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Synthesis and Crystal Structure of CpWOs₃(CO)₉ (μ-O)(μ-CHTol)(μ-H)

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In recent years alkylidyne cluster complexes have received considerable attention due to the potential surface intermediates of the μ₃-alkylidyne fragments in various catalytic reactions.[1] In previous work,[2] we have reported the synthesis and solution dynamics of a tungsten-triosmium *p*-xylylidyne complex, CpWOs₃(CO)₁₁(μ₃-CTol) (**1**, Cp=η⁵-C₅H₅, Tol=*p*−C₆H₄Me). Further investigation of **1** on the reactivity toward dihydrogen has revealed formation of an unexpected hydrido-*oxo*-alkylidene complex, CpWOs₃(CO)₉(μ-O)(μ-CHTol)(μ-H) (**2**). Herein we report details of the synthesis and crystal structure of compound **2**.

Experimental Section

General Comments. Solvents were dried prior to use. CpWOs₃(CO)₁₁(μ₃-CTol) was prepared as described in the literature.[2] All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. The progress of the reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, Silica Gel 560 F-254, E. Merck). Preparative TLC was carried out using glass-backed silica gel plates (20×20 cm) prepared from silica gel G (Type 60, E. Merck). Infrared spectra were obtained on a Nicolet 5-MX FT-IR spectrophotometer. ¹H-NMR (300 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were recorded by the staff of the Analytical Laboratory at the Lucky Ltd. using JEOL DX-300 mass spectrometer. All m/z values are referenced to ¹⁸⁴W and ¹⁹²Os.

Reaction of 1 with Dihydrogen. Compound **1** (20 mg, 0.016 mmol) was dissolved in toluene (25 mL) in a 250 mL glass pressure bottle. The resulting solution was degassed by the freeze-pump-thaw cycle and the bottle was charged with dihydrogen gas to a pressure of 50 psig. The resulting solution was heated at 110℃ for 2.5 h. Evaporation of the

Table 1. Crystal Data for **2**

formula	C₂₂H₁₄O₁₀WOs₃
f_w	1192.79
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	10.837(2)
b, Å	26.073(2)
c, Å	9.232(2)
β, deg	103.33(2)
V, Å³	2538(1)
Z	4
ρ(calcd), gcm⁻³	3.12
temp. ℃	21
λ(MoKα), Å	0.71069

solvent *in vacuo* and purification by preparative TLC (petroleum ether : dichloromethane = 1 : 2) gave CpWOs₃(CO)₉(μ-O)(μ-CHTol)(μ-H) (**2**, 0.0097 mmol, 60%, R_f=0.6) as an orange solid: ¹H-NMR (CDCl₃, 25℃) δ 7.06-6.44 (AB pattern, 4H), 5.94 (s, 5H), 5.52 (d, J=1.7 Hz, 1H), 2.41 (s, 3H), −18.05 (d, J=1.7 Hz, 1H); IR (C₆H₁₂) ν(CO) 2090 (s), 2064 (vs), 2026 (vs), 2014 (s), 2006 (m), 1990 (w), 1954 (w), 1937 (m), cm⁻¹; MS (70 eV) m/z 1198 (M⁺).

Crystal Structure of 2. Crystals of compound **2** suitable for an X-ray analysis were obtained by slow recrystallization from a mixture of petroleum ether and dichloromethane at −10℃. Space group and approximate cell dimensions of this crystal were determined by preliminary experiment using Weissenberg and precession photography.[3] The diffraction symmetry (2/m, C₂ₕ) and systematic absence (*h* 0 *l* for *h*+*l*=2n+1 and 0*k*0 for *k*=2n+1) uniquely defined the centrosymmetric monoclinic space group $P2_1/n$. An opaque dark red crystal of approximate orthogonal dimensions of 0.2×0.4 ×0.2 mm was mounted and aligned on a CAD-4 diffractometer. Details of the relevant crystallographic data are given in Table 1. The accurate cell parameters were refined from setting angles of 25 reflections with 10°<θ<14°, and intensity data for 3822 independent reflections in range 0≤h≤11, 0≤k≤28, −10≤l≤10 were collected using graphite-monochromated Mo Kα radiation and ω/2θ scan mode, ω-scan width=(0.8+0.35 tanθ)°, θ_max=25°. All data were converted to E_o values following correction for L-P and absorption factors. The four heavy atoms were located by using direct method (SDP)[4] and all non-hydrogen atoms were found on subsequent difference Fourier maps. The structure was refined by full-matrix least squares program with SHELX[5] and function minimized was Σω(|F_o|-|F_c|)², where ω=1.0/(σ²(F_o) +0.001834 F_o²). Independent reflections of 2790 [F_o>3σ(F_o)] were used for the structure refinement and number of parameters refined was 338. A final difference Fourier synthesis showed a number of small peaks in the vicinity of the heavy atoms. A bridging hydride ligand could not be located with any certainty. However, thirteen hydrogen atoms attached to the C(1), Cp and Tol moieties were calculated from the known stereochemistry by adopting the C-H distances of 1.08 Å and refined with isotropic thermal parameters. Neutral atomic scattering factors were used with W and Os corrected for anomalous dispersion.[6] Final reliability factors were R=

Table 2. Final Atomic Coordinates ($\text{Å} \times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) with Esd's for **2**

	x	y	z	U_{eq}*
Os1	6512(1)	3601(<1)	2646(1)	331
Os2	8870(1)	3083(<1)	3537(1)	294
Os3	8155(1)	3694(<1)	5747(1)	353
W	8897(1)	4091(<1)	3112(1)	375
O1	8924(16)	4354(6)	4907(17)	406
O11	3876(20)	4090(9)	2050(23)	728
O12	5484(21)	2571(9)	3247(22)	686
O13	6401(21)	3286(9)	−537(23)	766
O21	11636(20)	2933(10)	4979(32)	979
O22	9146(25)	2765(10)	464(30)	959
O23	8217(22)	2016(8)	4609(31)	886
O31	773(26)	3568(10)	7702(32)	1049
O32	7205(22)	4369(9)	7951(25)	744
O33	7233(21)	2715(8)	6859(22)	645
C11	4907(34)	3838(15)	2265(24)	755
C12	5940(35)	2927(10)	3041(26)	650
C13	6445(23)	3411(10)	643(27)	428
C21	10493(37)	2996(10)	4317(40)	737
C22	9026(31)	2875(15)	1622(46)	811
C23	8459(26)	2410(12)	4212(35)	620
C31	9696(36)	3629(11)	6799(58)	979
C32	7527(26)	4115(11)	7095(35)	541
C33	7567(27)	3071(12)	6409(30)	563
C1	7152(24)	4349(8)	1984(27)	384
C2	6688(26)	4860(9)	2369(25)	440
C3	6627(25)	5266(9)	1437(29)	481
C4	6347(28)	5759(11)	1862(30)	571
C5	6035(22)	5857(9)	3203(27)	396
C6	6075(22)	5439(10)	4172(30)	450
C7	6400(26)	4973(11)	3759(31)	517
C8	5746(26)	6395(9)	3701(36)	330
C51	10659(38)	3931(16)	2045(53)	859
C52	9822(35)	4158(17)	930(40)	765
C53	9589(54)	4626(17)	1334(63)	123
C54	10293(61)	4698(21)	2675(61)	141
C55	11005(29)	4234(31)	3229(43)	138

$$^*U_{eq} = \frac{1}{3}[U_{22} + \frac{1}{\sin^2\beta}(U_{11} + U_{33} + 2U_{13}\cos\beta]$$

0.0642, $\omega R = 0.0630$, with average $\Delta/\sigma = -0.001$, $\Delta\rho_{max}/\Delta\rho_{min} = 3.8/-2.2$ $e\text{Å}^{-3}$ in final $\Delta\rho$ map and $S = 1.3922$. Final positional parameters and U_{eq} for non-hydrogen atoms are given in Table 2. All calculations were carried out using MV/10000 and VAX−3400 computers.

Results and Discussion

The reaction of CpWOs$_3$(CO)$_{11}$(μ_3-CTol) (**1**) with dihydrogen under pressure (50 psig) at 110°C provides an orange crystalline product **2**, which is formulated as CpWOs$_3$(CO)$_9$(O)(CH-Tol)(H) on the basis of spectroscopic data. ^{1}H-NMR spectrum of **2** in CDCl$_3$ exhibits a hydride resonance at δ −18.05 (d, $J = 1.7$ Hz) and a downfield resonance at δ 5.52 (d, $J = 1.7$
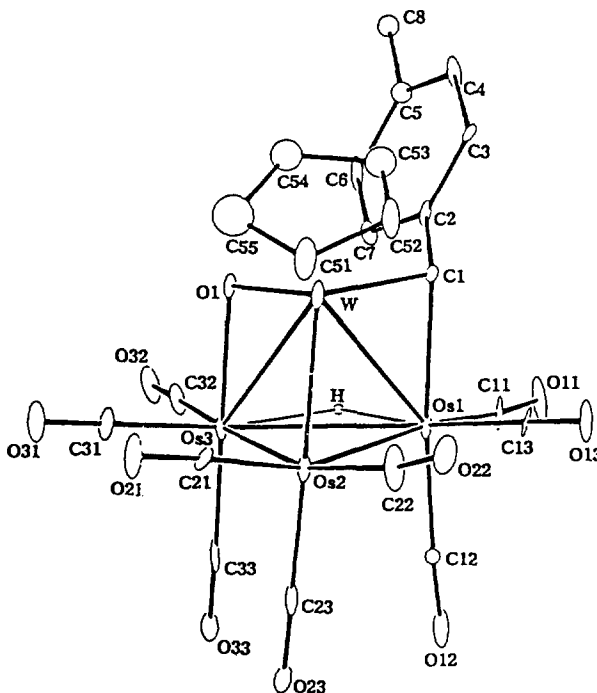
Figure 1. Molecular geometry and atomic labelling scheme for **2**. The μ-hydride ligand is shown in the predicted position.
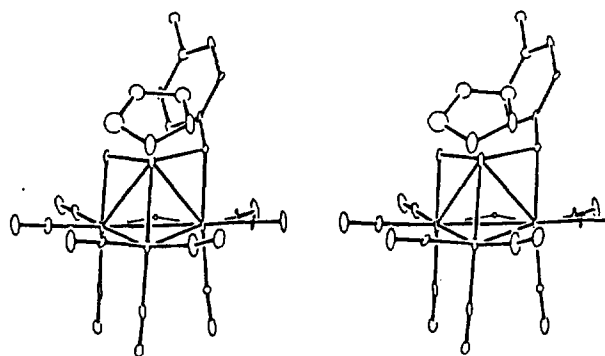
Figure 2. Stereoscopic view of **2**.

Hz) of the μ-alkylidene CH hydrogen. This observation indicates that reduction of the alkylidyne ligand in **1** by dihydrogen leads to the formation of hydrido alkylidene complex **2** and that the hydride and the alkylidene ligands in **2** bridge the adjacent metal-metal bonds. The molecular ion observed in the mass spectrum of **2** differs from that of **1** by 38 mass units, which suggests that **2** might have an *oxo* group (**1** −2CO+O+2H). Furthermore, infrared spectrum of **2** shows essentially identical with that of the structurally characterized complex, *syn*-CpMoOs$_3$(CO)$_9$(μ-O)(μ-CHCH$_2$Tol)(μ-H)[7], where the -CH$_2$Tol substituent on the alkylidene carbon oriented *syn* (to the μ-*oxo* ligand) with respect to the MoOs$_2$ face associated with the three edge bridging groups.

A single crystal X-ray diffraction study of **2** was carried out to ascertain the presence of the *oxo* ligand and the stereochemistry of the alkylidene moiety. The crystal contains an ordered arrangement of discrete CpWOs$_3$(CO)$_9$(μ-O)(μ-CHTol)(μ-H) molecules in contrast with a disordered structure of CpMoOs$_3$(CO)$_9$(μ-O)(μ-CHCH$_2$Tol)(μ-H) in the μ-*oxo*

Table 3. Interatomic Distances (Å) and Esd's for 2

(A) Metal-Metal Distances

Os(1)-Os(2)	2.839(1)	W-Os(1)	2.826(1)
Os(1)-Os(3)	3.013(1)	W-Os(2)	2.658(2)
Os(2)-Os(3)	2.833(1)	W-Os(3)	2.922(1)

(B) Metal-Alkylidene Distances

Os(1)-C(1)	2.20(2)	W-C(1)	2.05(3)

(C) Metal-Oxygen Distances

Os(3)-O(1)	2.13(2)	W-O(1)	1.79(2)

(D) Distances within the μ-CHTol Ligand

C(1)-C(2)	1.51(3)	C(4)-C(5)	1.38(3)
C(2)-C(3)	1.36(3)	C(5)-C(6)	1.40(3)
C(2)-C(7)	1.41(3)	C(5)-C(8)	1.53(3)
C(3)-C(4)	1.40(4)	C(6)-C(7)	1.34(4)

(E) Metal-Carbon (Carbonyl) Distances

Os(1)-C(11)	1.80(4)	Os(2)-C(23)	1.95(3)
Os(1)-C(12)	1.93(3)	Os(3)-C(31)	1.74(5)
Os(1)-C(13)	1.90(2)	Os(3)-C(32)	1.90(3)
Os(2)-C(21)	1.76(4)	Os(3)-C(33)	1.90(3)
Os(2)-C(22)	1.89(4)		

(F) Carbon-Oxygen (Carbonyl) distances

C(11)-O(11)	1.27(4)	C(23)-O(23)	1.14(4)
C(12)-O(12)	1.09(3)	C(31)-O(31)	1.28(5)
C(13)-O(13)	1.13(3)	C(32)-O(32)	1.15(3)
C(21)-O(21)	1.26(4)	C(33)-O(33)	1.11(3)
C(22)-O(22)	1.14(4)		

(C) Distances involving the Cp Ligand

W-C(51)	2.38(3)	C(51)-C(52)	1.34(5)
W-C(52)	2.46(3)	C(52)-C(53)	1.32(5)
W-C(53)	2.40(3)	C(53)-C(54)	1.31(7)
W-C(54)	2.29(3)	C(54)-C(55)	1.46(7)
W-C(55)	2.29(3)	C(55)-C(51)	1.33(6)

Table 4. Interatomic Angles (deg) and Esd's for 2

(A) Intermetallic Angles

Os(1)-Os(2)-Os(3)	64.2(0)	Os(2)-Os(1)-Os(3)	57.8(0)
Os(1)-Os(2)-W	61.8(0)	Os(2)-Os(1)-W	56.0(0)
Os(1)-Os(3)-Os(2)	58.0(0)	Os(2)-Os(3)-W	55.0(0)
Os(1)-Os(3)-W	56.8(0)	Os(2)-W-Os(3)	60.8(0)
Os(1)-W-Os(2)	62.3(0)	Os(3)-Os(1)-W	59.9(0)
Os(1)-W-Os(3)	63.2(0)	Os(3)-Os(2)-W	64.2(0)

(B) M-M-CO Angles

Os(2)-Os(1)-C(11)	170(1)	W-Os(2)-C(22)	98(1)
Os(3)-Os(1)-C(11)	119.4(7)	Os(1)-Os(2)-C(23)	105.3(8)
W-Os(1)-C(11)	133(1)	Os(3)-Os(2)-C(23)	99(1)
Os(2)-Os(1)-C(12)	80(1)	W-Os(2)-C(23)	162(1)
Os(3)-Os(1)-C(12)	92.2(7)	Os(1)-Os(3)-C(31)	144(1)
W-Os(1)-C(12)	135(1)	Os(2)-Os(3)-C(31)	88(1)
Os(2)-Os(1)-C(13)	89.3(8)	W-Os(3)-C(31)	95(1)
Os(3)-Os(1)-C(13)	145.8(8)	Os(1)-Os(3)-C(32)	116.5(9)
W-Os(1)-C(13)	95.4(7)	Os(2)-Os(3)-C(32)	174.5(9)
Os(1)-Os(2)-C(21)	158.6(7)	W-Os(3)-C(32)	123.4(8)
Os(3)-Os(2)-C(21)	101.1(8)	Os(1)-Os(3)-C(32)	93.9(7)
W-Os(2)-C(21)	98.3(8)	Os(2)-Os(3)-C(33)	85.3(9)
Os(1)-Os(2)-C(22)	98(1)	W-Os(3)-C(33)	138.5(9)
Os(3)-Os(2)-C(22)	159(1)		

(C) OC-Os-CO angles

C(11)-Os(1)-C(12)	91(2)	C(22)-Os(2)-C(23)	97(2)
C(11)-Os(1)-C(13)	95(1)	C(31)-Os(3)-C(32)	98(2)
C(12)-Os(1)-C(13)	90(1)	C(31)-Os(3)-C(33)	95(1)
C(21)-Os(2)-C(22)	93(1)	C(32)-Os(3)-C(33)	95(1)
C(21)-Os(2)-C(23)	92(1)		

(D) Os-C-O Angles

Os(1)-C(11)-O(11)	169(3)	Os(2)-C(23)-O(23)	180(1)
Os(1)-C(12)-O(12)	172(3)	Os(3)-C(31)-O(31)	173(4)
Os(1)-C(13)-O(13)	178(3)	Os(3)-C(32)-O(32)	177(3)
Os(2)-C(21)-O(21)	175(3)	Os(3)-C(33)-O(33)	177(3)
Os(2)-C(22)-O(22)	177(3)		

(E) Angles involving O(1) or C(1)

W-O(1)-Os(3)	95.9(7)	W-C(1)-Os(1)	83.2(9)
W-Os(3)-O(1)	37.5(4)	Os(1)-C(1)-C(2)	125(2)
Os(3)-W-O(1)	46.6(5)	W-C(1)-C(2)	120(2)
Os(2)-W-O(1)	103.9(5)	C(1)-W-O(1)	99.3(8)
Os(1)-W-O(1)	97.7(5)	Os(1)-W-C(1)	50.7(6)
Os(1)-Os(3)-O(1)	85.1(4)	Os(2)-W-C(1)	111.1(6)
Os(2)-Os(3)-O(1)	89.8(4)	Os(3)-Os(1)-C(1)	92.1(6)
Os(3)-W-O(1)	98.1(7)	Os(3)-W-C(1)	98.1(7)

(F) Angles within the μ-CHTol Ligand

C(1)-C(2)-C(3)	120(2)	C(4)-C(5)-C(8)	123(2)
C(1)-C(2)-C(7)	124(2)	C(5)-C(6)-C(7)	120(3)
C(2)-C(3)-C(4)	121(3)	C(6)-C(5)-C(8)	120(2)
C(3)-C(4)-C(5)	122(2)	C(6)-C(7)-C(2)	125(3)
C(4)-C(5)-C(6)	117(2)		

(G) Angles within the Cp Ligand

C(51)-C(52)-C(53)	109(4)	C(51)-C(55)-C(54)	100(3)
C(52)-C(53)-C(54)	107(5)	C(52)-C(51)-C(55)	112(5)
C(53)-C(54)-C(55)	111(4)		

and μ-alkylidene groups.[7] The overall molecular geometry and the atomic labelling scheme and stereoview of 2 are illustrated in Figures 1 and 2, respectively. Interatomic distances and angles are listed in Tables 3 and 4.

Although complex 2 is associated with 60 outer valence electrons as expected for a tetrahedral cluster,[8] the formal electron-counts at the individual metal atoms vary significantly, being 18 1/2e at Os(1), 17e at Os(2), 19 1/2e at Os(3) and 17e at W. It seems probable that the differences in metal-metal distances are related, in part, to these variations. The osmium-osmium distances are Os(2)-Os(3) 2.833(1), Os(1)-Os(2) 2.839(1) and Os(1)-Os(3) 3.013(1) Å and the tungsten-osmium distances are W-Os(2) 2.658(2), W-Os(1) 2.826(1) and W-Os(3) 2.922(1) Å. The longest of the metal-metal bonds, Os(1)-Os(3)=3.013(1) Å, is assigned to be associated with a single, unsupported μ-hydride ligand.[9] The presence of this bridging hydride ligand is further confirmed by the enlargement of the M-M-CO angles coplanar with and adjacent to the M-H-M linkage, <Os(1)-Os(3)-C(32)=116.5(9)° and <Os(3)-Os(1)-C(11)=119.4(7)°. The relatively short W-Os(2)=2.658(2) Å is believed to be due to formally electron-poor nature of W and Os(2) (17e each), which could be compensated for by increased bond order in the W-Os(2) linkage.[10]

The μ-oxo ligand [defined as O(1)] spans the W-Os(3) edge

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such that W-O(1)=1.79(2) Å, Os(3)-O(1)=2.13(2) Å, and <W-O(1)-Os(3)=95.9(7)°, which reveals the typical unsymmetrical edge-bridging *oxo* ligand. The presence of analogous W=O: →Os bonding has been found previously in μ-*oxo* tungsten complexes [W=O(av)=1.79 Å and Os-O(av)=2.16 Å] such as CpWOs₃(CO)₉(μ-O)(μ₃-CCH₂Tol),[11] *anti*-CpWOs₃(CO)₉(μ-O)(μ-CHCH₂Tol)(μ-H),[12] CpWOs₃(CO)₉(μ-O)(μ-C=CHTol)(μ-H),[13] CpWOs₃(CO)₈(μ-O)(μ₃-η²-C₂H₂)(μ-H),[10] CpWOs₃(CO)₉(μ-O)(μ-CHCH₂Tol)(μ-Cl),[14] CpWOs₃(CO)₈(PPh₂Me)(μ-O)(μ₃-CCH₂Tol),[15] and CpWOs₃(CO)₁₀(μ-O)(μ₃-CCH₂Tol).[16]

The μ-alkylidene ligand bridges the W-Os(1) edge, with W-C(1)=2.05(3) Å, Os(1)-C(1)=2.20(2) Å, and <W-C(1)-Os(1)=83.2(9)°. The configuration of C(1) is such that the C(1)-C(2) vector is oriented toward the μ-*oxo* ligand and the triangular W-Os(1)-Os(3) face. This configuration positions the Tol group *syn* to the W-Os(1)-Os(3) triangular face which is associated with three edge-bridging groups. The *syn* configuration of **2** adopted by the μ-alkylidene ligand places the bulky Cp and Tol moieties apart and avoids their steric congestion.[7]

All other features of the molecular geometry are within the expected range. Individual Os-CO distances range from 1.74(5) through 1.95(3) Å, C-O bond lengths range from 1.09 (3) through 1.28(5) Å and <Os-C-O angles are in the range 169(3)-180(1)°. Tungsten-carbon (Cp) distances vary from 2.29 (3) through 2.46(3) Å and carbon-carbon (Cp) distances are in the range 1.31(7)-1.46(7) Å.

In conclusion, the reaction of **1** with dihydrogen produces an unexpected hydrido-*oxo*-alkylidene complex CpWOs₃(CO)₉ (μ-O)(μ-CHTol)(μ-H) of *syn*-isomer as shown in Eq. (1). The source of the *oxo* ligand is not known at the moment. The

$$(1)$$
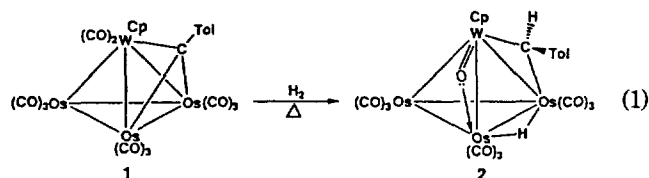
oxo ligand may be derived from a CO ligand by C-O bond scission or from other possible sources (O₂, H₂O, etc.). Note, however, that *oxo*-alkyne complexes CpWOs₃(CO)₈(μ-O)(μ₃-η²-C₂R₂)(μ-H) (R=H, Ph, Tol) were also produced by initial decarbonylation of the alkyne complexes CpWOs₃(CO)₁₀(μ₃-η²-C₂R₂)(μ-H) followed by thermolysis at 110℃.[17]

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Supplementary Material Available. Details of the crystallographic study of **2** are available from the authors (I.-H. S.).

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Convenient Method for the Synthesis of Unsymmetric Thioureas from Unreactive Amines Using Bu₂Sn(OAc)₂-SnCl₂

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We have been pursuing a synthetic program aimed at the potent H⁺/K⁺-ATPase inhibitor **1** which could have similar mechanistic behavior in biological system to FDA approved antiulcer agent, omeprazole **2**.[2,3] For the synthesis of com-