Scheme II

a R=CH$_2$CH$_2$
b R=CMe$_2$

(from 10a(α,β) only)
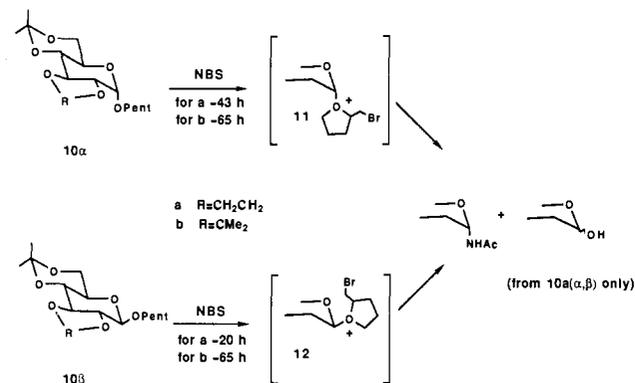
Ib), protonation of the glycosidic oxygen leads directly to the reactive intermediate **5**, which has the (presumed!) optimum geometry for cleavage leading to the cyclic oxocarbenium ion **6**. However, for the conjugate acid of the β-glycoside, **7**, a conformational change, **8** → **9**, is required in order to meet this antiperiplanar lone pair requirement.

The same geometric requirements should hold for the oxidative hydrolyses. Rationalization of the reaction (Scheme Ia) profits from the elegant studies of Bartlett[25] and subsequently Liotta, Maryanoff, and co-workers,[26] on the cyclization of γ-alkoxyalkenes, which established that formation of cyclic bromonium (**2**) and oxolanium (**3**) ions are reversible events. *Thus, it is reasonable to assume that, as with the protonated counterparts* **5** *and* **8** *or* **9**, *cleavage of the activated oxygen in* **3** *occurs in the rate-determining step.*[27]

Our test substrates were the tricyclic anomeric pair **10αa** and **10βa** which were prepared from 4-pentenyl glucopyranoside[6] by kinetic acetonation,[29] followed by reaction with 1,2-dichloroethane[30] under phase-transfer conditions.

These 6:6:6 trans–anti–trans systems (**10a**) are reminiscent of the steroidal substrates studied by Kirby and co-workers[20a] which, on the basis of molecular models, were judged to be "surprisingly easily converted, by a twist of ring B, into chair–twist-boat–chair conformation[s]..." In the hope of providing a more discriminating assessment, MM2 calculations have been applied to evaluate the strain energies of the relevant conformers of the methylene analogues shown in Figure 1. The results confirm that for the unrestrained pyranosides, the twist-boat lies $\sim$5 kcal/mol below the half-chair. *However, for the 6:6:6 systems, the twist-boat, far from being a local minimum, lies 2.5 kcal above the half-chair.*

For an even more stringent test, the bis-isopropylidene derivatives **10αb** and **10βb** were prepared according to the method of Debost and co-workers.[29] *Again, although molecular models suggest that the twist-boat is attainable (albeit with much more effort), the MM2 evaluation shows that it lies even higher than the corresponding half-chair conformer by 6 kcal.*

For an unrestrained pyranoside, such as 2-methoxypyran, where the twist-boat is a local minimum (Figure 1), it can be argued that β anomers react via that conformation in accordance with ALPH. However, for the restrained molecules with no such local minima, reaction of the β anomers, as with their α counterparts,

must proceed via the chair, and in accordance with ALPH, the α should be significantly more reactive.

The data in Scheme II show that the equatorial anomers, **10β** (**a** and **b**), reacted at comparable rates to their axial counterparts **10α** (**a** and **b**), although the latter should afford oxolanium ions **11**, in which a lone pair is presented to the leaving group, while for the former, a comparable alignment is energetically prohibited (Figure 1).

Since ALPH is not a viable option for the hydrolyses of **10β** an alternative rationalization is required. The chair-to-boat pathway **8** → **9**, as indicated by the Newmann projections I and III (Scheme Id), is seen to traverse a syn periplanar (eclipsed) rotamer, II, which is of intermediate energy. Rotamer II corresponds to a half-chair (or sofa) having (approximately) the same conformation as the cyclic ion **6**. It is therefore reasonable to postulate that II is the reactive conformation. *In this regard, it is instructive to note from Figure 1 that the energy required to attain the half-chair forms is virtually the same for all these substrates. Thus, the penalties of the restraining rings are inflicted subsequently, en route from the half-chair to the twist boat.*

The above results are reminiscent of syn elimination in amidine hydrolysis advocated by Perrin and Nunez[31] and to the principle of least nuclear motion advanced by Sinnott as an alternative to ALPH.[17] Our studies in this important area are continuing and will be reported in due course.

(31) Perrin, C. L.; Nunez, O. *J. Am. Chem. Soc.* **1986**, *108*, 5997.

Synthesis and Structure of a Capped Square-Pyramidal Five-Metal Oxo Cluster, [Fe$_2$Ru$_3$(CO)$_{14}$(μ_4-O)]$^{2-}$

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Main-group heteroatoms in low oxidation state organometallic cluster compounds are generally found in either interior positions or on the periphery as part of the cluster skeleton.[2] Carbide, nitride, and some phosphide clusters are known in which the C, N, or P occupies an interior position in a low oxidation state cluster. Many organometallic clusters containing sulfur have been prepared, and the sulfur atom is found as a peripheral component of these clusters.

Organometallic clusters containing the oxo ligand are much less numerous than organometallic carbides,[3] nitrides,[4] and sulfides.[2] Unlike C, N, or S, O has not been found in high coordination environments.[5] Until recently the highest coordination number of oxygen in an organometallic cluster was three.[6] Recently we found four-coordinate oxygen in a metal butterfly cluster.[7] We now describe the synthesis and characterization of

(25) Rychnovsky, S. D.; Bartlett, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3963.

(26) Reitz, A. b.; Nortey, S. O.; Maryanoff, B. E.; Liotta, B.; Monahan, III, R. *J. Org. Chem.* **1987**, *52*, 4191.

(27) Valuable evidence relating to these intermediates (and against a synchronous process) comes from the following observations: (i) bromonium ion **2** can be trapped as the bromohydrin by using very wet solvent;[5] (ii) the rates of oxidative[8] and acidic[28] hydrolyses slow down dramatically when electron-withdrawing groups, such as esters, are present at C-2, suggesting common rate-determining steps; (iii) even with sluggish substrates, the starting pentenyl glycosides are recovered with the olefinic residue intact.

(28) See, for example: Fraser-Reid, B.; Boctor, B. *Can. J. Chem.* **1969**, *47*, 393.

(29) Debost, J.-L.; Gelas, J.; Horton, D.; Mols, O. *Carbohydr. Res.* **1984**, *125*, 329.

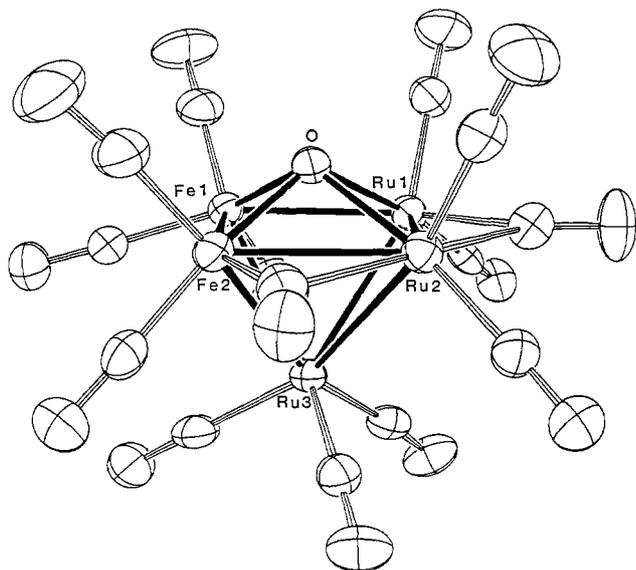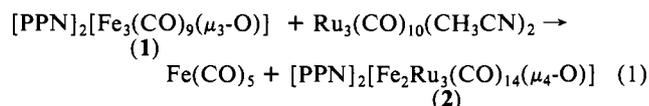(30) Cesare, P. D.; Gross, B. *Carbohydr. Res.* **1976**, *48*, 271.

(1) Current address: Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599–3290.

(2) Whitmire, K. H. *J. Coord. Chem. B* **1988**, *17*, 95.

(3) (a) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. (b) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203.

(4) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41.

(5) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.

(6) (a) Colombie, A.; Bonnet, J.-J.; Fompeyrine, P.; Lavigne, G.; Sunshine, S. *Organometallics* **1986**, *5*, 1154. (b) Gibson, C. P.; Huang, J.-S.; Dahl, L. F. *Organometallics* **1986**, *5*, 1676. (c) Bertolucci, A.; Freni, M.; Romiti, P.; Ciani, G.; Sironi, A.; Albano, V. G. *J. Organomet. Chem.* **1976**, *113*, C61. (d) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1983**, 246. (e) Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3763. (f) Ceriotti, A.; Resconi, L.; Demartin, R.; Longoni, G.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1983**, *249*, C35. (g) Gibson, C. P.; Rae, A. D.; Tomchick, D. R.; Dahl, L. F. *J. Organomet. Chem.* **1988**, *340*, C23.

(7) Schauer, C. K.; Shriver, D. F. *Angew. Chem.* **1987**, *99*, 275; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 255.

Communications to the Editor

J. Am. Chem. Soc., Vol. 111, No. 19, 1989 7663

Figure 1. Structure of the anion $[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]^{2-}$ in **3**, showing 50% probability ellipsoids.

a five-metal oxo cluster, $[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]^{2-}$. The five-metal environment presents the possibility of a five-coordinate heteroatom which is situated nearly in the square-basal plane, I, or a four-coordinate heteroatom capping the square base, II.
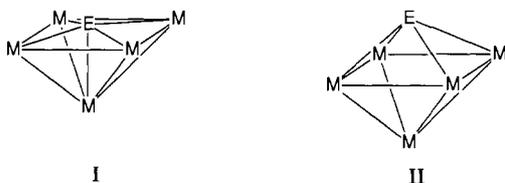
In an attempt to prepare a hexanuclear oxo cluster, PPN_2-$[Fe_3(CO)_9(\mu_3\text{-}O)]$ (PPN^+ = bis(triphenylphosphine)iminium cation), $\mathbf{1}^{6f}$ was mixed with 1 equiv of the labile cluster, $Ru_3(CO)_{10}(CH_3CN)_2^8$ in acetone at room temperature to generate instead a five-metal species $[PPN]_2[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]$, **2**, while liberating $Fe(CO)_5$, eq 1.

$$[PPN]_2[Fe_3(CO)_9(\mu_3\text{-}O)] \ + \ Ru_3(CO)_{10}(CH_3CN)_2 \rightarrow$$
$$(\mathbf{1})$$
$$Fe(CO)_5 + [PPN]_2[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)] \quad (1)$$
$$(\mathbf{2})$$

Brown crystals of **2** were obtained from CH_2Cl_2/Et_2O in 64% yield.[9] As these crystals prove unsuitable for crystallographic study, a metathesis reaction was carried out between **2** and excess $[BzMe_3N][BPh_4]$ in THF. Crystallization with THF/iPr_2O yields brown X-ray quality crystals of $[BzMe_3N]_2[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]\cdot[BzMe_3N][BPh_4]\cdot THF$, **3**.[10]

The structure of **3** was determined by single-crystal X-ray diffraction at $-120\ ^\circ C$.[11] The metal atoms in the cluster form a square pyramid, Figure 1, consisting of two iron atoms and two ruthenium atoms in the base and a third ruthenium atom at the apex of the pyramid. The $Fe(1)-Fe(2)$ bond distance of 2.509 (2) Å is shorter than the $Ru(1)-Ru(2)$ bond distance of 2.7117

(8) Å in the base of the M_5 pyramid of metal atoms.[12] The μ_4-O ligand caps the face of the "square" and extends away from the apical ruthenium with a distance 0.90 Å out of the four-metal plane. The apical ruthenium-to-oxygen (Ru(3)–O) distance of 2.994 Å is too long for significant bonding interaction. The oxygen ligand is closer to the two iron atoms (Fe(1)–O 1.957 (4) Å, Fe(2)–O 1.985 (5) Å versus Ru(1)–O 2.147 (4) Å, Ru(2)–O 2.126 (4) Å). The cluster has 12 terminal carbonyls with one bridging carbonyl between Ru(1) and Ru(2) in the square base and another bridging carbonyl between the basal Ru(2) and Fe(2) atoms.

When oxygen is considered to be a four-electron donor, the cluster valence electron count for $[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]^{2-}$ is 74, matching that expected for a square-pyramidal metal cluster.[13] A similar geometry is seen with the 74 electron clusters M_5-$(CO)_{15}(\mu_4\text{-}S)$ (M = Os,[14] Ru^{15}). As with the $M_5(CO)_{15}(\mu_4\text{-}S)$ clusters, $[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]^{2-}$ consists of a five-metal square pyramid with a capping heteroatom, and the capping ligand distance to the apical metal is too long to be considered bonding.

The oxo clusters in compounds **1** and **2** were characterized by ^{17}O NMR spectroscopy in acetone solution at room temperature on samples enriched with ^{17}O at the oxo ligand. Spectral peaks were referenced to the acetone oxygen resonance at δ = 569 ppm. As previously reported, the spectrum for **1** consists of two resonances: one for the ^{17}O enriched CO ligands (δ = 356 ppm) and the other for the μ_3-oxo ligand (δ = 107 ppm). The spectrum of **2** also consists of two resonances, but the ^{17}O enriched CO resonance is further down field (δ = 366 ppm), as is the μ_4-oxo resonance (δ = 156 ppm). For comparison, the μ_4-oxo resonance in the butterfly cluster $[PPN][Fe_3Mn(CO)_{12}(\mu_4\text{-}O)]$ is at δ = 93 ppm.[7]

Five-metal, 74-electron square-pyramidal clusters also exist with the μ_4-ligand as nitrogen or carbon and are similar to $[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]^{2-}$, except for the location and bonding of the heteroatom. Square-pyramidal clusters with oxygen or sulfur have a geometry in which the heteroatom is out of the four-metal plane and does not bond to the apical metal of the pyramid, II. However, square-pyramidal clusters with carbon or nitrogen have a geometry in which the ligand is only slightly displaced from the square array of metal atoms and is within bonding distance of the apical metal of the pyramid, I.

For example, the cluster $[Fe_5(CO)_{14}N]^{-16}$ has an apical Fe–N distance of 1.916 (8) Å, and this distance can be considered an iron–nitrogen bond. Similarly, the cluster $Fe_5(CO)_{15}C^{16}$ has a distance from the apical iron to the capping carbon of 1.96 (3) Å, another bonding interaction. Other organometallic clusters with carbide and nitride display similar separations of the heteroatom and the apical metal atom: $[Ru_5(CO)_{14}N]^-$, 2.14 (2) Å;[17] $Ru_5(CO)_{15}C$, 2.10–2.08 Å;[18] $Os_5(CO)_{15}C$, 2.06 Å;[19] $[Fe_4\text{-}Co(CO)_{14}C]^-$, 1.962 (5) Å;[20] and $[Fe_4Rh(CO)_{14}C]^-$, 1.980 (12) Å.[21]

The issue of interior versus peripheral position of C or S heteroatoms in M_5E clusters has been explored by extended Hückel molecular orbital calculations, and it was predicted that an organometallic M_5O cluster would have a peripheral O atom capping the square base, as observed in the present work.[22] In this

(8) Foulds, G. A.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *296*, 147.

(9) **2**: IR ν_{CO} (CH_2Cl_2) 2029 (vw), 1972 (vs), 1957 (vs), 1940 (ms), 1918 (m), 1808 (vw), 1761 (w) cm^{-1}.

(10) **3**: IR ν_{CO} (THF) 2029 (vw), 1972 (vs), 1956 (vs), 1924 (m), 1914 (m), 1824 (w), 1779 (w).

(11) $[BzMe_3N]_2[Fe_2Ru_3(CO)_{14}O]\cdot[BzMe_3N][BPh_4]\cdot THF$, M_r = 1641.03; orthorhombic, space group *Pbca* (No. 61); a = 18.179 (2) Å, b = 24.996 (3) Å, c = 31.754 (3) Å, V = 14429 (5) Å^3; Z = 8; D_{calcd} = 1.51 g cm^{-3}; μ(Mo Kα) = 10.7 cm^{-1}. The structure was solved by direct methods (SHELXS 86) and refined by using TEXSAN 4.0. Full-matrix least-squares refinement yielded $R(F)$ = 0.043 and $R_w(F)$ = 0.056 for 6532 reflections with $I > 3\sigma(I)$ measured on a CAD4 diffractometer up to 2θ = 45° at $-120\ ^\circ C$ (Mo Kα radiation, λ = 0.71069 Å).

(12) M–M bond distances, in Å: Ru1–Ru2 2.7117 (8), Ru1–Fe1 2.601 (1), Fe1–Fe2 2.509 (2), Fe2–Ru2 2.611 (1), Ru1–Ru3 2.8427 (9), Ru2–Ru3 2.8710 (8), Fe1–Ru3 2.735 (1), Fe2–Ru3 2.702 (1).

(13) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.

(14) Adams, R. D.; Horvath, I. T.; Segnuller, B. E.; Yang, L.-W.; *Organometallics* **1983**, *2*, 1301.

(15) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1988**, *7*, 503.

(16) Gourdon, A.; Jeannin, Y. *J. Organomet. Chem.* **1985**, *290*, 199.

(17) Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1985**, *4*, 45.

(18) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M.; McPartlin, M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 277.

(19) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 564.

(20) Hrljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* **1985**, *4*, 158.

(21) Tachikawa, M.; Sievert, A. C.; Muetterties, E. L.; Thompson, M. R.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1725.

(22) Halet, J.-F.; Saillard, J.-Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1986**, *5*, 139.

treatment a π-interaction between the heteroatom and the square metal array was identified as crucial for the heteroatom to lie in the plane of the four-metal base. Carbon and nitrogen atoms achieve this π-interaction because the p_z heteroatom energy is close to the metal atom d-orbital energies and dπ-pπ overlap is favorable. By contrast, the more electronegative sulfur and oxygen atoms have p-orbital energies well below those of the metals, which localizes an electron pair on the heteroatom. An unfavorable nonbonding interaction between the filled heteroatom p_z orbital and the filled metal d-π orbitals of the same symmetry is avoided by displacement of the heteroatom out of the basal plane of the cluster.

The μ_4 environment has been observed for oxygen on the low index faces of metals, c(2 × 2)O on Fe(100) being one example.[23] The present results indicate that the oxygen might take a capping position above the surface of this solid. In one report the interpretation of LEED data placed the oxygen atom 0.48 Å out of the Fe$_4$ plane,[24] and this agrees with low-energy ion scattering which places the oxygen 0.56 (5) Å out of the iron plane.[25] Thus the surface oxo ligand appears to be at a somewhat intermediate position and certainly not as far from the metal plane as observed in the present study of a cluster oxo complex.

Acknowledgment. This research was supported by the Department of Energy Grant No. DEFG02-ER13640.

Supplementary Material Available: Tables of crystal data, positional parameters, anisotropic thermal parameters, and bond distances and angles for [BzMe$_3$N]$_2$[Fe$_2$Ru$_3$(CO)$_{14}$(μ_4-O)]·[BzMe$_3$N][BPh$_4$]·THF (15 pages). Ordering information is given on any current masthead page.

(23) (a) Pignocco, A. J.; Pellissier, G. E. *J. Electrochem. Soc.* 1965, *112*, 1188. (b) Leygraf, C.; Ekelund, S. *Surf. Sci.* 1973, *40*, 609. (c) Simmons, G. W.; Dwyer, D. J. *Surf. Sci.* 1975, *48*, 373. (d) Bruker, C. F.; Rhodin, T. N. *Surf. Sci.* 1976, *57*, 523. (e) Bruker, C.; Rhodin, T. *J. Catal.* 1977, *47*, 214. (f) Brundle, C. R. *IBM J. Res. Develop.* 1978, *22*, 235. (g) Vink, T. J.; Gijzeman, O. C. J.; Geus, J. W. *Surf. Sci.* 1985, *150*, 14.
(24) Legg, K. O.; Jona, F.; Jepsen, D. W.; Marcus, P. M. *Phys. Rev. B.* 1977, *16*, 5271.
(25) van Zoest, J. M.; Fluit, J. M.; Vink, T. J.; van Hassel, B. A. *Surf. Sci.* 1987, *182*, 179.

Studies on the Molybdenum Cofactor. Determination of the Structure and Absolute Configuration of Form A

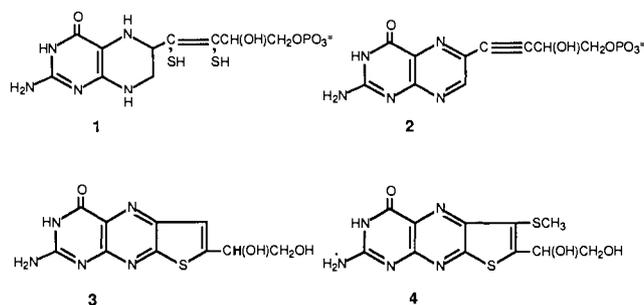Edward C. Taylor,* Partha S. Ray, and Ihab S. Darwish

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The molybdenum cofactor, which is present in all but one (nitrogenase) of the known molybdenum-containing enzymes, is a complex of Mo^{VI} with a unique sulfur-containing reduced pterin (molybdopterin) for which structure **1** has been suggested.[1,2] Several oxidative degradation products of molybdopterin have been isolated. Form A, derived from molybdopterin by oxidation of the pyrazine ring and removal of both sulfur atoms, has been assigned structure **2** on the basis of spectroscopic evidence, while Form B, which possesses a fused thiophene ring, retains one of

(1) Johnson, J. L.; Rajagopalan, K. V. *Proc. Natl. Acad. Sci. U.S.A.* 1982, *79*, 6856.
(2) Kramer, S. P.; Johnson, J. L.; Ribeiro, A. A.; Millington, D. S.; Rajagopalan, K. V. *J. Biol. Chem.* 1987, *262*, 16357.

the original sulfur atoms (**3**).[3-6] The structure of urothione, the urinary metabolite of the molybdenum cofactor, has recently been confirmed as **4** by an unequivocal total synthesis.[7] Despite this array of synthetic, degradative, and spectroscopic structural evidence, however, there has been to date no evidence bearing on the absolute configuration of the side chain secondary hydroxyl group in molybdopterin. We now describe an unequivocal, *stereospecific* synthesis of (dephospho) Form A (**2'**) which establishes the absolute chirality of its secondary hydroxyl group, and we present spectroscopic evidence which places the phosphate grouping on the primary side chain hydroxyl group (C-4'), as depicted in **2**.

Synthetic Studies: Determination of the Absolute Configuration of (Dephospho) Form A (2'). Our synthetic strategy was based upon a general procedure recently reported by us for the preparation of 6-alkynylpterins which employs a palladium-catalyzed coupling between 2-pivaloyl-6-chloropterin (**5**) and monosubstituted acetylenes. The pterins themselves can then be obtained by hydrolytic removal of the 2-pivaloyl protecting group.[8-10] (R)-Glyceraldehyde acetonide (from lead tetraacetate cleavage of 1,2:5,6-di-O-isopropylidene-D-mannitol)[11] was converted to the acetylene **7** by treatment with carbon tetrabromide and triphenylphosphine in methylene chloride to give the dibromoalkene **6** (55% yield), followed by reaction with 2 equiv of n-BuLi in THF (58% yield).[12] The resulting (S)-3,4-dihydroxybutyne acetonide (**7**) proved to be extremely difficult to purify and was coupled directly with 2-pivaloyl-6-chloropterin (**5**) in the presence of palladium acetate/tri-o-tolylphosphine/CuI to give **8**.[13] Hydrolysis of **8** with 0.5 N HCl in aqueous dioxane at gentle reflux removed both the acetonide and pivaloyl groups to give (S)-**2'** (Scheme I).[14] An analogous sequence of reactions starting from

(3) Johnson, J. L.; Hainline, B. E.; Rajagopalan, K. V. *J. Biol. Chem.* 1980, *255*, 1783.
(4) Rajagopalan, K. V.; Johnson, J. L.; Hainline, B. E. *Federation Proc.* 1982, *41*, 2608.
(5) Johnson, J. L.; Hainline, B. E.; Rajagopalan, K. V.; Arison, B. H. *J. Biol. Chem.* 1984, *259*, 5414.
(6) Rajagopalan, K. V. *Biochem. Soc. Trans.* 1985, *13*, 401.
(7) Taylor, E. C.; Reiter, L. A. *J. Am. Chem. Soc.* 1989, *111*, 285.
(8) Taylor, E. C.; Ray, P. S. *J. Org. Chem.* 1987, *52*, 3997.
(9) Taylor, E. C.; Ray, P. S. *J. Org. Chem.* 1988, *53*, 35.
(10) Taylor, E. C.; Ray, P. S. *Syn. Commun.* 1987, *17*, 1865.
(11) (a) Bauer, E. *Biochem. Prep.* 1952, *2*, 231. (b) Horton, D.; Jacques, G. *J. Org. Chem.* 1983, *48*, 1381. (c) An improved preparation of (R)-glyceraldehyde acetonide by sodium metaperiodate cleavage of 1,2:5,6-di-O-isopropylidene-D-mannitol has recently been described: Jackson, D. Y. *Synth. Commun.* 1988, *18*, 337.
(12) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* 1972, *36*, 3769.
(13) Representative coupling procedure: A mixture of **5** (0.5 g, 1.8 mmol), Pd(OAc)$_2$ (50 mg, 0.2 mmol), tri-o-tolylphosphine (136 mg, 0.4 mmol), CuI (42 mg, 0.4 mmol), Et$_3$N (3 mL), and (S)-**7** (0.5 g, 4 mmol) in MeCN (10 mL) was heated at 100 °C in a sealed tube for 16 h. Solvent was removed in vacuo, and the residue was chromatographed on silica gel, eluting with 1% MeOH in HCCl$_3$. The residual solid from evaporation of the fractions containing the product was recrystallized from ethanol to give 145 mg (20%) of **8** as a cream-colored microcrystalline powder, mp 240-241 °C: NMR (CDCl$_3$) δ 12.48 (br s, 1 H), 8.88 (s, 1 H), 8.37 (br s, 1 H), 4.99 (t, 1 H, J = 6.3 Hz), 4.28 (dd, 1 H, J = 6.6 Hz, 8.4 Hz), 4.12 (dd, 1 H, J = 6.3 Hz, 8.4 Hz), 1.55 (s, 3 H), 1.44 (s, 3 H), 1.36 (s, 9 H). Acceptable microanalytical data were obtained for C$_{18}$H$_{21}$N$_5$O$_4$. HRMS calcd m/z 371.1593, found 371.1604.
(14) (R)- and (S)-(dephospho) Form A: pale yellow solids, mp > 250 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.71 (s, 1 H), 4.44 (t, 1 H, J = 6.1 Hz), 3.53 d, 2 H, J = 6.1 Hz); UV λ$_{max}$ (0.1 N NaOH) nm (e) 270 (33 300), 380 (13 200).