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Preliminary communication

CATALYTICALLY REACTIVE (η^4-tetracyclone)$(CO)_2(H)_2Ru$ AND RELATED COMPLEXES IN DEHYDROGENATION OF ALCOHOLS TO ESTERS

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Summary

(η^4-Tetracyclone)$(CO)_3Ru$ and [(η^4-tetracyclone)$(CO)_2Ru]_2$ are catalyst precursors in the direct oxidation of primary alcohols to esters. Their use without a H-acceptor in an open reaction system leads to bimolecular dehydrogenation of primary alcohols to esters and also of secondary alcohols to ketones with evolution of H_2. The structure of (η^4-tetracyclone)$(CO)_2(H)_2Ru$ was assigned to a reaction intermediate observed during the catalysis. A catalytic cycle is proposed.

Catalytic cycles involving transition metal complexes are frequently characterized by a complex set of transformations. The elucidation of the mechanistic pathways of a catalysed reaction is fundamental to understanding of catalysis.

We previously attributed the unique direct transformation of alcohols to esters (eq. 1) to a hypothetical catalytically reactive Ru cluster [1,2]. A search for such a species led to our recent discovery [3], in the reaction mixture (eq. 1), of the mononuclear tetrahaptotetracyclonetricarbonylruthenium (1), and a related dimer, bis(tetrahaptotetracyclonedicarbonylruthenium) (2).

$$2RCH_2OH + 2PhC{\equiv}CPh \xrightarrow{Ru_3(CO)_{12}} RCO_2CH_2R + 2PhCH{=}CHPh \qquad (1)$$

$$PhC{\equiv}CPh + Ru_3(CO)_{12} \rightarrow$$

$$(\eta^4\text{-}Ph_4C_4CO)Ru(CO)_3 \; + \; [(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2 \qquad (2)$$

(1) (2)

Subsequently, these two complexes were independently prepared (eq. 2), and were found to be more reactive than $Ru_3(CO)_{12}$ in reaction 1 [3]. Thus, during

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catalysis $Ru_3(CO)_{12}$ is degraded by diphenylacetylene, via a complex but efficient set of transformations, to a mononuclear catalytically active species (1) and a related dimer (2). The important conclusion from these findings is that in reaction 1, PhC≡CPh functions not only as a H-acceptor but also as a catalyst precursor.

A major goal of our studies was to change reaction 1 from a catalytic H-transfer to a true dehydrogenation reaction, with formation of H_2 as the reduction product (eq. 3).

$$2RCH_2OH \xrightarrow{cat.} RCO_2CH_2R + 2H_2 \quad (3)$$

Only few homogeneously catalyzed dehydrogenation reactions are known [4—9]. Previously we concluded that such a process is not feasible on the basis of our experimental observation that reaction 1 did not take place in the absence of PhC≡CPh, the H-acceptor, in a closed or open reaction system [2]. Our present knowledge of the dual functionality of diphenylacetylene (vide supra) implies that in the above experiment we excluded not only the H-acceptor but also the catalyst precursor, thus rendering catalysis impossible. Repeating the experiment with 1 and 2, instead of $Ru_3(CO)_{12}$, and now omitting PhC≡CPh, clearly demonstrates that dehydrogenation, as described by reaction 3, does indeed, take place, and hydrogen is evolved. Complexes 1 and 2, each with $PhCH_2OH$ (neat) in an open reactor (145°C), generate 450 oxidation cycles as determined by GLC analysis, yielding benzyl benzoate. Under similar conditions (137°C), 1-pentanol (neat) yields 1-pentyl-n-pentanoate (250 cycles). The relative reactivities of 1, 2 and $Ru_3(CO)_{12}$ under various conditions are shown in Table 1.

TABLE 1

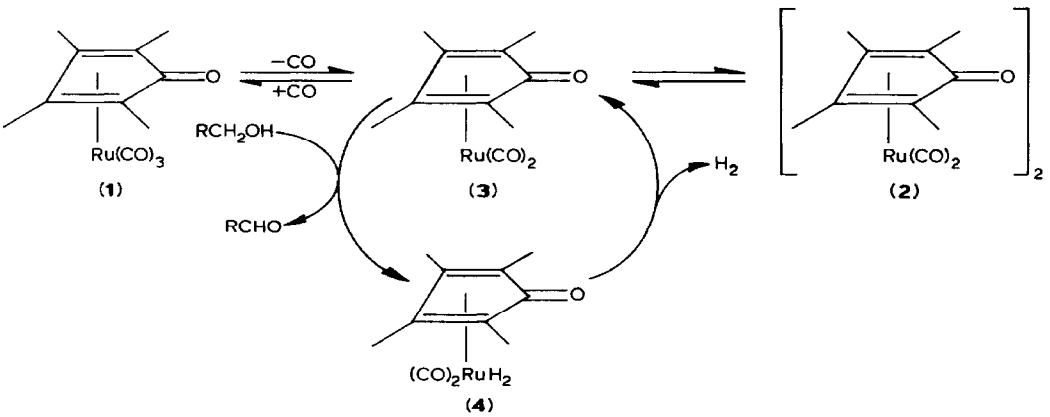
RELATIVE INITIAL RATES OF BENZYL ALCOHOL CONSUMPTION[a]

Catalyst	Reaction condition	Gas phase[b]	Relative initial rates
$Ru_3(CO)_{12}$	PhC≡CPh Closed system	Nitrogen	1.0
1	Open system	Nitrogen purge	1.9
1	Closed system	Nitrogen	0.9
2	Open system	Nitrogen purge	1.8
2	Closed system	Nitrogen	1.5[c]
2	Closed system	Nitrogen/Hydrogen 9/1	0.8[c]
2	Closed system	Hydrogen	0.5[c]

[a] ($PhCH_2OH$) 0.75 *M*; (catalyst) 0.015 *M* (in Ru) in 1-methylnaphthalene at 145°C. Rates were derived from the composition after 1 h of reaction as determined by GC analysis and were reproducible to ±5%. [b] A total pressure of 1 at. at room temperature was employed in closed systems; [c] Rates fell sharply after 1 h.

The following conclusions can be drawn from the data in Table 1: (a) The rates and final conversions diminish with an increase of hydrogen concentration (*P*). (b) With both 1 and 2, catalysis is less effective in a closed than in an open reaction system. This is attributed to the evolution, during catalysis, of CO and H_2 in the case of 1, and of H_2 in the case of 2 (vide infra). (c) In an open system, 1 and 2 behave similarly, but give faster reactions than $Ru_3(CO)_{12}$ in the presence of diphenylacetylene.

Although both 1 and 2 are reactive in reaction 3, they are coordinatively saturated 18*e* complexes and must still therefore be regarded as catalyst precursors. From the data of Table 1 we deduce that the true catalytic species is in fact the coordinatively unsaturated dicarbonyl complex 3 (Scheme 1).



SCHEME 1 (Phenyls are omitted)

Since it has a free coordination site, 3 is capable of oxidizing a primary alcohol to an aldehyde, and giving the dihydride 4 which regenerates 3 by thermal loss of H_2. Since it was rigorously established that aldehydes are intermediates in the overall transformation of alcohols to esters [1,2], the above basic oxidation cycle may also be applied to the second step, which involves an oxidative interaction of aldehyde, alcohol, and 3, conceivably in a metal bound hemiacetal intermediate.

The facts that 1 and 2 can be interconverted by the loss and addition of CO, and that both yield the same triphenylphosphine complex [3], strongly implicate undetected 3 as an active catalytic species. It is generated thermally, in situ, either from 1 by the loss of CO or from 2 by dissociation of the dimer (Scheme 1). On the other hand, the dihydride 4 was directly observed. The yellow benzene solution of 2, when subjected to hydrogen (500 psi) at 145°C for 1 h, turned colorless. The IR spectrum in hexane exhibits two CO bands at 2028, 1971 cm^{-1} and in CH_2Cl_2, 3535 (O—H), 2023, 1965 (CO), 1810 (Ru—H), 1550 (ring carbonyl) cm^{-1}. During the IR measurement, the above spectrum is gradually transformed into that of 2 (2040, 2010, 1982, 1550 cm^{-1}) with the concomitant reappearance of the yellow color. The above reaction was repeated in benzene-d_6 and the ^1H NMR spectrum was measured under a hydrogen blanket; a singlet at δ −9.31 ppm was observed and this gradually disappeared upon replacing the H_2 blanket by N_2. These results support structure 4 for the dihydride obtained by direct hydrogenation of 2 [10]. In solution, complex 4 is stable under hydrogen, reverts to the dimer 2 under nitrogen, decomposes when exposed to air, and could not be isolated in the solid state. That this complex is, in fact, associated with our catalytic reaction 3 in the presence of an alcohol was demonstrated by determining the IR spectrum of the reaction mixture with 4-

methylbenzyl alcohol and **2**; the carbonyl region of the mixture consists of the combinated spectra of **4** and **2**, with predominance of the former.

We have found that **2** also dehydrogenates secondary alcohols. Thus, 2-octanol and cyclohexanol (neat) in an open reactor at 145°C with **2**, give 2-octanone (558 cycles) and cyclohexanone (240 cycles), respectively.

The identification of the precatalytic complexes (**1**,**2**) and the catalytic species (**3**,**4**) is an important step in the understanding of the oxidative coupling reaction of alcohols to esters. It led us to complex **1**, which was reported a long time ago [11], but neither its chemistry nor its catalytic activity were previously explored. It also raises the question of the role of the cyclopentadienone ligand in the catalysis.

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10 The alternative structure (η^5-Ph_4C_5OH)$(CO)_2$(H)Ru for **4** cannot be ruled out. It would be consistent with the observed IR band at 3535 cm^{-1} (OH); we could not detect the corresponding ^1H resonance in the NMR spectrum of **4**, but it is possible that the H atoms (O—H and Ru—H) are involved in a fast exchange process.
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