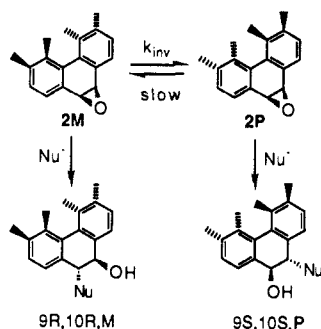
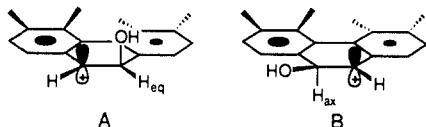


Figure 1. Circular dichroism spectra of the two conformational enantiomers of **2** at 0 °C in *n*-hexane. Activation parameters for inversion of configuration were derived from the temperature dependence of the decay of the CD transition at 230 nm.

Scheme I



possible diastereomeric carbocations **A** and **B** will be slow relative to the lifetime of the intermediates.



The hindered arene oxide, **2**, is considerably more sensitive to acid-catalyzed isomerization and solvolysis than the less strained 2,3,6,7-tetramethylphenanthrene 9,10-oxide (**3**).⁷ Solvolysis and rearrangement of **2** follows the rate law, $k_{\text{obs}} = k_0 + k_a[\text{H}_3\text{O}^+]$, with $k_a = (2.3 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $k_0 = (3.8 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$. In contrast, **3** solvolyzes more slowly under the same conditions with $k_a = (4.8 \pm 0.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_0 = (2.0 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$. Product distributions are essentially invariant with pH but differ markedly between the two isomers. Thus, solvolysis of **2** at pH 4, 7, and 10 gives 13–15% cis-dihydrodiol, 47–53% trans-diaxial-dihydrodiol, and 34–40% ketone whereas **3** yields 0.7–2.0% cis-dihydrodiol, 2.6–5.4% trans-diaxial-dihydrodiol, and 93–97% phenol. The larger amount of the trans solvolysis product from **2** at the expense of the NIH-shift product must derive in part from formation of the conformationally stable carbocation **A** (or its zwitterionic equivalent) with a pseudoaxial hydroxyl group that favors axial capture by solvent⁸ and from which transfer of the pseudo-equatorial hydride to form ketone is unlikely.^{4a,9} The ratio of the NIH-shift product and cis-dihydrodiol (products that are expected to arise only from carbocation **B**) varies from ca.

(7) Kinetics of solvolysis were followed at 255 nm in 25% $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ between pH 4 and 11 at 15 °C essentially as described by Whalen et al.^{3b} Products were analyzed by HPLC as previously described.^{1b} The positional isomer **3** was chosen as the reference compound for **2** to minimize the expected inductive effect of the methyl groups on the reaction. The inductive effect is obviously significant as judged from comparison of the rate constants above for solvolysis of **3** at 15 °C in 75% H_2O to those of phenanthrene 9,10-oxide [$k_a = (1.15 \pm 0.09) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_0 = (2.5 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$] at 30 °C in 100% H_2O .^{3b}

(8) Trans-dihydrodiol could also arise from equatorial trapping of carbocation **B** by solvent. However, this unlikely possibility would lead to the conformational diastereomer with quasiequatorial hydroxyl groups,^{2a} which is not observed.

(9) Nobes, R. H.; Rodwell, W. R.; Bouma, W. J.; Ransom, L. *J. Am. Chem. Soc.* **1981**, *103*, 1913.

50:1 in the solvolysis of **3** to about 3:1 with **2**.¹⁰ This suggests that the partitioning of this carbocation conformer to either ketone or cis-dihydrodiol is controlled to some extent by nonbonded interactions between the methyl groups at the 4- and 5-positions of **2**, which would tend to favor the less strained fully sp^3 -hybridized product.

As anticipated, complete transfer of chirality from the starting material to products is observed (Scheme I) under conditions where solvolysis or nucleophilic opening of **2** is much faster than pseudorotation ($k_{\text{obs}} \gg k_{\text{inv}}$). For example, all solvolysis products derived from **2M** at pH 4 exhibit an enantiomeric purity ($\geq 90\%$) that is indistinguishable from that of the hydrocarbon used to prepare **2M**.¹¹ In addition, the specific-base- or enzyme-catalyzed (glutathione *S*-transferase) addition of glutathione to **2M** or **2P** occurs stereospecifically with trans addition of the nucleophile to the oxirane carbon of *S* absolute configuration in the *M* antipode and to the *R* configured carbon of the *P* isomer. The unusual properties of the conformational enantiomers **2** are expected to be of considerable help in understanding the solution chemistry and enzyme-catalyzed reactions of arene oxides.

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Supplementary Material Available: Description of the synthesis and spectroscopic characterization of compounds **2**, **3**, and **4** (5 pages). Ordering information is given on any current masthead page.

(10) Preliminary experiments in H_2^{18}O at pH 4 indicate that the cis-dihydrodiol is derived largely ($>90\%$) if not exclusively from axial capture of carbocation **B** and that $<10\%$ of this product can be attributed to equatorial capture of conformer **A**.

(11) Solvolysis products were separated by reversed-phase HPLC after reduction of the ketone to the corresponding alcohol with NaBH_4 essentially as described by: Sayer, J. M.; Grossman, S. J.; Adusei-Poku, K. S.; Jerina, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 5068. The enantiomeric purity of each product was determined by HPLC on a chiral stationary phase of (+)-poly-(triphenylmethyl methacrylate).^{1b} The diastereomeric glutathione adducts of **2M** and **2P** were quantified by reversed-phase HPLC following: Cobb, D.; Boehlert, C.; Lewis, D.; Armstrong, R. N. *Biochemistry* **1983**, *22*, 805.

Oxidation of Primary Alcohols to Carboxylic Acids Made Easy at Iridium

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The oxidation of primary alcohols to carboxylic acids has no precedent for η^2 -dioxygen metal complexes.¹

In this communication we report on the synthesis and characterization of the peroxo complex [(triphos)IrCl(η^2 - O_2)] (**1**), which transforms primary alcohols into carboxylic acids [triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$]. Compound **1** is prepared as yellow, air-stable crystals by bubbling O_2 for 20 min through a CH_2Cl_2 (50

(1) For recent reviews on the synthesis and chemistry of metal dioxygen complexes, see: (a) Mimoun, H. *Metal Complexes in Oxidation*. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, p 317. (b) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1. For more recent and significant articles, see: (c) Lawson, H. J.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 6223. (d) Atwood, J. D. *Coord. Chem. Rev.* **1988**, *83*, 93. (e) van Asselt, A.; Trimmer, M. S.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 8254. (f) Mason, M. G.; Ibers, J. A. *Ibid.* **1982**, *104*, 5153.

and H₂O can be ruled out as we do not observe the formation of IrD. In contrast, a deuteride complex, namely, [(triphos)IrD(O₂CCD₃)]⁺, forms together with HDO when **1** is reacted with C₂D₂O₄. (ii) This reaction occurs also in CH₂Cl₂ with an equimolar amount of ethanol. (iii) Acetaldehyde does not react with **1** in CH₂Cl₂ unless 1 equiv of a protic acid such as triflic acid is added. Then a fast reaction occurs and the *cis*-chloride- η^2 -acetate derivative [(triphos)IrCl(O₂CMe)]BPh₄ (**8**) forms together with H₂O. (iv) When **1** (0.5 mmol) is reacted with a stoichiometric amount of C₂H₅OD and a 10-fold excess of R'CHO (R' = Pr, Bu, Ph), the formed η^2 -carboxylate hydride contains the aldehyde R' group and both acetaldehyde and HDO are the coproducts. (v) In the temperature range of -60 to 20 °C, ³¹P{¹H} NMR spectroscopy shows that the formation of **4** from C₂H₅OD is preceded by the appearance of an intermediate species. Complex **4** begins to form at -20 °C, and its concentration in solution increases as the temperature increases. Simultaneously, the concentration of the intermediate decreases until, at 0 °C, only **4** is present. The intermediate species exhibits an AMQ splitting pattern with $\delta_A = -27.38$, $\delta_M = -34.50$, and $\delta_Q = -35.48$ [J(AM) = J(AQ) = 19.50 Hz, J(MQ) = 26.60 Hz], which is typical for octahedral Ir(III) complexes containing three different ligands trans to triphos. A suitable intermediate could well be the hydroperoxo aldehyde complex A (Scheme I).

Registry No. **1**, 128549-58-6; **2**, 128549-59-7; **3**, 128549-61-1; **4**, 128549-63-3; **5**, 128549-65-5; **6**, 128549-67-7; **7**, 128549-69-9; **8**, 128549-71-3; [Ir₂Cl₂(C₈H₁₄)₄], 12246-51-4.

Supplementary Material Available: Analytical data for the new complexes and detailed preparation and characterization of [(triphos)IrCl(C₂H₄)] (1 page). Ordering information is given on any current masthead page.

Synthesis and Reactions of Tungsten(IV) Bis(imido) Complexes: Relatives of Bent Metallocenes

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Four-coordinate tungsten(IV) or molybdenum(IV) complexes are relatively rare.¹ The core geometry of such species may be either a paramagnetic tetrahedron (e.g., Mo(O-*t*-Bu)₄^{1a}), diamagnetic square plane (e.g., W(O-2,6-C₆H₃Me₂)₄^{1b}), or a diamagnetic flattened tetrahedron (e.g., W(S-*t*-Bu)₄^{1c}, Mo(S-2,4,6-C₆H₂Me₃)₄^{1d} or Mo(S-*t*-Bu)₄^{1e}). The recent synthesis of square-planar d⁴ Os(NAr)₂(PMe₂Ph)₂ (Ar = 2,6-C₆H₃-*i*-Pr₂)² raised the question as to whether analogous d² tungsten(IV) complexes could be prepared, and whether they would be planar or tetrahedral. We have now synthesized complexes of the type W(NAr)₂L₂ (L = a phosphine). They are diamagnetic, are believed to be tetrahedral species, and in contrast to Os(NAr)₂(PMe₂Ph)₂, react readily with π bonding ligands via five-coordinate intermediates.

W(NAr)₂Cl₂(dme)³ can be reduced readily with sodium amalgam in the presence of dimethylphenylphosphine in diethyl ether to give burgundy-colored, air-sensitive W(NAr)₂(PMe₂Ph)₂ (**1**) in 50–60% yield.⁴ ³¹P NMR data indicate that the phosphines are not lost readily from the metal on the NMR time scale in solution (J_{PW} = 465 Hz). So far, complexes analogous to **1** containing PPh₃, PMe₃, or P(OPh)₃ instead of PMe₂Ph have not been isolated, and no crystals of **1** have been obtained yet that are suitable for X-ray studies.

W(NAr)₂(PMe₂Ph)₂ reacts within 1–2 min with acetone in pentane to give orange-yellow W(NAr)₂(PMe₂Ph)(η^2 -OCMe₂) (**2a**) quantitatively. An X-ray study⁵ shows **2a** to be pseudotetrahedral, with W, P, O, and C lying in the pseudoplane that bisects the N–W–N angle (mean deviation of 0.034 Å; Figure 1). One imido ligand is close to linear (W–N–C = 168.8 (6)°) while the other is more bent (155.8 (5)°). Proton and carbon NMR spectra show the two imido ligands to be equivalent on the NMR time scale at 25 °C. One can rationalize the orientation of the imido groups' phenyl rings relative to each other and relative to the phosphine and acetone ligands on the basis of simple steric arguments. The C–O distance of 1.39 (1) Å suggests that **2a** is best described as an oxametallacyclopropane complex of W(VI); no ν_{CO} stretch could be observed above 1400 cm⁻¹. There are now many examples of complexes that contain a π -bound ketone or aldehyde.⁶

W(NAr)₂(PMe₂Ph)₂ reacts with propionaldehyde to give W(NAr)₂(PMe₂Ph)(η -OCH₂Et) (**2b**), in which the two imido ligands are inequivalent and the methylene protons in propionaldehyde are diastereotopic, consistent with **2b** being analogous to **2a**. Two isomers are observed; we propose one has a structure strictly analogous to that of **2a**, and the other a structure in which the carbon atom is in the position next to phosphorus.

The result of reactions of W(NAr)₂(PMe₂Ph)₂ with acetylenes or olefins appears to depend largely on the size of the added ligand. W(NAr)₂(PMe₂Ph)₂ reacts with (trimethylsilyl)acetylene and norbornene to give W(NAr)₂(PMe₂Ph)(HC≡CSiMe₃) (**2c**) and W(NAr)₂(PMe₂Ph)(norbornene) (**2d**), respectively. NMR spectra are consistent with a relatively rigid core geometry analogous to that found in **2a** in which neither (trimethylsilyl)acetylene nor norbornene rotates about the ligand(centroid)–metal axis. However, W(NAr)₂(PMe₂Ph)₂ reacts with acetylene and ethylene to form W(NAr)₂(PMe₂Ph)₂(C₂H₂) (**2e**) and W(NAr)₂(PMe₂Ph)₂(C₂H₄) (**2f**), respectively. The two ends of the acetylene and ethylene ligands are equivalent in each complex by NMR down to -80 °C, as are the two phosphine ligands. All data are consistent with their being distorted trigonal bipyramids containing axial phosphine ligands and imido ligands whose phenyl rings lie in the equatorial plane. NMR data alone cannot distinguish whether acetylene and ethylene lie in the WN₂ plane or are oriented perpendicular to it. We presume that five-coordinate intermediates are formed also in the reactions that give **2c** and **2d**.

We propose that all four-coordinate d² complexes reported here are pseudotetrahedral, since in a tetrahedron two imido ligands (each a 2 π , 1 σ donor) can form the maximum number of met-

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(4) See supplementary material for experimental details and analytical and NMR data.

(5) Crystals were mounted on glass fibers in air and coated in epoxy. Data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo K α radiation (space group P2₁/a with $a = 16.714$ (2) Å, $b = 12.343$ (1) Å, $c = 16.966$ (1) Å, $\beta = 91.909$ (7)°, $Z = 4$, FW = 730.62, and $\rho = 1.387$ g/cm³). A total of 5011 reflections (+ h , + k , $\pm l$) were collected in the range 3° < 2 θ < 55° with 3319 having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques (362 variables) using the TEXSAN crystallographic software package from Molecular Structure Corporation; final $R_1 = 0.037$, $R_2 = 0.037$. Full details can be found in the supplementary material.

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