred at this temperature for 18 h and cooled and opened to air. A brown solution is obtained which upon addition of 2 g of potassium chloride yielded a crude precipitate of the ruthenium-substituted polyoxometalate with a yield of 10.9 g (46%). The product was recrystallized twice from hot water, giving an overall yield of 24%. The elemental analysis was carried out by decomposing the polyoxometalate by boiling a solution of the polyoxometalate with 1 M NaOH for 3 h. The amount of ruthenium was determined gravimetrically as precipitated RuO_2. Tungsten was also determined gravimetrically as the hydroxyquinolate. Potassium, sodium, and zinc were determined by atomic absorption (GBC 903 single beam spectrometer). The water content was determined by thermogravimetric measurements of the polyoxometalate (Mettler TG 50 thermoanalytical balance). Anal. Calcd for $K_{11}Ru_2Zn_3W_{19}O_{68}\cdot15H_2O$: K, 6.99; Ru, 3.60; Zn, 3.50; W, 62.32; H_2O, 4.82. Found: K, 7.06; Ru, 3.56; Zn, 3.24; W, 61.30; H_2O, 4.69. The sodium salt was obtained by dissolution of potassium salt in 0.5 M solution of NaCl. Crystals for X-ray structure determination were obtained by slow evaporation in air of this solution at room temperature. Anal. Calcd for $Na_{11}\{[(WZnRu^{III}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot42H_2O$.: Na, 4.20; Ru, 3.35; Zn, 3.25; W, 58.00; H_2O, 12.55. Found Na, 4.46; Ru, 3.24; Zn, 3.19; W, 57.36; K 0.00; H_2O, 12.69. The X-ray crystal structure determination of the $Na_{11}\{[(WZnRu^{III}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot42H_2O$ polyoxometalate was carried out on a PW1100/20 Philips four-circle computer-controlled diffractometer. Data were measured at room temperature using Mo Kα ($\lambda = 0.710\,69$ Å) radiation. Crystals were in monoclinic crystal system with a $P2_1/c$ space group. The unit cell dimensions were $a = 13.069(3)$ Å, $b = 17.827(4)$ Å, $c = 24.182(5)$ Å, $\beta = 118.97(2)°$; volume = 4929(1) Å^3; $Z = 2$; $\rho_{calcd} = 4.06$ g/cm^3, and $2\theta = 45°$. Intensity data were collected using the $\omega-2\theta$ technique. The scan width, $\Delta\omega$, for each reflection was $1.00 + 0.35 \tan\theta$ with a scan speed of 3.0 deg/min. The number of unique reflections was 6689; the number of reflections with $I \geq 3\sigma_I$ was 4502. Intensities were corrected for Lorentzian polarization and absorption effects (μ(Mo Kα) = 237.50 cm^{-1}. All non-hydrogen atoms were found using the results of the SHELXS-86 direct method analysis. After several cycles of refinement on a VAX9000 computer using the TEXSAN structure analysis software, the positions of hydrogen atoms were calculated and added to the refinement process. Refinement proceeded to convergence by minimizing $\sum\omega(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 2.5 e/Å^3 scattered about the unit cell without significant feature. $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.051$; $R_\omega = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2} = 0.059$.

Instrumentation. Oxidation reaction products were characterized and quantisized using reference compounds when available by use of 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 whose initial identities were questionable were unambiguously identified using a gas chromatograph equipped with a mass selective detector (GC−MS Hewlett-Packard 5970A) equipped with the same column described above. IR spectra as KBr pellets or neat after evaporation of the solvent on the KBr plate were recorded on a Nicolet 510M FTIR instrument. UV−vis spectra were measured on a Hewlett-Packard 8452A diode array spectrometer. Cyclic voltammetry was measured on a BAS CV-1B instrument using a glassy carbon working electrode, a calomel reference electrode, and 0.5 M NaCl as the supporting electrolyte in aqueous solutions at pH = 7. ESR spectra (X-band) were taken with a Varian E-12 spectrometer at room temperature or at 120 K with a liquid nitrogen cryostat. Average magnetic susceptibilities were recorded at 5−100 K at a magnetic field of 100 G using a Squid magnetometer, Model MPMS-2, from Quantum Design.

Procedure for Catalytic Oxidation of Alkenes by Hydrogen Peroxide. Reaction progress for the oxidation of alkenes with hydrogen peroxide was monitored using gas chromatography. The most effective GC conditions for the rapid quantitation of products for the reactions of the alkenes involved the use of a 5% phenylmethylsilicone fused-silica capillary column, helium as the carrier gas, and temperature programming. Most reactions were carried out in a 5 mL vial equipped with cap and a stirring bar. Catalyst and substrate were dissolved in of 1,2-$C_2H_4Cl_2$. The solution was then heated to appropriate temperature, hydrogen peroxide was added, and the progress reaction was monitored by GC. GLC analysis was performed on aliquots withdrawn directly from the reaction mixture. Typically, substrate (0.7 mmol) was added to the solution of catalyst (0.2 μmol) in 1 mL of 1,2-$C_2H_4Cl_2$. To this was added 0.2 mL of 30% aqueous H_2O_2. The resulting biphasic mixture was stirred at 25 °C. Iodometric titration of hydrogen peroxide and also *tert*-butyl hydroperoxide was carried out by a modified procedure reported by Bruice[32] and required dissolving an aliquot of the reaction mixture in 95% ethanolic NaI containing 10% of acetic acid. From the absorbance of I_3^- at 360 nm ($\epsilon = 3.4 \times 10^4$ M^{-1} cm^{-1}) 100% of the theoretical 2 equiv/mol H_2O_2 (or *tert*-butyl hydroperoxide) was titrated.

Procedure for Catalytic Oxidation of Alkanes by *tert*-butyl hydroperoxide. Most reactions were carried out in a 5 mL vial equipped with cap and a stirring bar. Catalyst, substrate, and *tert*-butyl hydroperoxide were dissolved in 1 mL of 1,2-$C_2H_4Cl_2$. The solution was then heated to appropriate temperature. GLC analysis was performed after 24 h of stirring on aliquots withdrawn directly from the reaction mixture. Typically, substrate (0.93 mmol) was added to the solution of catalyst (0.085 μmol) in 1 mL of 1,2-$C_2H_4Cl_2$. To this was added 0.3 mL (2.3 mmol) of 70% aqueous *tert*-butyl hydroperoxide. The resulting mixture was stirred at 75 °C for 24 h.

Results and Discussion

Synthesis and Characterization of Noble Metal Substituted Polyoxometalates. The $K_{12}\{[WZnPd^{II}_2(H_2O)_2](ZnW_9O_{34})_2\}\cdot38H_2O$ and $K_{12}\{[WZnPt^{II}_2(H_2O)_2](ZnW_9O_{34})_2\}\cdot36H_2O$ compounds were prepared exactly as described in the literature,[28] and the product purity was verified by elemental analysis. The newer ruthenium analog, $Na_{11}\{[(WZnRu^{III}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot42H_2O$ could prepared by reacting $Na_{12}\{[WZn_3(H_2O)_2](ZnW_9O_{34})_2]\}\cdot46H_2O$ with $Ru^{II}[(CH_3)_2SO]_4Cl_2$ in a straightforward manner because the tetrakis(dimethyl sulfoxide)-

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(31) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204−209.

(32) Lee, W. A.; Bruice, T. C. *Inorg. Chem.* **1986**, *25*, 131−135.

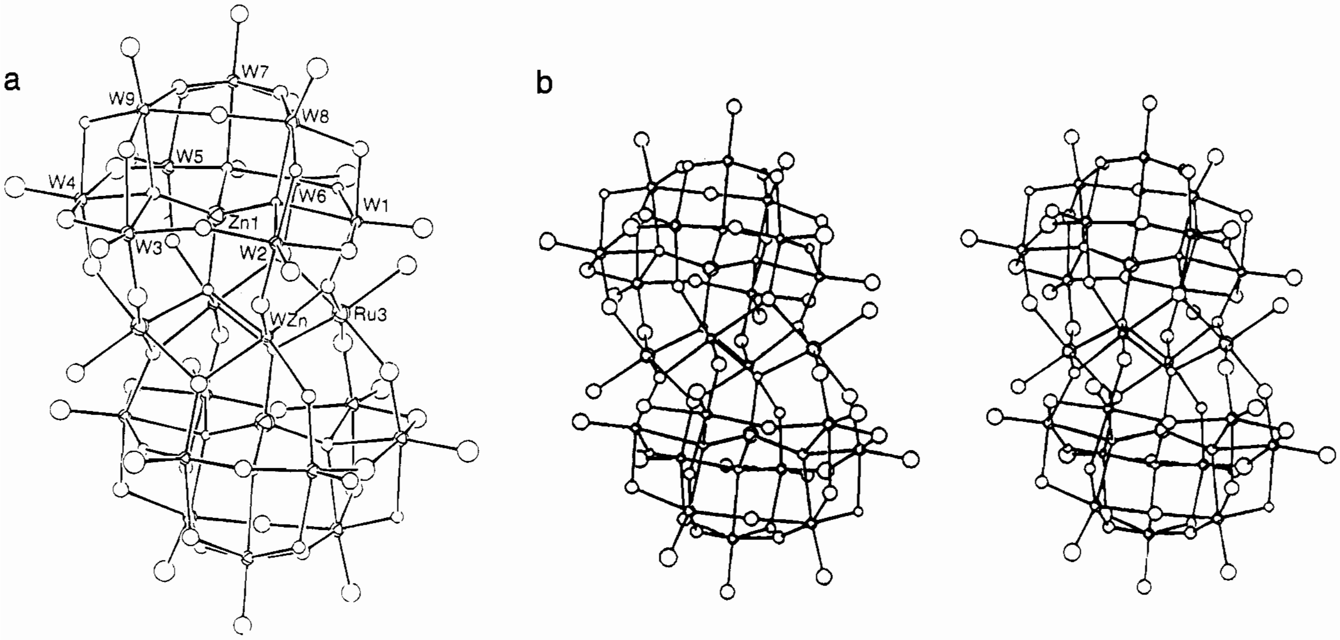

Figure 2. Ortep model (a) and stereoscopic view (b) of $[ZnWRu_2(Zn_2W_9O_{34})]^{11-}$.

ruthenium(II) reagent is a monomeric, well-defined, and relatively labile species compared to "$RuCl_3$" which is a poorly defined monomeric and polymeric mixture of mixed oxidation states which failed to give a definite single product upon reaction with the zinc polyoxometalate substrate. The reaction, however, is still slow in comparison to similar substitutions with 3d metals requiring a larger excess of ruthenium and longer heating periods. Following the successful substitution reaction, the *in situ* oxidation of the solution gives the air-stable tungstoruthenate (III) which was first precipitated as a potassium salt, recrystallized twice from hot water to remove any minor impurities, and then crystallized from a NaCl solution to form single crystals for X-ray diffraction analysis. The X-ray structure analysis, Figure 2, confirms a compound of the sandwich-type structure type previously found[28] with a WRuZnRu (Ru and W, Zn at opposing sides) ring between two B-XW_9O_{34} units. The large thermal coefficients found for the ruthenium atoms show that these positions are relatively labile. (For positional parameters, thermal coefficients, and intramolecular distances and bond angles, see Supporting Information.) Furthermore, the presence of only 11 sodium countercations indicates either a mixed ruthenium(II, III) polyoxometalate or a compound where the sixth labile ligand is hydroxy for one ruthenium(III) center and aquo for the other ruthenium(III) atom. No dimethylsulfoxide was observable as ligand for the ruthenium atom, though in the past such ligation has been found in more simple ruthenium substituted Keggin type polyoxometalates.[15] Likewise, the ruthenium polyoxometalate does not form a μ-oxo dimer as has been found for the ruthenium-substituted Dawson polyoxometalate derivatives in the presence of oxygen.[33] Magnetic susceptibility studies, presented below, show that a disubstituted ruthenium (III) polyoxotungstate, best formulated as $Na_{11}\{[WZnRu^{III}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot 42H_2O$, rather than a mixed valence compound, has been obtained.

The IR spectra, Figure 3, of the noble metal substituted polyoxometalates also indicate that these compounds are isostructural as the spectra are very similar to those of the zinc substituted starting material with the following features: W–O (terminal), 926 cm^{-1}; W–O–W (corner-sharing WO_6 octahedra), 881 cm^{-1}; W–O–W (edge-sharing octahedra), 765 cm^{-1}; a weak band at 546–575 cm^{-1}, probably attributable to noble metal–oxygen stretch vibrations. The UV–vis electronic spectra of the noble metal substituted compounds, Figure 4, all show the typical absorption at ~300 nm (ϵ = ~50 000 M^{-1} cm^{-1}) attributable to W–O–W charge transfer bands. In addition for the ruthenium compound a peak at 430 nm is observable due to O → Ru charge transfer. For the Pd and Pt compounds despite their dark color consistent with the presence of a reducing metal in the polyoxometalate framework (intervalence transfer bands of Pd or Pt–O–W) no definitive absorption peaks in the visible region are observed.

The cyclic voltammetry of all three noble metal substituted compounds are clean indicating that polyoxometalates of high purity have been obtained. For the ruthenium compound the cyclic voltammetry measurement is quite straightforward, Figure 5a, showing a reversible peak at +0.38 V attributed to a Ru(III) → Ru(IV) transition. In addition, a irreversible peak at +0.13 V designated to a Ru(III) → Ru(II) reduction was measured. The values of Ru(III/II) and Ru(IV/III) potentials are close to those found for $[Ru^{III}PW_{11}O_{39}]^{4-}$.[15] At negative potentials, typical reversible peaks are observed due to the reduction of the tungsten framework also observable in the $Na_{12}\{[WZn_3(H_2O)_2](Zn_2W_9O_{34})_2]\}\cdot 46H_2O$ starting material. The cyclic voltammetry measurements for the palladium and platinum compounds are significantly different and are more difficult to decipher. In the case of the palladium compound, Figure 5b, an irreversible peak apparently due to oxidation of Pd(II) → Pd(IV) is observed at +0.21 V. This potential is considerably lower than that ordinarily observed for Pd(II) in water, but this potential decrease is often observed for transition metal substituted polyoxometalates. At a low negative potential of −0.14 V, one or possibly two one-electron reductions are seen. This reduction at a relatively high potential might be due to a palladium-mediated reduction of the tungstate ligand as the nonsubstituted zinc polyoxometalate starting material is reduced at −0.7 V. The cyclic voltammetry spectrum of the platinum compound, Figure 5c, is similar to the one found for the palladium derivative with a significant shift to lower potentials. Thus, at −0.02 V there is an apparent two-electron oxidation of Pt(II) → Pt(IV), again significantly shifted compared to

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[33] Randall, W. J.; Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 1068–1071.

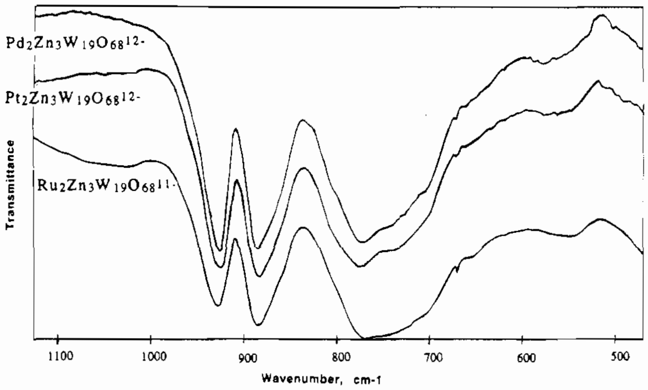

Figure 3. Infrared spectra of $K_{11}Ru_2(OH)(H_2O)Zn_3W_{19}O_{68}$ (A), K_{12}-$Pd_2(H_2O)_2Zn_3W_{19}O_{68}$ (B), and $K_{12}Pt_2(H_2O)_2Zn_3W_{19}O_{68}$ (C) in KBr pellets.

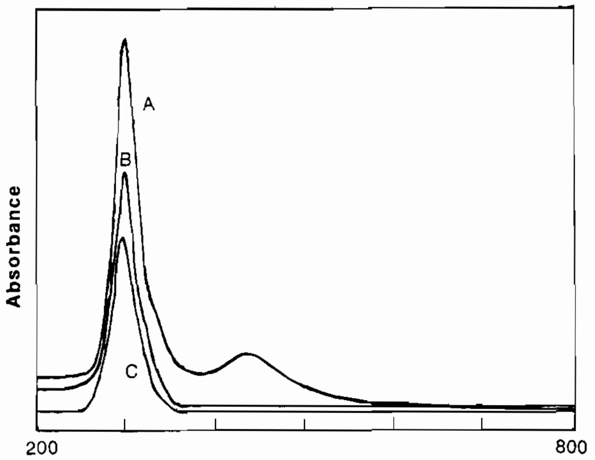

Figure 4. UV–vis spectra of 0.033 mM polyoxometalate in water: $K_{11}Ru_2(OH)(H_2O)Zn_3W_{19}O_{68}$ (A), $K_{12}Pd_2(H_2O)_2Zn_3W_{19}O_{68}$ (B), and K_{12}-$Pt_2(H_2O)_2Zn_3W_{19}O_{68}$ (C).

aqueous Pt(II). Reduction waves of the tungstate framework are not definitively observed.

Since the palladium and platinum derivatives are diamagnetic, magnetic susceptibility studies were done only on the ruthenium compound to determine the oxidation state of the ruthenium atoms and the magnetic interaction between the ruthenium centers. Temperature dependent magnetic susceptibility measurements from 5 to 100 K are presented in Figure 6. For a mixed-valent compound with one ruthenium (II) and one ruthenium(III) atom each,[34] the expected molar magnetic moment at 100 K for a mononuclear ruthenium (III) compound should be not more than 2.2 μB; however, from the measurements, a considerably higher molar magnetic moment of 4.48 μB was calculated. Thus, the compound should be formulated as a compound with two ruthenium(III) centers. Curiously, the Curie plot shows a linear behavior as a function of temperature. The linearity of the behavior coupled with the fact that the crystal structure shows that the ruthenium atoms are at ~5.2 Å apart discounts antiferromagnetic or ferromagnetic interactions between two ruthenium(III) atoms as the cause of the temperature dependence. Instead, the temperature dependence of magnetic moment can be explained by *spin–orbit* coupling as has been observed in the past for other ruthenium(III) compounds.[35] Our conclusions as to the noninteracting nature of the ruthenium(III) atoms were confirmed the EPR spectrum at 120 K of a polycrystalline sample of $Na_{11}\{[WZnRu^{III}{}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot 42H_2O$, Figure 7. A typical anisotropic spectrum for a ruthenium(III) $S = {}^1/_2$ spin system in an octahedral coordination with $g_{\parallel} = 1.80$ and $g_{\perp} = 2.30$ is plainly observed. The characterization of the noble metal substituted polyoxometalates shows that they are isostructural with similar first row transition metal substituted compounds with no discernible magnetic interactions between the two noble metal centers.

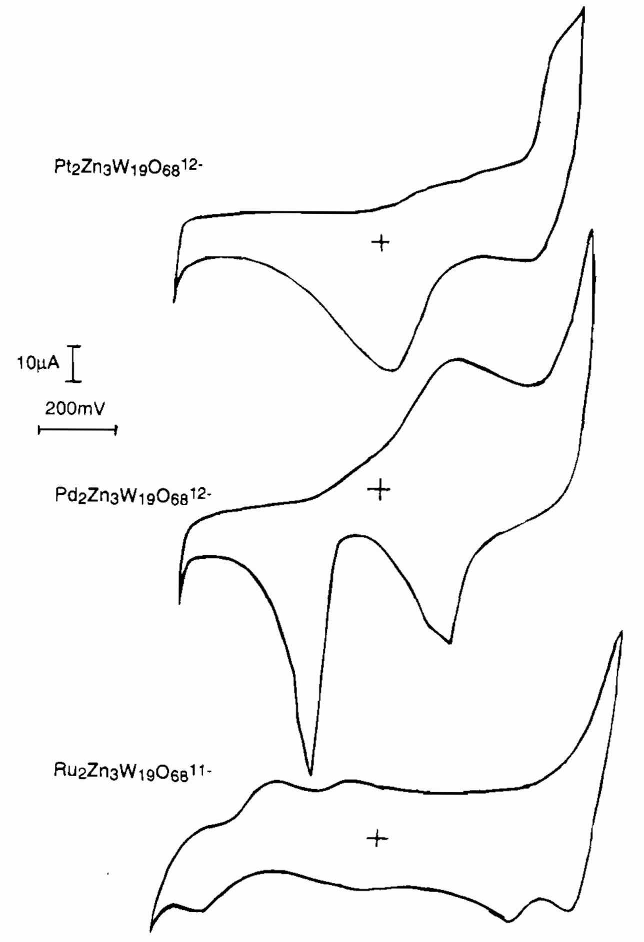

Figure 5. Cyclic voltammograms of 2 mM polyoxometalate in 0.5 M NaCl at a glassy-carbon working electrode with reference calomel electrode at the voltage sweep rate 100 mV/s: $K_{11}Ru_2(OH)(H_2O)Zn_3$-$W_{19}O_{68}$ (A), $K_{12}Pd_2(H_2O)_2Zn_3W_{19}O_{68}$ (B), and $K_{12}Pt_2(H_2O)_2Zn_3W_{19}O_{68}$ (C).

Catalytic Activity of Noble Metal Substituted Polyoxometalates. Alkene Oxidation. The synthetic route to methyltricaprylammonium salts of $[(WZnTM_2)(ZnW_9O_{34})_2]^{q-}$ (TM = Ru(III), Pd(II), Pt(II)) involves a methathetical exchange by addition of a stoichiometric amount of methyltricaprylammonium chloride in 1,2-dichloroethane to an aqueous solution of the potassium salt of the polyoxometalate. A stoichiometric amount of ammonium salt is used to avoid having excess methyltricaprylammonium chloride in the final product. The now hydrophobic polyoxometalate is then isolated by extraction into 1,2-dichloroethane.

For the oxidation of representative alkenes with 30% H_2O_2, in a typical reaction, 0.7 mmol of alkene was added to a solution of 0.2 μmol of catalyst in 1.0 mL of 1,2-dichloroethane. To this solution was added 2.0 mmol of 30% aqueous H_2O_2. The resulting biphasic reaction mixture was magnetically stirred at 25 °C for 24 h, and then the products were identified and quantified by GC, GC/MS and iodometric analysis. Product

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(34) Only low spin ruthenium species are considered, as intermediate or high spins have rarely been found for second row transition metals.

(35) Schneider, R.; Weyhermuller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4925–4934.

Table 1. Oxidation of Alkenes by H_2O_2 Catalyzed by Noble Metal Sandwich Complexes[a]

	products (conversion, mol %)		
alkene	$Pd_2Zn_3W_{19}O_{68}^{12-}$	$Pt_2Zn_3W_{19}O_{68}^{12-}$	$Ru_2Zn_3W_{19}O_{68}^{11-}$
cyclooctene	cyclooctene oxide (76)	cyclooctene oxide (77)	cyclooctene oxide (17)
cyclohexene	cyclohexene oxide (38) cyclohexen-2-ol (17) cyclohexen-2-one (30)	cyclohexene oxide (14) cyclohexen-2-ol (<0.1) cyclohexen-2-one (16)	cyclohexene oxide (3) cyclohexen-2-ol (0.7) cyclohexen-2-one (4)
1-octene	1-octene oxide (4.5)	1-octene oxide (6.1)	1-octene oxide (1.6)
cis-stilbene			*cis*-stilbene oxide (0.5) *trans*-stilbene oxide (0.5) benzaldehyde (5.5)

[a] Reaction conditions: 25 °C; time, 24 h; substrate, 0.7 mmol; polyoxometalate catalyst with methytricaprylammonium cation, 0.2 μmol, 30% H_2O_2, 2 mmol; and 1 mL of $1,2\text{-}C_2H_4Cl_2$ solvent. At the end of the reaction period all hydrogen peroxide was reacted. Reaction without polyoxometalate or using 0.20 μmol $Zn_5W_{19}O_{68}^{12-}$ gave no reaction with cyclooctene as substrate.

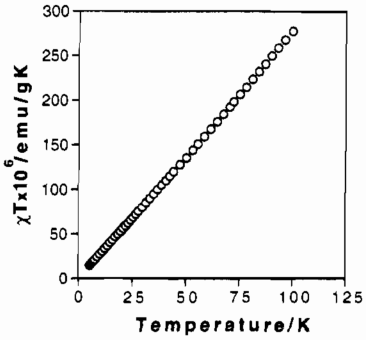


Figure 6. Plot of χT versus T for $K_{11}Ru_2(OH)(H_2O)Zn_3W_{19}O_{68}$.

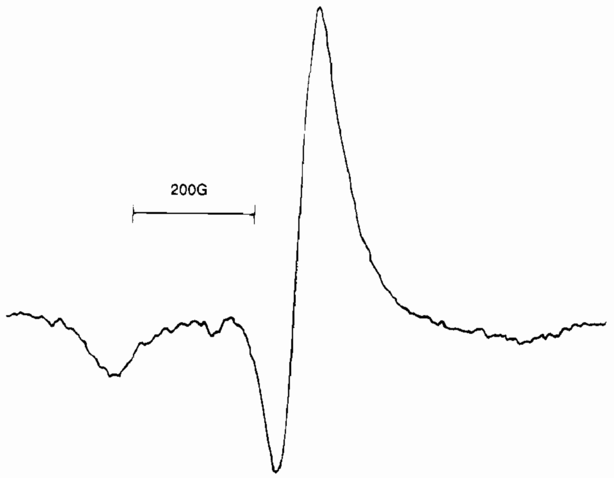


Figure 7. X-band ESR spectrum of a polycrystalline sample of K_{11}-$Ru_2(OH)(H_2O)Zn_3W_{19}O_{68}$ at 120 K (microwave 9.103 GHz; 20 mW/40 dB; modulation 10 G).

distributions for the oxidation of representative alkenes oxidation with H_2O_2 catalyzed by the three noble substituted polyoxometalates are summarized in Table 1. The results show that the palladium and platinum substituted compounds are similar catalysts with comparable reactivities and selectivities. For active substrates such as cyclooctene, conversions are high with moderate yields in hydrogen peroxide and excellent selectivity to the epoxidation product. For cyclohexene, which is highly susceptible to allylic oxidation, selectivity to epoxidation was significantly reduced. The difficult to epoxidize terminal alkene 1-octene gave low yields although turnover numbers were quite high in a very selective reaction. The ruthenium substituted compound was considerably less reactive with all substrates. The formation of allylic oxidation products even in the case of 1-octene indicates the major interaction of hydrogen peroxide with the ruthenium compound is homolytic cleavage generally leading to hydrogen peroxide dismutation or allylic oxidation via hydroperoxy and hydroxy radical intermediates. Epoxidation also was shown not to be stereoselective since with *cis*-stilbene as a substrate the ratio of *cis*/*trans* epoxide was one indicating a planar reaction intermediate. Interestingly, however, benzyl alcohol could be oxidized in high selectivity to benzaldehyde without significant formation of benzoic acid despite the relatively ease that benzaldehyde is autoxidized (54.3% yield, 2715 turnovers, 93% selectivity to benzaldehyde under conditions of Table 1). It is also interesting to compare the catalytic activity of the "sandwich" type disubstituted compounds with the monosubstituted Keggin compounds and the simple transition metal chloride salts, Table 2. In the case of the ruthenium substituted compound only the "sandwich" type compounds show activity whereas the others only decompose hydrogen peroxide. For the palladium substituted compounds the picture is somewhat different. A simple palladium chloride salt yields Wacker type ketonization reactions in the case of the linear terminal 1-octene and no catalytic activity for the cyclic alkenes. This reaction is typical for a Pd(II) compound. On the other hand the di- and monosubstituted palladotungstates have apparently similar reactivity for all three substrate types with *no* formation of ketones via palladium centered reactions, but with oxide products typical of tungsten−hydrogen peroxide oxidations. However, a closer look at the kinetic profiles of the oxidation of cyclooctene, Figure 8, shows that the monosubstituted Keggin palladotungstate has a S-type curve. This kinetic profile can be rationalized by the hydrogen peroxide mediated decomposition of the $PPdW_{11}O_{39}^{5-}$ to form the catalytically active $\{PO_4[WO(O_2)_2]_4\}^{3-}$ whose catalytically activity, however, is suppressed by the formation of the epoxide product.[27] The disubstituted $[(WZnPd^{II}_2)(ZnW_9O_{34})_2]^{12-}$ catalyst on the other hand showed a clean zero order reaction over a long time period of 24 h. This indicates that the disubstituted "sandwich" palladotungstate is the catalytically reactive species. In addition the reaction selectivity in the 1-octene oxidation would seem to indicate that this is a tungsten-centered reaction rather than a palladium-centered reaction. This is despite the fact that the non-noble metal substituted compound, $[(WZn_3)(ZnW_9O_{34})_2]^{12-}$, is inactive. The special effect of a neighboring transition metal to a tungsten center has already been observed and reported in the manganese case.[25,26] The stability of the disubstituted noble metal compounds to aqueous 30% hydrogen peroxide was also evaluated by use of a combination of electronic UV−vis and IR spectroscopy. In all cases, after 24 h of reaction at *no decline* in the concentration of the catalyst was observed as measured by the UV−vis spectrum, nor was any change in the IR spectrum noticeable.

The catalytic activity of the ruthenium compound was further investigated with a variety of additional oxidants, Table 3. As can be seen in the table the persulfate oxidant was very similar to hydrogen peroxide. Iodosylbenzene was not catalytically activated (a control experiment with no catalyst gave a similar

Table 2. Oxidation of Alkenes by H_2O_2 Catalyzed by Palladium Complexes[a]

	products (conversion, mol%)		
alkene	$Pd_2Zn_3W_{19}O_{68}^{12-}$	$PdW_{11}O_{39}^{5-}$	$PdCl_4^{2-}$
cyclo octene	cyclooctene oxide (76)	cyclooctene oxide (81)	
cyclo hexene	cyclohexene oxide (38) cyclohexen-2-ol (17) cyclohexen-2-one (30)	cyclohexene oxide (78) cyclohexen-2-ol (2) cyclohexen-2-one (11)	
1-octene	1-octene oxide (4.5)	1-octene oxide (5.6)	2-octanone (6.6)

[a] Reaction conditions were identical to those of Table 1.

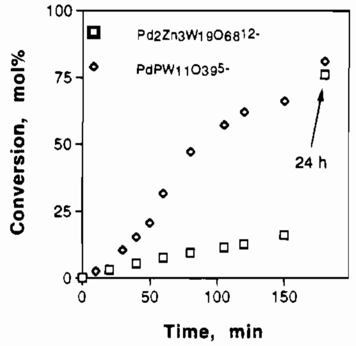


Figure 8. Time dependence of the generation of the cyclooctene oxide resulting from oxidation of cyclooctene (0.7 mmol) by H_2O_2 catalyzed by $Pd_2Zn_3W_{19}O_{68}^{12-}$ (0.2 μmol) and $PdPW_{11}O_{39}^{5-}$ (0.2 μmol) in 1,2-dichloroethane.

Table 3. Oxidation of Cyclooctene Catalyzed by $[ZnWRu_2(Zn_2W_9O_{34})]^{11-}$ Using Various Oxidants[f]

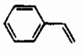
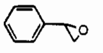
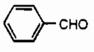
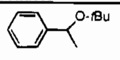
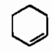
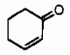
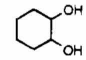
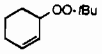
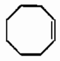
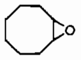
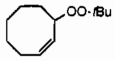
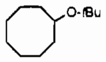
		conversion	
oxidant	products (% of total)	substrate	oxidant
H_2O_2[a]	cyclooctene oxide (100)	17.4	100
$KHSO_5$[b]	cyclooctene oxide (100)	16.0	97
PhIO[c]	cyclooctene oxide (100)	0.8	100
$NaIO_4$[d]	cyclooctene oxide (22) cycloctadione (78)	44.6	98
$(CH_3)_3COOH$[e]	cyclooctene oxide (100)	3.5	5.0

[a] 30% H_2O_2, 2 mmol. [b] $KHSO_5$, 2 mmol in 1 mL of H_2O. [c] PhIO, 0.2 mmol. [d] $NaIO_4$, 1 mmol in 1 mL of H_2O. [e] $[(CH_3)_3COOH]$, 2.3 mmol as 70% solution in water. [f] Reaction conditions: 25 °C; time, 24 h; substrate, 0.7 mmol; $[ZnWRu_2(Zn_2W_9O_{34})]^{11-}$ as methytricaprylammonium cation, 0.2 μmol; and oxidant, 1 mL of $1,2\text{-}C_2H_4Cl_2$ solvent.

yield). Sodium periodate was the most reactive with formation of the 1,2-cyclooctadione as the major product. This type of reaction of alkenes mediated by ruthenium-substituted polyoxometalates has been observed and detailed by us in the past.[16,17] The oxidation with *tert*-butyl hydroperoxide was very slow, but as no nonproductive decomposition was observed, reactions were performed at a higher temperature of 75 °C, Table 4. Although the reactivity was significantly higher, the selectivity of the reactions was severely reduced. In the case of cyclooctene and styrene, the addition product of *tert*-butyl alcohol to the alkene became the predominant reaction with less epoxidation and significant radical type reactions: allylic oxidation for cyclooctene and bond cleavage for styrene. In the oxidation of cyclohexene, allylic oxidation was predominant. As in the use of hydrogen peroxide, the stability of the noble metal substituted catalysts to *tert*-butyl hydroperoxide was evaluated by UV−vis and IR spectroscopy at reaction conditions, and no deterioration of the catalysts was observed.

Catalytic Activity of Noble Metal Substituted Polyoxometalates. Alkane Oxidation. Alkanes such as adamantane or cyclohexane are not oxidized by aqueous 30% H_2O_2 under conditions indicated in Table 1 or at higher temperatures. However, with *tert*-butyl hydroperoxide we have found that the noble metal sandwich complexes catalyze oxidation of alkanes at 75 °C. In the oxidation of cyclohexane, Table 5, one can see that the disubstituted "sandwich" type compounds are more reactive by one order of magnitude than the monosubstituted Keggin compounds previously reported on in the literature.[14] In the previous work the authors used a ratio cyclohexane/TBHP/catalyst (mol) 10600/177/1 and reached 125 turnovers for $MnPW_{11}O_{39}^{6-}$ as a best catalyst. Under our conditions with ratio cyclohexane/TBHP/catalyst (mol) 10900/27600/1 we have reached 79 turnovers for $MnPW_{11}O_{39}^{6-}$ and 720 turnovers for $[(WZnRu(III)_2)(ZnW_9O_{34})_2]^{11-}$ as a best catalyst. Interestingly, the platinum compound although somewhat less catalytically potent than the ruthenium and palladium analogs is also considerably less reactive in the decomposition of the oxidant. The manganese compound also has comparable reactivity to the noble metal substituted analogs. As a solvent, 1,2-dichloroethane is superior to benzene in contradiction to what was observed previously for the Keggin-substituted catalysts.

Table 4. Oxidation of Alkenes Catalyzed by $[ZnWRu_2(Zn_2W_9O_{34})]^{11-}$ Using *tert*-Butyl Hydroperoxide as Oxidant[a]

Substrate	Products, mol % of total products			Conversion, mol %
				
with catalyst	38	5	57	51
no catalyst	56	10	34	3
				
with catalyst	8	5	87	19
no catalyst	---	---	100	4
				
with catalyst	7	11	82	56
no catalyst	100	---	---	5

[a] Reaction conditions: temperature, 75 °C; time, 24 h, substrate, 0.93 mmol; $[ZnWRu_2(Zn_2W_9O_{34})]^{11-}$ as methytricaprylammonium cation, 0.085 μmol; *tert*-butyl hydroperoxide as 70% solution in water, 2.3 mmol; solvent, 1 mL of $1,2\text{-}C_2H_4Cl_2$.

Table 5. Oxidation of cyclohexane by *tert*-butyl hydroperoxide catalyzed by various polyoxometalates.

	ratio	conversion, mol %		
catalyst	$c\text{-}C_6H_{11}OH/$ $c\text{-}C_6H_{10}O$	C_6H_{12}	TBHP	turnover
$Ru_2Zn_3W_{19}O_{68}^{11-}$	1.26	6.45	98	720
$Pd_2Zn_3W_{19}O_{68}^{12-}$	0.77	5.67	97	623
$Pt_2Zn_3W_{19}O_{68}^{12-}$	0.67	4.41	55	483
$Mn_2Zn_3W_{19}O_{68}^{12-}$	1.25	6.78	97	741
$MnPW_{11}O_{39}^{4-}$[a]	0.65	1.80	97	79
$Ru_2Zn_3W_{19}O_{68}^{11-}$[c]	1.30	1.41	100	224

[a] Reaction conditions: temperature, 75 °C; time, 24 h; cyclohexane, 0.93 mmol; polyoxometalate as methytricaprylammonium cation, 0.085 μmol; *tert*-butyl hydroperoxide as 70% solution in water, 2.3 mmol; solvent, 1 mL of $1,2\text{-}C_2H_4Cl_2$. [b] Tetrahexylammonium salt. [c] In 1 mL of benzne as solvent.

Table 6. Oxidation of Adamantane by *tert*-Butyl Hydroperoxide Catalyzed by Various Polyoxometalates[a]

catalyst	ratio tertiary/ secondary	conversion, mol %		
		$C_{10}H_{16}$	TBHP	turnover
$Ru_2Zn_3W_{19}O_{68}{}^{11-}$	13.3	37	98	4000
$Pd_2Zn_3W_{19}O_{68}{}^{12-}$	9.9	27	80	2950
$Pt_2Zn_3W_{19}O_{68}{}^{12-}$	8.3	21	45	2300
$Mn_2Zn_3W_{19}O_{68}{}^{12-}$	12.1	45	94	5250

[a] Reaction conditions: temperature, 75 °C, time, 24 h; adamantane, 0.93 mmol; polyoxometalate as methytricaprylammonium cation, 0.085 μmol; *tert*-butyl hydroperoxide as 70% solution in water, 2.3 mmol; solvent, 1 mL of 1,2-$C_2H_4Cl_2$. Results are given as an average of three runs.

The best results were found for noble metal sandwich complexes in 1,2-dichloroethane as a solvent.

Better conversions and higher turnovers are obtained in the hydroxylation of adamantane, Table 6. In this case it is interesting to compare the oxidation product distributions between tertiary and secondary carbon−hydrogen bonds. For the ruthenium and manganese polyoxometalates a tertiary to secondary ratio of 12−13 was observed whereas for palladium and platinum polyoxometalates a ratio of 8−10 was found. The literature has shown that oxidation of adamantane by *tert*-butyl hydroperoxide catalyzed by ruthenium complexes[36−38] transition metal substituted polyoxometalates,[14,16,36] and several binuclear iron and manganese methane monoxygenase mimics[39,40] tertiary to secondary ratios in an interval of 8−10. In all these cases metal−oxo intermediates as active species has been suggested. Therefore, from our data, we can suggest that, for the palladium and platinum compounds, a metal oxo intermediate is the reactive catalytic species in the oxidation of alkanes by *tert*-butyl hydroperoxide. To the best of our knowledge, ratios for tertiary to secondary of 12−13 in the hydroxylation of adamantane have not been reported. However, since in the oxidation of adamantane by a benzoyloxy radical a higher tertiary or secondary ratio of 21 has been observed,[41] it is possible that for the ruthenium and manganese polyoxometalates in this work a metal *tert*-butyloxo or metal *tert*-butylperoxo intermediate could be generated as active species. Interestingly, there also appears to be a correlation between the Pd, Pt and Ru, Mn polyoxometalates as concerns the ratio of alcohol to ketone in the cyclohexane oxidation.

Certain activated alkylaromatic compounds could also be oxidized by *tert*-butyl hydroperoxide in the presence of $[(WZnRu^{III}{}_2)(ZnW_9O_{34})_2]^{11-}$ under the conditions of Table 6. Thus, ethylbenzene was oxidized to 66% acetophenone and 34% 1-(*t*-butylperoxy)ethylbenzene at 21.3% conversion (2506 turnovers). Similarly, 4-methoxytoluene was oxidized exclusively to 4-anisic acid at a 66% conversion (6200 turnovers). Toluene was not reactive.

Conclusions

Disubstituted noble metal (Pd, Pt, Ru) polyoxometalates have been prepared and characterized. Using peroxide type oxidants, we found that hydrogen peroxide is preferable for the oxidation of alkenes, whereas for alkanes *tert*-butyl hydroperoxide is a better oxidant. Kinetic measurements as well as UV−vis and IR spectroscopic measurements show the polyoxometalates to be stable over a period of many turnovers. In the future, more work will be carried out in order to further define the mechanisms of these oxidation reactions.

Acknowledgment. This research was supported by the Basic Research Foundation administered by the Israel Academy of Sciences and Humanities.

Supporting Information Available: For $Na_{11}\{[WZnRu^{III}{}_2(OH)(H_2O)](ZnW_9O_{34})_2\}\cdot 42H_2O$, tables of positional parameters, thermal coefficients, and intramolecular distances and bond angles and a figure showing the atom-labeling scheme (14 pages). Ordering information is given on any current masthead page.

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(36) Bressan, M.; Morvillo, A.; Romanello, G. *J. Mol. Catal.* **1992**, *77*, 283−288.

(37) Lau, T. C.; Che, C. M.; Lee, W. O.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1988**, 1406−1407.

(38) Murahashi, S. I.; Oda, Y.; Naota, T.; Kuwabara, T. *Tetrahedron Lett.* **1993**, *34*, 1299−1302.

(39) Menage, S.; Vincent, J. M.; Lambeaux, C.; Chottard, G.; Grand, A.; Fontecave, M. *Inorg. Chem.* **1993**, *32*, 4766−4773.

(40) Fish, R. H.; Fong, R. H. ; Oberhausen, K. J.; Konings, M. S.; Vega, M. C.; Christou, G.; Vincent, J. B.; Buchanan, R. M. *New J. Chem.* **1992**, *16*, 727−733.

(41) Fossey, J.; Lefort, D.; Masoudi, M.; Nedelec, J.-Y.; Sorba, J. *Can. J. Chem.* **1985**, *63*, 678−680.