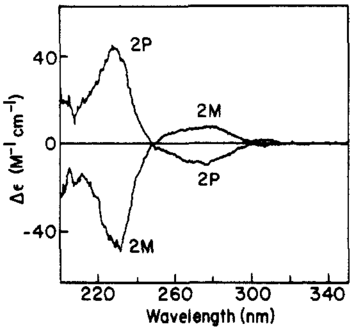
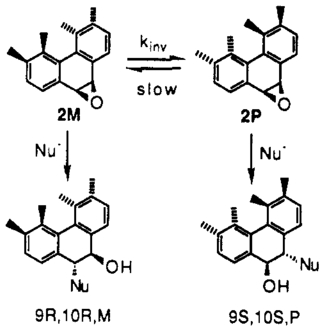
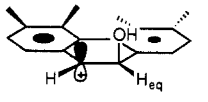


Figure 1. Circular dichroism spectra of the two conformational enantiomers of **2** at 0 °C in *n*-hexane. Activation parameters for inversion of configuration were derived from the temperature dependence of the decay of the CD transition at 230 nm.

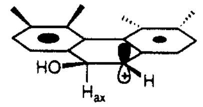
Scheme I



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



A



B

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, $k_{obs} = k_0 + k_a[H_3O^+]$, with $k_a = (2.3 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$ and $k_0 = (3.8 \pm 0.5) \times 10^{-4}\ s^{-1}$. In contrast, **3** solvolyzes more slowly under the same conditions with $k_a = (4.8 \pm 0.1) \times 10^2\ M^{-1}\ s^{-1}$ and $k_0 = (2.0 \pm 0.1) \times 10^{-5}\ s^{-1}$. 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 solvent[8] and from which transfer of the pseudoequatorial 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. 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 ($k_{obs} \gg k_{inv}$). For example, all solvolysis products derived from **2M** at pH 4 exhibit an enantiomeric purity (≥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.

Acknowledgment. This work was supported in part by Grants from the National Science Foundation (DMB 8716307) and the National Institutes of Health (GM 30910). R.N.A. is the recipient of an NIH Research Career Development Award (ES 00133). Compound **1** was generously supplied by Prof. M. S. Newman.

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.

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[7] Kinetics of solvolysis were followed at 255 nm in 25% CH_3CN/H_2O between pH 4 and 11 at 15 °C essentially as described by Whalen et al.[3g] 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 [$k_a = (1.15 \pm 0.09) \times 10^2\ M^{-1}\ s^{-1}$, $k_0 = (2.5 \pm 0.2) \times 10^{-5}\ s^{-1}$] at 30 °C in 100% H_2O.[3g]

[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 quasidiequatorial hydroxyl groups,[2a] which is not observed.

[9] Nobes, R. H.; Rodwell, W. R.; Bouma, W. J.; Random, L. *J. Am. Chem. Soc.* **1981**, *103*, 1913.

[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

Claudio Bianchini,* Andrea Meli, Maurizio Peruzzini, and Francesco Vizza

Istituto per lo Studio della Stereochimica ed
Energetica dei Composti di Coordinazione
CNR, Via J. Nardi 39, 50132 Firenze, Italy

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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 $[(triphos)IrCl(\eta^2\text{-}O_2)]$ (**1**), which transforms primary alcohols into carboxylic acids [triphos $= MeC(CH_2PPh_2)_3$]. Compound **1** is prepared as yellow, air-stable crystals by bubbling O_2 for 20 min thróugh a CH_2Cl_2 (50

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[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 significative 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.

0002-7863/90/1512-6726$02.50/0

Scheme I

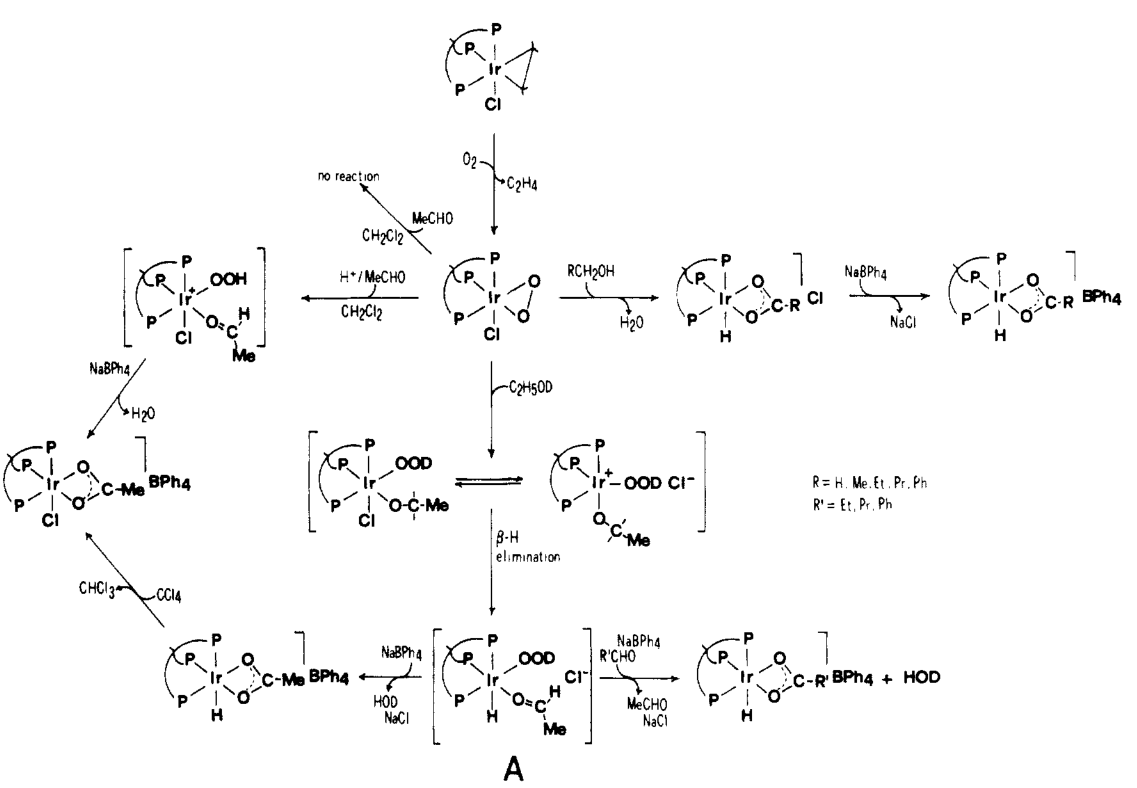

Table I. Selected Infrared and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ Nuclear Magnetic Resonance Data

		$^{31}P\{^1H\}$[b]				^1H[c]				^{13}C[d]
no.	IR[a]	pattern	$\delta(P_A)$	$\delta(P_M)$	$J(P_AP_M)$	δ(Ir-H)	$J(HP_{cis})$	$J(HP_{trans})$	$\delta(R\text{-}CO_2)$	$\delta(R\text{-}CO_2)$
1	823 ν(O-O)	AM_2	-32.41	-23.01	18.4					
3	2095 ν(Ir-H) 1547 ν(C=O)	AMQ	*e*			-7.09		*f*	9.70 (H)	*g*
4	2077 ν(Ir-H) 1502 ν(C=O)	AM_2	-10.60	-12.41	10.2	-4.41	11.7	163.6	2.04 (CH_3)	190.6
5	2084 ν(Ir-H) 1504 ν(C=O)	AM_2	-10.18	-11.65	10.2	-4.27	11.3	162.1		162.1
6	2077 ν(Ir-H) 1503 ν(C=O)	AM_2	-10.75	-12.25	10.1	-4.44	11.6	163.6	1.12, 2.36[h] (CH_3), (CH_2)	189.5
7	2076 ν(Ir-H) 1502 ν(C=O)	AM_2	-10.80	-12.27	10.0	-4.29	10.6	161.7	0.98, 1.68, 2.36[i] ($C_\gamma H_3$), ($C_\beta H_2$), ($C_\alpha H_2$)	188.7
8	1505 ν(C=O)	AM_2	-18.34	-31.81	18.0				1.99 (CH_3)	

[a] Nujol mulls, cm^{-1}. [b] CD_2Cl_2, 294 K, 121.42 MHz. [c] CD_2Cl_2, 298 K, 299.945 MHz. [d] CD_2Cl_2, 298 K, 75.429 MHz. [e] $\delta(P_A)$ -10.80, $\delta(P_M)$ -17.16, $\delta(P_Q)$ -33.56; $J(P_AP_M)$ = 23.5 Hz, $J(P_AP_Q)$ = 11.9 Hz, $J(P_MP_Q)$ = 12.7 Hz. [f] $J(HP_{cis})$ = 11.8 Hz, $J(HP_{cis})$ = 9.5 Hz, $J(HP_{trans})$ = 176.8 Hz. [g] Not recorded due to decomposition of the complex. [h] $J(HH)$ = 7.6 Hz. [i] $J(H_\alpha H_\beta) = J(H_\beta H_\gamma)$ = 7.3 Hz.

mL) solution of [(triphos)IrCl(C_2H_4)] (**2**)[2] (1 mmol) at room temperature, followed by addition of *n*-heptane (40 mL) (yield 95%). The formation of **1** is accompanied by C_2H_4 evolution (Scheme I). On the basis of its spectral data, **1** has an octahedral structure in which triphos caps a triangular face of the octahedron, and the three remaining coordination sites are occupied by a chloride and η^2-bonded dioxygen ligands (Table I).[3]

In a typical experiment, the peroxo[4] complex **1** (0.4 mmol) is added with stirring to neat alcohol (10 mL) previously deaerated by bubbling N_2 or Ar. In methanol, ethanol, or benzyl alcohol, **1** almost immediately dissolves to give colorless solutions from which off-white octahedral complexes [(triphos)IrH(O_2CR)]BPh_4 (R = H, **3**; Me, **4**; Ph, **5**) are precipitated by addition of $NaBPh_4$. The reactions with longer chain alcohols such as 1-propanol and 1-butanol are slower and are completed within 10 min at room temperature (R = Et, **6**; Pr, **7**). The *cis*-hydride–η^2-carboxylate complexes are obtained in good yields (85–95%) and are stable in the solid state and in solution, where they behave as 1:1 electrolytes. With the exception of the formate complex, which is unstable and eliminates CO_2, crystals can be obtained by recrystallization from CH_2Cl_2/alcohol mixtures. The hydride η^2-carboxylate structure of compounds **3**–**7** was also confirmed by comparison with the products of oxidative addition of the appropriate carboxylic acid to complex **2**.

The following observations, combined with previous evidence[5] on the chemistry of peroxo complexes, provide support for steps depicted in Scheme I. (i) Water is a side product of the reaction. Both H_2O hydrogens come from ethanol, one of the two being the OH hydrogen since ^1H NMR supports selective formation of HDO from C_2H_5OD. A deuterium exchange between C_2H_5OD

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(2) Details on the synthesis and characterization of this compound are given as supplementary material.

(3) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Fujiwara, Y.; Jintoku, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1988**, 210. (b) Janser, P.; Venanzi, L. M.; Bachechi, F. *J. Organomet. Chem.* **1985**, *296*, 229.

(4) In CH_2Cl_2 the compound liberates hydrogen peroxide by reaction with 2 equiv of a protic acid.

(5) (a) Jacobson, S. E.; Muccigrosso, D. A.; Mares, F. *J. Org. Chem.* **1979**, *44*, 921. (b) Atlay, M. T.; Preece, M.; Strukul, G.; James, B. R. *Can. J. Chem.* **1983**, *61*, 1332. (c) Bortolini, O.; Di Furia, F.; Modena, G. *J. Mol. Catal.* **1982**, *16*, 61.

and H_2O can be ruled out as we do not observe the formation of IrD. In contrast, a deuteride complex, namely, $[(triphos)IrD(O_2CCD_3)]^+$, forms together with HDO when **1** is reacted with C_2D_5OH. (ii) This reaction occurs also in CH_2Cl_2 with an equimolecular amount of ethanol. (iii) Acetaldehyde does not react with **1** in CH_2Cl_2 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 $[(triphos)IrCl(O_2CMe)]BPh_4$ (**8**) forms together with H_2O. (iv) When **1** (0.5 mmol) is reacted with a stoichiometric amount of C_2H_5OD 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, $^{31}P\{^1H\}$ NMR spectroscopy shows that the formation of **4** from C_2H_5OD 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; $[Ir_2Cl_2(C_8H_{14})_4]$, 12246-51-4.

Supplementary Material Available: Analytical data for the new complexes and detailed preparation and characterization of $[(triphos)IrCl(C_2H_4)]$ (1 page). Ordering information is given on any current masthead page.

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

Darryl S. Williams, Mark H. Schofield, Jens T. Anhaus, and Richard R. Schrock*

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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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., $Mo(O\text{-}t\text{-}Bu)_4$[1a]), diamagnetic square plane (e.g., $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$[1b]), or a diamagnetic flattened tetrahedron (e.g., $W(S\text{-}t\text{-}Bu)_4$,[1c] $Mo(S\text{-}2,4,6\text{-}C_6H_2Me_3)_4$,[1d] or $Mo(S\text{-}t\text{-}Bu)_4$[1e]). The recent synthesis of square-planar d^4 $Os(NAr)_2(PMe_2Ph)_2$ (Ar = $2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$)[2] raised the question as to whether analogous d^2 tungsten(IV) complexes could be prepared, and whether they would be planar or tetrahedral. We have now synthesized complexes of the type $W(NAr)_2L_2$ (L = a phosphine). They are diamagnetic, are believed to be tetrahedral species, and in contrast to $Os(NAr)_2(PMe_2Ph)_2$, react readily with π bonding ligands via five-coordinate intermediates.

$W(NAr)_2Cl_2(dme)$[3] can be reduced readily with sodium amalgam in the presence of dimethylphenylphosphine in diethyl ether to give burgundy-colored, air-sensitive $W(NAr)_2(PMe_2Ph)_2$ (**1**) in 50–60% yield.[4] ^{31}P 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 PPh_3, PMe_3, or $P(OPh)_3$ instead of PMe_2Ph have not been isolated, and no crystals of **1** have been obtained yet that are suitable for X-ray studies.

$W(NAr)_2(PMe_2Ph)_2$ reacts within 1–2 min with acetone in pentane to give orange-yellow $W(NAr)_2(PMe_2Ph)(\eta^2\text{-}OCMe_2)$ (**2a**) quantitatively. An X-ray study[5] 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]

$W(NAr)_2(PMe_2Ph)_2$ reacts with propionaldehyde to give $W(NAr)_2(PMe_2Ph)(\eta\text{-}OCHEt)$ (**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 $W(NAr)_2(PMe_2Ph)_2$ with acetylenes or olefins appears to depend largely on the size of the added ligand. $W(NAr)_2(PMe_2Ph)_2$ reacts with (trimethylsilyl)acetylene and norbornene to give $W(NAr)_2(PMe_2Ph)(HC{\equiv}CSiMe_3)$ (**2c**) and $W(NAr)_2(PMe_2Ph)(norbornene)$ (**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, $W(NAr)_2(PMe_2Ph)_2$ reacts with acetylene and ethylene to form $W(NAr)_2(PMe_2Ph)_2(C_2H_2)$ (**2e**) and $W(NAr)_2(PMe_2Ph)_2(C_2H_4)$ (**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 WN_2 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 d^2 complexes reported here are pseudotetrahedral, since in a tetrahedron two imido ligands (each a 2π, 1σ donor) can form the maximum number of met-

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(1) (a) Cayton, R. H.; Chisholm, M. H.; Clark, D. L.; Hammond, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 2751 and references therein. (b) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264. (c) Listemann, M. L.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 7207. (d) Roland, E.; Walborsky, E. C.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5795. (e) Otsuka, S.; Kamata, M.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3011. (f) Chisholm, M. H.; Cotton, F. A.; Extine, M. W. *Inorg. Chem.* **1978**, *17*, 1329.

(2) Anhaus, J. T.; Kee, T. P.; Schofield, M. H., Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642.

(3) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262–2275.

(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 Kα radiation (space group $P2_1/a$ 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/cm^3). A total of 5011 reflections ($+h,+k,\pm l$) were collected in the range $3° < 2\theta < 55°$ 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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0002-7863/90/1512-6728$02.50/0