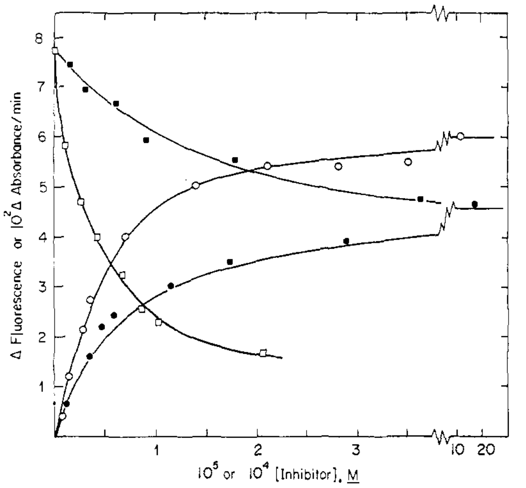

Figure 1. The interaction of the lactone I with hen egg white lysozyme. The change in the fluoresence of lysozyme (6.5×10^{-7} *M*) at 320 nm (excitation at 280 nm) in 0.005 *M* Na citrate–0.18 *M* NaCl, pH 5.0, at 23°, is plotted against the concentration of a I–II mixture with 13 mol % I (○, 10^5, *M*) or I–II mixture after hydrolysis of I at pH 9 for 30 min (●, 10^4, *M*). The rate of lysis of *M. lysodeikticus* cells (53 μg/ml) by 1.1×10^{-7} *M* lysozyme, followed by the change in absorbance at 450 nm, in 0.07 *M* Na phosphate, pH 6.2, at 30° is plotted against the concentration of a I–II mixture with 18 mol % I (□, 10^5, *M*) or a I–II mixture after hydrolysis of I at pH 6.0 in 0.3 *M* phosphate buffer for 4 hr (■, 10^4, *M*).

The dependence of the fluorescence changes upon the concentration of I obeys the equation for the formation of a 1:1 complex and yields an association constant of 3.6×10^6 M^{-1}.[10] Control experiments using the colorimetric tests for lactone[8] and reducing sugar[6] showed that during the period of measurement (about 1 min) for both fluorescence and lysis, there was less than 10 % hydrolysis of the lactone and 2 % cleavage of a glycosidic linkage.

On the basis of model building, Blake, *et al.*,[12] proposed that in a reactive lysozyme–substrate complex the pyranose ring which is bound in subsite D is strained from its normal chair conformation toward a half-chair conformation in which carbon atoms 1, 2, and 5, and the ring oxygen atom lie in the same plane, and that such strain is a cause of catalysis because it is relieved upon going to the transition state, which resembles an oxonium ion, the most favorable conformation for which is the half-chair one. A number of studies have supported this hypothesis.[13–17] The present study tests the strain hypothesis for the following reason: the most stable conformation for δ-lactones is the half-chair one,[18] and consequently I should bind more strongly to lysozyme in subsites A–D than the corresponding tetrasaccharide because the lactone ring can bind in subsite D without strain. In fact, the association constant for I is 36 times larger than that (10^5 M^{-1}) for tetra-*N*-acetylchitotetraose under the same conditions.[19] Moreover, the tetrasaccharide appears to bind predominantly only in subsites A–C; it thus avoids the unfavorable subsite D.[20] Studies on the binding of oligosaccharides consisting of alternating units of *N*-acetylglucosamine and *N*-acetylmuramic acid have shown that interaction of an *N*-acetylmuramic acid residue with subsite D contributes a factor of 10^{-2} to the association constant.[13] Since the factor is probably about the same for *N*-acetylglucosamine,[21] we estimate that I binds to lysozyme *3600 times more strongly* than tetra-*N*-acetylchitotetraose which is bound in the same mode (subsites A–D). Thus, relief of strain may account for a factor of 10^3–10^4 in catalysis.

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[21] The 3-lactyl side chain in subsite D probably does not interact strongly with the enzyme (ref 12).

Structure of Chloroaquobis(trimethylarsine)tetrakis(trifluoromethyl)rhodiacyclopentadiene. A Complex Containing Both Metal–Carbon σ Bonds and Coordinated Water

Sir:

We wish to report what we believe to be the first complete structural characterization of a solid complex containing both transition metal–carbon σ bonds and a coordinated water molecule. Previously the existence in solution of $[C_6H_5CH_2Cr(H_2O)_5]^{2+}$ [1] and $[(CH_3)_3Pt(H_2O)_3]^+$ [2] has been postulated, but no solids were isolated. More recently the complexes $[Rh(NH_3)_4(H_2O)R]SO_4$ (R = C_2H_5, C_2F_4H) have been isolated as solids and have been characterized by their infrared and nmr spectra.[3] The title compound, $RhCl(H_2O)(As(CH_3)_3)_2C_4(CF_3)_4$, is readily prepared by the decarbonylation of $RhCl(CO)(As(CH_3)_3)_2C_4(CF_3)_4$[4] in boiling benzene in the presence of moisture. It can also be prepared by exposing the yellow *solid* obtained by decarbonylating the carbonyl complex *in vacuo* at 80° (presumably $RhCl(As(CH_3)_3)_2C_4(CF_3)_4$) to moist air. The infrared spectrum of the complex shows bands due to coordinated water at 3550, 3350, and 1580 cm^{-1}, and the analytical data are in accord with the proposed formulation.[5]

The complex crystallizes from diethyl ether–petroleum ether (bp 30–60°) as pale yellow, wedge-shaped col-

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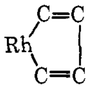
[5] *Anal.* Calcd for $C_{14}H_{20}F_{12}As_2OClRh$: C, 23.33; H, 2.80; F, 31.64; Cl, 4.92. Found: C, 23.42; H, 2.46; F, 30.33; Cl, 4.30.

umns. The systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$ observed on Weissenberg and precession photographs (Cu Kα radiation) uniquely determine the space group to be $P2_12_12_1$. The orthorhombic cell has dimensions a = 11.580 (1), b = 20.034 (1), c = 10.158 (1) Å, V = 2357 Å^3. No density was measured owing to the ready solubility of the complex in suitable media. A total of 2368 unique reflections having $\sin \theta/\lambda \leqq 0.6$ was collected on a Picker automated four-circle diffractometer using the θ–2θ scan procedure (Zr-filtered Mo Kα radiation). Of these, 777 were considered to be unobserved, and all data were corrected for absorption. The structure was solved by Patterson and difference Fourier techniques and refined by block-diagonal least-squares methods to convergence at a conventional residual of 0.06. All nonhydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms of the methyl groups have been included in the structure factor calculation.

A perspective view of the molecule is given in Figure 1. As in the case of the similar complex $RhCl(Sb(C_6H_5)_3)_2C_4(CF_3)_4 \cdot CH_2Cl_2$,[6] the fluorocarbon moiety is clearly σ bonded to the metal to give an essentially planar rhodiacyclopentadiene ring. The coordination about rhodium is thus that of a slightly distorted octahedron. There are two significant ways in which the present complex differs from the previous one. The first is a significantly longer Rh–Cl distance (2.446 (5) *vs.* 2.381 (3) Å; Δ/σ = 13). Two major factors contributing to this are a degree of bond weakening occasioned by the introduction of the sixth group into the coordination sphere of the metal and a substantial trans effect exerted by the alkyl group. Previously, alkyl groups bound to transition metals have been shown to exert strong trans influences in a number of Pt(II)[7] and Rh(III)[8] systems. That the latter contributes significantly to this bond lengthening can be inferred from the fact that the Rh–C distances are only slightly longer in the present complex. The second major difference is the pattern of C–C distances in the rhodium heterocycle. Whereas in the triphenylstibine complex all three C–C distances are substantially equal, here the C_2–C_3 distance is significantly longer ($\Delta/\sigma \sim 4$) than both C_1–C_2 and C_3–C_4 (see Figure 1), with the result that the four-carbon portion more closely resembles a *cis*-1,3-butadienylene moiety. Semiempirical molecular orbital calculations on models for these systems[9] show very clearly that the redistribution of charge within the molecule caused by the introduction of a sixth ligand into the coordination sphere is such that a more localized description of the bonding is appropriate for the six-coordinate species, *viz.*



These results further support our previous conclusions[5] that in the five-coordinate rhodiacycle there is significant π interaction between the metal and the fluorocarbon portion of the ring.

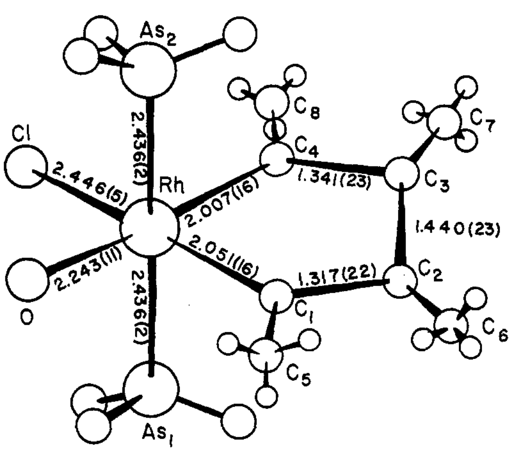


Figure 1. A perspective view of the molecule with the hydrogen atoms omitted for clarity. Relevant angles are: As_1–Rh–As_2, 178; As_1–Rh–Cl, 90; As_1–Rh–O, 87; As_2–Rh–Cl, 88; As_2–Rh–O, 92; Cl–Rh–O, 77; C_1–Rh–C_4, 80, O–Rh–C_4, 177; Cl–Rh–C_1, 175; Rh–C_1–C_2, 114; C_1–C_2–C_3, 114; C_2–C_3–C_4, 118; and C_3–C_4–Rh, 113°.

Although there appear to be no data available for a direct comparison, the Rh–O distance of 2.243 (11) Å probably represents a rather long bond to Rh(III) because of the trans effect noted above. In support of this it might be noted that an Ru–O distance of 2.12 (2) Å has been reported for $[RuCl_5(H_2O)]^{2-}$,[10] while the Rh–N distance trans to the C_2H_5 group in $[Rh(NH_3)_5(C_2H_5)]Br_2$ has been found to be 2.256 (8) Å.[8]

We are currently examining the details of the bonding in this type of complex more closely and the results, together with a complete account of the present structure, will be reported shortly.

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Electrochemistry of Natural Products. III. A Stereoselective, Stereospecific Phenol Coupling Reaction[1]

Sir:

We have previously reported[2] that the platinum-catalyzed oxygenation of racemic 1,2-dimethyl-7-hydroxy-6-methoxy-1,2,3,4-tetrahydroisoquinoline (**1**) gives three, separable pairs of enantiomers (**2**–**4**) of the carbon–carbon dimer, due to the centers of chirality

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[1] This work was supported by the National Science Foundation (GP-7601) and the National Institutes of Health (CA-10494). Part II: J. M. Bobbitt, H. Yagi, S. Shibuya, and J. T. Stock, *J. Org. Chem.*, in press.

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