in 1), which cannot bind to the protein, although competitively reduced the rate of retinal incorporation, was found to be inactive. ${ }^{8}$

The cells were also incubated with 11 -cis-dihydroretinals 8-11 and acyclic series 13-16 containing the same number of double bonds. The action spectral maxima of restored phototaxis are dependent on the conjugation length in both series. The action spectra peaks resulting from incorporation of tetraenals $8 / 13$ were at $472 / 461 \mathrm{~nm}$, trienals $\mathbf{9} / \mathbf{1 4}$ at $437 / 459 \mathrm{~nm}$, dienals $\mathbf{1 0} / \mathbf{1 5}$ at 489/446 nm, and monoenals 11/16 at $340 / 354 \mathrm{~nm}$. These aldehydes are linked to the photoreceptor via a $\mathrm{C}=\mathrm{N}^{+} \mathrm{H}$ bond as in other retinal proteins, since the maxima undergo progressive blue shifts with shorter conjugation, and the trend of phototaxis maxima restored by the acyclic series is similar to the absorption maxima of 11 -cis-dihydroretinals in bovine rhodopsin. ${ }^{9}$ The sharp change in opsin shifts ${ }^{6}$ that one observes between the trienals and dienals, e.g., $2370 \mathrm{~cm}^{-1}$ in 9 versus $11000 \mathrm{~cm}^{-1}$ in 10, suggests that a negative charge may be near the terminus of the conjugated system $\left.-\mathrm{C}_{(11)}=\mathrm{C}_{(12)}-\mathrm{C}_{(13)}=\mathrm{C}_{(14)}-\mathrm{C}_{(13}\right)=\mathrm{NH}^{+}$-, near $\mathrm{C}-10$ or $\mathrm{C}-11.7$ Hexenal 16 and even hexanal 17 (!) incorporated readily and, surprisingly, were as sensitive as other retinals, including 11-cis-retinal 7. The maximum for hexanal 17 ( 339 nm ) is at a shorter wavelength than that of hexenal $\mathbf{1 6}(354 \mathrm{~nm})$; this together with its red shift compared to hexanal in solution shows hexanal is also bound through $\mathrm{C}=\mathrm{N}^{+} \mathrm{H}$.

The activity of hexanal corroborates other results which suggest that a route other than cis-trans isomerization is possible for activation of Chlamydomonas rhodopsin. Upon photoexcitation of rhodopsins, electron density is redistributed toward the imine ( $\mathrm{C}=\mathrm{N}$ ) end of retinal causing a variety of events including cistrans isomerization. Although it is established that cis-trans isomerization occurs with visual pigments, ${ }^{10}$ it is not known whether this is the event responsible for visual transduction. Most experiments have measured the changes that retinal undergoes in the regulatory (binding) site and not the activation of the peripheral enzymatic site responsible for initiating the visual cascade.

Two mechanisms for the triggering of Chlamydomonas rhodopsin are conceivable. Charge redistribution in the photoexcited state, where the electron density moves toward $N,{ }^{11}$ acts (i) directly to activate rhodopsin or (ii) indirectly, via the possible subsequent step of syn/anti isomerization of the $\mathrm{C}=\mathrm{N}^{+} \mathrm{H}$ bond, to trigger phototaxis. In view of the positive phototaxis response of analogue 12, direct activation is more likely. Because of the possible homology among eukaryotic rhodopsins, ${ }^{2,12}$ a mechanism similar
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to that occurring in Chlamydomonas may be involved in triggering the activity of other rhodopsins. These aspects are currently under investigation.

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# $\left[\mathrm{Na}_{2} \mathrm{Fe}_{18} \mathrm{~S}_{30}\right]^{8-}$ : A High-Nuclearity Cyclic Cluster Generated Solely by Iron-Sulfur Bridge Bonding 

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Since its introduction, ${ }^{1}$ spontaneous self-assembly of iron-sulfur clusters from an iron salt, a sulfide source, and thiolate, halide, or areneoxide as a terminal ligand has proven to be a highly productive synthetic method. Clusters containing the cores $\left[\mathrm{Fe}_{2} \mathrm{~S}_{2}\right]^{2+}, 2-4$ linear $\left[\mathrm{Fe}_{3} \mathrm{~S}_{4}\right]^{1+4}$ cubic $\left[\mathrm{Fe}_{4} \mathrm{~S}_{4}\right]^{2+, 1+}, 1,2,5$ prismatic $\left[\mathrm{Fe}_{6} \mathrm{~S}_{6}\right]^{3+, 2+,}$ and $\left[\mathrm{Fe}_{6} \mathrm{~S}_{9}\right]^{2-4,7}$ have been obtained in good yield. Use of tertiary phosphine as a terminal ligand, usually in the presence of thiolate or halide, redirects the reaction pathways to new clusters containing basket $\left[\mathrm{Fe}_{6} \mathrm{~S}_{6}\right]^{2+, 1+,}$, stellated octahedral $\left[\mathrm{Fe}_{6} \mathrm{~S}_{8}\right]^{2+1+,}$, and monocapped prismatic $\left[\mathrm{Fe}_{7} \mathrm{~S}_{6}\right]^{3+10}$ cores. Further examination of the effects of different potential terminal ligands in assembly systems has afforded a remarkable cluster of unprecedented structure.

Treatment of a solution of 9.0 mmol of anhydrous $\mathrm{FeCl}_{3}$ in 70 mL of methanol at $5^{\circ} \mathrm{C}$ with a solution of 27 mmol of $\mathrm{Na}-$ [ $\mathrm{PhNC}(\mathrm{O}) \mathrm{Me}$ ] in 60 mL of methanol (generated in situ from equimolar acetanilide and sodium metal) afforded a yellow mixture, which was stirred for 30 min at $5^{\circ} \mathrm{C}$. A slurry of 12 mmol of $\mathrm{Li}_{2} \mathrm{~S}$ in 70 mL of methanol was slowly added, the reaction mixture was filtered after 1 h , and 9.0 mmol of $\left(n-\mathrm{Pr}_{4} \mathrm{~N}\right) \mathrm{Br}$ in 15 mL of methanol was added to the dark green filtrate. Over a 5 -day period a dark crystalline solid separated, which was collected, washed (ethanol), and dried in vacuo to afford 1.59 g

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Figure 1. Structure of $\left[\mathrm{Na}_{2} \mathrm{Fe}_{18} \mathrm{~S}_{30}\right]^{8-}$ showing $50 \%$ probability ellipsoids and the atom labeling scheme; primed and unprimed atoms are related by the inversion operation. Upper: planar projection emphasizing centrosymmetry. Lower: side-on view rotated $90^{\circ}$ from the upper view revealing thickness of the toroidal ring and noncluster ions $\mathrm{Na}\left(2,2^{\prime}\right)$. Distance ( $\AA$ ) and angle (deg) ranges are collected under idealized $C_{2 h}$ symmetry: $\mathrm{Fe}(1)-\mathrm{Fe}(2), 2.703-2.717 ; \mathrm{Fe}(2)-\mathrm{Fe}(3), 2.722-2.724 ; \mathrm{Fe}-$ (3) $-\mathrm{Fe}(4), \quad 2.701-2.725 ; \mathrm{Fe}(3)-\mathrm{Fe}(5), 2.672-2.702 ; \mathrm{Fe}(4)-\mathrm{Fe}(5)$, 2.738-2.783; $\mathrm{Fe}(4)-\mathrm{Fe}(7), 2.761-2.771 ; \mathrm{Fe}(1)-\mathrm{S}(1), 2.234-2.235 ; \mathrm{Fe}-$ (1)-S(2), 2.259-2.267; $\mathrm{Fe}(2)-\mathrm{S}(1), 2.207-2.210 ; \mathrm{Fe}(2)-\mathrm{S}(2), 2.227-$ 2.231; $\mathrm{Fe}(2)-\mathrm{S}(3), 2.361-2.385 ; \mathrm{Fe}(2)-\mathrm{S}(4), 2.227-2.258 ; \mathrm{Fe}(3)-\mathrm{S}(3)$, 2.296-2.310; $\mathrm{Fe}(3)-\mathrm{S}(4), 2.174-2.206 ; \mathrm{Fe}(3)-\mathrm{S}(5), 2.265-2.293 ; \mathrm{Fe}-$ (3)-S(6), 2.207-2.216; $\mathrm{Fe}(4)-\mathrm{S}(3), 2.287 ; \mathrm{Fe}(4)-\mathrm{S}(5), 2.273-2.303$; $\mathrm{Fe}(4)-\mathrm{S}(8), 2.347-2.355 ; \mathrm{Fe}(4)-\mathrm{S}(9), 2.240-2.245$; $\mathrm{Fe}(5)-\mathrm{S}(5)$, 2.2992.318; $\mathrm{Fe}(5)-\mathrm{S}(6), 2.216-2.230 ; \mathrm{Fe}(5)-\mathrm{S}(7), 2.202-2.210 ; \mathrm{Fe}(5)-\mathrm{S}(8)$, 2.345-2.645; $\mathrm{Na}(1)-\mathrm{S}(9), 2.871-2.907 ; \mathrm{Na}(1)-\mathrm{S}(10), 3.245 ; \mathrm{Na}(1)-\mathrm{S}-$ (15), 2.871; $\mathrm{Na}(1)-\mathrm{S}(2), 2.910 ; \mathrm{S}(1)-\mathrm{Fe}(1)-\mathrm{S}(2) 102.9-103.6 ; \mathrm{S}(1)-$ $\mathrm{Fe}(1)-\mathrm{S}\left(14^{\prime}\right) 117.6 ; \mathrm{S}(1)-\mathrm{Fe}(2)-\mathrm{S}(4)$ 111.7-114.5; $\mathrm{S}(1)-\mathrm{Fe}(2)-\mathrm{S}(2)$ 105.1-105.4; $\mathrm{S}(2)-\mathrm{Fe}(2)-\mathrm{S}(3) 107.2-107.5 ; \mathrm{S}(3)-\mathrm{Fe}(2)-\mathrm{S}(4) 100.4-$ 101.0; $\mathrm{S}(3)-\mathrm{Fe}(3)-\mathrm{S}(4)$ 104.1-105.0; $\mathrm{S}(3)-\mathrm{Fe}(3)-\mathrm{S}(5)$ 103.9-105.4; $\mathrm{S}(4)-\mathrm{Fe}(3)-\mathrm{S}(6) 116.5-121.3 ; \mathrm{S}(5)-\mathrm{Fe}(3)-\mathrm{S}(6) 102.4-103.8 ; \mathrm{S}(5)-\mathrm{Fe}-$ (4) $-\mathrm{S}(8) 104.4-105.4 ; \mathrm{S}(8)-\mathrm{Fe}(4)-\mathrm{S}(9) 103.4-103.5 ; \mathrm{S}(5)-\mathrm{Fe}(5)-\mathrm{S}(8)$ 103.6-104.6; $\mathrm{S}(7)-\mathrm{Fe}(5)-\mathrm{S}(8) 102.4-103.3 ; \mathrm{S}(8)-\mathrm{Fe}(5)-\mathrm{S}\left(8^{\prime}\right) 112.4$. Esd's: $0.003-0.005(\mathrm{Fe}-\mathrm{Fe} / \mathrm{S}), 0.006-0.009(\mathrm{Na}-\mathrm{S}) \mathrm{Fe}-\mathrm{S}$, and $0.1-0.2$ (angles).
( $35 \%$, based on Fe ) of product. Large black crystals resulted from ether diffusion into an acetonitrile solution at $5^{\circ} \mathrm{C} .{ }^{11}$ Thus far,

[^1]we have found no anion other than amidate that supports formation of this product.

An X-ray diffraction study of the black crystals established the stoichiometry $\left(n-\mathrm{Pr}_{4} \mathrm{~N}\right)_{6} \mathrm{Na}_{4}\left[\mathrm{Fe}_{18} \mathrm{~S}_{30}\right] \cdot 14 \mathrm{MeCN} .{ }^{11}$ The compound crystallizes in triclinic space group $P \overline{1}$. The cluster, which binds two sodium ions in its interior and is thus formulated as $\left[\mathrm{Na}_{2} \mathrm{Fe}_{18} \mathrm{~S}_{30}\right]^{8-}$, is depicted in two views in Figure 1. The $\mathrm{Fe}_{18} \mathrm{~S}_{30}$ portion is a cyclic cluster of toroidal shape and is the largest $\mathrm{Fe}-\mathrm{S}$ cluster yet prepared. The cluster has imposed $C_{i}$ symmetry but closely approaches $C_{2 h}$ symmetry, this being broken mainly by the positions of the two $\mathrm{Na}^{+}$ions. Because of the large number of independent parameters in the real symmetry, the metric data in Figure 1 are collected under the idealized symmetry. ${ }^{12}$ Cluster lateral dimensions are $13.320\left(\mathrm{~S}(1) \cdots \mathrm{S}\left(1^{\prime}\right)\right) \times 15.975\left(\mathrm{~S}(7) \cdots \mathrm{S}\left(7^{\prime}\right)\right)$ $\AA$. The 18 Fe atoms are nearly coplanar, with the largest deviation from the plane being $\pm 0.154 \AA$ by $\mathrm{Fe}(4)$; the majority are $<0.11$ $\AA$. The maximum thickness of the toroid is ca. $3.3 \AA$ (twice the vertical displacement of $\mathrm{S}(5)$ from the $\mathrm{Fe}_{18}$ mean plane).

As all other $\mathrm{Fe}-\mathrm{S}$ clusters, $\left[\mathrm{Na}_{2} \mathrm{Fe}_{18} \mathrm{~S}_{30}\right]^{8-}$ is constructed by the fusion of nonplanar $\mathrm{Fe}_{2} \mathrm{~S}_{2}$ rhombs. Here 24 rhombs are connected by a combination of edge- and corner-sharing such that there are $20 \mu_{2}-\mathrm{S}$, eight $\mu_{3}-\mathrm{S}$, and two $\mu_{4}-\mathrm{S}$ atoms, excluding interactions with $\mathrm{Na}^{+}$. Every $\mathrm{FeS}_{4}$ unit is tetrahedral. The structure is recognizable as the conjoint of $2 \mathrm{Fe}_{3} \mathrm{~S}_{4}+2 \mathrm{Fe}_{6} \mathrm{~S}_{9}$ cores, as found in $\left[\mathrm{Fe}_{3} \mathrm{~S}_{4}(\mathrm{SR})_{4}\right]^{3-4}$ and $\left[\mathrm{Fe}_{6} \mathrm{~S}_{9}(\mathrm{SR})_{2}\right]^{4-4,7}$ respectively, supported by four additional $\mu_{2}-\mathrm{S}$ bridges. Of independent portions, tetrahedra centered at $\mathrm{Fe}\left(9^{\prime}, 1,2\right)$ and joined by parallel edge-sharing constitute a $\mathrm{Fe}_{3} \mathrm{~S}_{4}$ subunit, and $\mathrm{Fe}(3-8)+\mathrm{S}(3,5-12)$ a $\mathrm{Fe}_{6} \mathrm{~S}_{9}$ subunit. These are bridged by $\mu_{3}-\mathrm{S}(3)$ from $\mathrm{Fe}_{6} \mathrm{~S}_{9}$ and by $\mu_{2}-\mathrm{S}(4)$. In thiolate clusters of these cores, $S(3,4)$ and $S(4)$ are analogous to terminal ligands in $\left[\mathrm{Fe}_{3} \mathrm{~S}_{4}(\mathrm{SR})_{4}\right]^{3-}$ and $\left[\mathrm{Fe}_{6} \mathrm{~S}_{9}(\mathrm{SR})_{2}\right]^{4-}$, respectively. The cyclic topography is effectuated by simultaneous edge- and corner-sharing of tetrahedra at $\mathrm{Fe}(4,7)$ which reroutes the fused rhombs from the nearly linear arrangement in the $\mathrm{Fe}_{3} \mathrm{~S}_{4}$ subunit $\left(\mathrm{Fe}\left(9^{\prime}\right)-\mathrm{Fe}(1)-\mathrm{Fe}(2)=164.0(1)^{\circ}\right)$. The pattern is repeated in the other half of the cluster. Bond distances and angles are not exceptional, as shown by the mean $\mathrm{Fe}-\mathrm{Fe}$ distance of 2.727 (32) $\AA$ and (with several exceptions) the trend of $\mathrm{Fe}-\mathrm{S}$ mean bond lengths $\mathrm{Fe}-\mu_{4} \mathrm{~S}(2.35 \AA)>\mathrm{Fe}-\mu_{3} \mathrm{~S}(2.29 \AA)>\mathrm{Fe}-\mu_{2} \mathrm{~S}(2.25 \AA)$. Although the cluster is mixed-valence $(14 \mathrm{Fe}(\mathrm{III})+4 \mathrm{Fe}(\mathrm{II}))$, there is no structural evidence for localized valence sites.

Encapsulated within the toroidal cavity, in a manner similar to a crown ether, are two sodium ions, $\mathrm{Na}\left(1,1^{\prime}\right)$. These are monosolvated and make four bonding contacts to sulfide over the range 2.871 (6) -2.910 (7) $\AA$. Two additional sodium atoms, $\mathrm{Na}\left(2,2^{\prime}\right)$, are situated above and below the cluster at $\mathrm{Na}-\mathrm{S}=$ 3.007 (9)-3.027 (8) $\AA$ and are trisolvated.

In addition to containing core units of three discrete $\mathrm{Fe}-\mathrm{S}$ clusters, $\left[\mathrm{Na}_{2} \mathrm{Fe}_{18} \mathrm{~S}_{30}\right]^{8-}$ also exhibits fragments corresponding to units in synthetic $\mathrm{Fe}-\mathrm{S}$ phases but with increased bridging modality. These include tetrahedral $\mathrm{FeS}_{4}$ sites as in $\mathrm{Na}_{5} \mathrm{FeS}_{4}$, ${ }^{13}$ edge-shared $\mathrm{FeS}_{4}$ tetrahedra as in $\mathrm{Na}_{3} \mathrm{FeS}_{3}$, ${ }^{14}$ and the ${ }_{\infty}^{1}\left[\mathrm{FeS}_{2}\right]$ chains of $\mathrm{M}^{1} \mathrm{FeS}_{2}{ }^{15}$ and $\mathrm{Na}_{3} \mathrm{Fe}_{2} \mathrm{~S}_{4}{ }^{16}$ Edge- and corner-sharing are also found in $\mathrm{Ba}_{7} \mathrm{Fe}_{6} \mathrm{~S}_{14}$, ${ }^{17}$ with the former building $\mathrm{Fe}_{3} \mathrm{~S}_{6} \mathrm{~S}_{2 / 2}$ clusters which are linked in chains by the latter interaction. In [ $\left.\mathrm{Na}_{2} \mathrm{Fe}_{18} \mathrm{~S}_{30}\right]^{8-}$, corner-shared atoms $\mathrm{S}(3,5,8,10,11)$ are part of incomplete cubane $\mathrm{Fe}_{3} \mathrm{~S}_{4}$ subunits (e.g., $\mathrm{Fe}(3-5) \mathrm{S}(3,5,6,8)$ ) reminiscent of the $\mathrm{Fe}_{3} \mathrm{Se}_{4}$ units in $\mathrm{Ba}_{3} \mathrm{Fe}_{3} \mathrm{Se}_{7}$. ${ }^{18}$

It is the combination of tetrahedral Fe stereochemistry and the feasibility of $\mu_{2,3,4^{-}} \mathrm{S}$ bridging modes that permits the multiple connectivity patterns of $\mathrm{Fe}_{2} \mathrm{~S}_{2}$ rhombs evident in nine stable $\mathrm{Fe}-\mathrm{S}$
(12) Under $C_{i}$ symmetry, the independent dimensions of bonded atoms are $12 \mathrm{Fe}-\mathrm{Fe}$ and $36 \mathrm{Fe}-\mathrm{S}$ distances and $28 \mathrm{Fe}-\mathrm{S}-\mathrm{Fe}$ and $54 \mathrm{~S}-\mathrm{Fe}-\mathrm{S}$ angles. Under idealized $C_{2 h}$ symmetry, where the $C_{2}$ axis contains $\mathrm{Fe}\left(1,1^{\prime}\right)$ and the mirror plane contains $\mathbf{S}\left(7,7^{\prime}, 8,8^{\prime}, 9,9^{\prime}\right)$, the number of independent parameters is reduced by one-half.
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cluster core structures. ${ }^{19} \quad\left[\mathrm{Na}_{2} \mathrm{Fe}_{18} \mathrm{~S}_{30}\right]^{8-}$ 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 $\mathrm{Na}^{+}$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 ( $\lambda_{\text {max }}\left(\epsilon_{\mathrm{M}}\right) 300$ ( 81100 ), 320 (sh), 396 ( 76400 ), 520 (sh), 600 (sh, 32700 ) 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 $\left[\mathrm{Na}_{2} \mathrm{Fe}_{18} \mathrm{~S}_{30}\right]^{8-}$ will be the subjects of future reports.

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Supplementary Material Available: Table of atom positional parameters for ( $n$ - $\left.\mathrm{Pr}_{4} \mathrm{~N}\right)_{6} \mathrm{Na}_{4}\left[\mathrm{Fe}_{18} \mathrm{~S}_{30}\right] \cdot 14 \mathrm{MeCN}$ (2 pages). Ordering information is given on any current masthead page.
(19) This statement excludes organometallic clusters; cluster structural types are illustrated elsewhere. ${ }^{8 \mathrm{c}}$ The largest discrete cyclic assembly based on planar metal units is $\mathrm{Ni}_{8}\left(\mathrm{SCH}_{2} \mathrm{COOEt}\right)_{16}$ : Dance, I. G.; Scudder, M. L.; Secomb, R. Inorg. Chem. 1985, 24, 1201
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## Heterobimetallic Catalysts for the Oxidation of Alcohols: $\left[\mathrm{Os}(\mathrm{N}) \mathrm{R}_{\mathbf{2}}\left(\mathrm{CrO}_{4}\right)\right]^{-}\left(\mathrm{R}=\mathrm{CH}_{\mathbf{3}}, \mathrm{CH}_{\mathbf{2}} \mathrm{SiMe}_{\mathbf{3}}\right)$

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Chromate salts and other chromium(VI) oxides have been widely used as oxidizing agents for a variety of substrates ${ }^{1}$ including alcohols. ${ }^{2}$ These oxidants are frequently used in large excess ${ }^{3}$ 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

[^2]Table I. Alcohol Oxidation Catalyzed by $\left[\mathrm{NBu}_{4}\right]\left[\mathrm{Os}(\mathrm{N})\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}\left(\mathrm{CrO}_{4}\right)\right.$

${ }^{a}$ The reactions were run in air, $5 \mathrm{~mol} \%$ catalyst, $\mathrm{CH}_{3} \mathrm{CN}, 70^{\circ} \mathrm{C}, 72$ h. ${ }^{b}$ Conversion to aldehyde/ketone was measured by GLC and ${ }^{1} \mathrm{H}$ NMR. No other organic products were formed. (Turnover number $=$ mol product $/ \mathrm{mol}$ catalyst). ${ }^{\text {c }}$ The reaction was run as above with 10 $\mathrm{mol} \% \mathrm{Cu}\left(\mathrm{O}_{2} \mathrm{CCH}_{3}\right)_{2}$ 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 $\mathrm{CrO}_{4}{ }^{2-}$ 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-[ $\left.\mathrm{NBu}_{4}\right]\left[\mathrm{Os}(\mathrm{N})\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2^{-}}\right.$ $\left.\left(\mathrm{CrO}_{4}\right)\right]$ (1) and $c i s-\left[\mathrm{PPh}_{4}\right]\left[\mathrm{Os}(\mathrm{N}) \mathrm{Me}_{2}\left(\mathrm{CrO}_{4}\right)\right]$ (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 $\left[\mathrm{NBu}_{4}{ }_{4}\right]\left[\mathrm{Os}(\mathrm{N})\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$ or $\left[\mathrm{PPh}_{4}\right]\left[\mathrm{Os}(\mathrm{N})\left(\mathrm{CH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$ with silver chromate in methylene chloride gave silver chloride and $\mathbf{1}$ or 2 , respectively. 9.10 The
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(9) $\left[\mathrm{NBu}^{\mathrm{n}}{ }_{4}\right]\left[\mathrm{Os}(\mathrm{N})\left(\mathrm{CH}_{2} \mathrm{SiCH}_{3}\right)_{2}\left(\mathrm{CrO}_{4}\right)\right]:$ IR $\left(\mathrm{KBr}\right.$, pellet, $\left.\mathrm{cm}^{-1}\right) 1111 \mathrm{~s}$ ( $\mathrm{Os}-\mathrm{N}$ ), 948 vs ( $\mathrm{Cr}-\mathrm{O}$ ), 928 vs ( $\mathrm{Cr}-\mathrm{O}$ ); ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{CD}_{2} \mathrm{Cl}_{2}, 500 \mathrm{MHz}, 293$ K) $\delta 3.18\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 2.08\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OsCH}_{2} \mathrm{SiMe}_{3}\right), 1.63(\mathrm{~m}, 4 \mathrm{H}$ $\left.\mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.43\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.02(\mathrm{t}, 6 \mathrm{H}$, $\left.\mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.09\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{OsCH}_{2} \mathrm{SiCH}_{3}\right) ;{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right.$ $500 \mathrm{MHz}, 293 \mathrm{~K}) \delta 59.27\left(\mathrm{NCH}_{2}\right), 24.25\left(\mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 20.12$ $\left(\mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 13.78\left(\mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 5.59\left(\mathrm{OsCH}_{2} \mathrm{SiMe}_{3}\right), 0.81$ $\left(\mathrm{OsCH}_{2} \mathrm{SiCH}_{3}\right)$. Anal. Calcd for $\mathrm{OsCrN}_{2} \mathrm{Si}_{2} \mathrm{O}_{4} \mathrm{C}_{24} \mathrm{H}_{58}$ : $\mathrm{C}, 39.11 ; \mathrm{H}, 7.93$; N, 3.80. Found: C, 39.07 ; H, 8.02; N. 3.80 .
(10) cis- $\left[\mathrm{PPh}_{4}\right]\left[\mathrm{Os}(\mathrm{N}) \mathrm{Me}_{2}\left(\mathrm{CrO}_{4}\right)\right]:$ IR $\left(\mathrm{KBr}\right.$, pellet, $\left.\mathrm{cm}^{-1}\right) 1109 \mathrm{~s}(\mathrm{Os}-\mathrm{N})$, 956 vs ( $\mathrm{Cr}-\mathrm{O}$ ), 922 vs ( $\mathrm{Cr}-\mathrm{O}$ ), 795 m ( $\mathrm{Cr}-\mathrm{O}$ ); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right.$, $293 \mathrm{~K}) \delta 2.27\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OsCH}_{3}\right), 8.0-7.5(\mathrm{~m}, 10 \mathrm{H}, \mathrm{PPh})$. Anal. Calcd for $\mathrm{OsCrNPO}_{4} \mathrm{C}_{26} \mathrm{H}_{26}: \mathrm{C}, 45.28 ; \mathrm{H}, 3.80 ; \mathrm{N}, 2.03$. Found: $\mathrm{C}, 45.14 ; \mathrm{H}, 3.84$; N, 1.97.


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[^1]:    (11) Experimental. All reactions and manipulations were performed under anaerobic conditions. Diffraction data were collected on a Nicolet P3F diffractometer at $20^{\circ} \mathrm{C}$ with use of graphite-monochromatized Mo $\mathrm{K} \alpha$ radiation. An empirical absorption correction was applied. Crystal parameters are $a=$ 16.286 (8) $\AA, b=16.718$ (8) $\AA, c=17.902$ (9) $\AA, \alpha=115.28$ (3) $)^{\circ}, \beta=91.07$ (4) ${ }^{\circ}, \gamma=101.64(4)^{\circ}, V=4287$ (3) $\AA^{3}$, and $Z=1$. From 17179 total reflections ( $\pm h, \pm k,+l$ ), the structure was solved with 6102 unique data ( $3^{\circ}$ $\leq 2 \theta \leq 50^{\circ}, I \geq 3 \sigma(I)$. All Fe and S atoms were located by direct methods (MULTAN) and all other non-hydrogen atoms by Fourier techniques (CRYSTALS). Isotropic refinement converged at $R=11.0 \%$. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at calculated positions in the final stages of refinement. Anisotropic refinement converged at $R\left(R_{w}\right)=6.47(8.30) \%$.

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