

cluster core structures.¹⁹ $[\text{Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$ is the tenth such cluster and is the first meaningfully describable as cyclic and one of the very few *chalcogenide* clusters of any kind devoid of terminal ligands.^{20,21} Its sulfide-rich interior should render it a receptive host, a purely inorganic version of a crown ether, to other metals by Na^+ substitution. Lastly, the absorption spectrum of the crystal used in the X-ray determination is identical with that of a bulk sample. This intense, characteristic spectrum (λ_{max} (ϵ_{M}) 300 (81 100), 320 (sh), 396 (76 400), 520 (sh), 600 (sh, 32 700) nm, acetonitrile) ensures that the present cluster is different from the green chromophore formed in aqueous alkaline solutions of iron salts and alkali metal sulfides.²² The reactivity and electronic structural properties of $[\text{Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$ will be the subjects of future reports.

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Supplementary Material Available: Table of atom positional parameters for $(n\text{-Pr}_4\text{N})_6\text{Na}_4[\text{Fe}_{18}\text{S}_{30}] \cdot 14\text{MeCN}$ (2 pages). Ordering information is given on any current masthead page.

(19) This statement excludes organometallic clusters; cluster structural types are illustrated elsewhere.^{8c} The largest discrete cyclic assembly based on planar metal units is $\text{Ni}_8(\text{SCH}_2\text{COOEt})_{16}$; Dance, I. G.; Scudder, M. L.; Secomb, R. *Inorg. Chem.* **1985**, *24*, 1201.

(20) The only other examples involve M(I) clusters in which the metal coordination number is two or three. (a) $[\text{Cu}_{12}\text{S}_8]^{4+}$: Betz, P.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 311. (b) $[\text{Au}_{12}\text{S}_8]^{4+}$: Marbach, G.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 715. (c) $[\text{Au}_4\text{Te}_4]^{4+}$ and $[\text{KAu}_9\text{Te}_7]^{4+}$: Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 432.

(21) Among metal halide clusters, $[\text{Cu}_4\text{I}_6]^{2-}$ and $[\text{Cu}_8\text{I}_{11}]^{5-}$ exhibit this property: Bowmaker, G. A.; Clark, G. R.; Yuen, D. K. P. *J. Chem. Soc., Dalton Trans.* **1976**, 2329. Rath, N. P.; Holt, E. M. *J. Chem. Soc., Chem. Commun.* **1985**, 665.

(22) Taylor, P.; Shoesmith, D. W. *Can. J. Chem.* **1978**, *56*, 2797. Solutions of $[\text{Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$ are brown.

Heterobimetallic Catalysts for the Oxidation of Alcohols: $[\text{Os}(\text{N})\text{R}_2(\text{CrO}_4)]^-$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{SiMe}_3$)

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Chromate salts and other chromium(VI) oxides have been widely used as oxidizing agents for a variety of substrates¹ including alcohols.² These oxidants are frequently used in large excess³ but can also be used catalytically in conjunction with secondary oxidants.⁴ None of these employ dioxygen as the secondary oxidant. Problems in the use of chromium(VI) complexes as oxidation reagents include the lack of selectivity in oxidations, safety hazards associated with the use of large quantities of toxic compounds, and the need for aqueous acidic or basic conditions for reactions of chromate salts.

These problems could be eliminated by incorporating the chromate moiety in a heterobimetallic complex. Selectivity could be improved due to substrate binding to one metal center and oxidation by the other. The presence of organic ligands would

Table I. Alcohol Oxidation Catalyzed by $[\text{NBu}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{CrO}_4)]^-$

	57 (11.4) 100 (20) ^c
	28 (5.9) 99 (19.8) ^c
	34 (7.3)
	17 (3.7)
	13 (2.8)
	9 (2.0)

^a The reactions were run in air, 5 mol% catalyst, CH_3CN , 70 °C, 72 h. ^b Conversion to aldehyde/ketone was measured by GLC and ¹H NMR. No other organic products were formed. (Turnover number = mol product/mol catalyst). ^c The reaction was run as above with 10 mol% $\text{Cu}(\text{O}_2\text{CCH}_3)_2$ added.

increase solubility in nonaqueous media. Also, incorporation of a metal capable of activating dioxygen could allow the oxidation reaction to become catalytic and reduce the environmental hazards. A number of coordination compounds containing CrO_4^{2-} bound to another transition-metal center are known.^{5,6} No organometallic complexes containing the chromate group have been reported previously, however. The dialkyl-nitridoosmium(VI) moiety is well suited to be part of a bimetallic oxidation catalyst since certain osmium(VI) complexes can be air oxidized,⁷ precursors to heterobimetallic complexes are readily available,⁸ and these precursors are stable to oxidation.

We report here the first metal alkyl complexes containing coordinated chromate group, *cis*- $[\text{NBu}^n_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{CrO}_4)]^-$ (**1**) and *cis*- $[\text{PPh}_4][\text{Os}(\text{N})\text{Me}_2(\text{CrO}_4)]^-$ (**2**), and on their reactions with alcohols. They are catalysts for the selective oxidation of primary and secondary alcohols. These chromate complexes are unique in their ability to use molecular oxygen as the secondary oxidant. Selectivity is improved with primary alcohols converted exclusively to aldehydes and other functional groups unaffected by the catalyst.

The reactions of $[\text{NBu}^n_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2]$ or $[\text{PPh}_4][\text{Os}(\text{N})(\text{CH}_3)_2\text{Cl}_2]$ with silver chromate in methylene chloride gave silver chloride and **1** or **2**, respectively.^{9,10} The

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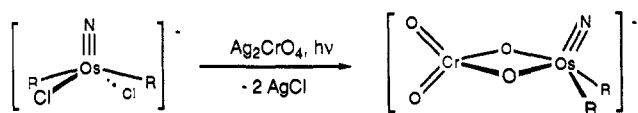
(7) (a) Willstätter, R.; Sonnenfeld, E. *Chem. Ber.* **1913**, *46*, 2952. (b) Périchon, J.; Palous, S.; Buvet, R. *Bull. Soc. Chim. Fr.* **1963**, 982-988. (c) Cairns, J. F.; Roberts, H. L. *J. Chem. Soc. C* **1968**, 640-642.

(8) (a) Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493-7496. (b) Shapley, P. A.; Kim, H. S.; Wilson, S. R. *Organometallics* **1988**, *7*, 928-933.

(9) $[\text{NBu}^n_4][\text{Os}(\text{N})(\text{CH}_2\text{SiCH}_3)_2(\text{CrO}_4)]^-$: IR (KBr, pellet, cm^{-1}) 1111 s (Os-N), 948 vs (Cr-O), 928 vs (Cr-O); ¹H NMR (CD_2Cl_2 , 500 MHz, 293 K) δ 3.18 (m, 4 H, NCH_2), 2.08 (s, 2 H, $\text{OsCH}_2\text{SiMe}_3$), 1.63 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.43 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.02 (t, 6 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.09 (s, 9 H, $\text{OsCH}_2\text{SiCH}_3$); ¹³C{¹H} NMR (CD_2Cl_2 , 500 MHz, 293 K) δ 59.27 (NCH_2), 24.25 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.12 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.78 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.59 ($\text{OsCH}_2\text{SiMe}_3$), 0.81 ($\text{OsCH}_2\text{SiCH}_3$). Anal. Calcd for $\text{OsCrN}_2\text{Si}_2\text{O}_4\text{C}_{24}\text{H}_{58}$: C, 39.11; H, 7.93; N, 3.80. Found: C, 39.07; H, 8.02; N, 3.80.

(10) *cis*- $[\text{PPh}_4][\text{Os}(\text{N})\text{Me}_2(\text{CrO}_4)]^-$: IR (KBr, pellet, cm^{-1}) 1109 s (Os-N), 956 vs (Cr-O), 922 vs (Cr-O), 795 m (Cr-O); ¹H NMR (CDCl_3 , 300 MHz, 293 K) δ 2.27 (s, 3 H, OsCH_3), 8.0-7.5 (m, 10 H, PPh). Anal. Calcd for $\text{OsCrNPO}_4\text{C}_{26}\text{H}_{26}$: C, 45.28; H, 3.80; N, 2.03. Found: C, 45.14; H, 3.84; N, 1.97.

reactions proceeded only in the light. When the syntheses were attempted in an opaque vessel, no product was obtained. The IR and NMR spectra of these new chromate complexes suggests a similar structure with *cis*, bidentate chromate ligands. The IR bands associated with the chromate group in 1 and 2 are similar to those of $[\text{Co}(\text{NH}_3)_4(\text{CrO}_4)][\text{NO}_3]$, in which there is bidentate coordination of the ligand.¹¹



1. R = CH₂SiMe₃; 2. R = Me

These osmium and ruthenium chromate complexes are quite thermally stable. Heating them in the solid state or in solution to 100 °C causes no decomposition. They are also stable to air and water. Even though these species are anionic, the presence of the alkyl groups and large organic counterion makes them soluble in a variety of organic solvents including toluene and diethyl ether.

The osmium chromate complex, *cis*-[NBuⁿ][Os(N)(CH₂SiMe₃)₂(CrO₄)], catalytically oxidizes a variety of alcohols with high selectivity. Primary alcohols are oxidized exclusively to aldehydes and secondary alcohols to ketones. No carboxylic acids or esters could be detected in the reaction mixtures by gas chromatography or ¹H NMR. The reaction requires molecular oxygen, which is reduced to water.

In a typical reaction, a magnetically stirred mixture of *cis*-[NBuⁿ][Os(N)(CH₂SiMe₃)₂(CrO₄)] (8 mg, 0.01 mmol, 5 mol%), alcohol (0.2 mmol), anisole (0.12 mmol, internal standard), and acetonitrile (2.0 mL) was heated to 70 °C for 72 h under air. Conversion of alcohol to aldehyde or ketone, as determined by gas chromatography and ¹H NMR, ranged from 57% to 9% depending on the nature of the alcohol. Similar results were obtained when the reactions were performed in a closed system under O₂, either in a pressure bottle or in a sealed NMR tube. No reaction occurred in the absence of the catalyst.

The rate of oxidation and yield of product depended on the nature of the substrate and reaction conditions. Oxidation of benzylic and allylic alcohols proceeded more rapidly than the oxidation of primary alcohols, and primary alcohols were oxidized more rapidly than secondary alcohols. Tertiary alcohols were not oxidized. In contrast, potassium chromate in aqueous acidic acid solution oxidizes hindered alcohols faster than less hindered alcohols. In the oxidation of benzyl alcohol to benzaldehyde, the rate and yield of the reaction increased when the reaction was run under oxygen (30 psi) or in air in the presence of cupric acetate.^{12,13}

The less bulky osmium chromate complex, 2, was more active for alcohol oxidation. Benzyl alcohol was oxidized in air with 79% conversion to benzaldehyde in 12 h. Again, the aldehyde was the only product of the reaction.¹⁴

The osmium chromate complex, 1, is chemoselective for the oxidation of hydroxy groups. Neither triphenylphosphine nor olefins (cyclohexene, styrene) reacted with the osmium chromate complex under alcohol oxidation conditions. No oxidation of the double bond occurred in the catalytic oxidation of 2-cyclohexenol to 2-cyclohexanone. No reaction with carbon monoxide or pyridine was observed.

In all of the reactions with alcohols performed in air, 1 was eventually converted to a yellow-green species which has not yet been fully characterized. This product was not active for alcohol

oxidation. Even though the osmium chromate complex is stable to water at room temperature, it may be decomposing under the reaction conditions with water formed as a byproduct.

The osmium-chromate complexes have a number of advantages over currently employed Cr(VI) complexes in the oxidation of alcohols. They are thermally stable and soluble in organic solvents. They are highly selective, giving only aldehyde in the oxidation of primary alcohols. The chemoselectivity allows their use in the presence of triphenylphosphine, olefins, amines, and ethers. They are unique with respect to other chromium(VI) reagents in their ability to activate molecular oxygen in the catalytic oxidation of alcohols.¹⁵ The reaction is slow, however, and deactivation of the catalysts with the water produced may be occurring over time. Since ruthenium complexes are generally more powerful oxidants than the corresponding osmium species,¹⁶ and ruthenium complexes oxidize alcohols,¹⁷ we are now investigating the reactivity of the ruthenium-chromate complexes, [Ru(N)R₂(CrO₄)]⁻, in alcohol oxidations.

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Supplementary Material Available: Experimental procedures and physical data for the new compounds (1) *cis*-[NBuⁿ][Os(N)(CH₂SiMe₃)₂(CrO₄)], (2) *cis*-[PPh₄][Os(N)(CH₃)₂(CrO₄)], (3) *cis*-[NBuⁿ][Ru(N)(CH₂SiMe₃)₂(CrO₄)], and (4) *cis*-[PPh₄][Ru(N)(CH₃)₂(CrO₄)] (2 pages). Ordering information is given on any current masthead page.

(15) Transition-metal complexes have been previously shown to use molecular oxygen in alcohol oxidation reactions, but other functional groups are also oxidized by these catalysts. See: (a) Solar, J. P.; Mares, F.; Diamond, S. E. *Catal. Rev.-Sci. Eng.* **1985**, *27*, 1-28. (b) Gagne, R. R.; Marks, D. N. *Inorg. Chem.* **1984**, *23*, 65-74. (c) Hamilton, D. E.; Drago, R. S.; Zombeck, A. J. *Am. Chem. Soc.* **1987**, *109*, 374-379. (d) Bedell, S. A.; Martell, A. E. *J. Am. Chem. Soc.* **1985**, *107*, 7909-7913. (e) Groves, J. T.; Quinn, R. J. *Am. Chem. Soc.* **1985**, *107*, 5790-5792.

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A Hybrid Sequence-Selective Ribonuclease S

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Chemists and biologists are focusing considerable effort on the design of selective catalysts for the synthesis and modification of complex molecules. One approach involves modifying the specificity of existing enzymes either by altering active site residues via site-directed mutagenesis or by selectively introducing new binding domains into enzymes. We recently applied this latter strategy to the construction of a hybrid enzyme capable of site-selectively hydrolyzing single-stranded DNA and RNA.^{1,2} We now report the design of a second hybrid enzyme based on this strategy. A sequence-selective ribonuclease has been generated by selectively fusing an oligodeoxyribonucleotide binding site of defined sequence to the relatively nonspecific enzyme bovine pancreatic ribonuclease A.

Ribonuclease A (RNase A) is a well-characterized stable enzyme, 124 amino acids in length, that hydrolyzes the phosphodiester bonds of single-stranded RNA preferentially to the 3' side

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(2) Zuckermann, R. N.; Corey, D. C.; Schultz, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 1614.

(11) Coomber, R.; Griffith, W. P. *J. Chem. Soc. A* **1968**, 1128-1131.

(12) Cu^{II}/O₂ has been used to aid in the reoxidation of other transition-metal complexes. See: (a) Nyberg, E. D.; Pribich, D. C.; Drago, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 3538-3544. (b) Mimoun, H.; Machirant, M. M. P.; de Roch, I. S. *J. Am. Chem. Soc.* **1978**, *100*, 5437-5443.

(13) No catalytic oxidation occurred in the absence of the osmium chromate complex. A mixture of potassium chromate and cupric acetate converted a very small amount of benzyl alcohol (2.7% conversion, 0.51 TO) to oxidation products.

(14) Concentrations of reactants were the same as above: 0.01 mmol catalyst, 0.2 mmol benzyl alcohol, in 2.0 mL of acetonitrile.