Organometallics **1985,** *4,* 1887–1888

Communications

Synthesis and Reactivity of the Hydroxymethyl Complex of Rhodium Octaethylporphyrin

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Received March 12, 1985

Summary: The hydroxymethyl complex of rhodium octaethylporphyrin [RhOEP(CH_2OH)], prepared by the reaction of RhOEP(H) with formaldehyde or by the reduction of RhOEP(CHO) by diisobutylaluminum hydride, is found to react with RhOEP(H) to reductively eliminate methanol and to insert carbon monoxide to form the hydroxyacyl complex RhOEP(C(O)CH_2OH).

Metallohydroxymethyl complexes (M–CH_2OH) have been implicated as key intermediates in the catalyzed hydrogenation of carbon monoxide.[1] Complexes of this type are generally prepared as kinetic products from the reaction of metallocarbonyl or metalloformyl species with hydride reducing agents and are generally unstable with respect to dissociation into metal hydride and aldehyde units (reaction 1).[2] A thermodynamically stable hydroxymethyl complex of rhodium octaethylporphyrin [RhOEP(CH_2OH)], I, has been prepared in benzene solution by the reaction of the RhOEP(H) with excess formaldehyde (reaction 2). Either polymeric paraformaldehyde or aqueous monomeric formaldehyde has been used successfully in reaction 2. The equilibrium constant for reaction 2 is too large [$K^{298} > 10^4$] to be conveniently measured by NMR methods. Compound I can be alternately prepared by reacting performed metalloformyl with a hydride reducing agent such as diisobutylaluminum hydride (reaction 3). The yield of I from reaction 2 is essentially quantitative, whereas reaction 3 produces only 30% of the hydroxymethyl complex. Compound I has been obtained as a pure solid, but well-defined crystals have not been observed. This hydroxymethyl complex has been characterized by ^1H and ^{13}C NMR techniques as well as mass spectral analysis.[3] Compound I has a sharp triplet hydroxyl ^1H NMR even in the presence of excess water or alcohols, indicating that proton exchange is slower than that for organic alcohols. Addition of D_2O to a C_6D_6 solution of I produces the deuterated compound [RhOEP(CH_2OD)] in a period of 30 min as monitored by the disappearance of the hydroxyl resonance in the ^1H NMR.

$$\mathrm{M(CHROH)} \rightarrow \mathrm{M{-}H} + \mathrm{RC(O)H} \qquad (1)$$

$$\mathrm{RhOEP(H)} + \mathrm{CH_2O} \xrightleftharpoons{C_6D_6} \mathrm{RhOEP(CH_2OH)} \qquad (2)$$

$$\mathrm{RhOEP(H)} + \mathrm{CO} \rightleftharpoons \mathrm{RhOEP(CHO)} \xrightarrow[2.\mathrm{H_2O}]{1.\mathrm{HAlR_2}} \mathrm{RhOEP(CH_2OH)} \qquad (3)$$

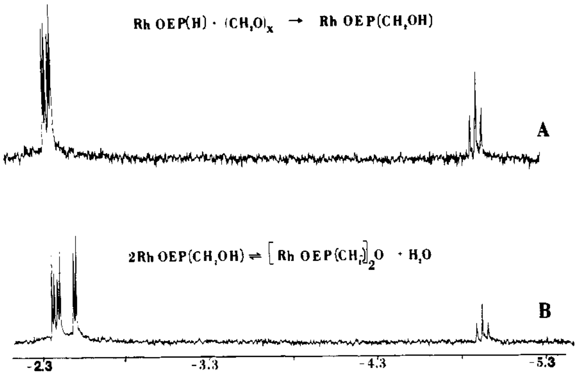

Figure 1. (A) High-field region of ^1H NMR of RhOEP(CH_2OH) in C_6D_6 (time = 0). (B) ^1H NMR of solution A demonstrating the equilibrium of RhOEP(CH_2OH) and [RhOEP(CH_2)]$_2$O (time = 16 h).

Compound I is found to undergo an intermolecular self-condensation reaction to form an equilibrium distribution with a symmetrical metallo ether [(RhOEP(CH_2))$_2$O], II (reaction 4, Figure 1). Compound II has been characterized in benzene solution by proton NMR using carbon-12 and carbon-13 labeled formaldehyde.[4] The three-bond coupling constant $^3J_{^{13}COCH_2} = 6.1$ Hz observed when using carbon-13 enriched formaldehyde is particularly characteristic of compound II and similar in value to analogous organic ethers, $^3J_{^{13}COCH_3} = 5.7$ Hz.[5]

$$2\mathrm{RhOEP(CH_2OH)} \rightleftharpoons [\mathrm{RhOEP(CH_2)}]_2\mathrm{O} + \mathrm{H_2O} \qquad (4)$$

Intermolecular reductive elimination of methanol via the hydroxymethyl intermediate is frequently postulated as an important step in the catalytic reduction of carbon monoxide.[1] In the presence of RhOEP(H) compound I reacts quantitatively to form methanol and the bimetallic complex $(RhOEP)_2$ (reaction 5). To our knowledge, this is the first reported reductive elimination of methanol through a well-characterized metallohydroxymethyl intermediate.

$$\mathrm{RhOEP(CH_2OH)} + \mathrm{RhOEP(H)} \xrightarrow[8h]{80\ ^\circ C} \mathrm{(RhOEP)_2} + \mathrm{CH_3OH} \qquad (5)$$

The insertion of carbon monoxide into a metal–alkyl bond is frequently proposed as the key intermediate in carbon–carbon bond forming catalytic processes.[1] Both

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(2) (a) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981,** *219,* 353. (b) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980,** *102,* 1927. (c) Elroi, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1978,** *100,* 5540. (d) May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982,** *234,* C49. (e) Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983,** *2,* 1461.

(3) ^1H NMR of I (C_6D_6): using ^{12}C formaldehyde, δ −2.34 [d or d ($^2J_{Rh-CH_2} = 3.4$ Hz, $J_{CH_2OH} = 8.6$ Hz)], −4.84 [t ($J_{CH_2OH} = 8.6$ Hz)]; using ^{13}C formaldehyde, δ −2.34 [$^1J_{^{13}CH} = 162.0$ Hz], −4.84 [$^2J_{^{13}COH} = 3.6$ Hz]. ^{13}C NMR (proton decoupled): $Rh^{13}CH_2OH$ δ +54.5 [d ($^2J_{Rh^{13}C} = 24.4$ Hz)]. MS: *m/e* 666 (M^+).

(4) ^1H NMR of II (C_6D_6): using ^{13}C formaldehyde, δ −2.44 [d ($2J_{RhCH2}$ = 3.6 Hz)]; using ^{13}C formaldehyde, δ −2.44 [d of d ($^1J_{^{13}CH} = 155.0$ Hz, $^3J_{^{13}COCH} = 6.1$ Hz)].

(5) Dreeskamp, H.; Hildenbrand, K.; Pfisterer, G. *Mol. Phys.* **1969,** *17,* 429.

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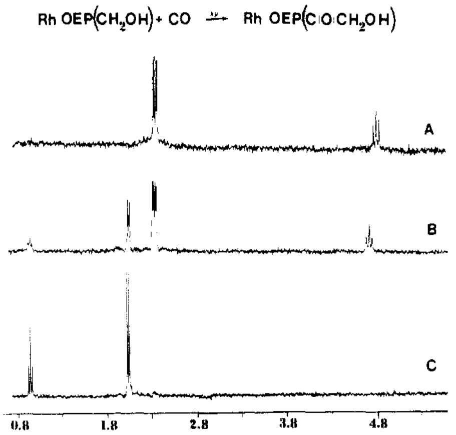

Figure 2. (A) High-field region of the ^1H NMR of RhOEP-(CH_2OH) pressurized with CO (P_{CO} = 320 torr) in C_6D_6 (time = 0). (B) ^1H NMR of solution A irradiated (hν > 445) for 30 min. (C) ^1H NMR of pure RhOEP[C(O)CH_2OH].

compound I and the corresponding alkyl complex RhOEP(CH_3) photolytically incorporate carbon monoxide to form the corresponding acyl derivatives (reactions 6 and 7). In a typical experiment the alkyl complex was irradiated, using a band path filter (hν > 445), for 90 min in the presence of 300 torr of carbon monoxide, at ice–water temperatures. The methylacyl complex III was characterized by comparison with authentic samples prepared by published procedures.[6] The hydroxyacyl complex IV has been characterized by proton and carbon-13 NMR and IR as well as mass spectra analysis (Figure 2).[7] The overall conversion to the hydroxyacyl complex IV is limited by the simultaneous photoinduced transformation of the hydroxymethyl complex I into metal hydride and formaldehyde. Further conversion to the hydroxyacyl species is accomplished by thermally regenerating the hydroxymethyl compound, followed by continued photolysis. A comparison of NMR and IR spectra for III and IV is compatible with the presence of intramolecular hydrogen bonding between the hydroxy and carbonyl functionalities, which has also been noted for the only previously reported metallohydroxyacyl complex.[8]

$$\mathrm{ROEP(CH_3) + CO \xrightarrow{h\nu} \underset{III}{RhOEP[C(O)CH_3]}} \qquad (6)$$

$$\mathrm{RhOEP(CH_2OH) + CO \xrightarrow{h\nu} \underset{IV}{RhOEP[C(O)CH_2OH]}} \qquad (7)$$

The rhodium porphyrin system has demonstrated many of the most important steps postulated[1] in the catalytic reduction of CO to organic products. The key steps in this process usually include (a) the activation of molecular hydrogen, (b) the incorporation of carbon monoxide into the metal–hydride to form the metalloformyl, (c) the reduction of the metalloformyl to the hydroxymethyl complex, and either (d) reductive elimination of methanol or (e) incorporation of another molecule of carbon monoxide to form the corresponding hydroxyacyl (Scheme I). Reaction steps a, b, d, and e have been observed and characterized in the rhodium porphyrin system.[9,10] Further studies of the catalytic reduction of the metalloformyl to the hydroxymethyl complex (step c) as well as the intermolecular reductive elimination of the hydroxyacyl to glycoaldehyde (step f) are now in progress.

Scheme I

$$\text{(a)} \quad \mathrm{M{-}M + H_2 \rightleftharpoons 2M{-}H}$$

$$\text{(b)} \quad \mathrm{M{-}H + CO \rightleftharpoons M{-}C(O)H}$$

$$\text{(c)} \quad \mathrm{M{-}C(O)H + H_2 \rightarrow M{-}CH_2OH}$$

$$\text{(d)} \quad \mathrm{M{-}CH_2OH + M{-}H \rightarrow M{-}M + CH_3OH}$$

$$\text{(e)} \quad \mathrm{M{-}CH_2OH + CO \rightarrow M{-}C(O)CH_2OH}$$

$$\text{(f)} \quad \mathrm{M{-}C(O)CH_2OH + M{-}H \rightarrow M{-}M + HC(O)CH_2OH}$$

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, DOE Grant No. DE-AC02-84ER-13133.

Registry No. I, 83691-18-3; II, 97645-15-3; III, 83691-22-9; IV, 97645-16-4; RhOEP(H), 63372-77-0; $(RhOEP)_2$, 63439-10-1; RhOEP(CH_3), 36643-85-3; CH_2O, 50-00-0.

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[7] ^1H NMR of IV (C_6D_6): using ^{12}C carbon monoxide and ^{12}C formaldehyde, δ −2.01 [d (J_{CH_2OH} = 5.8 Hz)], −0.88 [*t* (J_{CH_2OH} = 5.8 Hz)]; using ^{13}C carbon monoxide with ^{13}C formaldehyde, δ −2.01 [d of d ($^1J_{^{13}CCH_2}$ = 2.9 Hz, J_{CH_2OH} = 5.8 Hz)]. ^{13}C NMR (proton decoupled): δ +202.3 [d ($^1J_{Rh^{13}C}$ = 34.2 Hz)]. IR (cm^{-1}, KBr): ν_{CO} 1697, ν_{OH} 3424 (br). MS: *m/e* 694 (M^+).

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Generation and Stabilization of the 3,3-Diphenyl-1,2,4-thiadiarsete Unit at a Transition Metal

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Received April 16, 1985

Summary: The reaction of [Co(As_2S)(triphos)]BF_4 [triphos = 1,1,1-tris[(diphenylphosphino)methyl]ethane], which contains the thiadiarsiranediyl ring η^3 bonded to the metal, with a tenfold excess of diphenyldiazomethane produces the dark red complex [Co{SAsC(Ph)$_2$As}(triphos)]BF_4. An X-ray structural determination has shown that the [Co{SAsC(Ph)$_2$As}(triphos)]$^+$ cation contains the four-membered 3,3-diphenyl-1,2,4-thiadiarsete unit 1,2,4-η^3 linked to the Co(triphos) moiety. Such unprecedented four-membered ring is obtained through insertion of the diphenylcarbene into the homoatomic bond of the thiadiarsiranediyl unit.

Mononuclear metal complexes containing the homocyclic E_3 (E = P,[1] As[2]) or the heterocyclic E_2X (E = P, X = S, Se;[3] E = As, X = S[4]) inorganic units η^3 bonded to a

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