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Supplementary Material Available: Tables of final positional and thermal parameters, interatomic distances and angles, and general temperature factor expressions (24 pages); tables of observed and calculated structure factor amplitudes (72 pages). Ordering information is given on any current masthead page.

Alkene Oxidation Catalyzed by a Ruthenium-Substituted Heteropolyanion, $SiRu(L)W_{11}O_{39}$: The Mechanism of the Periodate Mediated Oxidative Cleavage

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Abstract: A ruthenium-substituted heteropolyanion $SiRu(H_2O)W_{11}O_{39}{}^{5-}$ was synthesized and characterized. The hydrophobic quaternary ammonium salt of the heteropolyanion $((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$ was used as a catalyst for the oxidation of alkenes with *tert*-butyl hydroperoxide, potassium persulfate, iodosobenzene, and sodium periodate as primary oxidants. Reactivity and selectivity were found to be dependent on the oxidant used; several different types of oxidation processes could be identified including allylic oxidation, epoxidation, and oxidative cleavage. Use of sodium periodate as oxidant enabled selective bond cleavage with aldehydes as the exclusive product. Different product selectivity and UV–vis and IR spectra of the ruthenium heteropoly compound in the presence of the various oxidants shows that unique mechanisms are operating in each case. A series of further experiments into the oxidation of styrene derivatives to benzaldehydes by sodium periodate including investigation of the reaction kinetics, substituent effects, and isotope incorporation enabled the formulation of a reaction mechanism. The reaction proceeds by interaction of the styrene with the catalyst forming a metallocyclooxetane which rearranges in the rate-determining step to a cyclic diester through two different transition states depending on the ring substituent. In the final step the cyclic diester decomposes yielding the cleavage products.

Introduction

The vast field of heteropolyanion chemistry has historically been centered around the preparation, structure, properties, and analytical chemistry applications of these compounds.[1] Only recently has the potential use of heteropolyanions as catalysts slowly gained recognition, both as Brönsted acid[2] and oxidation catalysts.[3] Heteropolyanions are attractive as robust oxidation catalysts because the exclusively inorganic nature of the anions makes them inherently stable toward decomposition under extreme oxidation conditions. Perusal of the literature reveals that liquid phase oxidation reactions catalyzed by heteropolyanions may be divided into four categories based on the type of reaction performed. The first category includes reactions where the heteropolyanion catalyst, HPC, generally $PV_2Mo_{10}O_{40}{}^{5-}$ is used in electron-transfer-type oxidations, eq 1. Substrates in the context of the above reaction

$$\text{substrate} + HPC_{ox} \rightarrow \text{product} + HPC_{red} \qquad (1)$$

$$HPC_{red} + \tfrac{1}{2}O_2 \rightarrow HPC_{ox} + H_2O$$

may be organic molecules as in the oxidation of sulfides,[4] dehydrogenation of dienes,[5] and the oxidative cleavage of ketones.[6] Substrates may be of an inorganic nature as in the oxidation of hydrogen bromide to molecular bromine[7] or primary catalysts such as Pd(0) (product is Pd(II)) as in the Wacker-type oxidation of ethylene to acetaldehyde[8] or acetoxylation of aromatics.[9] Systems whereby heteropolyanions undergo photoactivation represent a second group of reactions and include the dehydrogenation of alcohols[10] and alkanes.[11] A third set of reactions are those where complete molybdenum or tungsten Keggin anions have been used as catalysts in tandem with hydrogen peroxide in oxidations of alcohols,[12] allyl alcohols,[13] alkenes,[14] and alkynes[15] which are typical of molybdenum and tungsten catalytic centers.

The fourth category of reactions where heteropolyanions are used as liquid phase oxidation catalysts is based on transition-

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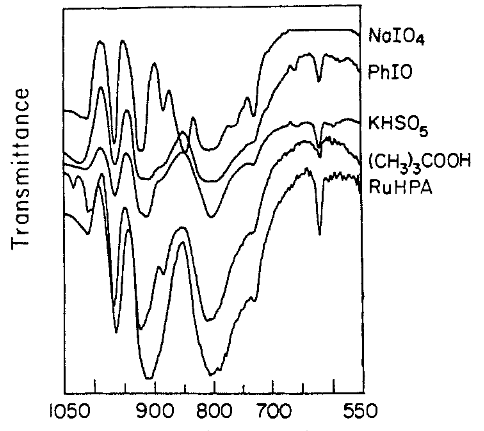

Figure 1. IR spectra of the QSiRuW catalyst.

metal-substituted heteropolyanions. In this type of reaction a transition metal (M) such as manganese or cobalt is ligated by an unsaturated or lacunary heteropolyanion (L) such as $SiW_{11}O_{39}^{8-}$ yielding for example $SiCo^{II}(H_2O)W_{11}O_{39}^{6-}$. Reactions are postulated to occur at the substituted transition-metal center with the bulk of the heteropolyanion acting as an inorganic ligand.[16] This concept has been utilized to date for first row transition metals only (Fe(III), Mn(II), Co(II), and Cu(II)) and includes only three examples: the epoxidation of alkenes by iodosobenzene,[17] the hydroxylation of alkanes by *tert*-butyl hydroperoxide,[18] and the oxidation of hindered phenols by dioxygen.[19]

In this manuscript we report on the synthesis and characterization of the second row ruthenium substituted heteropolyanion $SiRu^{III}(H_2O)W_{11}O_{39}^{5-}$ and its use as a catalyst for the oxidation of alkenes and alkanes with various oxidants such as potassium monopersulfate, *tert*-butyl hydroperoxide, iodosylbenzene, and sodium periodate.[20] Reactions with the various oxidants show that reactions in the presence of sodium periodate are highly selective. For example, $SiRu^{III}(H_2O)W_{11}O_{39}^{5-}$ (SiRuW) catalyzed oxidation of styrene and its derivatives to corresponding benzaldehyde with selectivity >99%, eq 2. In order to gain more

$$ArCH{=}CH_2 + NaIO_4 \xrightarrow{SiRuW} ArCHO \qquad (2)$$

insight into this reaction system kinetic and mechanistic studies were performed which enable the presentation of a plausible mechanistic scheme and reveal novel insights into the catalytic oxidation chemistry of transition-metal-substituted heteropolyanions.

Results and Discussion

Synthesis and Characterization of the Ruthenium Heteropolyanion. The ruthenium heteropolyanion, $SiRu^{III}(H_2O)W_{11}O_{39}^{6-}$, was prepared by a synthetic route similar to that used for preparation of the analogous rhodium compound, $SiRh^{III}(H_2O)W_{11}O_{39}^{5-}$.[21] Thus, equimolar amounts of $K_8SiW_{11}O_{39}$[22] and $RuCl_3{\cdot}xH_2O$ were mixed, and the resulting ruthenium heteropolyanion was precipitated by methanol. The sticky solid obtained was titurated twice with acetone yielding the desired crystalline $K_5SiRu^{III}(H_2O)W_{11}O_{39}{\cdot}xH_2O$. A hydrophobic form of SiRuW which could be used for reactions in apolar organic solvents was attained by replacing the potassium cation by a hydrophobic quaternary tetrahexylammonium cation yielding the catalyst used in all the oxidation systems, $((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$.

Table I. The Oxidation of Alkenes Catalyzed by $((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$[a]

Substrate Cyclohexene

	products				
oxidant	epoxide	en-2-one	en-2-ol	adipic acid	other[b]
$KHSO_5$				67 (4)	<0.1
$NaIO_4$				1.3	31.2[c]
PhIO	3.1 (0.1)	4.1 (0.1)	1.0 (0.1)	1.1	2.7
t-BuOOH		28.7 (1.3)	1.3 (1.5)		25.2

Substrate 1-Octene

	products		
oxidant	1-octene oxide	heptanoic acid	other[b]
$KHSO_5$	10.3	30.1 (1.0)	18.5[d]
$NaIO_4$		1.8	
PhIO	5.1	7.7	7.5
t-BuOOH		<0.1	10.3 (0.5)

Substrate Styrene

	products				
oxidant	PhCHO	PhCOOH	$PhCH(O)CH_2$	$PhCH_2CHO$	other[b]
$KHSO_5$	3.3	95 (6.2)			
$NaIO_4$	98				
PhIO	34.5	11.2 (0.3)	6.8 (0.5)	4.9 (0.1)	
t-BuOOH	20.3	6.1	2.4	3.1	18.4 (3.4)

[a] Reduction conditions: Substrate, 1 mmol; QSiRuW, 0.002 mmol; 1,2-dichloroethane, 5 mL; oxidant, 5 mmol; temperature, 60 °C; time, 2 h (4 h for 1-octene). Reactions with $NaIO_4$ and $KHSO_5$ were performed with 5 mL of water. Analysis was by GLC, and the yields of product are given as the percentage of product formed from the substrate. Yields in reactions performed in the absence of catalyst where applicable are given in parentheses. Adipic acid yields were found by isolation of the acid from the aqueous phase. The conversion of TBHP was quantitative coupled with formation of *tert*-butyl alcohol. [b] Unidentified products, yields were calculated by area integration of the GLC peaks. [c] Adipaldehyde. [d] 2-Octanol.

The ruthenium heteropoly species were analyzed, and the results (see Experimental Section) were compatible with the molecular formulas $K_5SiRu^{III}(H_2O)W_{11}O_{39}{\cdot}15H_2O$ and $((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$ for the water soluble and hydrophobic SiRuW compounds, respectively. The IR spectrum of $((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$ (QSiRuW), given in Figure 1 (bottom spectrum—RuHPA) is virtually identical with analogous spectra of other transition-metal-substituted heteropolyanions[23] and shows the absorptions at 1009 cm^{-1} for terminal W=O, 963 cm^{-1} for the tetrahedral Si–O, and 913 and 805 cm^{-1} for the two types of bridging W–O–W. The Ru–O absorptions could not be resolved, but literature precedent[24] indicates absorptions at about 800 cm^{-1} which coincide with the W–O–W peaks. The UV–vis spectrum, Figure 2, of QSiRuW in 1,2-dichloroethane is characterized by a strong absorption band at 266 nm (log ϵ 4.70) and a weak band at 434 nm (log ϵ 3.80). The maximum at 266 nm is attributable to a W ← O charge-transfer band (CT),[25] and the lower energy band at 434 nm corresponds to a $^1A_g \leftarrow {}^1T_{2g}$ transition and indicates an approximately octahedral weak field coordination of the ruthenium(III) cation.[21]

The QSiRuW compound was further characterized by taking its ESR spectrum in dichloromethane solution at 100 K, Figure 3. The spectrum shows a peak at $g_\perp = 2.05$ and a minimum at $g_\parallel = 1.85$. This ESR spectrum is typical of a ruthenium(III) octahedral metal center coordinated by oxo or aqua ligands with a low-spin d^5 electronic configuration.[26] The redox properties of QSiRuW were investigated by cyclic voltammetry in di-

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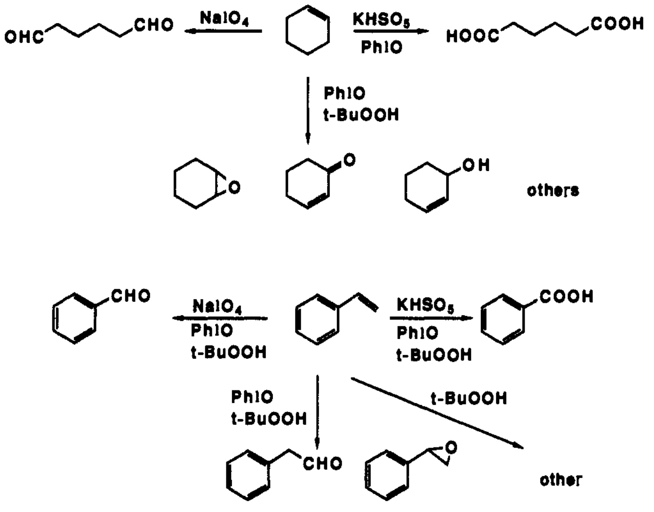
Table II. Total Rates of Reaction to Identifiable Oxidation Products[a]

oxidant	reaction rate, mol substrate/mol catalyst, h styrene	 cyclohexene	 1-octene
$NaIO_4$	245	81	2.2
$KHSO_5$	245	168	50
PhIO	140	23	16
t-BuOOH	80	75	0.25

[a] The data was computed by use of the reaction conditions described for Table I taking into account the yield when the reaction was terminated.

Scheme I



chloromethane with tetrabutylammonium tetrafluoroborate as supporting electrolyte. The QSiRu(III)W compound is oxidized irreversibly probably to the QSiRu(IV)W compound at a potential of +0.95 V vs SCE and is reversibly reduced in a series of one-electron reductions to the mixed valence W(V)–W(VI) compounds at potentials of −0.3 to −1.0 V vs SCE.

Oxidations Catalyzed by the Ruthenium Heteropolyanion. The ruthenium heteropolyanion was used as a catalyst in the oxidation of hydrocarbons[20] with four different primary oxidants, *tert*-butyl hydroperoxide (TBHP), potassium monopersulfate, sodium periodate, and iodosylbenzene. The results for the oxidation of alkenes are summarized in Tables I and II and schematically in Scheme I. The results show that in the presence of TBHP the catalytic system is highly active, but the nonproductive decomposition, eq 3, of the hydroperoxide to *tert*-butyl alcohol and dioxygen is substantial. Depending on the substrate one can discern several

$$ROOH \rightarrow ROH + \tfrac{1}{2}O_2 \qquad (3)$$

oxidative processes including allylic oxidation (cyclohexene) and epoxidation and bond cleavage (styrene), but in all cases selectivity is marred by various nonselective radical reactions leading to a large diversity of unidentified products. The use of potassium monopersulfate (oxone, $KHSO_5$) as primary oxidant also yields a highly reactive oxidation system. In this case selectivity is also high to the alkene cleavage product, carboxylic acids. In the case of 1-octene where oxidation is slower, acid-catalyzed hydration yielding 2-octanol was significant apparently because of the high acidity of oxone. Oxidations by $KHSO_5$ which is in effect an inorganic hydroperoxide[27] are also accompanied by significant decomposition of the oxidant to dioxygen and potassium hydrogen sulfate. Furthermore, oxidation of organic substrates with hydrogen peroxide failed with QSiRuW, and only decomposition of hydrogen peroxide to water and dioxygen was observed. Oxidations with sodium periodate are very selective to alkene cleavage, aldehydes (or ketones) being the major or only products. However, reactivity is strongly dependent on the nucleophilicity of the carbon–carbon double bond. Thus, reactivity decreased in the series styrene > cycloalkene > primary alkene. Finally iodosylbenzene is the least active of the oxidants used and leads to a variety of oxidation processes including epoxidation, allylic oxidation, and carbon–carbon bond cleavage and also a variety of unidentified reaction pathways.

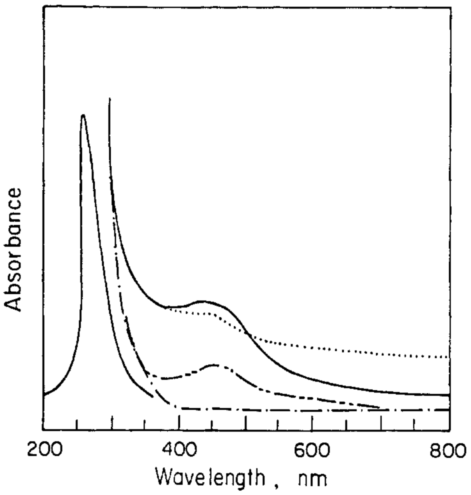


Figure 2. UV–vis spectra of the QSiRuW catalyst: (—) QSiRuW; (– – – –) QSiRuW + $KHSO_5$; (···) QSiRuW + *t*-BuOOH; —·— QSiRuW + PhIO or $NaIO_4$.

It is apparent from the different reactivity and selectivity found in the various QSiRuW-catalyzed reacions that a number of different catalytic cycles are possible and the relative rates of each process are functions of the primary oxidant and the relative reactivity of the organic substrate. The different interactions between the ruthenium heteropolyanion catalyst and the various oxidants can be viewed spectroscopically by UV–vis, Figure 2, and IR, Figure 1. Upon addition of TBHP or $KHSO_5$ to a 0.02 mM solution of QSiRuW in 1,2-dichloroethane one finds an identical red shift of the d–d transition from 434 to 456 nm in the UV–vis spectra. The red shift may possibly be due to oxidation of the Ru(III) to Ru(IV). Evaporation of the organic solvent and isolation of the catalyst followed by pelletization with KBr also gave virtually identical IR spectra. These spectra are only slightly different from the spectra of the original QSiRuW compound, the major modification being the appearance of a weak peak or shoulder at 883 cm^{-1} upon addition of the hydroperoxide. The similar interaction of both hydroperoxides with the ruthenium heteropolyanion seems to indicate a similar preliminary catalyst–oxidant interaction with formation of the same (possibly a peroxo complex) active catalytic precursor. The considerably different reactivity and selectivity may therefore be due to different secondary interactions of the oxidant with a substrate–catalyst intermediate or the operation of multiple mechanisms.

The sodium periodate and iodosylbenzene interact in an entirely different manner with QSiRuW. Addition of these oxidants to QSiRuW in 1,2-dichloroethane cause the original brown solution to clear which is born out in the UV–vis spectra, Figure 2, by the disappearance of the absorption band at 434 nm. In the case of iodosylbenzene removal by filtration of the oxidant (it is insoluble in the organic phase) causes the solution to slowly revert (1 h) to a brown solution with a UV–vis spectra identical with that of QSiRuW with TBHP or $KHSO_5$. The IR spectra of the reisolated catalyst was also identical with those spectra of ruthenium heteropolyanion catalyst isolated after addition of the hydroperoxides. On the other hand, when the aqueous phase of sodium periodate is separated from the catalyst in the organic phase, the solution retains the same UV–vis spectrum without change indefinitely. Isolation of the catalyst followed by IR reveals a significantly different spectrum, Figure 1. The peak at 883 cm^{-1} becomes very distinct, the Si–O band is shifted from 913 to 925 cm^{-1}, and a new absorption is revealed at 848 cm^{-1}. The latter may be tentatively assigned to a Ru–O band.[28] One may conclude that the

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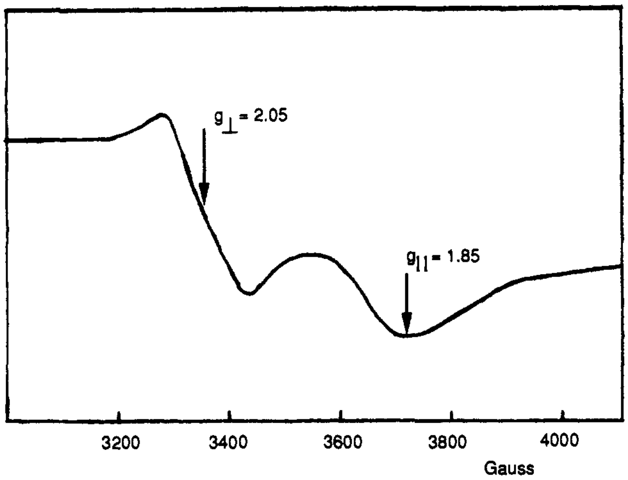

Figure 3. The ESR spectrum of QSiRuW in dichloromethane at 100 K.

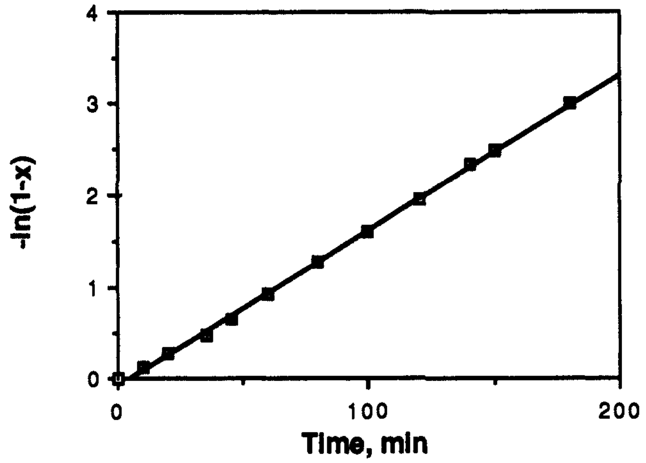

Figure 4. The reaction profile for the oxidation of styrene (first order). Reaction condition: 1 mmol of styrene, 0.001 mmol of QSiRuW, 5 mmol of $NaIO_4$, 5 mL of 1,2-dichloroethane, and 5 mL of water, temperature 60 °C.

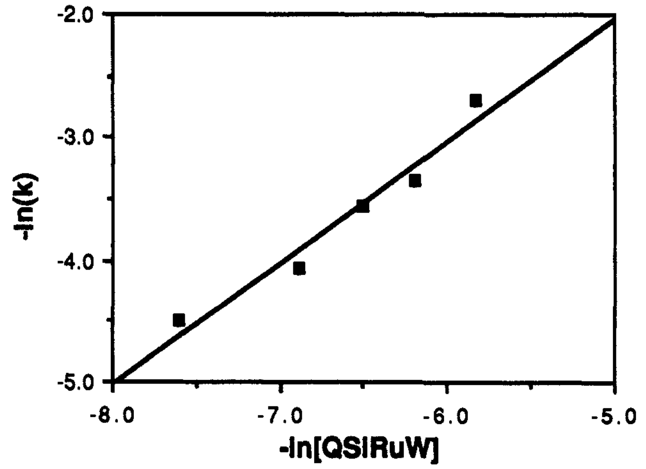

Figure 5. The reaction rate as a function of the catalyst concentration. Reaction condition: 1 mmol of styrene, 5 mmol of $NaIO_4$, 5 mL of 1,2-dichloroethane, and 5 mL of water, temperature 60 °C.

sodium periodate and iodosylbenzene interact in a different manner with the ruthenium heteropolyanion, and together with the hydroperoxides at least three catalyst–oxidant interactions are possible.

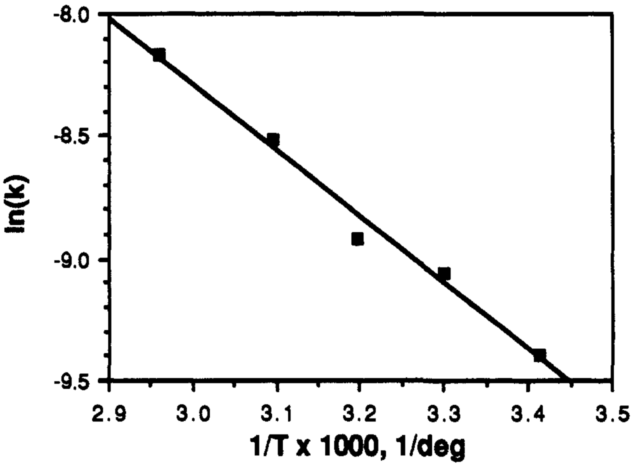

Figure 6. The reaction rate as a function of temperature. Reaction condition: 1 mmol of styrene, 0.001 mmol of QSiRuW, 5 mmol of $NaIO_4$, 5 mL of 1,2-dichloroethane, and 5 mL of water.

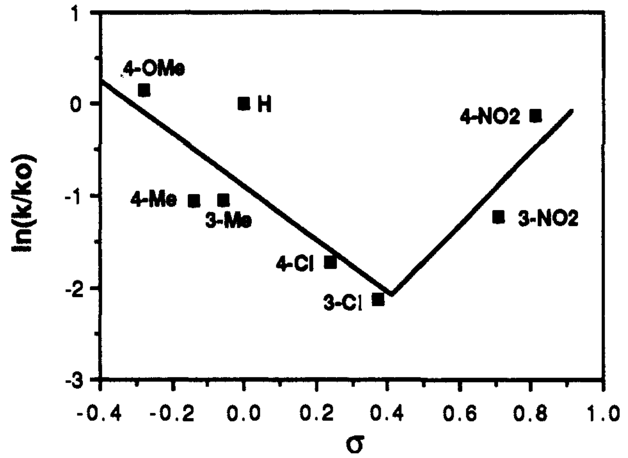

Figure 7. The reaction rate as a function of ring substituents. Reaction condition: 1 mmol of styrene derivative, 0.001 mmol of QSiRuW, 5 mmol of $NaIO_4$, 5 mL of 1,2-dichloroethane, and 5 mL of water, temperature 60 °C.

The Mechanism of Alkene Oxidation by Sodium Periodate. As stated above alkenes were cleaved in high selectivity to aldehydes by sodium periodate in the presence of QSiRuW, eq 2. The fact that the aromatic aldehydes formed were not oxidized to the corresponding acids is unique and provided impetus for further investigation into the catalytic system. The standard substrate chosen was styrene, and the first stage was to determine the kinetic behavior of the reaction. A typical reaction system consisted of mixing 1 mmol of styrene and 0.001 mmol of QSiRuW (0.1 mol %) in 5 mL of 1,2-dichloroethane and 5 mmol of $NaIO_4$ in water at 60 °C. The reaction profile gave the best fit for first order in styrene, Figure 4, with an observed rate constant, $k_{obs} = 2.83 \times 10^{-4}\ s^{-1}$ ($r = 1.0$). One may note that the kinetics are linear up to quantitative conversions (1000 turnovers), and no catalyst decomposition was visibly discerned or could be implicated by departure from the first-order linear reaction kinetics. The reaction was also found to be zero order in sodium periodate. In order to compute the reaction order in the catalyst a series of kinetic runs were made at various initial catalyst concentrations. The measured rate constant is a function of the catalyst concentration, eq 4. A plot of ln (k_{obs}) vs ln ([QSiRuW]), Figure 5, gave a slope

$$k_{obs} = k'[\mathrm{QSiRuW}]^{\nu} \Rightarrow \ln(k_{obs}) = \nu \ln([\mathrm{QSiRuW}]) + \ln(k') \quad (4)$$

$\nu = 0.99$ ($r = 0.98$) so that one may conclude that the reaction is first order in the catalyst, and the full rate equation is given as eq 5. The reaction rate as a function of temperature was

$$\mathrm{rate} = k[\mathrm{QSiRuW}][\mathrm{styrene}] \quad (5)$$

measured between 20 °C and 60 °C and plotted by using the Arrhenius equation, Figure 6. The computed activation energy

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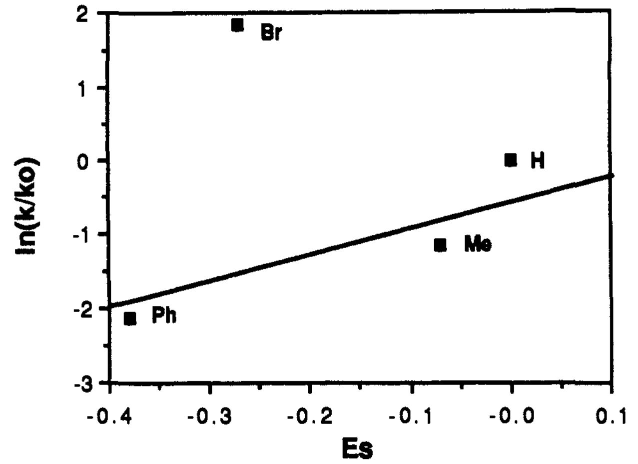

Figure 8. The reaction rate as a function of substitution at the α carbon. Reaction condition: 1 mmol of styrene derivative, 0.001 mmol of QSiRuW, 5 mmol of $NaIO_4$, 5 mL of 1,2-dichloroethane, and 5 mL of water, temperature 60 °C.

(E_a) was 5.25 Kcal/mol, and the activation parameters were $\Delta H^{\ddagger} = 4.58$ Kcal/mol and $\Delta S^{\ddagger} = -50.4$ eu at 60 °C.

The effect of substituents on the styrene substrates was also investigated. Ring substitution at the meta and para positions gave a nonlinear Hammett plot, Figure 7. The curve was concave up with relatively high ρ values ($\rho_1 = -3.0$ and $\rho_2 = 4.1$) which indicates a definite change of mechanism when going from electron-donating to electron-withdrawing substituents.[29] The steric effect at the benzyl carbon was also investigated for $PhCR{=}CH_2$ (R = H, Me, Ph, Br) as a Taft plot, Figure 8. One can see the expected linear effect for the substituents R = H, Me, and Ph as a function of their steric bulk, however Br as a substituent is a significant outlier.

Before suggesting and discussing a possible reaction mechanism it is worthy to describe several additional important experimental observations. During the course of the oxidation of styrene one may have expected the formation of intermediates such as styrene oxide or its hydrolysis product styrene glycol, however neither of these compounds could be found in GLC analysis even in trace amounts. Furthermore the rate of oxidation of styrene oxide ($k_{obs} = 3.0 \times 10^{-4}\ s^{-1}$) was similar to that found for styrene. Styrene glycol was cleaved to benzaldehyde at a significantly faster rate ($k_{obs} = 1.4 \times 10^{-2}\ s^{-1}$), but the catalyst QSiRuW did not affect the rate of this reaction. Therefore, it seems unlikely that the epoxide is a reaction intermediate, although the glycol remains a potential intermediate, if not formed from the epoxide. The oxidation of $PhCH{=}C(CN)_2$ proceeded at a very sluggish rate ($k_{obs} = 1.05 \times 10^{-6}\ s^{-1}$) even though other substrates with electron-withdrawing substituents e.g., 4-nitrostyrene ($k_{obs} = 2.5 \times 10^{-4}\ s^{-1}$), reacted at a rate comparable to that found for styrene.

Key experimental findings concern the role of water in the oxidative cleavage of styrene. Reactions carried out with solid sodium periodate failed. It could be construed that such reactions failed because of lack of interfacial contact. However, reactions performed by using tetrabutylammonium periodate dissolved in the organic phase in the absence of water were likewise unsuccessful. The UV–vis spectrum of QSiRuW and $(C_4H_9)_4N^+IO_4^-$ showed a red shift of the d–d transition band relative to the catalyst in the absence of oxidant, Figure 9. Addition of water to a reaction with $(C_4H_9)_4N^+IO_4^-$ caused the oxidative cleavage to commence with a concurrent change in the UV–vis spectrum. The low-temperature ESR spectra of this key catalytic intermediate was also measured, Figure 10. The spectrum is, as may have been expected, different than that of the original Ru(III) catalyst and shows a single peak at $g = 2.11$. Since heavy transition metals generally retain a low-spin character, the existence of an ESR spectrum would seem to indicate the presence of a paramagnetic Ru(V) or Ru(VII) species, low-spin Ru(IV) and Ru(VI) being diamagnetic. To our knowledge there are no literature precedents for Ru(V) ESR spectra of this type, whereas the single Ru(VII) ESR[30] reported spectrum of $[RuO_4(OH)_2]^{3-}$ gave a single peak at a different field ($g = 1.9$).

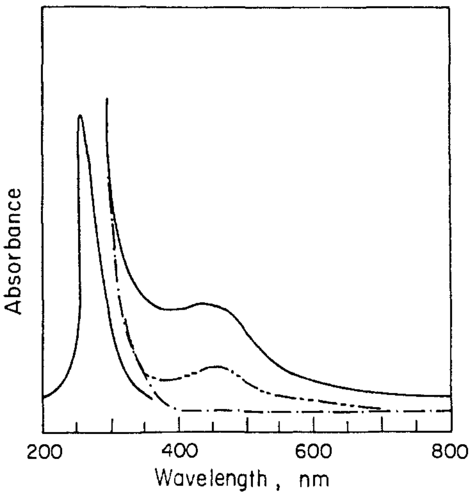

Figure 9. The UV–vis spectra of QSiRuW in the presence of $(C_4H_9)_4IO_4$: (—) QSiRuW; (– – – –) QSiRuW + $(C_4H_9)_4NIO_4$; (— · —) QSiRuW + $(C_4H_9)_4NIO_4$ and H_2O.

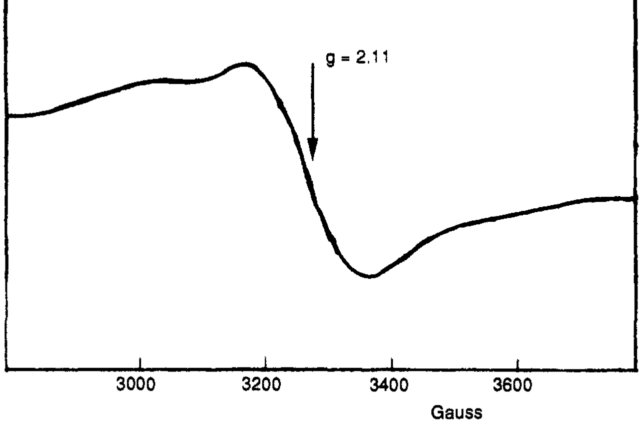

Figure 10. The ESR spectrum of catalyst after addition of $NaIO_4$ and water. The sample was prepared by addition of an excess of $NaIO_4$ and water to QSiRuW dissolved in 1,2-dichloroethane at 60 °,C, and the spectrum was taken at 100 K.

Table III. ^{18}O Isotope Incorporation into the Benzaldehyde Derivative[a]

substrate	^{18}O incorporation
4-methoxystyrene	0.20
styrene	0.45
4-chlorostyrene	0.70
4-nitrostyrene	0.25

[a] Reaction conditions: 50 μmol of styrene derivative, 0.10 μmol of QSiRuW, and 250 μmol of tetrabutylammonium periodate were dissolved in 500 μL of 1,2-dichloroethane in a stirred reaction vial at 60 °C. After 5 min 100 μL of $H_2{}^{18}O$ (90%) was added. After 2 min the reaction was quenched by cooling, and the isotope incorporation in the benzaldehyde product was computed by GC-MS analysis. Values are given as $ArCH^{18}O$/total ArCHO.

The role of the water in the reaction mechanism was further investigated and clarified by the following experiment. Styrene and $(C_4H_9)_4N^+IO_4^-$ were dissolved in 1,2-dichloroethane, and $H_2{}^{18}O$ was added to the reaction mixture. The amount of ^{18}O

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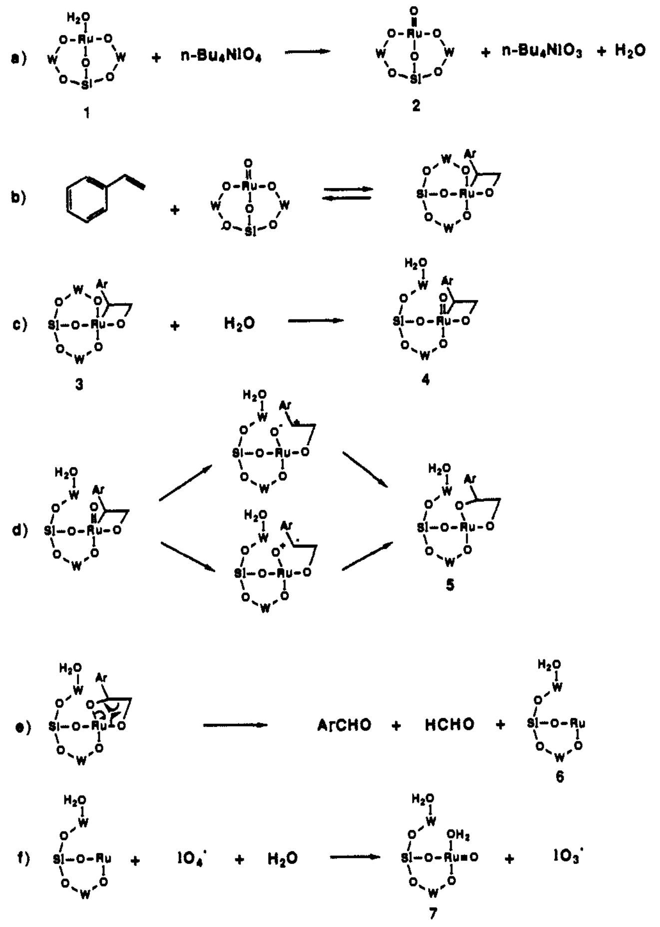
Scheme II



found in the benzaldehyde cleavage product was then measured by GLC-MS analysis, Table III. Analysis was performed at short reaction times (2 min)[31] to minimize isotope exchange between $H_2{}^{18}O$ and $(C_4H_9)_4N^+IO_4^-$ or benzaldehyde. The results with various ring-substituted styrenes show that ^{18}O incorporation is inversely proportional to the trend of the Hammett plot.

Taking into account all the results described above we wish to suggest the following reaction mechanism for the oxidative cleavage of styrenes by periodate in the presence of QSiRuW and H_2O, Scheme II. The original catalyst, **1** (QSiRu(III)W), is oxidized by $(C_4H_9)_4N^+IO_4^-$ to a higher valent ruthenium-oxo compound (Figure 9, the peak at 434 is shifted to 463 nm), which taking into account only a normal redox interaction should be a ruthenium(V) heteropolyanion, **2**. The latter may possibly interact with the styrene derivative forming a metallocyclooxetane, **3**. Such compounds have been postulated previously for chromyl chloride,[32] permanganate,[33] and ruthenate and perruthenate[34] oxidations. The next step in such a reaction mechanism[34] is the breaking of the ruthenium–carbon bond together with the formation of a carbon–oxygen bond yielding a cyclic ruthenium(V) diester. In the absence of water this step cannot take place because the required oxygen atom is bound to the neighboring tungsten atom. The addition of water enables the breaking of the tungsten–oxygen bond forming the metallocyclooxetane, **4**. The cyclic diester, **5**, may now be formed in the rate-determining step (step d) by two possible pathways through transition states of similar energy since the Hammett plot shows that the reaction is similarly accelerated both by electron-donating and electron-withdrawing ring substituents and a change of mechanism when going from one to the other. Electron-donating groups will stabilize a transition state with a positive charge at the benzylic carbon (ρ_1 is large and negative), and electron-withdrawing groups will stabilize transition states with a negative charge at the benzylic carbon (ρ_2 is large and positive). When the reaction is carried out with $H_2{}^{18}O$, ^{18}O isotope incorporation at the benzylic carbon (precursor to benzaldehyde) will be greatest for the slowest reaction because of the greater probability of exchange of the oxygen on the ruthenium with the neighboring water ligand on the tungsten as is borne out in Table III. The cyclic diester then is cleaved in a commonly accepted concerted manner[32-34] to yield benzaldehyde and formaldehyde products on the one hand and the reduced ruthenium intermediate, **6**, on the other hand. The latter is reoxidized by periodate in the presence of water to yield **7**. The latter may rereact with the styrene directly yielding the metallocycloeoxetane, **4**. In fact in the "normal" reaction system where reactions carried out with aqueous sodium periodate, **7** is formed directly from **1** (compare UV–vis Figure 1 and Figure 9), and the latter reacts with the styrene derivative to give **4**, eq 6.

$$1 + NaIO_{4(aq)} \rightarrow 7 + NaIO_{3(aq)} \qquad (6)$$

$$7 + ArCH{=}CH_2 \rightarrow 4$$

The mechanism described in Scheme II and eq 6 satisfactorily explains all the experimental results. The action of aqueous sodium periodate on QSiRuW irreversibly yields a compound **7**, the UV–vis and IR spectra thereof are given in Figures 1 and 2. Step d is the rate-determining step of the reaction, and therefore the rate is proportional to the concentration of **4** which is formed by the fast reaction of the catalyst (in the presence of $NaIO_4$) and styrene. Thus, the reaction mechanism requires the reaction to be be first order in the catalyst and the organic substrate as is indeed found, Figures 3 and 4. Activation parameters derived by using the Arrhenius equation show a highly unfavorable entropy of activation ($\Delta S^{\ddagger} = -50.4$ eu) which is consistent with a highly ordered transition state as presented in Scheme II. Bulky substituents at the benzylic carbon decrease the reaction rate as may be expected because the formation of the carbon–oxygen bond is sterically hindered. The anomalously fast reaction rate found for the oxidation of α-bromostyrene is due to the fact that the Br substituent may stabilize both possible transition states by either field or resonance effects. The mechanism naturally also explains the absence of even traces of styrene oxide or styrene glycol; the cleavage products are formed directly from the olefin. The very slow oxidation of $PhCH{=}C(CN)_2$ as opposed to 4-nitrostyrene may be explained by a change in the rate-determining step in the oxidation of the former. The presence of the two cyano substituents reduces the nucleophilicity or electron density of the double bond to such a degree that the rate-determining step is transferred to the formation of the electrophile–nucleophile adduct, **4**. This same trend may be observed for reactions outside the styrene series where it was found that cyclic and acyclic olefins were oxidized at considerably lower rates, Table I.

Conclusion

A ruthenium heteropolyanion, $SiRu(H_2O)W_{11}O_{39}{}^{5-}$, has been synthesized and characterized. The heteropolyanion with a hydrophobic counter cation oxidizes alkenes with four oxidants, *tert*-butyl hydroperoxide, potassium persulfate, iodosobenzene, and sodium periodate with different reactivity and selectivity in each case. Especially unique is the selective catalytic cleavage of olefins to aldehydes in the presence of sodium periodate. Spectroscopic investigation of the catalyst behavior in the presence of the various oxidants reveal at least three interactions. A mechanistic scheme applicable to the catalytic oxidative cleavage of styrenes by periodate has been suggested which explains the reaction kinetics, substituent effects, and the role of water in the oxidation reaction.

Experimental Section

Materials and Instruments. In general reagents and solvents used were of the highest purity commerciably available. Olefins were purified by

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(31) At longer reaction times there was full isotope incorporation due to exchange reactions.

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passing them over a neutral alumina column prior to use in order to remove any peroxides or inhibitors present. 4-Nitrostyrene was prepared in two stages by nitrating (β-bromoethyl)benzene with fuming nitric acid to yield a mixture of 2- and 4-nitro-(β-bromoethyl)benzene. The 4-nitro-(β-bromoethyl)benzene was then purified by crystallization from heptane (yield 60%). The 4-nitro-(β-bromoethyl)benzene dissolved in toluene was then treated with an excess of 50% NaOH in the presence of polyethylene glycol 400 as catalyst[35] at room temperature which after crystallization from hexane gave 4-nitrostyrene (mp 29 °C, yield 90%, purity GLC 99%). Iodosobenzene was prepared by the common literature method.[36]

The following research instruments were used: atomic absorption, GBC 603 single beam spectrometer; UV-vis, Hewlett Packard 8452 diode parray spectrometer; FTIR, Analect FX 6260; ESR, Brucker ESP300; GLC, Hewlett Packard 5890 equipped with an FID detector, a Model 3396 integrator, and 10-m cross-linked FFAP megabore column (i.d. 0.53 mm with a 1.0 μm coating); GC-MS, Hewlett Packard 5970 A with a mass selective detector; cyclic voltammetry, BAS CV-IB voltammograph with a glassy carbon working electrode and a Ag/AgCl reference electrode.

Preparation of $SiRu(H_2O)W_{11}O_{39}^{5-}$. $K_5SiRu(H_2O)W_{11}O_{39}$ was prepared by first dissolving 1.0 mmol of $K_8SiW_{11}O_{39}$[22] in 100 mL of water at 80 °C. After the unsaturated heteropolyanion was completely dissolved (about 30 min) 1.05 mmol of $RuCl_3 \cdot H_2O$ dissolved in a small amount of water was slowly added, and the mixture was stirred at 90 °C for 30 min. The solution was cooled to 50 °C, and 80 mL of methanol was added which precipitated a brown-black sticky solid. The solid was filtered at the pump and then was twice titurated with acetone to yield the black crystalline $K_5SiRu(H_2O)W_{11}O_{39}$ with a 70% yield. The ruthenium heteropolyanion was analyzed by using atomic absorption to determine potassium and ruthenium[37] and gravimetric analysis for Si and W as SiO_2[38] and the 8-hydroxyquindinotungstate,[39] respectively. Water of hydration was found by thermogravimetric analysis. The analysis yields the molecular formula $K_5SiRu(H_2O)W_{11}O_{39} \cdot 15H_2O$, and the calculated (found) percentages are K, 6.00 (6.04); Si, 0.86 (0.73); Ru, 3.10 (3.01); W, 62.05 (60.82); H_2O, 8.84 (8.52).

$((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$ was prepared by vigorously mixing 0.5 mmol of $K_5SiRu^{III}(H_2O)W_{11}O_{39}$ dissolved in 20 mL of water with 2.6 mmol of $(C_6H_{13})_4NHSO_4$ in 30 mL of dichloromethane. After the ruthenium heteropolyanion was entirely transferred into the organic phase, phases were separated, the organic phase was dried with $MgSO_4$, and the solvent was removed yielding a crystalline $((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$ in a 95% yield. The calculated (found) percentages for the organic counter cation are C, 30.68 (30.29); H, 5.72 (5.48); N, 1.54 (1.28).

Typical Procedure for the Oxidatin of Olefins. Reactions were performed in a 25-mL flask equipped with a thermostated oil bath and a magnetic stirrer. Thus 0.002 mmol of $((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$ and 1.0 mmol of substrate in 5 mL of 1,2-dichloroethane were mixed with 5 mmol of oxidant at 60 ± 2 °C. The oxidants were added in 5 mL of water in the case of sodium periodate and potassium persulfate, as a solid in the case of iodosobenzene and as a liquid in the case of *tert*-butyl hydroperoxide (technical grade 70%). Samples were taken at the appropriate intervals and analyzed by GLC. Peaks were standardized by using the available reference compounds.

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Models for Diferrous Forms of Iron-Oxo Proteins. Structure and Properties of $[Fe_2BPMP(O_2CR)_2]BPh_4$ Complexes

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Abstract: A series of bimetallic complexes, $[M^{II}M'^{II}BPMP(O_2CR)_2]X_2$ where BPMP is the anion of 2,6-bis[[bis(2-pyridylmethyl)amino]methyl]-4-methylphenol, has been synthesized to serve as models for the diferrous forms of iron-oxo centers in proteins. Complex **1** (M = M′ = Fe, R = C_2H_5, X = BPh_4, solvate = 0.8 CH_2Cl_2) has been characterized by X-ray diffraction methods as having a (μ-phenoxo)bis(μ-carboxylato)diiron core. **1** crystallizes in the triclinic space group $P\bar{1}$ with cell constants: a = 12.607 (6) Å, b = 15.113 (13) Å, c = 16.601 (6) Å, α = 81.42 (6)°, β = 88.88 (4)°, γ = 67.89 (5)°, Z = 2, V = 2879.4 Å^3. From 11 192 reflections (of 13 865 where $I(\mathrm{obsd}) > \sigma(I)$) collected at 175 K, the structure was solved by the Patterson method and refined anisotropically to R = 0.058 and R_w = 0.074. The metal centers in **1** have distinct six-coordinate environments but have similar structural parameters. They have been characterized as high-spin Fe(II) centers by electronic spectral, NMR, Mössbauer, and EPR methods with the help of the analogous heterobimetallic complexes such as the $Fe^{II}Zn^{II}$ and $Fe^{II}Ga^{III}$ derivatives. Most interestingly, **1** and **2** (M = M′ = Fe, R = Ph, X = BPh_4) exhibit low field EPR signals near g = 16, similar to those reported for deoxyhemerythrin azide, reduced methane monooxygenase and reduced ribonucleotide reductase. The signal for **1** has an intensity that is enhanced in parallel mode ($\mathbf{B}_1 \parallel \mathbf{B}$), a characteristic of integer spin systems, and has a temperature dependence indicative of a ground-state transition. Analysis of EPR spectra shows that the two iron sites of **1** are ferromagnetically coupled. Depending on the sign of the zero-field splitting parameters D_i of the individual Fe(II) sites, both a weak and a strong coupling scheme are compatible with the data. Similar but significantly less intense signals are observed for analogous $Fe^{II}Zn^{II}$ or $Fe^{II}Ga^{III}$ complexes, as expected for the S = 2 centers in these complexes.

In recent years, dinuclear iron-oxo centers have emerged as a common structural component in the active sites of several metalloproteins.[1] These centers have important functional roles in hemerythrin,[2] ribonucleotide reductase,[3] methane monooxygenase,[4] and the purple acid phosphatases.[5] The prototype and best characterized member of this class of proteins is hemerythrin (Hr),

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