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Activation of a C–H bond by a rhodium A-frame complex under hydroformylation conditions: carbonylation of styrene to 1-indanone

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Abstract

The cationic rhodium A-frame complex $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ is active as a hydroformylation catalyst at elevated temperature and pressure. In addition to the expected aldehydes, significant yields of linear and cyclic ketones are produced. Surprisingly, when the solvent is THF, but not methanol, carbonylation of styrene with cyclization to form 1-indanone also occurs, demonstrating the ability of the A-frame complex to non-photolytically activate a C–H bond.

Keywords: C–H bond activation; Cyclic carbonylation; Hydroformylation; 1-Indanone; Rhodium A-frame complex

1. Introduction

A wide range of catalysts are known to be active for carbonylation of alkenes to aldehydes and ketones [1]. Binuclear dppm-bridged (dppm: bis(diphenylphosphino)methane) A-frame complexes of rhodium(I) are catalytically active for hydrogenation [2,3], hydroformylation [2,4], and the water gas shift reaction [2,5]. In an earlier work, it was shown that the presence of carbon monoxide suppresses the hydrogenation catalytic activity of the cation $[Rh_2(\mu\text{-}Cl)CO_2(\mu\text{-}dppm)_2]^+$ by forming the CO bridged cation $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]^+$ [4,6]. However, at higher temperature and pressure reactions of the unsaturated substrates with hydrogen and carbon monoxide are catalyzed by the latter cation [4]. Under strenuous hydroformylation conditions, cationic Pd(II)-diphosphine complexes also catalyze carbonylation of alkenes to ketones [7]. However, related dinuclear complexes have lower activity [8]. Herein, the catalyzed reactions of either phenylacetylene or styrene with a mixture of hydrogen and carbon monoxide, in various solvents, will be described. Not only is hydrogenation of phenylacetylene to styrene and hydroformylation of styrene to the corresponding aldehydes catalyzed, but carbonylation of each to linear and cyclic ketones also occurs.

In THF, but not in methanol, styrene undergoes a combination of carbonylation and C–H bond activation to afford significant amounts of a surprising product, 1-indanone. This represents the first observation of C–H bond activation by an A-frame complex [8]. Significantly, it does so under non-photolytic conditions.

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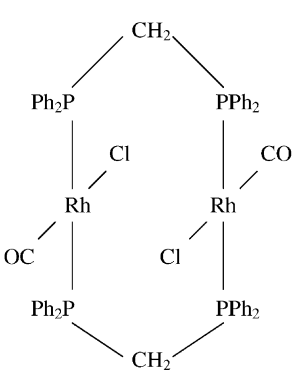

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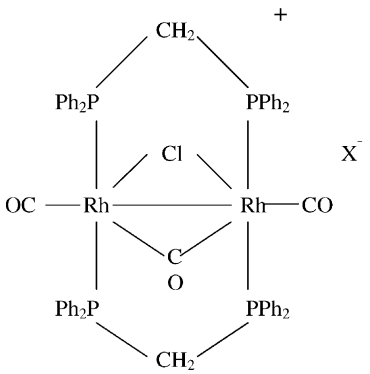


2, $X^- = BPh_4^-$

3, $X^- = SnCl_3^-$

2. Experimental

All reactions were performed in dry, oxygen-free solvents, under the conditions reported in Table 1.

$[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$ (**1**) [2,9], and $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2]^+[BPh_4]^-$ (**2**), [6] were prepared as previously described. The corresponding complex containing the trichlorostannio anion, $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2]^+[SnCl_3]^-$ (**3**), was prepared by the stoichiometric reaction of **1** with $SnCl_2{\cdot}2H_2O$ in a mixture of dichloromethane and methanol under an atmosphere of CO [4,10], followed by evaporation of a majority of the solvents, filtration and drying under vacuum.

All catalytic reactions were performed in a glass-lined, thermostatted stirrer reactor (Parr, model 5464) with a capacity of 160 cm^3. The reactor was charged with a solution (50 cm^3) of catalyst and substrate, pressurized at room temperature, and then heated to a selected reaction temperature, typically 150 °C. Aliquots of solution were extracted at intervals, and were analyzed by gas chromatography (Finnegan 4000/5000).

3. Results and discussion

Under an atmosphere containing no CO, $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2]^+[BPh_4]^-$ (**2**) reversibly

Table 1
Reactions of Phenylacetylene or Styrene with CO and H_2[a]

Catalyst	X	Solvent	Time (h)	H_2/CO	PhC_2H (%)	PhC_2H_3 (%)	PhC_2H_5 (%)	Aldehyde/ acetal (%)	*n*/*iso*	DPP (%)	DPCP (%)	Indanone (%)
Substrate: phenylacetylene												
2	BPh_4	MeOH	3.5	1:1	Trace	96	0.3	Trace	–	1	3	–
2	BPh_4	MeCN	17	1:1	2	97	0.4	Trace	–	–	–	–
3	$SnCl_3$	MeOH	3	1:1	Trace	99.5	0.2	–	–	–	–	–
3	$SnCl_3$	THF	29	1:1	3.5	50	0.6	6.5	0.31	39	2	–
Substrate: styrene												
2	BPh_4	MeOH	47	1:1	–	43	2.4	41	2.1	11.5	2.5	–
2	BPh_4	THF	69	1:1	–	17	5	21	3.1	20	31.5	5
3	$SnCl_3$	MeOH	22.5	1:1	–	96.5	1.4	1.7	2.45	–	–	–
3	$SnCl_3$	THF	25	1:1	–	44	1	19	0.31	–	27	11

[a] 1.0 MPa; 150 °C; $[Rh_2(\mu\text{-Cl})(CO)_2\ (\mu\text{-CO})(\mu\text{-}Ph_2PCH_2PPh_2)_2][X]$.

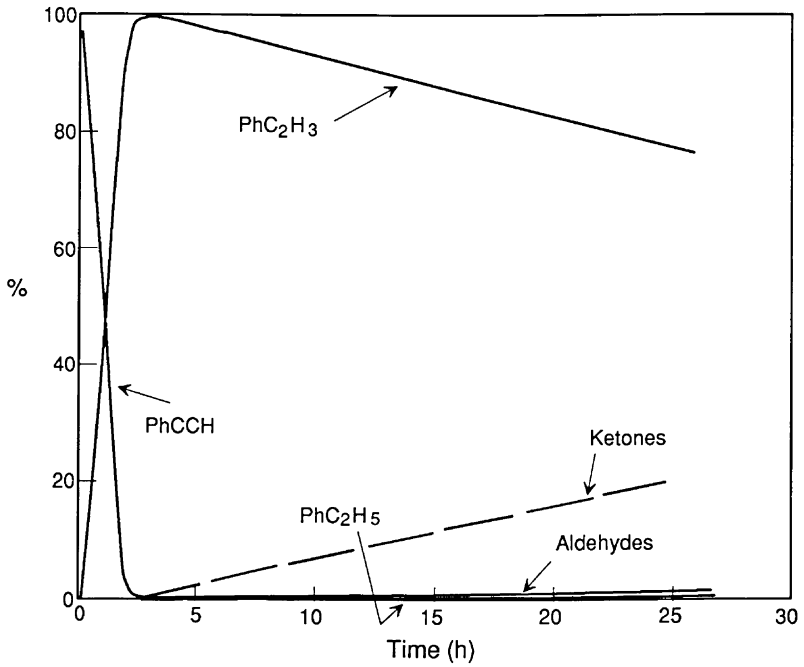


Fig. 1. Reaction of phenylacetylene (1.00 cm^3) with H_2 and CO (1:1; 1:03 mPa) catalyzed by a solution of $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][SnCl_3]$ (28 mg) in methanol (50 cm^3) at 150 °C.

dissociates to form CO and the corresponding cationic complex containing no bridging CO ligand [6]. However, the CO-bridged cation is very stable under an atmosphere of CO and H_2 [4] or CO alone [6]. The $[SnCl_3]^-$ salt of the same cation, **3**, is also stable under an atmosphere of CO [10].

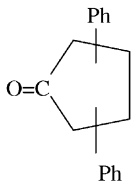
Under a 1:1 mixture of CO and H_2, either **2** or **3** catalyzes the hydrogenation of phenylacetylene to styrene, with high selectivity, within a few hours at 50–150 °C, in various solvents (Table 1; Figs. 1 and 2). Only in THF are significant amounts of phenylpropionaldehydes and diphenyl-3-pentanone (DPP) concurrently formed, by subsequent hydroformylation of styrene (Fig. 2).

Reactions of styrene with CO and H_2, catalyzed by either **2** or **3**, afford a variety of products. The product distribution is dependant upon the natures of both the solvent and the anion of the complex catalyst (Table 1). Hydrogenation of styrene to ethylbenzene is a minor reaction (Eq. (1)) when using either catalyst, in any solvent. The major reactions are hydroformylation of styrene to *n*- and *iso*-phenylpropionaldehyde and to DPP (Eq. (2)), and cyclization of two molecules of styrene with one molecule of CO to a mixture of cyclic carbonylation products comprising four isomers of diphenylcyclopentanone (DPCP) (Eq. (3)).

$$\mathrm{PhCH:CH_2 + H_2 \rightarrow PhCH_2CH_3} \quad (1)$$

$$\mathrm{PhCH:CH_2 + H_2 + CO \rightarrow PhCH_2CH_2CHO + PhCH(CH_3)CHO + (PhC_2H_4)_2CO} \quad (2)$$

$$\mathrm{2PhCH{:}CH_2 + CO \rightarrow}$$



(3)

A surprising product produced when the reaction was performed in THF, but not in methanol, was 1-indanone (Eq. (4)). This showed the ability of the A-frame complex cation to activate a C–H bond. In contrast to the activation of C–H bonds by alkyl phosphine complexes of rhodium [11,12], this reaction

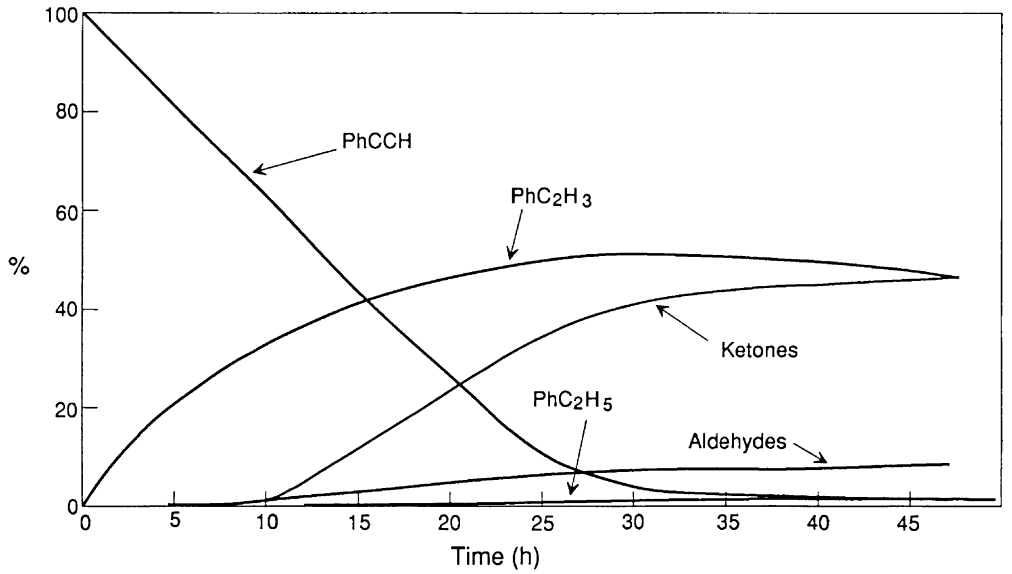
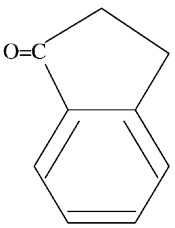


Fig. 2. Reaction of phenylacetylene (1.00 cm^3) with H_2 and CO (1:1; 1:03 mPa) catalyzed by a solution of [Rh_2(μ-Cl)(CO)$_2$(μ-CO)(μ-dppm)$_2$][$SnCl_3$] (28 mg) in THF (50 cm^3) at 150 °C.

occurred under non-photolytic conditions. To effect closure of the five-membered ring, an aromatic C–H bond must be activated to enable formation of the C–C bond between carbonyl carbon and aromatic carbon. Although 1-indanone was not the major product, the proportions were nevertheless substantial (5 and 11%).

$$\mathrm{PhCH{:}CH_2 + CO \rightarrow}$$  (4)

Although reaction (4) was unexpected, a related reaction is known: insertion of CO into a C–H bond. A series of reactions have been reported in which a C–H bond is activated under photolytic conditions in the presence of rhodium phosphine complexes [11,12]. Complexes having alkyl phosphine ligands, especially PMe_3, were shown to be much more active than the corresponding aryl phosphine or phosphite ligands [12]. However, the di-rhodium complex [Rh_2Cl_2(CO)$_2$ (μ-dmpm)$_2$] (dmpm is $Me_2PCH_2PMe_2$), the core structure of which is the same as complex **1** had very low activity for carbonylation of benzene to benzaldehyde when compared with mononuclear complexes. When there was no irradiation, no C–H bond activation occurred, and none of the catalysts was active for carbonylation of hydrocarbons [11,12].

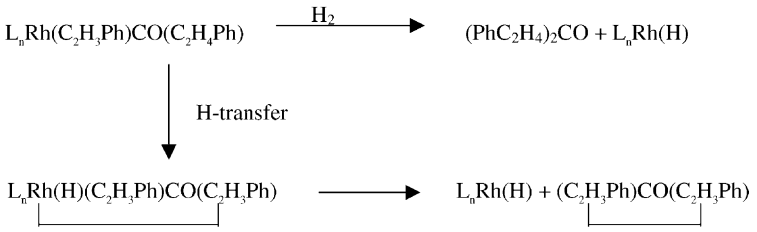
3.1. Proposed mechanism of formation of ketones

The mechanism for hydroformylation of alkenes to aldehydes necessarily includes formation of acyl-metal intermediate complexes [8,13], herein shown as [L_nMCOR]. Subsequent reactions of the coordinatively unsaturated acyl complex with hydrogen (or a hydrido-complex) affords product aldehydes, and regenerates the catalytically active hydrido-metal complex (Eq. (5); L_n is the sum of all ligands except acyl or H).

$$L_n\mathrm{MCOR} + \mathrm{H_2} \rightarrow L_n\mathrm{MH} + \mathrm{RCHO} \quad (5)$$

There are two possible mechanisms of formation of linear ketones. In a mononuclear mechanism, insertion of a second molecule of substrate into the acyl–metal bond (Eq. (6)), and subsequent reaction with hydrogen, affords the ketone and regenerates the

active hydrido-complex. Alternatively, in a binuclear elimination reaction, reaction of the acyl complex intermediate with its precursor alkyl complex [13] affords the ketone and a dinuclear complex (Eq. (7)).



(8)

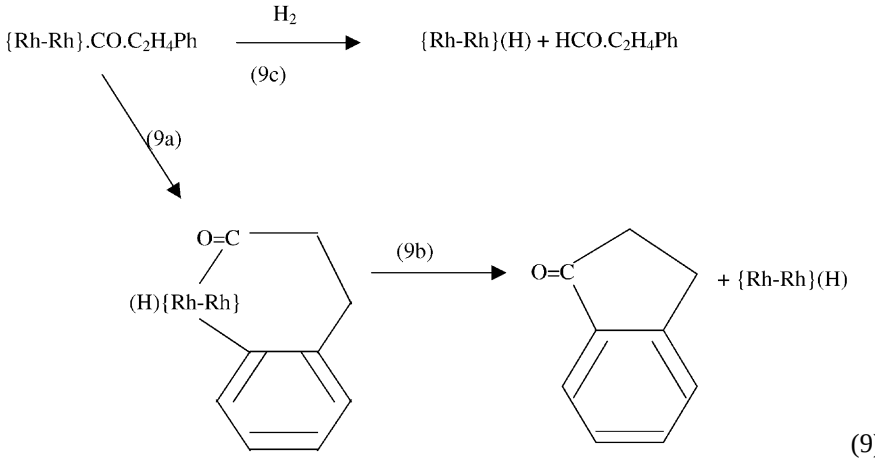
Subsequent reaction of this dinuclear complex with hydrogen regenerates the active hydrido-complex.

$$L_n\mathrm{RhCOC_2H_4Ph} + \mathrm{PhCH:CH_2} \rightarrow L_n\mathrm{Rh(C_2H_3Ph)CO(C_2H_4Ph)} \quad (6)$$

$$L_n\mathrm{RhCOC_2H_4Ph} + L_m\mathrm{Rh(C_2H_4Ph)} \rightarrow (\mathrm{PhC_2H_4})_2\mathrm{CO} + L_n\mathrm{RhRhL}_m \quad (7)$$

When THF is the solvent, selectivity to cyclic ketones, DPCP, is very high (Eq. (3)), and is essentially independent of the anion. It is difficult to reconcile formation of a cyclic product with a binuclear elimination mechanism, as in Eq. (7). However, by simple hydrogen addition or hydrogen transfer, respectively, the product of Eq. (6) can form both linear and cyclic ketone products (Eq. (8)). Therefore, insertion reaction (Eq. (6)) is considered to be the mechanism of formation of ketones, and binuclear elimination (Eq. (7)) is not considered to make a significant contribution to formation of these products.

The formation of 1-indanone, that occurs when THF is the solvent, also requires hydrogen transfer, in this case from aromatic carbon to rhodium, for formation of the acyl complex intermediate. It cannot be determined unequivocally from the present data whether the hydrogen transfers to the same rhodium that has the acyl ligand, or to the other rhodium of the dinuclear complex catalyst. However, formation of 1-indanone is not formed in the presence of $[RhCl(CO)(PPh_3)_2]$, and has not previously been reported for carbonylation or hydroformylation reactions using any of the other numerous complexes of rhodium that are active catalysts for these reactions [1,13]. Therefore, the proximate second rhodium center of the A-frame complex clearly has a significant catalytic role. Consequently, the following mechanism is tentatively proposed (Eq. (9); {Rh–Rh} represents the A-frame complex intermediate, without illustration of the non-participating pendant or bridging ligands).



(9)

The product of the sequence of reactions (9a) and (9b) resembles that from an intramolecular Pauson–Khand reaction [14]. However, 1-indanone cannot be formed from styrene without activation of an aromatic C–H bond, and so this mechanism is quite distinct from that of the Pauson–Khand reaction. Reaction (9c) is the product elimination step of a conventional hydroformylation reaction (Eq. (2)).

It is noteworthy that, in each case the products requiring a hydrogen transfer from carbon to rhodium, DPCP (Eq. (8)) and 1-indanone (Eq. (9)), are formed when THF is the solvent, but not methanol. Thus the nature of the solvent is significant, although its role is not clear.

Finally, a note should be made of the role of the anion. Whereas $[BPh_4]^-$ is essentially a non-coordinating ion, $[SnCl_3]^-$ has moderate Lewis acidity [15] and can coordinate to rhodium or other metals [16,17], or to unbound donor sites of ligands. In either methanol or THF, catalyst **2**, containing the $[BPh_4]^-$ anion, exhibited significant selectivity to formation of the linear ketone DPP (Eq. (2)). When catalyst **3**, with the $[SnCl_3]^-$ anion, was used, no significant selectivity to DPP was observed. A possible explanation for this observation is that the $[SnCl_3]^-$ anion participates in the mechanism by coordinating to a mechanistically important site on one or more of the intermediate complexes, thereby suppressing formation of DPP. The $[SnCl_3]^-$ ion is a participating component of hydroformylation catalyst systems comprising chloroplatinum complexes dissolved in chlorostannate ionic liquids [15].

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