yellow at ca. 200 °C. The electronic spectra of **1** in a 320–520-nm range is shown in Figure 2. Clearly an isosbestic point is observable at 389 nm. The mechanism of this spectral change is not clear at this moment but indicates that the double bond of **1** must be more twisted at higher temperatures than in the solid state at −70 °C.

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Registry No. 1, 74465-53-5.

Supplementary Material Available: A stereoview of packing of molecules in crystal, tables of atomic parameters, anisotropic temperature factors, mean-square displacement tensor of atoms, and structure factors (27 pages). Ordering information is given on any current masthead page.

Reactions of Carbon Monoxide and Alkyl Isocyanides with Rhodium Octaethylporphyrin Species: Metalloformyl and Formimidoyl Complexes

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Metalloformyl species are frequently invoked as a key intermediate in the metal-catalyzed reduction of CO by H_2.[1] We have recently observed that RhOEP(H) reacts with CO to produce RhOEP(CHO) (I), which is the first reported formyl complex prepared by the reaction of a metal hydride complex with carbon monoxide.[2] We now wish to report on the alternate preparation of I by using H_2O as a source of hydrogen, the molecular structure of I, and the formation of a metalloformimidoyl complex from the reaction of RhOEP(H) with an alkyl isocyanide.

The metalloformyl complex RhOEP(CHO) (I) can be alternatively prepared by reactions 1, 2, or 3.[3] Substitution of D_2 and

$$\mathrm{RhOEP(H) + CO \rightleftarrows RhOEP(CHO)} \quad (1)$$

$$\mathrm{(RhOEP)_2 + H_2 + 2CO \rightleftarrows 2RhOEP(CHO)} \quad (2)$$

$$\mathrm{(RhOEP)_2 + H_2O + 3CO \rightarrow 2RhOEP(CHO) + CO_2} \quad (3)$$

D_2O, respectively, in reactions 2 and 3 produces the deuterated formyl RhOEP(CDO) and identifies D_2 and D_2O as alternate sources of the formyl hydrogen. Reaction 2 undoubtedly occurs through formation of RhOEP(H) by reaction 4. Reaction 3 is

$$\mathrm{(RhOEP)_2 + H_2 \overset{C_6H_6}{\rightleftarrows} 2RhOEP(H)} \quad (4)$$

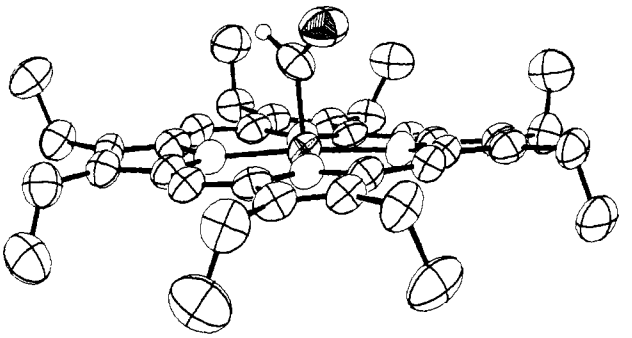

Figure 1. ORTEP representation for RhOEP(CHO). Bond lengths and angles for the RhCHO unit are as follows: Rh–C, 1.896 (6) Å; C–O, 1.175 (5) Å; C–H, 1.09 (1) Å; Rh–C–O, 129.6 (5)°; Rh–C–H, 129.9 (4)°.

thought to occur by formation of RhOEP(H) in the water gas shift (WGS)[4] reaction (reactions 5–7). Some of the intermediate

$$\mathrm{(RhOEP)_2 + CO + H_2O \rightarrow RhOEP(CO_2H) + RhOEP(H)} \quad (5)$$

$$\mathrm{RhOEP(CO_2H) \rightleftarrows RhOEP(H) + CO_2} \quad (6)$$

$$\mathrm{2RhOEP(H) \rightleftarrows (RhOEP)_2 + H_2} \quad (7)$$

RhOEP(H) formed in the WGS reaction is utilized by reaction 1 in producing the formyl complex I. This system is capable of catalyzing the WGS reaction even though most of the active catalyst, $(RhOEP)_2$, is converted to compound I, because reactions 1 and 2 are reversible. A transient species observed in the ^1H NMR spectrum for reaction 3 is tentatively assigned to the intermediate metallocarboxylic acid complex, $RhOEP(CO_2H)$.

RhOEP(CHO) (I) is characterized in beznene solution by ^1H and ^{13}C NMR spectroscopy (δ_{CHO} 2.90, J_{Rh-H} = 1.75 Hz, $J_{^{13}C-H}$ = 200 Hz; $\delta_{^{13}CHO}$ = 194.4). The formyl complex I has been crystallized and fully characterized by single-crystal X-ray structure determination.[5] An ORTEP representation of the molecule along with bond distances and angles for the Rh(CHO) unit is given in Figure 1.

Isocyanides (R—N≡C:) have similar reactivity patterns but generally enhanced reactivity when compared to carbon monoxide and are used to model and define the range of potential carbon monoxide reactivity. Metallohydrides of Ru,[6] Os,[7] Pt,[8] and Zr[9] are observed to react with isocyanides to produce metalloformimidoyl (M—CH=NR) species, while the corresponding reactions with carbon monoxide failed to yield observable metalloformyl complexes. We find that RhOEP(H) reacts with *n*-butyl isocyanide (BuNC) to produce the metalloformimidoyl RhOEP(—

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(3) Reactions 1, 2, and 3 are carried out in sealed NMR tubes by using C_6D_6 as the solvent at ambient laboratory temperatures. Reaction 1 is virtually quantitative (>95%) by NMR measurements when the pressure of carbon monoxide is greater than 300 torr. This reaction is complicated only by the possibility of converting RhOEP(H) into $(RhOEP)_2$ and H_2. Reaction 2 is essentially the same as 1 except that the pressure of H_2 gas (100 mm) assures complete conversion to the formyl. Reaction 3 when carried out with a fivefold excess of H_2O and $P_{CO} \sim 300$ torr again produces compound I in near quantitative yield by NMR observation. Attempts to isolate I by removal of the solvent under vacuum always results in contamination by RhOEP(H) and $(RhOEP)_2$ due to reversibility of reactions 1 and 2. Evaporation of a benzene solution of I, under a stream of CO, results in crystals of RhOEP(CHO) used in the structure determination.

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(5) RhOEP(CHO) crystallizes as a benzene solvate. The crystals are triclinic ($P\bar{1}$ space group) with lattice parameters a = 10.564 (4) Å, b = 12.257 (4) Å, c = 15.266 (7) Å, α = 77.38 (3)°, β = 94.31 (4)°, and γ = 100.30 (3)°. The structure was refined by using 3843 nonzero reflections for which $I > 3\sigma(I)$ out of a total of 6609 independent reflections. Corrections were made for absorption with an absorption coefficient of 4.799. The structure was refined to an R index of 0.052 by using anisotropic temperature factors for all nonhydrogen atoms and isotropic factors for all hydrogens. All hydrogens were located by difference Fourier methods.

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(7) (a) Collins, T. J.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1976**, 1044. (b) Adams, R. D.; Bolembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579. (c) Clark, G. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2556.

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CH=NBu) (II)[10] and that compound II can also be formed by using H_2O as a source of hydrogen in a reaction analogous to the WGS reaction (reaction 9). Reaction 9 is proposed to occur

$$RhOEP(H) + BuNC \rightarrow RhOEP(CH{=}NBu) \quad (8)$$

$$(RhOEP)_2 + H_2O + 3BuNC \rightarrow 2RhOEP(CH{=}NBu) + BuNCO \quad (9)$$

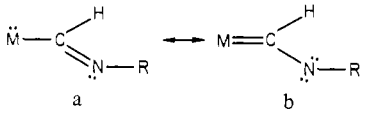
through an intermediate analogous to the metallocarboxylic acid in the WGS reaction. The RhOEP(H) produced in reactions

$$(RhOEP)_2 + BuNC + H_2O \rightarrow RhOEP(C(OH){=}NBu) + RhOEP(H) \quad (10)$$

$$RhOEPnC(OH){=}NBu) \rightarrow RhOEP(H) + BuNCO \quad (11)$$

10 and 11 subsequently reacts with BuNC to produce the formimidoyl complex II by reaction 8.

The C-N stretching frequency for RhOEP(CH=NBu) (ν_{CN} = 1624 cm^{-1}) is similar to that of $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH{=}NCH_3)$ (ν_{CN} = 1617)[9] and organic analogues ($\nu_{CN} \sim 1625$) but is substantially higher than values reported for metalloformimidoyls ($\nu_{C=N}$ = 1550-1580 cm^{-1})[6-8] where back-π-bonding (resonance structure b) is expected to be more important. Similarly, the



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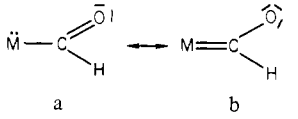
ν_{CO} value of 1700 cm^{-1} for RhOEP(CHO) is higher than for any previously reported metalloformyl (ν_{CO} = 1570-1640).[11]

Prior to this report, $\eta^5\text{-}C_5H_5Re(Ph_3P)(NO)(CHO)$ was the only metalloformyl to be structurally characterized.[12] A relatively short Re-C distance (2.055 Å), the C-O bond distance of 1.22 Å, and a ν_{CO} of 1558 cm^{-1} indicate the importance of back-π-bonding (resonance structure b) in this complex. RhOEP(CHO)



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has a much shorter C-O distance (1.175 Å) and higher ν_{CO} (1700 cm^{-1}), suggesting that the $Rh^{III}OEP$ unit may be relatively ineffective in back-π-bonding with the formyl group. RhOEP(CHO) is more like an organic aldehyde (resonance structure a) than previously reported metalloformyls, and this may be expected to produce different patterns of formyl group reactivity. The short Rh-C distance of 1.869 (6) Å in I compared to 2.031 (6) Å in $RhOEP(CH_3)$[13] is partially attributed to the differences in carbon hybridization.

The ability of rhodium octaethylporphyrin dimer to activate and transfer hydrogen to carbon monoxide indicates relevance to Fischer-Tropsch chemistry. We are presently studying the reactivity patterns of the coordinated formyl group in I, including hydrogen reduction, and evaluating the conditions required to establish a catalytic cycle. RhOEP(H) is the first of a potential large class of metallomacrocycles that could produce related chemistry. Mechanistic studies of reaction 1 and a survey of carbon monoxide reactivity with metallomacrocycle hydrides are expected to reveal the generality of formyl complex formation with metallomacrocycles and establish criteria for stabilizing the coordinated formyl unit. We presently believe that the rigid macrocycle, relatively high metal oxidation state [Rh(III)], and the normal covalent bond forming ability of rhodium(II) all contribute to stabilizing the metalloformyl unit in RhOEP(CHO).

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Registry No. I, 79666-16-3; II, 80010-78-2; CO, 630-08-0; RhOEP(H), 63372-77-0; $(RhOEP)_2$, 63439-10-1; BuNC, 2769-64-4.

(10) Reactions 8 and 9 are virtually quantitative when carried out in sealed NMR tubes using C_6D_6 as the solvent and fivefold excesses of BuNC and H_2O. Rh(CH=NBu) can be isolated as an air-stable crystalline solid by removing the solvent under vacuum. RhOEP(—CH=NBu): IR (Nujol mull) $\nu_{C=N}$ = 1624 cm^{-1}; ^1H NMR (C_6D_6) δ -2.48 (—CH=NBu, $J(CH{=}NCH_2)$ = 6.0 Hz), $\delta_{CH=NCH_2-}$ 0.36; Porphyrin resonances δ_{C-H} = 10.42, δ_{CH2} = 4.11, δ_{CH_3} 2.06.

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A Formal Total Synthesis of Fusidic Acid[1]

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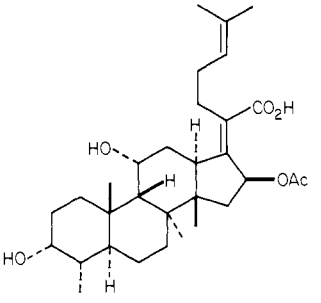
Of the many tetracyclic triterpenes of the dammarane series, fusidic acid (**1**) is the most potent antibiotic, and it possesses the broadest spectrum of biological activity.[3] Since it was first reported in 1962,[4] the clinical importance of **1** has been established,[5] and a wealth of knowledge has been accumulated in regard to its chemical modification and degradation.[3] We now report the formal total synthetic of fusidic acid.



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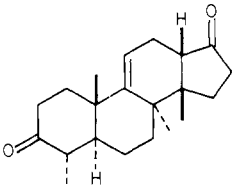

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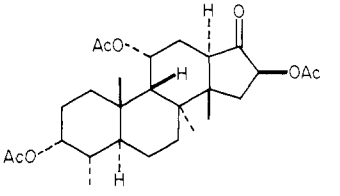

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(2) National Research Service Award, 1979-1981, National Institute of Allergy and Infectious Diseases.

(3) For an excellent review, see: von Daehne, W.; Godtfredsen, W. O.; Rasmussen, P. R. *Adv. Appl. Microbiol.* **1979**, *25*, 95.

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