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 nm, trienals 9/14 at 437/459 nm, dienals 10/15 at 489/446 nm, and monoenals 11/16 at 340/354 nm. These aldehydes are linked to the photoreceptor via a $C=N^+H$ 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 shifts⁶ that one observes between the trienals and dienals, e.g., 2370 cm⁻¹ in 9 versus 11 000 cm⁻¹ in 10, suggests that a negative charge may be near the terminus of the conjugated system $-C_{(11)} = C_{(12)} - C_{(13)} = C_{(14)} - C_{(15)} = NH^+$, near C-10 or 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 16 (354 nm); this together with its red shift compared to hexanal in solution shows hexanal is also bound through $C = N^+H$.

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 (C=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 C=N+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

(9) (a) Honig, B.; Dinur, U.; Nakanishi, K.; Balogh-Nair, V.; Gawinowicz, M. A.; Arnaboldi, M.; Motto, M. G. J. Am. Chem. Soc. 1979, 101, 7084–7086. These earlier studies used 9-cis- rather than 11-cis-dihydroretinals

7084-7086. These earlier studies used 9-cis-rather than 11-cis-ohinydroretinals due to synthetic ease. (b) For 11-cis series, see: Koutalos, Y.; Ebrey, T. G.; Tsuda, M.; Park, M.-H.; Lien, T.; Odashima, K.; Shimizu, N.; Derguini, F.; (10) (a) Hubbard, R.; Kropf, A. Proc. Natl. Sci. U.S.A. 1958, 44, 130-139. (b) Akita, H.; Tanis, S. P.; Adams, M.; Balogh-Nair, V.; Nakanishi, K. J. Am. Chem. Soc. 1980, 102, 6370-6372. (c) Gawinowincz, M. A.; Balogh-Nair, V.; Sabol, J. S.; Nakanishi, K. J. Am. Chem. Soc. 1977, 99, 7720-7721. (d) Shichi, H. Biochemistry of Vision; Academic Press: New York. 1983 York, 1983.

(12) (a) Findlay, J. B. C.; Pappin, D. J. C. Biochem. J. 1986, 238, 625-642. (b) Findlay, J. B. C. Photobiochem. Photobiophys. 1986, 13, 213-228.

(13) Fang, J.-M.; Carriker, J. D.; Balogh-Nair, V.; Nakanishi, K. J. Am. Chem. Soc. 1983, 105, 5162-5164.

(14) Kolling, E.; Gartner, D.; Oesterhelt, D.; Ernst, L. Angew. Chem., Int. Ed. Engl. 1984, 23, 81-82.
 (15) Akhtar, M.; Jallo, L.; Johnson, A. H. Chem. Commun. 1982, 44-46.
 (16) Croteau, A.; Termini, J. Tetrahedron Lett. 1983, 24, 2481-2484.
 (17) Descu, D.; Chur, M., Lin, P. S. H. Bkrokeker, Photokici, 1981, 23

(17) Denny, M.; Chun, M.; Liu, R. S. H. Photochem. Photobiol. 1981, 33, 267-269

(18) M.-Szeweykowska, M.; Pardoen, J. A.; Dobbelstein, D.; Van Am-(19) M.-Szeweykowska, M., Fardoen, J. A., Doboestein, D., Van Antsterdam, L. J. P.; Lugtenburg, J. Eur. J. Biochem. 1984, 140, 173–176.
(19) Jayathirtha Rao, V.; Zingoni, J. P.; Crouch, R.; Denny, M.; Liu, R. S. H. Photochem. Photobiol. 1985, 41, 171–174.
(20) Corey, E. J.; Enders, D.; Bock, M. G. Tetrahedron Lett. 1976, 7–10.

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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[Na₂Fe₁₈S₃₀]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 correst $[Fe_2S_2]^{2+,2-4}$ linear $[Fe_3S_4]^{1+,4}$ cubic $[Fe_4S_4]^{2+,1+,1,2,5}$ prismatic $[Fe_6S_6]^{3+,2+,6}$ and $[Fe_6S_9]^{2-4,7}$ 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 $[Fe_6S_6]^{2+,1+,8}$ stellated octahedral $[Fe_6S_8]^{2+,1+,9}$ and monocapped prismatic $[Fe_7S_6]^{3+10}$ 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 FeCl₃ in 70 mL of methanol at 5 °C with a solution of 27 mmol of Na-[PhNC(O)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 °C. A slurry of 12 mmol of Li₂S in 70 mL of methanol was slowly added, the reaction mixture was filtered after 1 h, and 9.0 mmol of $(n-Pr_4N)Br$ 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

(2) Berg, J. M., Holli, K. H. In *Iron-Supar Proteins*, Spiro, T. G., Ed., Interscience: New York, 1982; Chapter 1.
 (3) (a) Reynolds, J. G.; Holm, R. H. *Inorg. Chem.* 1980, *19*, 3257. (b) Cleland, W. R., Jr.; Averill, B. A. *Inorg. Chem.* 1984, *23*, 4192. (c) Han, S.; Czernuszewicz, R. S.; Spiro, T. G. *Inorg. Chem.* 1986, *25*, 2276.

(4) Hagen, K. S.; Watson, A. D.; Holm, R. H. J. Am. Chem. Soc. 1983, 105, 3905.

(5) (a) Christou, G.; Garner, C. D. J. Chem. Soc., Dalton Trans. 1979,
(5) (a) Christou, G.; Garner, C. D. J. Chem. Soc., Dalton Trans. 1979,
1033. (b) Hagen, K. S.; Watson, A. D.; Holm, R. H. Inorg. Chem. 1984, 23,
2984. (c) Saak, W.; Pohl, S. Z. Naturforsch. 1985, 408, 1105. (d) Müller,
A.; Schladerbeck, N.; Bögge, H. Chimia 1985, 39, 24. (e) Rutchik, S.; Kim, S.; Walters, M. A. *Inorg. Chem.* 1988, 27, 1515.
(6) (a) Coucouvanis, D.; Kanatzidis, M. G.; Dunham, W. R.; Hagen, W.

R. J. Am. Chem. Soc. 1984, 106, 7998. (b) Kanatzidis, M. G.; Hagen, W. R.; Dunham, W. R.; Lester, R. K.; Coucouvanis, D. J. Am. Chem. Soc. 1985, 107, 953. (c) Kanatzidis, M. G.; Salifoglou, A.; Coucouvanis, D. Inorg. Chem. 1986, 25, 2460.

(7) (a) Christou, G.; Sabat, M.; Ibers, J. A.; Holm, R. H. Inorg. Chem. 1982, 21, 3518. (b) Strasdeit, H.; Krebs, H.; Henkel, G. Inorg. Chem. 1984, 23, 1816

(8) (a) Snyder, B. S.; Reynolds, M. S.; Noda, I.; Holm, R. H. Inorg. Chem (a) Snyder, B. S.; Reynolds, M. S.; Noda, I.; Holm, R. H. Inorg. Chem.
1988, 27, 595. (b) Snyder, B. S.; Holm, R. H. Inorg. Chem. 1988, 27, 2339.
(c) Reynolds, M. S.; Holm, R. H. Inorg. Chem., submitted for publication.
(d) Snyder, B. S.; Holm, R. H., unpublished results.
(9) (a) Agresti, A.; Bacci, M.; Cecconi, F.; Ghilardi, C. A. Inorg. Chem.
1985, 24, 689. (b) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.;
Zanello, P. J. Chem. Soc., Dalton Trans. 1987, 831.
(10) Noda, I.; Snyder, B. S.; Holm, R. H. Inorg. Chem. 1986, 25, 3851.

0002-7863/88/1510-6589\$01.50/0 © 1988 American Chemical Society

^{(8) (}a) Liu, R. S. H.; Asato, A. E. Tetrahedron 1984, 40, 1931-1969. (b) Chromophores that neither restored phototaxis nor affected incorporation of *trans*-retinal include methyl ketones, e.g., β -ionone and the C₁₈ ketone (13-one in 1), and aldehydes that carry a ring 5-6 carbons removed from C=N⁺H,

^{(1) (}a) Herskovitz, T.; Averill, B. A.; Holm, R. H.; Ibers, J. A.; Phillips, W. D.; Weiher, J. F. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 2437. (b) Averill, B. A.; Herskovitz, T.; Holm, R. H.; Ibers, J. A. J. Am. Chem. Soc. **1973**, *95*, 3523.

⁽²⁾ Berg, J. M.; Holm, R. H. In Iron-Sulfur Proteins; Spiro, T. G., Ed.;

S(7



S(1)



Figure 1. Structure of [Na2Fe18S30]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° from the upper view revealing thickness of the toroidal ring and noncluster ions Na(2,2'). Distance (Å) and angle (deg) ranges are collected under idealized C_{2h} symmetry: Fe(1)-Fe(2), 2.703-2.717; Fe(2)-Fe(3), 2.722-2.724; Fe-(3)-Fe(4), 2.701-2.725; Fe(3)-Fe(5), 2.672-2.702; Fe(4)-Fe(5), 2.738-2.783; Fe(4)-Fe(7), 2.761-2.771; Fe(1)-S(1), 2.234-2.235; Fe-(1)-S(2), 2.259-2.267; Fe(2)-S(1), 2.207-2.210; Fe(2)-S(2), 2.227-2.231; Fe(2)-S(3), 2.361-2.385; Fe(2)-S(4), 2.227-2.258; Fe(3)-S(3), 2.296-2.310; Fe(3)-S(4), 2.174-2.206; Fe(3)-S(5), 2.265-2.293; Fe-(3)-S(6), 2.207-2.216; Fe(4)-S(3), 2.287; Fe(4)-S(5), 2.273-2.303; Fe(4)-S(8), 2.347-2.355; Fe(4)-S(9), 2.240-2.245; Fe(5)-S(5), 2.299-2.318; Fe(5)-S(6), 2.216-2.230; Fe(5)-S(7), 2.202-2.210; Fe(5)-S(8), 2.345-2.645; Na(1)-S(9), 2.871-2.907; Na(1)-S(10), 3.245; Na(1)-S-105.1-105.4; S(2)-Fe(2)-S(3) 107.2-107.5; S(3)-Fe(2)-S(4) 100.4-101.0; S(3)-Fe(3)-S(4) 104.1-105.0; S(3)-Fe(3)-S(5) 103.9-105.4; S(4)-Fe(3)-S(6) 116.5-121.3; S(5)-Fe(3)-S(6) 102.4-103.8; S(5)-Fe-(4)-S(8) 104.4-105.4; S(8)-Fe(4)-S(9) 103.4-103.5; S(5)-Fe(5)-S(8) 103.6-104.6; S(7)-Fe(5)-S(8) 102.4-103.3; S(8)-Fe(5)-S(8') 112.4. Esd's: 0.003-0.005 (Fe-Fe/S), 0.006-0.009 (Na-S) Fe-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 °C.11 Thus far,

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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 (n-Pr₄N)₆Na₄[Fe₁₈S₃₀]·14MeCN.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 $[Na_2Fe_{18}S_{30}]^{8-}$, is depicted in two views in Figure 1. The $Fe_{18}S_{30}$ portion is a cyclic cluster of toroidal shape and is the largest Fe-S cluster yet prepared. The cluster has imposed C_i symmetry but closely approaches C_{2h} symmetry, this being broken mainly by the positions of the two 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 (S(1)--S(1')) × 15.975 (S(7)--S(7')) Å. The 18 Fe atoms are nearly coplanar, with the largest deviation from the plane being ± 0.154 Å by Fe(4); the majority are <0.11 Å. The maximum thickness of the toroid is ca. 3.3 Å (twice the vertical displacement of S(5) from the Fe₁₈ mean plane).

As all other Fe–S clusters, $[Na_2Fe_{18}S_{30}]^{8-}$ is constructed by the fusion of nonplanar Fe2S2 rhombs. Here 24 rhombs are connected by a combination of edge- and corner-sharing such that there are 20 μ_2 -S, eight μ_3 -S, and two μ_4 -S atoms, excluding interactions with Na⁺. Every FeS₄ unit is tetrahedral. The structure is recognizable as the conjoint of $2Fe_3S_4 + 2Fe_6S_9$ cores, as found in $[Fe_3S_4(SR)_4]^{3-4}$ and $[Fe_6S_9(SR)_2]^{4-4.7}$ respectively, supported by four additional μ_2 -S bridges. Of independent portions, tetrahedra centered at Fe(9',1,2) and joined by parallel edge-sharing constitute a Fe₃S₄ subunit, and Fe(3-8) + S(3,5-12) a Fe₆S₉ subunit. These are bridged by μ_3 -S(3) from Fe₆S₉ and by μ_2 -S(4). In thiolate clusters of these cores, S(3,4) and S(4) are analogous to terminal ligands in [Fe₃S₄(SR)₄]³⁻ and [Fe₆S₉(SR)₂]⁴⁻, respectively. The cyclic topography is effectuated by simultaneous edge- and corner-sharing of tetrahedra at Fe(4,7) which reroutes the fused rhombs from the nearly linear arrangement in the Fe₃S₄ subunit $(Fe(9')-Fe(1)-Fe(2) = 164.0 (1)^{\circ})$. The pattern is repeated in the other half of the cluster. Bond distances and angles are not exceptional, as shown by the mean Fe-Fe distance of 2.727 (32) Å and (with several exceptions) the trend of Fe-S mean bond lengths Fe- μ_4 S (2.35 Å) > Fe- μ_3 S (2.29 Å) > Fe- μ_2 S (2.25 Å). Although the cluster is mixed-valence (14Fe(III) + 4Fe(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, Na(1,1'). These are monosolvated and make four bonding contacts to sulfide over the range 2.871 (6)-2.910 (7) Å. Two additional sodium atoms, Na(2,2'), are situated above and below the cluster at Na-S =3.007 (9)-3.027 (8) Å and are trisolvated.

In addition to containing core units of three discrete Fe-S clusters, $[Na_2Fe_{18}S_{30}]^{8-}$ also exhibits fragments corresponding to units in synthetic Fe-S phases but with increased bridging modality. These include tetrahedral FeS₄ sites as in Na₅FeS₄,¹³ edge-shared FeS₄ tetrahedra as in Na₃FeS₃,¹⁴ and the $\frac{1}{\omega}$ [FeS₂] chains of M¹FeS₂¹⁵ and Na₃Fe₂S₄,¹⁶ Edge- and corner-sharing are also found in Ba₇Fe₆S₁₄,¹⁷ with the former building Fe₃S₆S_{2/2} clusters which are linked in chains by the latter interaction. In [Na₂Fe₁₈S₃₀]⁸⁻, corner-shared atoms S(3,5,8,10,11) are part of incomplete cubane Fe₃S₄ subunits (e.g., Fe(3-5)S(3,5,6,8)) reminiscent of the Fe₃Se₄ units in Ba₃Fe₃Se₇.¹⁸

It is the combination of tetrahedral Fe stereochemistry and the feasibility of $\mu_{2,3,4}$ -S bridging modes that permits the multiple connectivity patterns of Fe2S2 rhombs evident in nine stable Fe-S

⁽¹¹⁾ Experimental. All reactions and manipulations were performed under anaerobic conditions. Diffraction data were collected on a Nicolet P3F diffractometer at 20 °C with use of graphite-monochromatized Mo Ka radiation. An empirical absorption correction was applied. Crystal parameters are a = 16.286 (8) Å, b = 16.718 (8) Å, c = 17.902 (9) Å, $\alpha = 115.28$ (3)°, $\beta = 91.07$ (4)°, $\gamma = 101.64$ (4)°, V = 4287 (3) Å³, and Z = 1. From 17 179 total reflections ($\pm h, \pm k, +1$), the structure was solved with 6102 unique data (3° $\leq 2\theta \leq 50^\circ$, $I \geq 3\sigma(I)$). All Fe and S atoms were located by direct methods (MULTAN) and all other non-hydrogen atoms by Fourier techniques (CRYS-TALS). 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 $R(R_w) = 6.47 (8.30)\%$.

⁽¹²⁾ Under C_i symmetry, the independent dimensions of bonded atoms are 12 Fe-Fe and 36 Fe-S distances and 28 Fe-S-Fe and 54 S-Fe-S angles. Under idealized C_{2k} symmetry, where the C_2 axis contains Fe(1,1') and the mirror plane contains S(7,7',8,8',9,9'), the number of independent parameters is reduced by one-half.

 ⁽¹³⁾ Klepp, K. O.; Bronger, W. Z. Anorg. Allg. Chem. 1986, 532, 23.
 (14) Müller, P.; Bronger, W. Z. Naturforsch. 1979, 34B, 1264.

 ^{(15) (}a) Boon, J. W.; MacGillavry, C. H. Recl. Trav. Chim. Pays-Bas
 1942, 61, 910. (b) Bronger, W. Z. Anorg. Allg. Chem. 1968, 359, 225.
 (16) Klepp, K.; Boller, H. Monatsh. Chem. 1981, 112, 83.
 (17) Grey, I. E.; Hong, H.; Steinfink, H. Inorg. Chem. 1971, 10, 340.

⁽¹⁸⁾ Hong, H. Y.; Steinfink, H. J. Solid State Chem. 1972, 5, 93.

cluster core structures.¹⁹ $[Na_2Fe_{18}S_{30}]^{8-}$ 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 $[Na_2Fe_{18}S_{30}]^{8-}$ will be the subjects of future reports.

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Supplementary Material Available: Table of atom positional parameters for $(n-Pr_4N)_6Na_4[Fe_{18}S_{30}]$ ·14MeCN (2 pages). Ordering information is given on any current masthead page.

(22) Taylor, P.; Shoesmith, D. W. Can. J. Chem. 1978, 56, 2797. Solutions of $[Na_2Fe_{18}S_{30}]^{8-}$ are brown.

Heterobimetallic Catalysts for the Oxidation of Alcohols: $[Os(N)R_2(CrO_4)]^-$ (R = CH₃, CH₂SiMe₃)

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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

(2) (a) Piancatelli, G.; Scettri, A.; D'Auria, M. Synthesis 1982, 245-258.
(b) Collins, J. C.; Hess, W. W.; Frank, F. J. Tetrahedron Lett. 1968, 3363-3366.

(3) Sharpless, K. B.; Akashi, K. J. Am. Chem. Soc. 1975, 97, 5927-5928.
(4) (a) Corey, E. J.; Barette, E.-P.; Magriotis, P. A. Tetrahedron Lett. 1985, 26, 5855-5858.
(b) Muzart, J. Tetrahedron Lett. 1986, 27, 3139-3142.
(c) Kanemoto, S.; Oshima, K.; Matsubara, S.; Takai, K.; Nozaki, H. Tetrahedron Lett. 1983, 24, 2185-2188.





^aThe reactions were run in air, 5 mol% catalyst, CH₃CN, 70 °C, 72 h. ^bConversion to aldehyde/ketone was measured by GLC and ¹H NMR. No other organic products were formed. (Turnover number = mol product/mol catalyst). ^cThe reaction was run as above with 10 mol% Cu(O₂CCH₃)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-[NBuⁿ₄][Os(N)(CH₂SiMe₃)₂-(CrO₄)] (1) and cis-[PPh₄][Os(N)Me₂(CrO₄)] (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 $[NBu^{n}_{4}][Os(N)(CH_{2}SiMe_{3})_{2}Cl_{2}]$ or $[PPh_{4}][Os(N)(CH_{3})_{2}Cl_{2}]$ with silver chromate in methylene chloride gave silver chloride and 1 or 2, respectively.^{9.10} The

(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,

(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.

1988, 7, 928-933. (9) $[NBu^{n}_{4}][Os(N)(CH_{2}SiCH_{3})_{2}(CrO_{4})]$: IR (KBr, pellet, cm⁻¹) 1111 s (Os-N), 948 vs (Cr-O), 928 vs (Cr-O); ¹H NMR (CD₂Cl₂, 500 MHz, 293 K) δ 3.18 (m, 4 H, NCH₂), 2.08 (s, 2 H, OsCH₂SiMe₃), 1.63 (m, 4 H, NCH₂CH₂CH₂CH₃), 1.43 (m, 4 H, NCH₂CH₂CH₂CH₃), 1.02 (t, 6 H, NCH₂CH₂CH₂CH₃), 0.09 (s, 9 H, OsCH₂SiCH₃); ¹³C[¹H] NMR (CD₂Cl₂, 500 MHz, 293 K) δ 59.27 (NCH₂), 24.25 (NCH₂CH₂CH₂CH₃), 0.81 (NCH₂CH₂CH₂CH₃), 1.3.78 (NCH₂CH₂CH₂CH₃), 5.59 (OsCH₂SiMe₃), 0.81 (OsCH₂SiCH₃). Anal. Calcd for OsCrN₂Si₂O₄C₂₄H₅₈: C, 39.11; H, 7.93; N, 3.80. Found: C, 39.07; H, 8.02; N, 3.80.

(10) cis-[PPh₄][Os(N)Me₂(CrO₄)]: IR (KBr, pellet, cm⁻¹) 1109 s (Os-N), 956 vs (Cr-O), 922 vs (Cr-O), 795 m (Cr-O); ¹H NMR (CDCl₃, 300 MHz, 293 K) δ 2.27 (s, 3 H, OsCH₃), 8.0–7.5 (m, 10 H, PPh). Anal. Calcd for OsCrNPO₄C₂₆H₂₆: C, 45.28; H, 3.80; N, 2.03. Found: C, 45.14; H, 3.84; N, 1.97.

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⁽¹⁹⁾ This statement excludes organometallic clusters; cluster structural types are illustrated elsewhere.^{8c} The largest discrete cyclic assembly based on *planar* metal units is Ni₈(SCH₂COOEt)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) $[Cu_{12}S_{9}]^{4-}$: Betz, P.; Krebs, B.; Henkel, G. Angew. Chem., Int. Ed. Engl. **1984**, 23, 311. (b) $[Au_{12}S_{9}]^{4-}$: Marbach, G.; Strähle, J. Angew. Chem., Int. Ed. Engl. **1984**, 23, 715. (c) $[Au_{4}Te_{4}]^{4-}$ and $[KAu_{9}Te_{7}]^{4-}$: Haushalter, R. C. Angew. Chem., Int. Ed. Engl. **1985**, 24, 432.

⁽²¹⁾ Among metal halide clusters, $[Cu_4I_6]^{2-}$ and $[Cu_8I_{13}]^{5-}$ 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.

⁽¹⁾ For reviews, see: (a) Cainelli, G.; Cardillo, G. Chromium Oxidations in Organic Chemistry; Springer-Verlag: Berlin, 1984. (b) Wiberg, K. B. Oxidation in Organic Chemistry; Academic Press: 1965. (c) Muzart, J. Bull. Soc. Chim. Fr. **1986**, 65-77. (d) Sheldon, R. A.; Kochi, J. K. Metal Catalyzed Oxidations of Organic Compounds; Academic Press: New York, 1981; Chapter 6.

^{(5) (}a) Briggs, S. H. C. J. Chem. Soc. 1919, 67. (b) Genchev, MI. Natura (Plovdiv) 1971, 4, 63-66. (c) Casabo, J.; Ribas, J.; Coronas, J. M. J. Inorg. Nucl. Chem. 1974, 38, 886-887. (d) Sharma, C. L.; Sharma, S. J. Inorg. Nucl. Chem. 1977, 39, 1240-1241. (e) Mineely, P. J.; Scott, D. L. Aust. J. Chem. 1987, 40, 387-393.

⁽⁶⁾ A cyclopentadienylrhenium dichromate complex has also been prepared by W. A. Herrmann, personal communication.