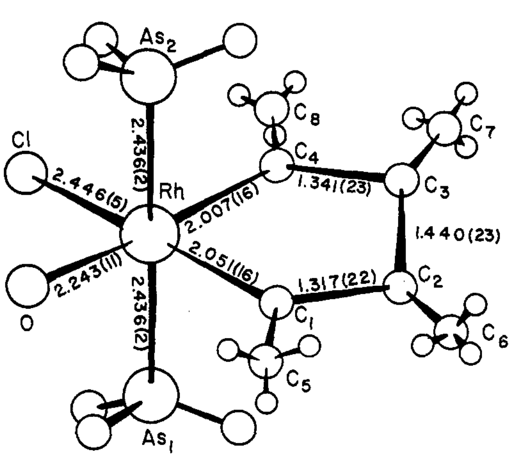
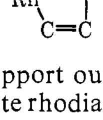


Figure 1. A perspective view of the molecule with the hydrogen atoms omitted for clarity. Relevant angles are: As_1–Rh–As_2, 178; As_1–Rh–Cl, 90; As_1–Rh–O, 87; As_2–Rh–Cl, 88; As_2–Rh–O, 92; Cl–Rh–O, 77; C_1–Rh–C_4, 80, O–Rh–C_4, 177; Cl–Rh–C_1, 175; Rh–C_1–C_2, 114; C_1–C_2–C_3, 114; C_2–C_3–C_4, 118;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

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.

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.

Acknowledgments. We are indebted to Dr. Charles Fritchie for the use of the diffractometer and to the National Science Foundation (Grants No. GP-8066 and GP-16380) and the Gulf Research and Development Corp. for support of this work.

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(6) J. T. Mague, *Inorg. Chem.*, **9**, 1610 (1970).

(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 5.

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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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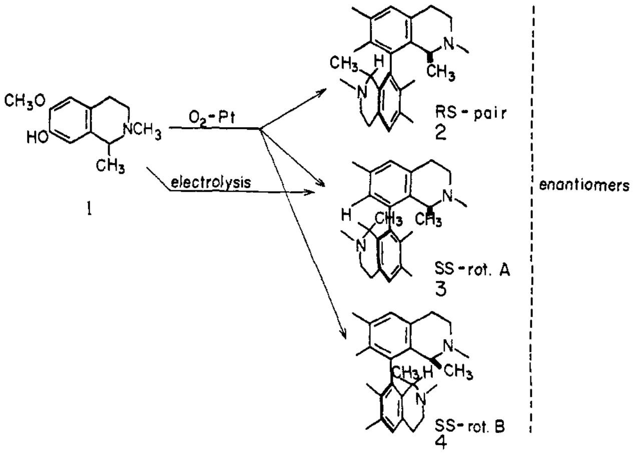
at the diphenyl linkage and at C-1 of the isoquinoline systems (Scheme I). The same three pairs of isomers were obtained in our laboratory when the $K_3Fe(CN)_6$ oxidation of racemic 1[3] was repeated. We have now found that the electrolytic oxidation[4] of racemic 1 yields *only one* (tlc, nmr, and isolation) of the enantiomeric pairs in 69% yield (77% conversion). The carbon–oxygen dimer[2] was isolated in 7% yield.

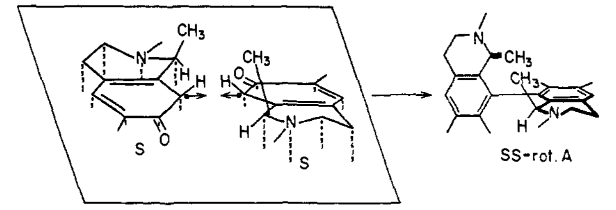
Scheme I. Oxidative Coupling of Racemic **1**



This single isomer, mp 226–227°, corresponds to one of the two crystalline isomers of the dimer. The structure is thought to be **3** based upon the following evidence. Electrolytic oxidation of the pure enantiomers of **1**[5] gave the enantiomers of the same dimer which was isolated from racemic **1** [*S* isomer, 62% yield, 72% conversion; *R* isomer, 66% yield, 87% conversion]. The dimers had equal and opposite ORD curves. Thus, C-1 of the two isoquinoline rings in the electrolysis product must have the same configuration, as in **3** and **4**. Furthermore, ferricyanide oxidation of the enantiomers of **1** gave a mixture of two isomers which must be **3** and **4**. One was identical with the product from the electrolytic oxidation, and the other had spectral properties identical with those of another one of the original isomers.[2] The final establishment of **3** as the structure of the electrolysis product depends upon the nmr spectra of these two compounds. In **4**, the methyl groups are close to the oxygens and the protons should exhibit nmr peaks downfield from those generated by the methyl protons of **3** which lie more over the benzene rings (partially due to a methyl–methyl repulsion which does not exist in **4**). The spectra in dimethyl-d_6 sulfoxide of the two isomers from the $K_3Fe(CN)_6$ oxidation show *C*-methyl doublets at δ 0.71 and 1.17. The product of the electrolysis shows the δ 0.71 peak and is therefore **3**. In **1**, this peak appears at δ 1.22, slightly downfield from both **3** and **4** due to the absence of any positive effect of the ring current (of the additional aromatic ring in the dimers).

These results are best explained as resulting from a surface reaction on the graphite electrode as shown in Scheme II between two radicals. Such radicals are considered[6] to be the reacting species in oxidative coupling reactions. If the reacting molecules are adsorbed to the surface with the methyl groups sticking up, only those having identical configurations can come close enough together to couple. Otherwise methyl–methyl hindrance is severe. The formation of **3** in preference to **4** requires that the molecules lie in planes which are not parallel with the electrode surface. These planes are so tipped that the aromatic ring, or the flatter portion, is closer to the surface than the more bulky heterocyclic rings, a quite logical circumstance.

Scheme II. Oxidative Coupling of (*S*)-**1** on a Surface



Thus, the reaction is stereoselective in that only molecules of identical configuration couple, and stereospecific in that only one of two possible rotational isomers is formed.

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[3] M. Tomita, Y. Masaki, and K. Fujitani, *Chem. Pharm. Bull.*, **16**, 257 (1968).

[4] The oxidation was carried out on a graphite felt electrode in excess sodium methoxide (3.3 mol) in wet CH_3CN at a potential of 0.04 V *vs.* standard calomel electrode using tetraethylammonium perchlorate as an electrolyte. A conventional two-compartment system was used.

[5] Racemic **1** was resolved through its *p*-toluoyltartaric acid salts. The enantiomers were correlated with carnegine of known absolute configuration (A. R. Battersby and T. P. Edwards, *J. Chem. Soc.*, 1214 (1960); E. Späth, *Chem. Ber.*, **62**, 1021 (1929)): *R* isomer, mp 182–182.5°, $[\alpha]^{22}D$ +29.2° (*c* 1, $CHCl_3$); *S* isomer, mp 182.5–183°, $[\alpha]^{22}D$ −29.8° (*c* 1, $CHCl_3$).

[6] H. Musso in "Oxidative Coupling of Phenols," W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, New York, N. Y., 1967, p 1.

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Complexes of Ozone with Carbon π Systems

Sir:

π complexes have frequently been proposed as the result of the initial attraction between ozone and olefinic or aromatic systems.[1-5] For example, in the competition between ozonolysis and epoxide formation during ozonation of hindered olefins (*e.g.*, 1-mesityl-1-phenylethylene), a π complex precursor is suggested either to enter into 1,3-dipolar cycloaddition (ozonolysis route) or convert to a σ complex (epoxide route *via* O_2 loss).[2]

We wish now to report data which to our knowledge constitute the first characterization of complexes between ozone and sp^2 carbon systems.

Ozonation of 1-mesityl-1-phenylethylene at −78° in various solvents[2] or even at −120° (Freon-11 or -12) resulted in the ready absorption of 1 mol equiv of ozone and the simultaneous release of molecular oxygen with formation of the corresponding epoxide.

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[4] D. G. Williamson and R. J. Cvetanovic, *ibid.*, **90**, 4248 (1968).

[5] P. S. Bailey, F. E. Potts, III, and J. W. Ward, *ibid.*, **92**, 230 (1970).