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Preliminary communication

PREPARATION OF HETEROBIMETALLIC COMPOUNDS CONTAINING OCTAETHYLPORPHYRINRHODIUM AND THEIR REACTIONS WITH HYDROGEN AND CARBON MONOXIDE

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Summary

Octaethylporphyrinrhodium dimer ($[Rh(OEP)]_2$) reacts with a series of transition metal dimers (M′–M′; M′ = $Mn(CO)_5$; $Mo(CO)_3Cp$; $Ru(CO)_2C_5Me_5$) to form metal–metal bonded heterobimetallic compounds ((OEP)Rh–M′). The heterobimetallic compounds reported in this paper react with H_2 and CO to produce M′–H and equilibrium quantities of Rh(OEP)(H) and Rh(OEP)(CHO).

Recent interest in heterobimetallic compounds has been motivated in part by their potential use as precursors to hydrogenation catalysts utilizing two different metallohydride units [1–3]. We have previously reported the synthesis and structural characterization of Rh(OEP)–In(OEP), which does not react with hydrogen and carbon monoxide under ambient conditions [4]. In this paper, we report a series of heterobimetallic compounds containing the octaethylporphyrinrhodium fragment that react with molecular hydrogen and carbon monoxide under mild conditions to form two independent metallohydrides.

Octaethylporphyrinrhodium dimer ($[Rh(OEP)]_2$) reacts with $[Mn(CO)_5]_2$, $[CpMo(CO)_3]_2$, and $[Cp'Ru(CO)_2]_2$ in benzene to form the metathesis products (OEP)Rh–$Mn(CO)_5$ (**1**), (OEP)Rh–$Mo(CO)_3Cp$ (**2**), and (OEP)Rh–$Ru(CO)_2Cp'$ (**3**) (eq. 1).

$$[Rh(OEP)]_2 + M'–M' \rightarrow 2\ (OEP)Rh–M' \qquad (1)$$

$$(M'\text{-}Mn(CO)_5,\ Mo(CO)_3Cp,\ Ru(CO)_2Cp';\ Cp = \eta^5\text{-}C_5H_5;\ Cp' = \eta^5\text{-}C_5(CH_3)_5)$$

In contrast, the Rh(OEP)–In(OEP) complex was prepared by nucleophilic displacement (eq. 2).

$$Rh(OEP)^- + In(OEP)Cl \rightarrow Rh(OEP)–In(OEP) + Cl^- \qquad (2)$$

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TABLE 1

PROTON NMR AND CARBONYL STRETCHING FREQUENCIES FOR THE HETEROBIMETALLIC COMPOUNDS 1, 2, AND 3

(OEP)Rh–Mn(CO)$_5$	(OEP)Rh–Mo(CO)$_3$Cp	(OEP)Rh–Ru(CO)$_2$Cp′
δ_{meso} 10.17 (s)	δ_{meso} 10.16 (s, 4 H)	δ_{meso} 9.94 (s, 4 H)
	δ(Cp) 2.44 (s, 5 H)	δ(Cp′) −0.06 (s, 15 H)
ν(CO) 2046, 2000, 1981	ν(CO) 2000, 1940, 1896	ν(CO) 1985, 1931

[a] NMR data in ppm in C_6D_6 solutions at room temperature. [b] IR data in cm^{-1}, taken in KBr discs at room temperature.

Metathesis of $[Rh(OEP)]_2$ and M′–M′ is the preferred synthetic technique because no side products are produced, facilitating purification.

Compounds **1**, **2**, and **3** were prepared by addition of a slight molar excess of M′–M′ to benzene solutions of $[Rh(OEP)]_2$. Under ambient laboratory conditions, formation of **1** and **2** was quantitative after 12 h at 25 °C. Complete formation of compound **3** required temperatures of 80–90 °C and reaction times in excess of 72 h. The heterobimetallics could be purified by removal of excess M′–M′ by vacuum sublimation, followed by recrystallization from benzene/light petroleum ether. All three heterobimetallic compounds form quantitatively at 25 °C within 2 h when irradiated with near-UV light (Rayonet RMR-400 Photochemical Reactor, 300 nm source). We believe that the rate-determining step in this reaction is M′–M′ bond homolysis, which is promoted by UV radiation [5].

Compounds **1**, **2**, and **3** are dark red solids and have been partially characterized by IR and NMR spectroscopy [6] (Table 1). Crystals suitable for X-ray structure determination have not yet been obtained. One of the most prominent spectroscopic features of compounds **2** and **3** is the unusually high field chemical shift of the Cp or Cp′ proton resonance, which arises from the magnetic anisotropy of the porphyrin unit (Table 1). Carbonyl stretching frequencies in **1**, **2**, and **3** indicate the presence of only terminal CO ligands which is consistent with the absence of an available adjacent coordination site on the Rh(OEP) fragment.

Synthesis of the heterobimetallics by reaction 1 is an important feature of these systems because it assures that **1**, **2**, and **3** are the thermodynamic products. Formation of the Rh(OEP)–M′ species by reaction 1 is essentially quantitative at room temperature, as evidenced by proton NMR spectra. The instrumental limits of detection indicate that the equilibrium constants for reaction 1 must exceed 500 ($K_1^{298} > 500$; $\Delta G < -15$ kJ/mol). We believe that the Rh–M′ bond energies in **1**, **2**, and **3** are larger than the average of the Rh–Rh and M′–M′ bond energies, and this originates in large part from elimination of the interporphyrin repulsion present in $[Rh(OEP)]_2$.

Preparation of heterobimetallics containing the Rh(OEP) fragment was motivated by the possibility of coupling the unusual reactivity of Rh(OEP)(H) with CO and CH_2O (reactions 4, 6) [7,8] with the potential reducing abilities of diverse metallohydrides as represented in model reactions 5 and 7.

$$\mathrm{Rh(OEP){-}M' + H_2 \rightleftarrows Rh(OEP)(H) + M'{-}H} \tag{3}$$

$$\mathrm{Rh(OEP)(H) + CO \rightleftarrows Rh(OEP)(CHO)} \tag{4}$$

$$\mathrm{Rh(OEP)(CHO) + M'{-}H \rightleftarrows Rh(OEP){-}M' + CH_2O} \tag{5}$$

$$\mathrm{Rh(OEP)(H) + CH_2O \rightleftarrows Rh(OEP)(CH_2OH)} \tag{6}$$

$$\mathrm{Rh(OEP)(CH_2OH) + M'{-}H \rightleftarrows Rh(OEP){-}M' + CH_3OH} \tag{7}$$

The heterobimetallics **1**, **2**, and **3** accomplish reaction 3 in the presence of H_2 and CO, and the resulting Rh(OEP)(H) proceeds to form equilibrium concentrations of the formyl complex by reaction 4 (Fig. 1). Proton NMR was used to follow the disappearance of intermetallic peaks and concurrent appearance of the diagnostic metallohydride resonances [9]. In the absence of carbon monoxide, reaction 3 does not occur at an appreciable rate. The mechanism for reaction 3 probably involves coordination of CO to the Rh(OEP) fragment of the heterobimetallics with concurrent weakening of the metal–metal bond and subsequent metal–metal bond cleavage.

The formation of two chemically diverse hydride species by reaction 3 may prove to be useful for some hydrogenation reactions, but the metallohydrides formed from **1**, **2**, and **3** do not reduce Rh(OEP)(CHO) by reaction 5. We are currently evaluating

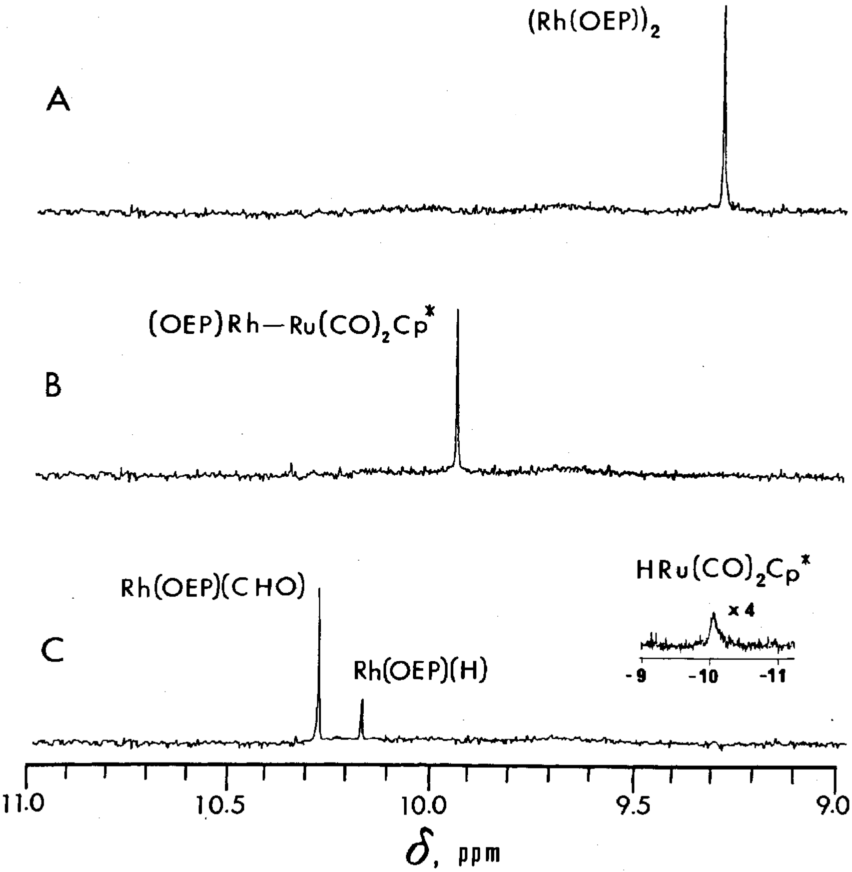

Fig. 1. Porphyrin Methine Proton NMR spectra (C_6D_6). A. $[\mathrm{Rh(OEP)}]_2$. B. (OEP)Rh–Ru(CO)$_2$Cp′. C. Reaction of (OEP)Rh–Ru(CO)$_2$Cp′ with 120 torr H_2, 280 torr CO (δ(*H*-Ru(CO)$_2$Cp′) −10.08 ppm).

a series of transition metal di- and tri-hydrides for their ability to hydrogenate the coordinated formyl unit.

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9 ^{1}H NMR Chemical shifts observed in this work: $\delta(H\text{-Mn(CO)}_5)$ -7.94 ppm; $\delta(H\text{-Mo(CO)}_3\text{Cp})$ -5.47 ppm (s, 1 H); $\delta(\text{H-Mo(CO)}_3Cp$ 4.51 ppm (s, 5 H); $\delta(H\text{-Ru(CO)}_2\text{Cp}')$ -10.08 ppm (s, 1 H); $\delta(\text{H-Ru(CO)}_2Cp')$ 1.67 ppm (s, 15 H). For comparison with previous reports of metallohydride ^{1}H NMR data see references 10–13.

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