The rate constants for the reaction of *i*-PrOH (k_i) and *t*-BuOH (k_t) with $1^{\bullet+}$ were also determined by flash photolysis: k_i = 5.5 (3) × 10^7 and k_t = 1.8 (1) × 10^7 M^{-1} s^{-1}. Interestingly, a comparison of the rate constants for MeOH, *i*-PrOH, and *t*-BuOH reveals a relative reactivity of ≈5:3:1, respectively. This shows that the *nucleophilic ring-opening of $1^{\bullet+}$ is remarkably insensitive to the steric environment of the nucleophile.* Some insight into this surprising observation may be provided by theory.

Molecular orbital calculations show that one-electron oxidation can be accompanied by large structural distortions.[18] For example, despite a one-electron bond energy of ≈50 kcal mol^{-1}, the ethane cation radical is calculated to have a C–C bond length of ca. 2 Å and a H–C–C bond angle of only 98°.[19] Similar structural changes have been calculated for cyclopropane cation radicals.[20] These structural changes are expected to lead to an "early" transition state for nucleophilic displacements on one-electron C–C bonds, which, in turn, should diminish steric effects on the reactions. The near equal reactivity of $1^{\bullet+}$ with MeOH, *i*-PrOH, and *t*-BuOH is consistent with this expectation.

In summary, arylcyclopropane cation radicals undergo nucleophilic substitution by a variety of nucleophiles with inversion of configuration at carbon. Furthermore, these substitution reactions have both diminished steric requirements and large reaction rate constants. Currently, we are investigating the reaction characteristics of other nucleophilic one-electron bond cleavages.

Acknowledgment. We thank Professor H. M. Walborsky (Florida State University) for sending us a generous sample of optically enriched **12** and Professor S. S. Shaik (Ben-Gurion University) for several enlightening discussions and for his encouragement. Research support was provided by the National Science Foundation (CHE86-10404) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Stereochemistry of the Oxidative Addition of an Epoxide to Platinum(II): Relevance to Catalytic Reactions of Epoxides

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Received September 27, 1989

The activation of epoxides by transition-metal catalysts (A → B, Scheme I) is thought to occur by oxidative addition. Only a few examples of oxametallacyclobutane products have been isolated or fully characterized, and the mechanism for their preparation by oxidative addition has not been determined unambiguously.[1-3] The overall catalytic cycle shown in Scheme I may occur with overall retention of stereochemistry, as has been demonstrated by using the reagent *trans*-$\overline{\mathrm{CHDCHDO}}$ with a copper(I) catalyst. It is not known whether this cycle occurs by double retention or double inversion of stereochemistry.[2,3] Other related reactions are complicated by hydrogen atom migration or exchange.[4,5]

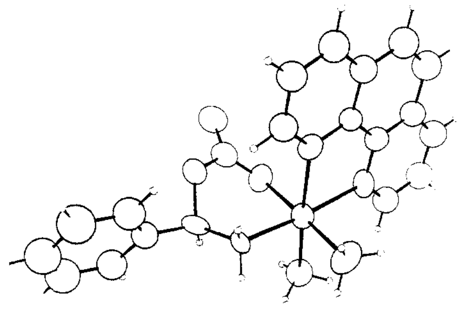
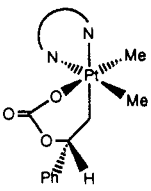
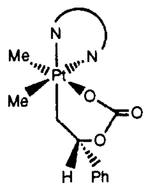


Figure 1. A view of the structure of complex **2-RΔ**.

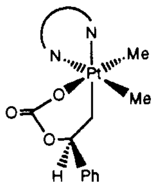
The recent discovery of the conversion A → C shown in Scheme I, L_nM = [$PtMe_2$(1,10-phenanthroline)] (**1**), in which the intermediate B is trapped by carbon dioxide to give the stable metallacarbonate C,[5,6] provides a reaction for which the stereochemistry of epoxide oxidative addition can be assessed.[7] The product of reaction of styrene oxide, carbon dioxide, and **1** can adopt two diastereomeric forms, each of which has two enantiomeric forms.[8] The isomers **2-RΔ**/**2-SΛ** and **2-RΛ**/**2-SΔ** are possible, in which R/S and Λ/Δ describe the chiralities at carbon and platinum, respectively.[8] NMR studies reveal that both diastereomers are present in a ratio of ≈5:1, but resonances cannot be assigned to a specific diastereomer.[7,8]



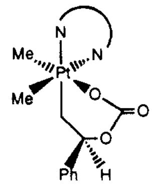
2-SΛ



2-RΔ



2-RΛ



2-SΔ

Reaction of (*R*)-styrene oxide and CO_2 with **1** gave crystals of **2** in two crystalline forms. Thin colorless platy crystals[9] were readily grown on many occasions from methylene chloride solutions layered with pentane. These crystals were not suitable for a Bijvoet study. From one recrystallization attempt, a single, pale yellow, prismatic crystal was obtained, which was cut into three pieces. The smallest fragment, of dimensions 0.45 × 0.45 × 0.45 mm, was used in the X-ray determination,[10] while the other two were used for NMR experiments, vide infra. The molecular structure was shown to be that of the **2-RΔ** isomer by the Bijvoet method, Figure 1. Thus retention of configuration at the chiral carbon center is observed on oxidative addition of the epoxide.[11] When either the single-crystal fragments or the platy crystals were

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(8) There are several other possible isomers; however, only those containing the stable *fac*-trialkylplatinum(IV) units are viable, and mer isomers need not be considered.

(9) Orthorhombic, space group $P2_12_12_1$, with cell dimensions a = 9.757 (6) Å, b = 27.47 (2) Å, c = 7.122 (4) Å, V = 1909 $Å^3$, Z = 4.

(10) $\overline{\mathrm{Pt(CH_3)_2\{CH_2CH(C_6H_5)OC(O)O}}\}$(phen), monoclinic, space group $P2_1$, a = 11.185 (2) Å, b = 14.622 (3) Å, c = 6.350 (2) Å, β = 105.77 (2)°, V = 999.5 (7) $Å^3$, Z = 2, λ (Mo Kα) = 0.71073 Å, Zr prefilter, μ = 711.6 mm^{-1}, R_1 = 0.0658 and R_2 = 0.0683. The data were processed by using the Enraf-Nonius Structure Determination Package.

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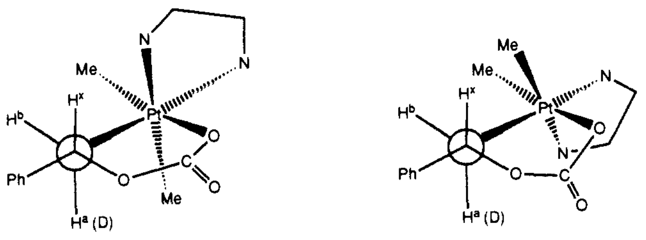
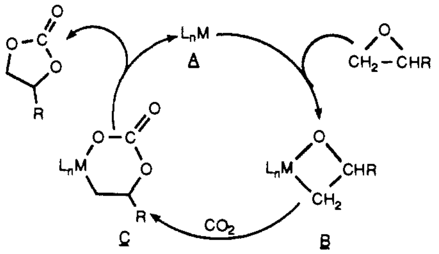


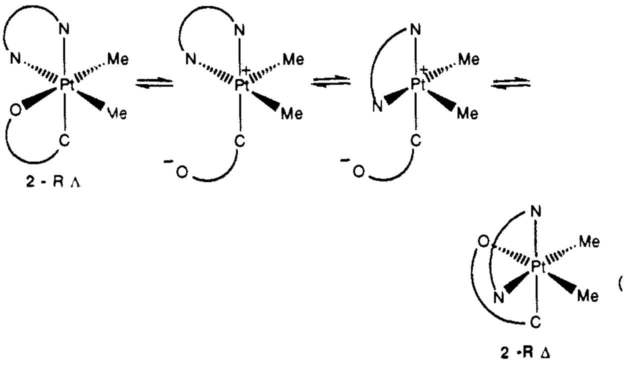
2-RΛ **2-RΔ**

Figure 2. Diagram of the MMX minimized structures of 2-RΛ and 2-RΔ, showing a view down the CHPh-CH_2 bond. The optimized dihedral angles used in calculating the coupling constants ^3J(HH) were H^xCCH^b = 60 (5)° and 63 (2)°, H^xCCH^a = 173 (4)° and 171 (2)° for the RΔ/SΛ and RΛ/SΔ diastereomers.

Scheme I

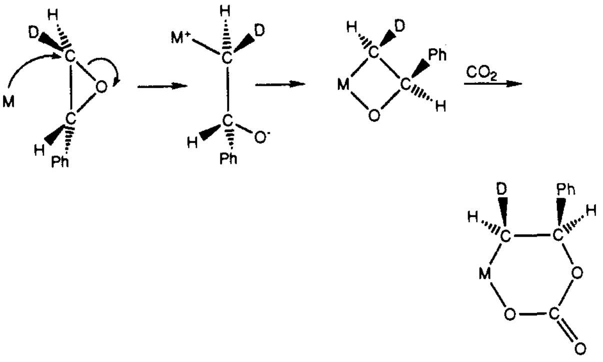


dissolved, the NMR spectrum indicated the presence of a mixture of diastereomers; hence interconversion between 2-RΔ and 2-RΛ is facile under these conditions. This probably occurs by dissociation of the Pt-O bond, followed by pseudorotation and recoordination as shown in eq 1.



(1)

The reaction of *trans*-CHDCHPhO, CO_2, and **1** gave [$PtMe_2${*cis*-CHDCHPhOC(O)O}(phen)] (2-D). Investigations using NMR techniques have shown that the product has *cis*-1-D,2-Ph stereochemistry (Figure 2). On the basis of crystallographic data for the RΔ isomer (Figure 1) and MMX data for both the RΔ and RΛ isomers (Figure 2),[12] each isomer is expected to give $^3J(H^aH^x)$ = 11-13 Hz and $^3J(H^bH^x)$ = 0-3 Hz.[13] The observed coupling constants are in good agreement (see supplementary material, Table SX). Of critical importance to this investigation is the absence of the coupling constant $^3J(H^aH^x)$ in both isomers of 2-D (Table SX). The stereochemistry is therefore determined with confidence, and the result shows that the reaction forming 2-D occurs with inversion of stereochemistry at the CHD center. An S_N2 mechanism for the oxidative addition, in which the metal attacks at the less sterically hindered carbon atom, can be inferred as shown in eq 2, M = [$PtMe_2$(phen)].



(2)

Acknowledgment. The NSERC of Canada and the Academic Development Fund of the University of Western Ontario are thanked for financial support of this research. L.G. is grateful for the award of an NSERC postdoctoral scholarship.

Supplementary Material Available: Tables SI-SVII, SIX, and SX, comprising crystal data and experimental conditions, atomic positional and thermal parameters, bond distances and angles, weighted least-squares planes, selected torsion angles, selected friedel pairs, and ^1H NMR data for **2** (9 pages); Table SVIII, comprising structure amplitudes for **2** (16 pages). Ordering information is given on any current masthead page.

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(11) This is not a trivial experiment since metallacycles undergo many types of rearrangements which could lead to racemization or inversion at that carbon center.[4-6] In particular, platinacyclobutanes undergo ready skeletal isomerization. Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

(12) We cannot tell if the second crystalline form contains molecules in the RΛ configuration, but we can be confident that the chirality at the carbon is *R*. Similarly, because of the equilibration, we cannot tell if RΔ is the major diastereomer in solution. Molecular mechanics calculations suggest that RΛ is more stable by ≈0.8 kcal mol^{-1} than RΔ. This would give an equilibrium constant $K = [R\Lambda]/[R\Delta] \approx 3.9$ in the absence of differential solvation effects. The calculations were made by using the MMX force field developed by K. Gilbert and J. J. Gajewski (Indiana University). Good agreement was found by using starting structures based on the X-ray data for 2-RΔ or using a "hand-drawn" structure. The metallacycle configuration with equatorial phenyl groups was found to be 1.5-2.5 kcal mol^{-1} more stable than that with axial phenyl groups for both diastereomers.

(13) Haasnoot, C. A. G.; DeLeeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1981**, *36*, 2783. The extent of inversion at the CHD center is estimated to be at least 90%.

(14) The reductive elimination step in the catalytic cycle[2] would then also occur with inversion, that is by dissociation of the Pt-O bond followed by S_N2 attack by the O^- center on the Pt-CH_2 group, to give overall retention of stereochemistry.

Synthesis of Helical Poly-β-pyrroles. Multiple Atropisomerism Resulting in Helical Enantiomorphic Conformations

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Received July 27, 1989
Revised Manuscript Received January 19, 1990

We have been interested in designing large conformationally flexible molecular arrays that have a predictable secondary

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