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Preliminary communication

CATALYSIS WITH TRICARBONYL-*tetrahapto*-CYCLOPENTADIENONE-RUTHENIUM(0) COMPLEXES. A WATER-GAS TYPE REACTION

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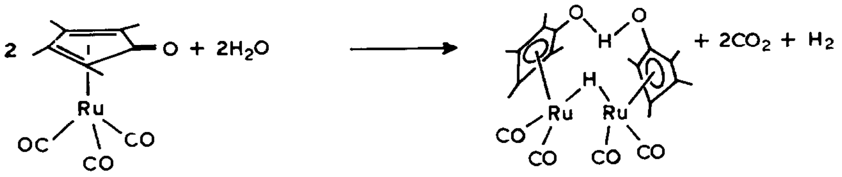
Summary

With water tricarbonyl-*tetrahapto*-tetraphenylcyclopentadienoneruthenium(0) (**1**) undergoes a water-gas type reaction whereby a coordinated CO is oxidized to CO_2, and gives the dimeric complex, which was isolated in high yield. A catalytic reduction of ketones with CO and water under mild conditions has been developed, and a catalytic cycle proposed. A turnover frequency of 1.2 min^{-1}, which is increased by a factor of ca. 6 by the presence of sodium carbonate, has been observed in the reactions with cyclohexanone.

Complexes of the type $(\eta^4\text{-CPD})(CO)_3Fe$ (CPD = substituted cyclopentadienones) have been known for over thirty years [1–11]. Their synthesis and chemistry were investigated mainly by Reppe, Hubel, Weiss, Wilkinson and their co-workers [1–9]. Three crystal structures of complexes with variously substituted CPD ligands have been determined by X-ray diffraction [12–14]. Isoelectronic Ru complexes are scarce [15,16]. The potential catalytic activity of this type of complex in organic reactions has not been explored.

The X-ray structure of tricarbonyl-*tetrahapto*-tetraphenylcyclopentadienone-ruthenium(0) (**1**) [17], demonstrates the tetrahapticity of the CPD ligand. The near equivalence of the three carbon–carbon bond lengths of the CPD ligand (1.44, 1.44, 1.45 Å) as well as the high frequency CO infrared stretching bands (2081, 2026, 2005 cm^{-1}) of **1** suggested weak Ru–CO coordination bonds and possibly a high reactivity towards nucleophiles.

The latter possibility was substantiated by an experiment in which a solution of **1** in acetone was mixed with an aqueous solution of sodium carbonate. The reaction (eq. 1) was complete after 45 min at room temperature and gave **2** (91%) the structure of which was recently determined by X-ray crystallography [18]. There was a slower reaction when water was used in place of the aqueous sodium carbonate, in this case the amount of CO_2 in the nitrogen stream was determined by trapping with BaO and that in solution by infrared spectroscopy (2335 cm^{-1}).



(1)

(1) (CPD Phenyls are omitted) (2)

The course of this transformation can be described by eqs. 2 and 3. Formation of carbon dioxide as well as **2** clearly points to the oxidation by water of a coordination carbon monoxide molecule. Nucleophilic attack by water on a coordinated CO with subsequent decarboxylation (a WGSR type process) is most likely. This step must give an organometallic dihydride complex, which we have formulated as **3** [18] (eq. 2). The formation of **2** requires now the loss of one dihydrogen molecule from **3** (eq. 3).

$$\underset{(\mathbf{1})}{(\eta^4\text{-}Ph_4C_4CO)(CO)_3Ru} + H_2O \rightarrow (\eta^5\text{-}Ph_4C_4COH)(CO)_2RuH + CO_2 \qquad (2)$$

$$2\underset{(\mathbf{3})}{(\eta^5\text{-}Ph_4C_4COH)(CO)_2RuH} \rightarrow \mathbf{2} + H_2 \qquad (3)$$

Complex **2** is a precatalyst in hydrogenation of various organic substrates by dihydrogen [20]. When subjected to hydrogen pressure at ca. 100°C, it was converted into **3** [20]. Complex **3** could not be isolated in the solid state, and is stable only in solution under a hydrogen blanket.

The following experiments were carried out:

(a) A THF solution of **1** containing water was heated under nitrogen at 105°C for 3 h in a closed glass-lined reactor. The infrared spectrum of the resulting solution showed CO stretching bands at 2014 and 1955 cm^{-1} which were assigned to **3** and was identical with that of the solution obtained by hydrogenation of **2** in THF with dihydrogen.

(b) When the above solution was left at room temperature under nitrogen, **3** was slowly converted into **2**, as indicated by the clean infrared spectral changes.

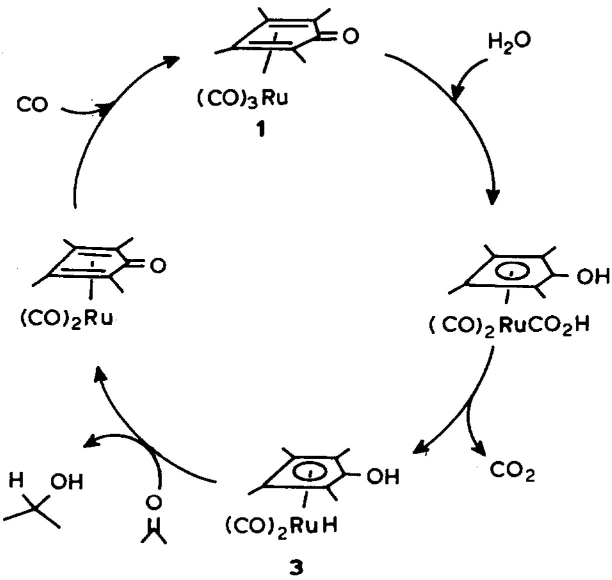
These two transformations, which are depicted in eqs. 2 and 3, must therefore represent the pathway for the overall conversion of **1** into **2** (eq. 1).

The above results suggested the possibility of incorporating eq. 2 into a catalytic cycle (Scheme 1). Preliminary experiments with several ketones (Table 1) demonstrate the viability of this cycle.

It should be noted that the above cycle can operate without added base, but a small quantity of sodium carbonate accelerates the reduction (cyclohexanone) and takes it to completion within 2 h at an average rate of 1.2 turnover per minute (Table 1). Steric effects were evident for some of the substrates that were examined.

Variation of the CO pressure from 250 to 1000 psi does not affect the rate of hydrogenation of cyclohexanone, indicating fast coordination of CO (Scheme 1). The dependence of the rate on both the added base and the nature of the ketone seems to be inconsistent with the proposed rate-limiting step (Scheme 1). This problem must await further kinetic studies.

Infrared monitoring of the hydrogenation solution for the reaction of cyclohexanone in THF, which remains pale yellow and homogeneous throughout, indi-



SCHEME 1.

cates the exclusive presence of **1**. It is only after the removal of carbon monoxide that **3** is exclusively present as shown by the IR bands at 2014 and 1955 cm^{-1}.

Addition of water to **1** (Scheme 1) releases a proton, which is taken up by the oxygen atom of the ring carbonyl. Probably, the formation of **3** is initiated by an acid–base type interaction of a water molecule with the oxygen atom of the CPD ligand in **1**. Supporting this is the observation that although η^4-$[(CF_3)_4C_4CO](CO)_3Ru$ exhibits CO IR stretching bands (2130, 2085 br cm^{-1}) at frequencies significantly higher than those of **1**, it is unreactive in reaction 1 or in the reduction of ketones with CO and water. Its CPD carbonyl group (ν 1740 cm^{-1}) must be substantially less basic than that of **1** (ν 1655 cm^{-1}). Thus, a reactive CO ligand is not the sole requirement for interaction with water.

TABLE 1

HYDROGENATION OF KETONES WITH $CO + H_2O$ AND 1

(Reaction conditions: [ketone] 1.0 *M*; $[(Ph_4C_4CO)(CO)_3Ru]$ 7×10^{-3} *M*; $[H_2O]$ 2.8 *M*; *P*(CO) 500 psi; Temp. 105°C in THF. Conversion and turnover values are at 4 h reaction time. The identity and yields of products were determined by GLC)

Ketone	Alcohol	Conversion (%)	Turnovers
Acetone	Isopropanol	53	76
Cyclohexanone	Cyclohexanol	33	47
Cyclohexanone [a]	Cyclohexanol	98	140
Diisopropyl ketone	Diisopropylcarbinol	16	23
Acetophenone	1-phenylethanol	25	36

[a] Sodium carbonate (0.1 mmol) was added to 10 ml of the solution, the conversion and turnover values are after 2 h of reaction.

Neither alkenes nor alkynes could be hydrogenated under the experimental conditions described. Consequently hydrogenation of ketones with water and CO in the presence of **1** is a selective catalytic process.

Unfortunately the isoelectronic iron complex $(\eta^4\text{-}Ph_4C_4CO)(CO)_3Fe$ [3] shows very little catalytic activity, and decomposes to give a heterogeneous mixture under the conditions used.

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