Having demonstrated that the cyclization was stereospecific in the predicted sense (compare the cyclization of **4** to the iodolactonization of 3-methyl-4-pentenoic acid)[2], we sought to apply this transformation in systems where it would result in the introduction of two new chiral centers and provide intermediates more closely related to our synthetic targets. When allyl methyl urethane **7a**[8] (Chart I) was treated with $I^+(\text{collidine})_2ClO_4^-$ (**5b**, X = I;[6] 12 h, refluxing CH_2Cl_2), only traces of a new compound were detected by TLC. Similarly, **7b**[8] was unreactive. However, under the same conditions, the corresponding *tert*-butyl urethanes **8a** and **8b** did undergo cyclization with **5b**.[9] These reactions were regio- and stereospecific, affording **11a** and **11b** respectively[10] (Table I). The formation of the six-membered ring products was unexpected; the oxazolidones were not detected in these cyclizations. This change in regiochemistry (compare **4** → **6**) corresponds to nucleophilic attack on an intermediate halonium ion at the site of greater positive charge (see additional discussion below).

We reasoned that a substituent that stabilizes a positive charge less effectively than phenyl might be expected to allow closure to the oxazolidone. To test this hypothesis, we prepared urethanes **9** and **10**. Urethane **9b** (the major isomer from the Wittig procedure)[8] gave, as predicted, a significant amount of the oxazolidone **12c**[10] (**12b**:**12c** = 1:2). Urethane **10b** (the major isomer from the Wittig procedure)[8] showed even greater tendency to go to the oxazolidone product (**13b**:**13c** = 1:5).

The trans-compounds **9a** and **10a** did not behave as predicted, however. Each afforded (stereospecifically) only the six-membered ring product[10] (**12a** and **13a**, respectively).

The results of these product studies are consistent with a mechanism (Scheme I) in which two concerted diastereoselective additions to the olefinic bond may occur. Cation I is favored when the aryl substituent is capable of assisting the stabilization of positive charge at the γ-carbon (i.e., when R^1 or R^2 = phenyl and when R_2 = *o*-cyanophenyl or *p*-nitrophenyl).[11] Cation II is favored in the absence of this stabilization (i.e., when $R^1 = R^2$ = H) or when the stabilization afforded by the substituent is counterbalanced by the steric interaction of R^1 and the α-hydrogen (R^1 = *o*-cyanophenyl or *p*-nitrophenyl) in I. Either cation, I or II, may lose the R^3 group (*tert*-butyl easily or methyl more slowly) to afford a cyclic urethane product.

The potential of the halonium-initiated cyclization of allylic urethanes, a reaction that is not only stereospecific but subject to regiochemical control, will be investigated for the synthesis of stereochemically complex natural products.

Acknowledgment. We would like to acknowledge helpful discussion with Professor Bert Fraser-Reid. Robert E. Babine assisted in acquiring decoupled spectra on Brown University's Bruker WM250 spectrometer, which was purchased with funds from the National Science Foundation and from Montedison, SPA (Milan, Italy). This work was supported by the National Institutes of Health (AI-18665). K.A.P. is pleased to acknowledge additional support in the form of a Teacher–Scholar Award from the Camille and Henry Dreyfus Foundation.

Supplementary Material Available: Partial ^1H NMR data for the debrominated urethane A and its stereoisomer and ^1H NMR data for halourethanes **11a**,**b**, **12a–c**, and **13a–c** (2 pages). Ordering information is given on any current masthead page.

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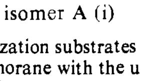
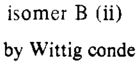
(7) Raney nickel hydrogenolysis afforded the debrominated urethane, designated here as isomer A. A mixture of isomer A and its epimer had been prepared (by Grignard addition to the protected prolinal) and subjected to NMR analysis. At 250 MHz the proton spectrum of the mixture showed two completely nonsuperimposable sets of signals (data in supplementary material). The isomer with the smaller coupling constant between protons on the oxazolidone ring and the higher field chemical shifts for these protons (the isomer obtained by debromination of **6**) was tentatively assigned the trans structure by analogy to assignments in the literature (see: Herweh, J. E.; Foglia, T. S.; Swern, D. *J. Org. Chem.* **1968**, *33*, 4029. Spassow, S. L.; Stefanovsky, J. N.; Kurtev, B. J.; Fodor, G. *Chem. Ber.* **1972**, *105*, 2462). This assignment was confirmed by inspection of the ^{13}C NMR spectrum of the mixture ($\delta(CH_3)$ 21.1 and 15.8) and that of isomer A ($\delta(CH_3)$ 21.1). For an analogous ^{13}C assignment, see: Overman, L. E.; Bell, K. L. *J. Am. Chem. Soc.* **1981**, *103*, 1851.



isomer A (i)



isomer B (ii)

(8) All cyclization substrates were prepared by Wittig condensation of the required phosphorane with the urethane of prolinal. Geometric isomers were separated by chromatography on silica gel or by fractional crystallization.

(9) A similar effect of the alkyl "leaving group" on halonium-initiated cyclizations of γ,δ-unsaturated ethers to tetrahydrofurans has been noted by Bartlett. See: Tychnovsky, S. D.; Bartlett, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3963.

(10) The cyclic urethanes **11a–13a** and **11b–13b** exhibited carbonyl absorption in the 1690–1705-cm^{-1} range. Stereochemistry was assigned on the basis of proton–proton coupling constants (see supplementary material). For **12c** and **13c**, IR 1750 cm^{-1}, the trans relationship of H_b and H_c was assigned on the basis of coupling constants (see supplementary material); the threo relationship of the centers bearing H_a and H_b was assigned by assuming that addition to the double bond was anti as it was in cyclizations affording the isomeric **12b** and **13b** as well as **12a** and **13a**.

(11) This is reminiscent of substituent effects that control ring size in concerted, cationic polyolefin cyclizations; see the discussion in the following: Parker, K. A.; Johnson, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 2556. A substituent effect in the *inter*molecular opening of iodonium and bromonium ions has previously been noted; see: Hassner, A. *Acc. Chem. Res.* **1969**, *4*, 9. L'abbe, G.; Hassner, A. *J. Org. Chem.* **1971**, *36*, 258.

(12) **Note Added in Proof:** For the stereochemistry of cyclization of some homoallylic urethanes, see the following: Wang, Y.-F.; Izawa, T.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1982**, *103*, 6465.

Unusual Ligand Replacement: Displacement of η^5-Cyclopentadienyl by η^6-Arenes in the Syntheses of $H_3(\eta^6\text{-}X)RhOs_3(CO)_9$ ($X = C_6H_6$, $C_6H_5CH_3$). Crystal and Molecular Structure of $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$

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We recently described general approaches to the preparation of mixed metal clusters that contain a triosmium unit.[1] Among the compounds reported is the paramagnetic cluster $H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$ (Figure 1), obtained from the reaction of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with $H_2Os_3(CO)_{10}$ in the presence of H_2. Attempts to prepare the rhodium analogue gave only very small amounts of a paramagnetic substance for which analytical data could not be obtained. However, in the course of this work we did observe displacement reactions that we believe to be without precedent in mono-η^5-cyclopentadienyl complexes.

We find that when $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ reacts with $H_2Os_3(CO)_{10}$ in the presence of H_2 in a solvent that is a potential η^6 ligand (benzene and toluene), the cyclopentadienyl molecule is replaced by a solvent molecule (eq 1; $X = C_6H_6$, $C_6H_5CH_3$). The second

$$H_2Os_3(CO)_{10} + (\eta^5\text{-}C_5H_5)Rh(CO)_2 \xrightarrow[H_2]{X} H_3(\eta^6\text{-}X)RhOs_3(CO)_9 + H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10} \quad (1)$$

product of the above reaction, $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$, has been reported previously[1] from the reaction of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with $H_2Os_3(CO)_{10}$ in the absence of H_2.

In a typical reaction $H_2Os_3(CO)_{10}$ was allowed to react with a 2-fold excess of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in toluene with prepurified hydrogen slowly bubbled through the reaction mixture at 90 °C for 72 h. Orange-red $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$ (25% based on $H_2Os_3(CO)_{10}$) and greenish brown $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ (8%) were isolated by TLC (silica 80:20 hexane/benzene). Or-

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(1) Shore, S. G.; Hsu, W. L.; Weisenberg, C. R.; Caste, M. L.; Churchill, M. R.; Bueno, C. *Organometallics* **1982**, *1*, 1405.

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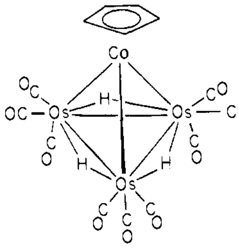

Figure 1. Structure of $H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$.

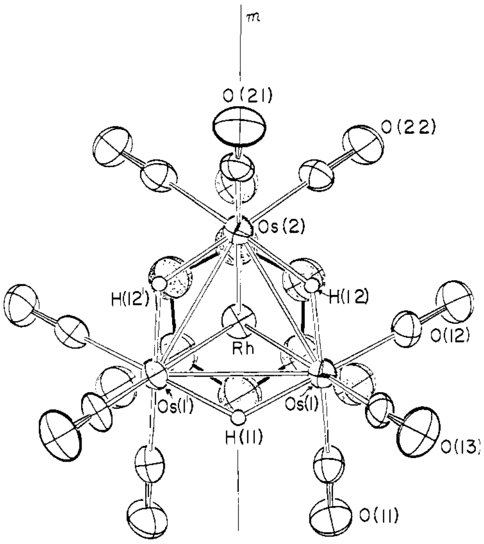

Figure 2. Observed structure of the $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$ molecule. The toluene ligand is subject to a 3-fold disorder that manifests itself only in the appearance of three methyl substituents each of one-third normal occupancy. Atoms of the toluene ligand have been stippled, and the bridging hydride ligands have been artificially reduced in an attempt to clarify this picture. The crystallographic mirror plane is vertical (ORTEP-II diagram).

ange-red $H_3(\eta^6\text{-}C_6H_6)RhOs_3(CO)_9$ (10%) was similarly prepared. In both reactions, a small amount of unidentified brown solid [ν_{CO} (hexane) 2080 w, 2065 s, 2045 w (sh), 2039 vs, 2006 vs, 1995 vs, 1962 m, 1932 vw, 1830 vw, 1808 m cm^{-1}] was obtained. All of these compounds are air-stable.

Infrared spectra of $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$ [ν_{CO} (hexane) 2070 w, 2048 s, 1999 vs, 1984 m, 1950 vw cm^{-1}] and $H_3(\eta^6\text{-}C_6H_6)RhOs_3(CO)_9$ [ν_{CO} (hexane) 2070 w, 2048 s, 1994 vs, 1978 m, 1945 vw cm^{-1}] are very similar to those of the isostructural clusters $H_3(\eta^5\text{-}C_5H_5)MOs_3(CO)_9$ [M = Co, Ni (Figure 1)].[1] The structure of $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$ is described below. It is equivalent to these structures. Proton [(acetone-d_6, −60 °C δ 6.68 (s, 6 H), −17.43 (s, 3 H)] and ^{13}C [(CH_2Cl_2, −60 °C) δ 176.9 (s, 3 C), 172.1 (d, J = 9 Hz, 6 C)] NMR spectra of $H_3(\eta^6\text{-}C_6H_6)RhOs_3(CO)_9$ are consistent with this structural arrangement.

The molecular structure of $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$ has been determined by means of a full three-dimensional X-ray diffraction study.[2] The molecule has crystallographically dictated C_s(m) symmetry; a 3-fold disorder of the methyl group on the toluene ligand, coupled with the intrinsic 3-fold symmetry of the $(\mu\text{-}H)_3Os_3(CO)_9$ moiety, leads to the entire observed ensemble having approximate C_{3v} symmetry. (Figure 2 shows the molecule viewed down the noncrystallographic 3-fold axis.)

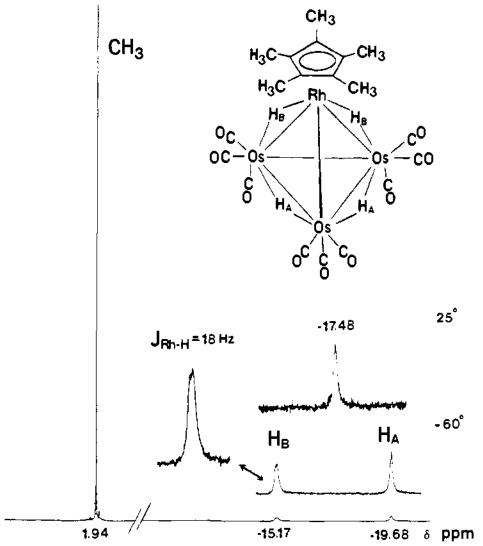

Figure 3. Proton NMR spectra of $H_4(\eta^5\text{-}C_5(CH_3)_5)RhOs_3(CO)_9$ in $CDCl_3$.

The rhodium atom is bonded to an η^6-tolyl ligand and to three osmium atoms, while each osmium atom is linked to the rhodium atom, two other osmium atoms, two bridging hydride ligands, and three terminal carbonyl ligands. The three bridging hydride ligands were located directly from difference Fourier syntheses and were well behaved during least-squares refinement.

Metal-metal distances (Å) are as follows: Os(1)–Os(1′) = 2.888 (1), Os(1)–Os(2) = Os(1′)–Os(2) = 2.888 (1), Os(1)–Rh = Os(1′)–Rh = 2.702 (1), and Os(2)–Rh = 2.703 (1). The bridging hydride ligands are all in symmetrical locations with Os(1)–H(11) = Os(1′)–H(11) = 1.75 (7), Os(1)–H(12) = Os(1′)–H(12′) = 1.74 (9) and Os(2)–H(12) = Os(2)–H(12′) = 1.72 (8). Corresponding angles (deg) are as follows: Os(1)–H(11)–Os(1′) = 111 (5), and Os(1)–H(12)–Os(2) = Os(1′)–H(12′)–Os(2) = 113 (5). Other distances of note include Os–CO = 1.887 (11)–1.927 (13) and Rh–C(arene) = 2.257 (29)–2.308 (18).

In other attempts to prepare a paramagnetic rhodium analogue of $H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$, we undertook reaction 1 in an inert solvent (heptane). In this case $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ was the only identifiable product. However, when $Rh(\eta^5\text{-}C_5(CH_3)_5)(CO)_2$ was used as the rhodium reagent in heptane, the new cluster $H_4(\eta^5\text{-}C_5(CH_3)_5)RhOs_3(CO)_9$ was obtained in 16% yield, and when toluene was used as the solvent, the yield was increased to 36%. Infrared [ν_{CO} (hexane) 2082 m, 2060 s, 2050 s, 2012 s, 1920 m, 1985 s, 1972 w (sh), 1943 vw cm^{-1}] and proton NMR (Figure 3) spectra of $H_4(\eta^5\text{-}C_5(CH_3)_5)RhOs_3(CO)_9$ are similar to those of $H_4(\eta^5\text{-}C_5H_5)RhOs_3(CO)_9$.[1] There was no evidence for toluene displacing pentamethylcyclopentadienyl in this case.

Acknowledgment. We thank the National Science Foundation for support of this work through Grants CHE 79-18149 (to S.G.S.) and CHE 80-23448 (to M.R.C.); 300-MHz FT NMR spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant CHE-7910019).

Registry No. $H_2Os_3(CO)_{10}$, 41766-80-7; $(\eta^5\text{-}C_5H_5)Rh(CO)_2$, 12192-97-1; $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$, 84237-81-0; $H_3(\eta^6\text{-}C_6H_6)RhOs_3(CO)_9$, 84237-82-1; $Rh(\eta^5\text{-}C_5(CH_3)_5)(CO)_2$, 32627-01-3; $H_4(\eta^5\text{-}C_5(CH_3)_5)RhOs_3(CO)_9$, 84237-83-2; Rh, 7440-16-6; Os, 7440-04-2; toluene, 108-88-3; benzene, 71-43-2.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters and observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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[2] Crystal data for $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$ are as follows: space group $C2/m$ (No. 12) with a = 14.178 (2) Å, b = 14.683 (2) Å, c = 10.205 (1) Å, β = 92.89 (1)°, V = 2121.6 (6) Å^3, and ρ(calcd) = 3.20 g cm^{-3} for mol wt = 1020.78 and Z = 4. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer and the structure solved by direct methods (MULTAN), difference Fourier syntheses, and full-matrix least-squares refinement. Final discrepancy indices are R_F = 3.9% and R_{wF} = 4.0% for all 1964 independent reflections with $4° < 2\theta < 50°$ (Mo Kα radiation) and R_F = 3.2% and R_{wF} = 3.8% for those 1726 data with $|F_o| > 3\sigma(|F_o|)$. All crystallographic computations were carried out on a Nova 1200 computer using the Syntex XTL structure-solving package (as modified at SUNY at Buffalo).