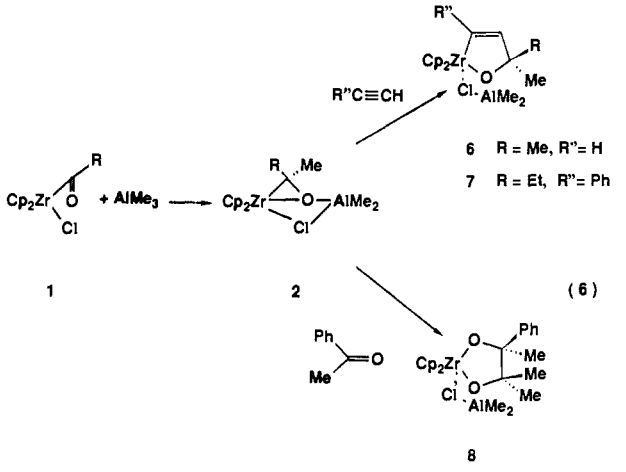
of the aluminum reagent in this case is to lower the barrier for rotation of the acyl ligand to a geometry most favorable for migration of the alkyl group (eq 3).

The role of the aluminum reagent in the isomerization of the alkyl acyl **3** to the ketone complex **2** models the behavior of Lewis-acidic metal oxides which serve as supports for heterogeneous Fischer–Tropsch catalysts. Shriver's results[22] demonstrate that molecular Lewis acids and aluminum oxides promote CO migratory insertion reactions. Our results imply that Lewis-acidic centers also promote further reduction of an acyl ligand.

The ketone complexes **2** react cleanly with acetylenes, ethylene, and ketones in reactions that promise to be of considerable synthetic utility. Treatment of the ketone complexes with acetylene or phenylacetylene generates the oxymetallacyclopentenes **6** and **7**, respectively (eq 6).[24,25] These reactions can be conveniently run in one pot starting from acyl complexes **1**. The oxymetallacycle **7** is produced regioselectively in 71% yield from the acyl **1b**. Treatment of the ketone complexes with ethylene yields saturated analogues of **6**. Hydrolysis of **6** or **7** yields the tertiary unsaturated alcohols.[26] Acetophenone reacts rapidly with the ketone complex **2a** to give **8**. The diolate **8** decomposes in solution above 10 °C but could be characterized spectroscopically[27] and by hydrolysis to the 1,2-diol Me(Ph)C(OH)C(OH)Me$_2$ (**9**) (eq 6).[28]



We have demonstrated that aluminum reagents promote the intramolecular reductive coupling of an alkyl and an acyl ligand to give ketone complexes. The aluminum reagent performs a dual role in these reactions: it acts as a reagent in the formation of the ketone complexes and it stabilizes and prevents dimerization of the ketone complexes by coordinating to the ketone ligand.[29] In the absence of coordinated Me$_2$AlCl, group 4 ketone complexes dimerize readily[3] and are much less reactive than the monomeric ketone complexes **2**. Further studies will investigate the role of these complexes as models for intermediates in catalytic processes and as reagents in organic synthesis.

Acknowledgment. We gratefully acknowledge the financial support of the Department of Energy and the National Institute of Health. R.M.W. was supported in part by a W.R. Grace Fellowship and a SOHIO fellowship in catalysis. K.R.C. was supported by a Summer Undergraduate Research Fellowship (SURF). We thank Dr. D. A. Straus for many helpful discussions.

Formation, Structures, and Reactivity of *cis*-Hydroxy-, *cis*-Methoxy-, and *cis*-Mercaptoiridium Hydrides. Oxidative Addition of Water to Ir(I)

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Received May 16, 1986

Although mononuclear hydrido hydroxy complexes may play an important role in "water activation", including the water gas shift reaction,[1a,e] olefin and nitrile hydration,[1b] exchange reactions,[1b,d] and photodissociation of water,[1c] only few of them are known. The early-transition-metal complexes of this type[2] tend to dimerize, whereas the late-transition-metal complexes[1,3] tend to be unstable[1,3b,d] in the absence of excess water, probably because of an unfavorable formation constant. None of these complexes has been crystallographically characterized. We report here the isolation, properties, and crystallographic characterization, revealing some unusual features, of a stable, mononuclear hydrido hydroxy complex formed by facile water oxidative addition to Ir(I). A rare example of a mononuclear hydrido methoxy complex derived from it is also described. For comparison a hydrido mercapto complex is also presented.

Addition of excess purified water to a red suspension of Ir(PMe$_3$)$_4$$^+PF_6$$^-$ (**1**)[4] (Scheme I) in THF results in bleaching. Evaporation of the solvent under vacuum yields almost pure *cis*-IrH(OH)(PMe$_3$)$_4$$^+PF_6$$^-$ (**2**) as a white solid. Crystallization from THF by vapor diffusion of benzene leads to colorless crystals of pure **2** in 85% yield. The structure of **2** is unambiguously assigned based on IR, ^{1}H NMR, ^{31}P NMR, and elemental analysis.[5]

The *cis*-hydrido hydroxy **2** is air and thermally stable and does not undergo reductive elimination of water even at 100 °C. In contrast, the strongly basic *trans*-hydridohydroxyplatinum complexes[1a,b,3b] and hydridorhodium complexes containing outer-sphere hydroxide[1c,d,e] eliminate water readily, probably by deprotonation, and are stable only in the presence of a large excess of water. The cis configuration of **2** results in a relatively low tendency of the hydroxide ligand to dissociate (lack of hydride trans effect) and thus a diminished tendency to form water by deprotonation. Indeed, **2** is a relatively weak base. However, **2** undergoes ex-

(24) **6** (R = Me, R" = H): ^{1}H NMR (C$_6$D$_6$) δ 6.35 (d, J = 10.9 Hz, 1 H), 5.71 (d, J = 10.9 Hz, 1 H), 5.68 (s, 10 H), 1.24 (s, 6 H), −0.24 (s, 6 H); ^{13}C NMR (C$_6$D$_6$) δ 175.5 (CH), 140.4 (CH), 112.1 (Cp), 90.8 (CO), 29.3 (CH$_3$), −4.13 (CH$_3$). Anal. Calcd for C$_{17}$H$_{24}$OClAlZr: C, 51.30; H, 6.08; Cl, 8.91. Found: C, 51.26, H, 6.10; Cl 8.98. Yield: 55% from **1a**.

(25) **7** (R = Et, R" = Ph): ^{1}H NMR (C$_6$D$_6$) δ 7.24 (m, 2 H), 7.12 (m, 3 H), 5.85 (s, 5 H), 5.75 (s, 5 H), 5.43 (s, 1 H), 1.68 (m, J = 7.08 Hz, 3 H), 1.49 (m, J = 7.08 Hz, 2 H), −0.21 (s, 3 H); ^{13}C NMR (C$_6$D$_6$) δ 186.0 (C), 154.0 (Ph), 139.0 (CH), 126.2 (Ph), 113.2 (Cp), 112.6 (Cp), 92.1 (CO), 36.8 (CH$_3$), 28.9 (CH$_2$), 10.56 (CH$_3$). Anal. Calcd for C$_{24}$H$_{30}$OClZrAl: C, 59.05; H, 6.19. Found: C, 59.14; H, 6.30. Yield: 71% from **1b**.

(26) Hydrolysis of **6** with H$_2$O affords 2-methyl-3-buten-2-ol in 70% yield (GC).

(27) **8**: ^{1}H NMR (C$_6$D$_6$) δ 7.24 (m, Ph), 6.05 (s, 5 H), 6.02 (s, 5 H), 1.46 (s, 3 H), 1.43 (s, 3 H), 0.88 (s, 3 H), −0.14 (s, 3 H), −0.21 (s, 3 H).

(28) **9**: ^{1}H NMR (C$_6$D$_6$) δ 7.35 (m, Ph), 1.41 (s, 3 H), 1.09 (s, 3 H), 0.98 (s, 3 H). Anal. (C$_{11}$H$_{16}$O$_2$) C, H. Mp 80–81 °C, uncorrected; lit. mp 83–84 °C: Roger, R. *J. Chem. Soc.* **1925**, *124*, 518. Yield: 50% from **1a**.

(29) Coordinated Me$_2$AlCl performs a similar role in stabilizing the reactive alkylidene ligand in the Tebbe reagent Cp$_2$Ti=CH$_2$·AlMe$_2$Cl. (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1980**, *102*, 6876.

(1) (a) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941. (b) Yoshida, T.; Matsuda, T.; Okano, T.; Otsuka, S. *Ibid* **1979**, *101*, 2027. (c) Yoshida, T.; Okano, T.; Otsuka, S. *Ibid.* **1980**, *102*, 5966. (d) Yoshida, T.; Okano, T.; Saito, K.; Otsuka, S. *Inorg. Chim. Acta* **1980**, *44*, L135. (e) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 3411.

(2) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

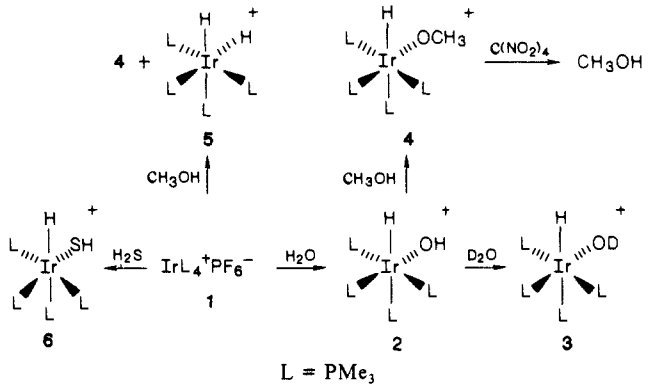
(3) (a) Gillard, R. D.; Heaton, B. T.; Vaughan, D. *J. Chem. Soc. A* **1970**, 3126. (b) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543. (c) Chaudred, B. N.; Cole hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (d) James, B. R.; Preece, M.; Robinson, S. D. *Adv. Chem. Ser.* **1982**, *196*, 145. (e) Gotzig, R.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *285*, 99.

(4) Thorn, D. L. *Organometallics* **1982**, *1*, 197.

(5) **2**: IR (Nujol) 2068 (s, Ir–H), 3620 cm^{-1} (s, sh, O–H); ^{1}H NMR (pyridine-d_5) δ 1.445 (d, J = 8 Hz, 9 H, PMe$_3$), 1.601 (superimposed t + d, J_1 = 14, J_2 = 8 Hz, 27 H, 3PMe$_3$), −1.40 (br s, 1 H, OH; disappears upon D$_2$O addition), −11.19 (d of q, $J_{P\text{-}H,trans}$ = 147, $J_{P\text{-}H,cis}$ = 19 Hz, 1 H, Ir H); ^{31}P{^{1}H} NMR (pyridine-d_5) δ −41.92 (d of d, J_1 = 20, J_2 = 16 Hz, 2 P), −47.94 (d of t, J_1 = 12, J_2 = 20 Hz, 1 P), −53.93 (d of t, J_1 = 16, J_2 = 12 Hz, 1 P). ^{31}P NMR (pyridine-d_5) δ −41.92 (m, 2 P, P trans to P), −47.94 (d of m, J = 147 Hz, 1 P, P trans to H), −53.93 (m, 1 P, P trans to OH).

0002-7863/86/1508-6387$01.50/0

Scheme I



change reactions involving the OH group. Upon addition of excess D_2O, **2** yields exclusively the hydrido deuteroxy complex *cis*-$IrH(OD)(PMe_3)_4^+PF_6^-$ (**3**), confirming that a reductive elimination–oxidative addition sequence is not involved.[6] Exposure of **3** to air results in regeneration of **2**. Upon dissolution of **2** in methanol and removal of the solvent in vacuo, quantitative formation of the hydrido methoxy complex *cis*-$IrH(OMe)(PMe_3)_4^+PF_6^-$ (**4**) results. Spectroscopic characterization of this white crystalline complex is unambiguous.[7] Few other hydrido alkoxy complexes have been reported.[3b,e,6,8] **4** is air and thermally stable and does not change upon heating at 70 °C. However, it does undergo oxidatively induced methanol reductive elimination. Thus, addition of 1 equiv of $C(NO_2)_4$ results in immediate methanol formation in 85% yield.

It is noteworthy that complex **4** cannot be obtained cleanly from reaction of **1** with methanol. Rather, a mixture of **4** with the dihydrido complex *cis*-$Ir(H)_2(PMe_3)_4^+PF_6^-$ (**5**)[9] is formed.[10] This observation indicates that (a) oxidative addition of methanol to **1**[11] involves a coordinatively unsaturated Ir(III) intermediate (which undergoes competing β-hydride elimination and PMe_3 association). This intermediate is most likely formed by reaction of the 14e complex $Ir(PMe_3)_3^+$ with methanol, consistent with a concerted oxidative addition mechanism. (b) OH substitution in **2** does not involve predissociation of a phosphine ligand (which would likely result in at least some β elimination to **5**). (c) The hydrido methoxy complex **4** is kinetically stabilized, as a result of the tightness by which the small PMe_3 ligand is bound to Ir(III).[12]

The hydrido mercapto complex *cis*-$IrH(SH)(PMe_3)_4^+PF_6^-$ (**6**) was also prepared for comparison. Passage of H_2S through a suspension of **1** in THF leads to bleaching. Filtration of the white precipitate followed by crystallization from CH_3CN/C_6H_6 by vapor diffusion of pentane leads to the thermally stable **6** in 90% yield.[13,14] In contrast to **2**, the SH ligand does not undergo exchange with alcohols, perhaps because the softer SH ligand binds more strongly to iridium than OH (vide infra).

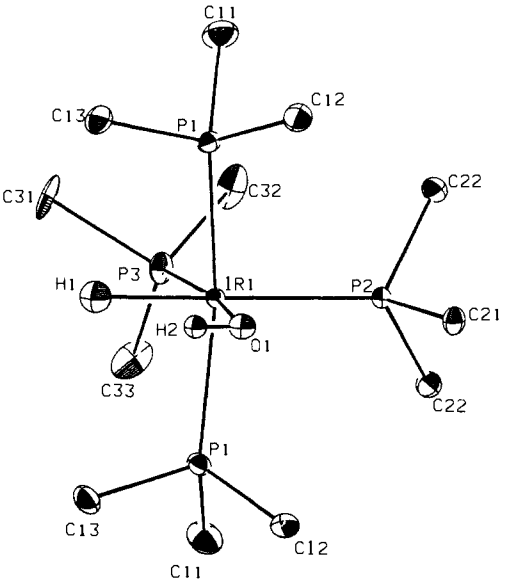


Figure 1. ORTEP drawing of a molecule of **2**. Selected bond distances (Å) and angles (deg): Ir1–P1 2.337 (1); Ir1–P2 2.369 (2); Ir1–P3 2.259 (2); Ir1–O1 2.119 (5); Ir1–H1 1.712 (76); Ir1–H2 2.2374; H1–H2 2.4418; O1–Ir1–H1 93 (2); Ir1–O1–H2 91 (7).

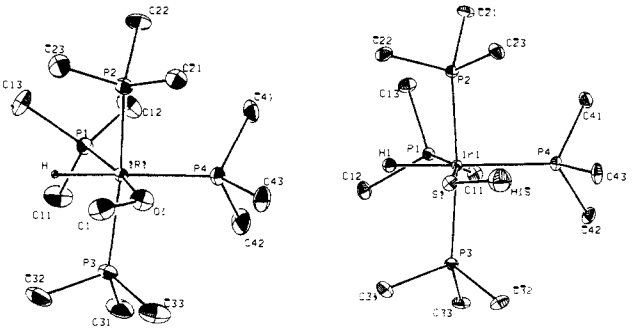


Figure 2. ORTEP drawings of molecules of **4** (left) and **6** (right). Selected bond distances (Å) and angles (deg): **4**: Ir1–P1 2.274 (3); Ir1–P2 2.336 (3); Ir1–P3 2.345 (3); Ir1–P4 2.374 (3); Ir1–O1 2.118 (8); Ir1–H 1.813 (84); O1–C1 1.334 (16); Ir1–O1–C1 119.4 (9); O1–Ir1–H 76 (3). **6**: Ir1–S1 2.437 (1); Ir1–P1 2.298 (1); Ir1–P2 2.355 (1); Ir1–P3 2.343 (1); Ir1–P4 2.378 (1); Ir1–H1 1.642 (48); S1–H1S 1.321 (66); S1–Ir1–H1 76 (2); Ir1–S1–H1S 111 (3).

An X-ray diffraction study of complexes **2**, **4**, and **6** was carried out (Figures 1 and 2).[15] As expected, the octahedral geometry

(6) Similarly, only the ethoxy group in η^5-$C_5Me_5IrH(OEt)(PPh_3)$ exchanges with CD_3CD_2OD: Newman, L. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 5314.

(7) **4**: IR (Nujol) 2045 (s, Ir–H), 1070 cm^{-1} (s, O–CH_3) ^1H NMR (pyridine-d_5) δ 1.393 (d, J = 8 Hz, 9 H, PMe_3), 1.590 (d, J = 10 Hz, 9 H, PMe_3), 1.645 (t, J = 3.5 Hz, 18 H, $2PMe_3$) 3.637 (d, J = 6 Hz, 3 H, OCH_3), −11.365 (d of q, $J_{P-H,trans}$ = 145, $J_{P-H,cis}$ = 19 Hz). $^{31}P\{^1H\}$ NMR (pyridine-d_5) δ −40.34 (d of d, J_1 = 20, J_2 = 16 Hz, 2 P, P trans to P) −46.76 (d of t, J_1 = 21, J_2 = 12 Hz, P trans to H; coupled spectrum shows d of m, J_{P-H} = 145 Hz), −56.72 (d of t, J_1 = 12, J_2 = 16 Hz, 1 P, P trans to OH).

(8) For examples of early-transition-metal hydrido alkoxy complexes, see: (a) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723. (b) Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (c) Ito, T.; Ohki, T.; Nakano, T. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 169.

(9) Preparation of *cis*-$H_2Ir(PMe_3)_4^+Cl^-$ by H_2 addition to $Ir(PMe_3)_4^+Cl^-$ has been described: (a) Herskovitz, T., unpublished work. (b) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580.

(10) A ratio of **4**/**5** ≈ 3 is obtained at an initial concentration of [**1**] ≈ 6 × 10^{-2} M.

(11) $Pt(PEt_3)_3$ reacts with methanol to form unisolable $[PtH(PEt_3)_3]OCH_3$.[3b] $Pt(PR_3)_2$ (R = *i*-Pr, cyclohexyl) yields *trans*-$PtH_2(PR_3)_2$: Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134. The spectroscopically observable *cis*-$OsH(OMe)(PMe_3)_4$ decomposes to *cis*-$OsH_2(PMe_3)_4$.[3e]

(12) For other examples of kinetically stabilized Ir(III) and Rh(III) PMe_3 complexes, see: Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.

(13) **6**: IR (Nujol) 2043 (s, Ir–H); ^1H NMR (CD_3CN) δ 1.56 (d, J = 8 Hz, 9 H, PMe_3), 1.80 (superimposed, t + d, J_1 = 4, J_2 = 9.5 Hz, 27 H, $3PMe_3$), −2.05 (d of sextets, J_1 = 16, J_2 = 2 Hz, 1 H, SH), −12.72 (d of q, $J_{P-H,trans}$ = 136, $J_{P-H,cis}$ = 18 Hz, 1 H, IrH). $^{31}P\{^1H\}$ NMR(CD_3CN) δ −46.4 (d of t, J_1 = 14, J_2 = 17 Hz, 1 P), −49.4 (t, J = 20 Hz, 2 P) −58.3 (d of t, J_1 = 14, J_2 = 21 Hz, 1 P).

(14) Formation of $IrCl(H)(SH)CO(PPh_3)_2$ by reaction of $IrCl(CO)(PPh_3)_2$ with H_2S has been reported: (a) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 5325. (b) Singer, H.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2516. (c) Hsieh, M. L.; Zingaro, R. A.; Krishnan, V. *Int. J. Sulfur Chem.* **1971**, *1*, 197. (d) Mueting, A. M.; Boyle, P.; Pignolet, L. H. *Inorg. Chem.* **1984**, *23*, 44 (includes crystal structure).

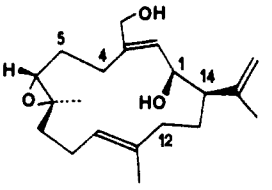
(15) Crystal data for **2**: $IrP_5F_6OC_{12}H_{38}$, irregular sphere, ~0.31 × 0.29 × 0.29 mm, orthorhombid, *Pnma* (No. 62), a = 14.540 (2) Å, b = 12.015 (1) Å, c = 13.613 (2) Å, from 25 reflections, T = −100 °C, V = 2378.2 Å^3, Z = 4, FW = 659.51, D_c = 1842 g/cm^3, μ(Mo) = 59.70 cm^{-1}, R = 0.027, R_w = 0.027. Crystal data for **4**: $IrP_5F_6OC_{13}H_{40}$, thin plate, ~0.06 × 0.35 × 0.36 mm, monoclinic b, $P2_1/n$ (No. 14), a = 10.932 (5) Å, b = 15.680 (6) Å, c = 14.553 (6) Å, β = 91.52 (3)°, from 50 reflections, T = −100 °C, V = 2493.7 Å^3, Z = 4, FW = 673.53, D_c = 1.794 g/cm^3, μ(Mo) = 56.96 cm^{-1}, R = 0.054, R_w = 0.048. Crystal data for **6**: $IrSP_5F_6C_{12}H_{38}$, colorless, plate, ~0.15 × 0.30 × 0.33 mm, from acetonitrile/benzene by vapor diffusion of pentane, monoclinic b, $P2_1/n$ (No. 14), a = 14.381 (2) Å, b = 14.789 (2) Å, c = 11.363 (2) Å, β = 90.96 (1)°, from 50 reflections, T = −100 °C, V = 2416.4 Å^3, Z = 4, FW = 675.57, D_c = 1.857 g/cm^3, μ(Mo) = 59.56 cm^{-1}, R = 0.027, R_w = 0.028. All details are included in the supplementary material.

of these complexes is distorted by the relatively small size of the hydride ligand. On the basis of the Ir-P distances in **2**, **4**, and **6** and in *cis*-$IrH(CH_2OH)(PMe_3)_4^+PF_6^-$,[9b] the following trans influence order is obtained: H > CH_2OH > P > SH > OCH_3 > OH. This implies that the Ir-OH bond is the least covalent.[16] Indeed, this bond is 0.029 Å longer than Ir-OCH_3. This order is in agreement with the observed exchange reactivity of OH and unreactivity of SH toward methanol.

It is interesting to note the relatively small Ir-O-H angle of 91 (±7)° and the orientation of the OH ligand in **2**. For comparison, the Ir-S-H angle in **6** is 111 (±3)° with the SH pointing away from the hydride, and the Ir-O-CH_3 angle in **4** is 119.4 (±0.9)°. This may be a result of an interaction between the hydridic Ir-H and the OH proton, although the distance $H_1\cdots H_2$ of 2.441 Å is too large to represent a normal hydrogen bond. MO calculation aimed at clarifying the nature of this interaction are in progress, as are other studies on the reactivity and mechanism of formation of the above complexes.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles and intermolecular distances for compounds **2**, **4**, and **6** (15 pages); tables of structure factor amplitudes for **2**, **4**, and **6** (15 pages). Ordering information is given on any current masthead page.

(16) A relatively low trans effect of OH compared to other ligands was indicated on the basis of spectroscopic data: (a) Chatt, J.; Heaton, B. T. *J. Chem. Soc. A* **1968**, 2475. (b) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.



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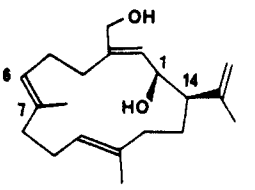

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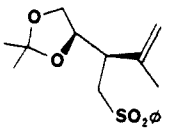

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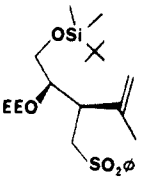

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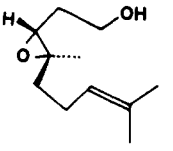

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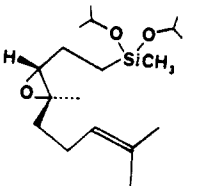

6

Total Synthesis of (-)-Asperdiol

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Received May 8, 1986

Asperdiol (**1**) is a cembranoid marine natural product which has been isolated from the extracts of Caribbean gorgonians of the *Eunicea* genus.[1] The extracts had been shown to be active in vivo against the National Cancer Institute's P-388 lymphocytic leukemia assay and several other cancer cell lines. The activity was traced to asperdiol and the structure and the absolute configuration were determined by X-ray crystallography.[1] Two total syntheses of the racemate of **1** have been described.[2] A total synthesis of (+)-desepoxyasperdiol (**2**) has been performed in our laboratory.[3] In this paper we describe the first total synthesis of (-)-asperdiol.

The presence of the C-6, C-7 epoxide in **1** made it necessary to follow an approach that differed significantly from the one used for **2**. The retrosynthetic cleavage of the macrocycle led to three fragments. The two large fragments include C-4 through C-12 and C-13 through C-2. The remaining carbon atoms, C-3 and C-20, comprise the third fragment. Each of the two large fragments included two of the asymmetric centers of the final product, therefore a convergent and enantioselective synthesis appeared possible. A synthesis of sulfone **3**, the starting point for the total synthesis, from (2*R*,3*S*)-4-benzyloxy-2,3-epoxy-1-butanol has been described.[3] It will be necessary to distinguish the two alcohol groups of **3** later in the synthesis so it is most efficient to protect them with orthogonal protecting groups at an early stage.

Acetonide exchange in dimethoxyethane-ethylene glycol was catalyzed by Amberlyst IR-120 at 45 °C for 1 h to produce the diol in 85% yield. The primary alcohol was converted to the *tert*-butyldimethylsilyl ether in 87% yield by treatment in *N*,*N*-dimethylformamide at 23 °C for 1 h with 1.2 equiv of *tert*-butyldimethylsilyl chloride and 2.5 equiv of imidazole.[4] The secondary alcohol was protected as the ethoxyethyl derivative (99% yield) by pyridinium tosylate catalyzed reaction with ethyl vinyl ether in dichloromethane. The choice of the ethoxyethyl protecting group was crucial to the success of the synthesis. This was unfortunate, because the presence of the asymmetric acetal carbon of the protecting group made the interpretation of NMR spectra tedious. The two stereocenters at C-1 and C-14 of **1** are present in **4**. The carbanion stabilizing group at C-13 allows the formation of the C-12, C-13 bond through a nucleophilic displacement reaction.

A synthesis of the C-13, C-2 fragment from homogeraniol was conceptually very simple. The asymmetric epoxidation of homoallylic alcohols according to Sharpless' conditions, however, leads to products with a modest degree of enantioselectivity.[5] Therefore an alternative approach was followed. (2*R*,3*R*)-2,3-Epoxygeraniol was prepared from geraniol.[6] The optical purity of this material was determined to be >95% by analysis of the (+)-MTPA ester.[7] The conversion of (2*R*,3*R*)-2,3-epoxygeraniol to (3*R*,4*R*)-3,4-epoxyhomogeraniol (**5**) was undertaken next. Epoxygeraniol was converted in quantitative yield to the labile mesylate by treatment with 1.2 equiv of methanesulfonyl chloride and 1.5 equiv of tri-

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