Observation of a Neutral Metallo-formyl Complex Formed by the Reaction of Rhodium Octaethylporphyrin Hydride with Carbon Monoxide

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Summary Rhodium octaethylporphyrin hydride, RhOEP(H) (OEP = octaethylporphyrin), reacts with carbon monoxide to form a neutral metallo-formyl complex.

METAL-FORMYL complexes have been considered as probable intermediates in the metal catalysed reduction of CO by H_2 and thus have been of recent interest.[1] Metal-formyl complexes are relatively rare when compared with the acyl derivatives, but a number of formyl complexes have been observed[2–5] and several structurally characterized.[6,7] The most general method for preparing metal-formyl species is the borohydride reduction of a co-ordinated CO group.[7] To our knowledge there has been no previous report of a metal-formyl complex which forms either from the reaction of a metal hydride with CO or by the reaction of H_2 and CO with a metal complex. We report herein that the formyl complex RhOEP(CHO) (**1**) (OEP = octaethylporphyrin) resulted from the reaction of RhOEP(H) with CO in benzene solvent [equation (1)]. RhOEP(H) was formed reversibly

$$\mathrm{RhOEP(H)} + \mathrm{CO} \rightarrow \underset{(\mathbf{1})}{\mathrm{RhOEP(CHO)}} \qquad (1)$$

by the reaction of $(\mathrm{RhOEP})_2$ with H_2 and thus compound (**1**) could be formed from the reaction of $(\mathrm{RhOEP})_2$ with H_2 and CO. The formyl complex (**1**) is indefinitely stable in the solid state or in a benzene solution in contact with CO (200 Torr). When an isolated sample of compound (**1**) was dissolved in degassed benzene, there was a slow reaction (24 h) which produced $(\mathrm{RhOEP})_2$, thus demonstrating the reversible formation of (**1**).

The formyl complex (**1**) has been characterized by i.r., ^{1}H n.m.r., and mass spectral studies. The ^{1}H n.m.r. spectra shown in the Figure were taken on samples prepared by treating a benzene solution of RhOEP(H) with carbon monoxide (600 mmHg) in a sealed n.m.r. tube. Formation of the formyl group was indicated by the appearance of a doublet [δ 2·90, J (^{103}Rh–H) 1·75 Hz] with a relative intensity of one hydrogen per rhodium porphyrin unit. Formyl-hydrogen chemical-shifts in other metal-formyl complexes are in the range of δ 14—16. Porphyrin ring-current effects are responsible for the high-field position of the formyl hydrogen (δ 2·90) in RhOEP(CHO). The ^{1}H n.m.r. spectrum of the ^{13}CO derivative of compound (**1**) shows further splitting of this resonance [J(^{13}C–H) 200 Hz], consistent with a formyl hydrogen. The carbon-13 n.m.r. spectrum of RhOEP(^{13}CHO) shows a doublet of doublets due to ^{103}Rh and ^{1}H coupling [δ (^{13}C) 194·4 p.p.m. (CHO); J(^{13}C–H) 200, J(^{13}C–^{103}Rh) 29 Hz] which demonstrates that the carbonyl carbon is directly bonded to both one hydrogen atom and one rhodium atom.

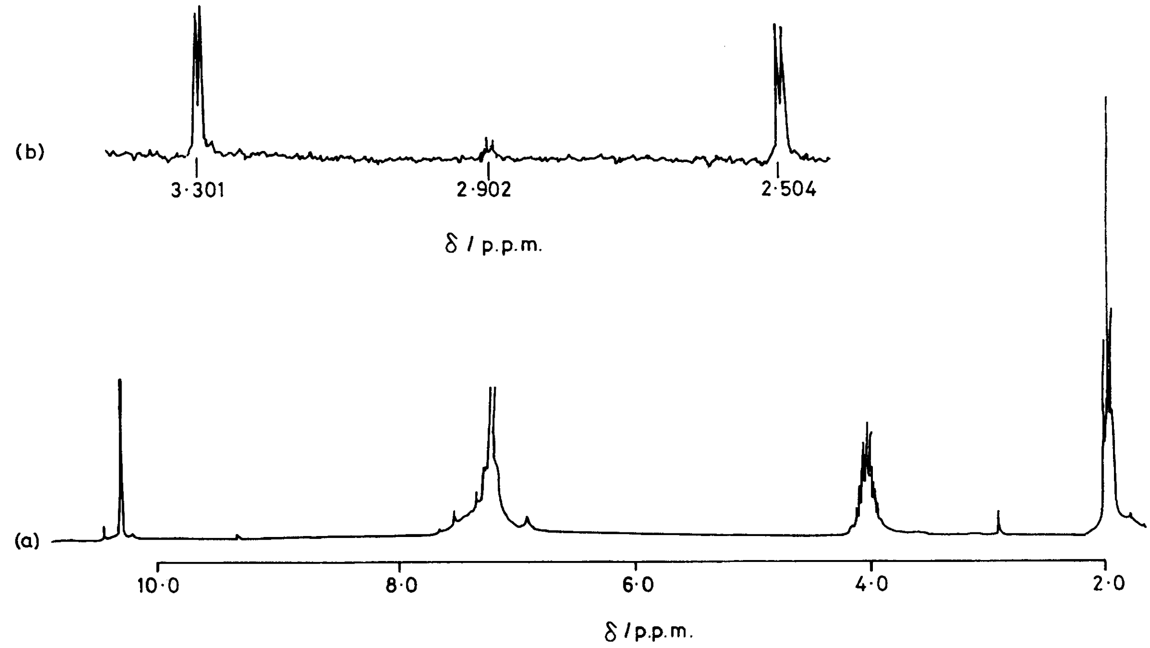

FIGURE. (a) ^{1}H N.m.r. (250 MHz) of RhOEP(CHO) in C_6H_6 (δ relative to tetramethylsilane). (b) ^{1}H N.m.r. of the formyl hydrogen in RhOEP(^{13}CHO).

RhOEP(CHO) has been crystallized and shows a strong ν_{CO} band (Nujol mull) at 1700 cm^{-1} which shifts to 1667 cm^{-1} in the ^{13}C-labelled carbonyl derivative. The ν_{CO} value for compound (**1**) is similar to that of organic aldehydes (1690—1730 cm^{-1}), but substantially higher than the values reported for other metallo-formyls (1550—1650 cm^{-1}). This probably reflects the smaller contribution of d–π back-bonding [M=C(H)–O⁻] by the Rh^{III} porphyrin group compared with complexes of metals in lower oxidation states.[7]. The Rh–C bond in compound (**1**) is probably best described as a normal covalent bond between the half-filled Rh d_{z^2} and formyl-carbon sp^2 hybrid orbitals with relatively little Rh-formyl π-bonding.

Little is known about the mechanism of formation of compound (**1**) by reaction 1. We presently favour a radical-like reaction pathway similar to our observations on the reactivity of $(RhOEP)_2$ with trialkylphosphites,[8] but this is under investigation.

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