Preliminary communication

PHOTOCHEMICAL HYDROFORMYLATION CATALYSIS USING RUTHENIUM COMPLEXES

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Summary

The catalytic hydroformylation of ethylene and propylene is promoted photochemically by the ruthenium(0) complexes $Ru(CO)_3(PPh_3)_2$, $Ru(CO)_4$-(PPh_3) and $Ru_3(CO)_{12}$ under UV irradiation at low pressure (ca. 500 torr H_2/CO, 1/1) and ambient temperature. Subsequent hydrogenation of the aldehydes is also observed. The photolyses are performed in benzene solution, and result in competitive hydroformylation and hydrogenation of the olefin to yield a product mixture of alkane, aldehydes and alcohols. The use of ^{13}CO shows that the ligands in $Ru(CO)_3(PPh_3)_2$ exchange readily under photolysis, and that under catalytic conditions $Ru(CO)_3(PPh_3)_2$ is slowly converted to $Ru(CO)_4(PPh_3)$ as the only observable Ru species in solution. Incorporation of ^{13}C into the carbonyl position of propanal and the C(1) position of 1-propanol is observed directly by NMR spectroscopy. The tetracarbonyl complex exchanges CO readily at ambient temperature, and upon irradiation under H_2 forms the unstable dihydride complex $RuH_2(CO)_3(PPh_3)$. A mechanism is proposed for the observed hydroformylation in which the photochemical step is thought to be generation of a coordinatively unsaturated Ru species.

The photogeneration of catalytically active species represents an area of current interest in homogeneous catalysis [1]. Recently, Mirbach and coworkers have examined the influence of UV irradiation on cobalt and rhodium hydroformylation catalysts as elevated pressures [2, 3]. A variety of results were obtained for the different systems including photochemical promotion and photochemical inhibition of the catalysis, and changes in the principle products and product distributions. In this communication we report that the ruthenium(0) complexes $Ru(CO)_3(PPh_3)_2$, $Ru(CO)_4(PPh_3)$ and $Ru_3(CO)_{12}$ promote hydroformylation of ethylene and propylene photochemically under low pressure at

ambient temperature. Under these conditions subsequent hydrogenation to the corresponding alcohol is also achieved. Previous reports of Ru complex catalyzed hydroformylation have been made by Wilkinson et al. [4], using $Ru(CO)_3(PPh_3)_2$, and $Ru_3(CO)_{12}$, and by Pino et al. [5], and by Laine [6] with $Ru_3(CO)_{12}$. In these studies the hydroformylation catalysis was carried out at 120°C and 100 atm H_2/CO, and at 150°C and >70 atm, respectively.

In the present study catalysis experiments were performed in NMR tubes with products identified and quantified by ^1H or ^{13}C NMR spectroscopy or by GC analysis. In a typical run, 2.6×10^{-5} mol of the gaseous olefin was condensed into a sample tube containing 1.0—2.5 mg of ruthenium complex in 0.5 ml of C_6D_6. The tube was then sealed under 500—600 torr of H_2/CO (1/1) and photolyzed with a 200 Watt Hg-Xe lamp through a pyrex filter resulting in a mixture of hydrogenation and hydroformylation products. For the reaction involving ethylene catalyzed by $Ru(CO)_3(PPh_3)_2$, ethane, propionaldehyde, 1-propanol and a trace of 3-pentanone are observed directly in the ^1H NMR spectrum, and the first three products are identified separately by GC analysis. The ratio of hydrogenation to hydroformylation products for this system corresponds to approximately 2/1, and of the hydroformylation products, the proportion of propanol to propanal increases throughout the course of the reaction. With larger amounts of ethylene, as many as nine turnovers of products are observed for this closed reaction system. The same products are also found when $Ru(CO)_4(PPh_3)$ and $Ru_3(CO)_{12}$ are employed as the catalysts.

Propylene also undergoes photochemical hydroformylation and hydrogenation using $Ru(CO)_3(PPh_3)_2$ as the catalyst. Both straight and branched chain aldehydes are produced in a 3.9/1 n/iso ratio with propane, n-butanol and isobutanol formed as the other products. For propylene, hydrogenation is favored even more over hydroformylation than is the case for ethylene with a product ratio of C_3H_8 to combined butanals + butanols of ca. 4/1. When styrene is employed as the olefin, only hydrogenation to ethylbenzene is seen upon photolysis of a benzene-d_6 solution of $Ru(CO)_3(PPh_3)_2$ under H_2/CO; no hydroformylation products are detected.

Further studies on the system with $Ru(CO)_3(PPh_3)_2$ as the catalyst and C_2H_4 as the olefin provide insight into the nature of the active catalyst and the mechanism of catalysis. By alternately photolyzing the sample and placing it in the dark we are able to show that reaction only occurs during photolysis. The system is thus photoassisted and not merely photoinitiated. While small amounts of $RuH_2(CO)_2(PPh_3)_2$ can be detected at early reaction times, our studies indicate that under the conditions used for hydroformylation $Ru(CO)_3$-$(PPh_3)_2$ is converted completely to $Ru(CO)_4(PPh_3)$.

That $Ru(CO)_4(PPh_3)$ is the principal species in solution was demonstrated by ^{13}C NMR spectroscopy using an $H_2/^{13}CO$ mixture to react with ethylene. After several minutes of photolysis, both ^{13}CO incorporation into $Ru(CO)_3(PPh_3)_2$ and the formation of $Ru(CO)_4(PPh_3)$ are observed, indicating facile substitution of ^{13}CO for both CO and PPh_3. $Ru(CO)_3(PPh_3)_2$ exhibits a triplet at 208.53 ppm with $J(PC)$ of 16 Hz, while $Ru(CO)_4(PPh_3)$ appears as a doublet at 204.41 ppm with $J(PC)$ of 4 Hz [7]. After 11 h of photolysis, the ^{13}C NMR spectrum shows only the resonance at δ 204 ppm indicating $Ru(CO)_4(PPh_3)$ as the only observable ruthenium carbonyl species in solution with the resonance

at δ 208 ppm due to $Ru(CO)_3(PPh_3)_2$ no longer seen. Photolysis beyond the point at which $Ru(CO)_4(PPh_3)$ is the only observed Ru species in solution results in further hydroformylation and hydrogenation of ethylene. The conversion of $Ru(CO)_3(PPh_3)_2$ to $Ru(CO)_4(PPh_3)$ under catalysis conditions is further corroborated by infrared spectroscopy. When a concentrated solution of $Ru(CO)_3(PPh_3)_2$ and ethylene under synthesis gas is photolyzed, bands at 2060, 1977, and 1936 cm^{-1} consistent with $Ru(CO)_4(PPh_3)$ are observed in the IR spectrum. This sample, however, was not photolyzed until the complete disappearance of $\nu(CO)$ attributable to $Ru(CO)_3(PPh_3)_2$.

In addition to establishing $Ru(CO)_4(PPh_3)$ as the principal species in solution, the use of $H_2/^{13}CO$ leads to direct observation of ^{13}C isotope incorporation into propionaldehyde at the carbonyl position and into 1-propanol at the C(1) position. This is seen by resonances at δ 200.12 and 63.99 ppm for the respective products in the ^{13}C NMR spectrum, and by the large ^{13}C coupling exhibited in the ^1H NMR spectrum by the hydrogen atoms bound to the ^{13}C isotope. The chemical shifts for 1-propanal and 1-propanol are δ 9.23 ppm (d, $J(CH)$ 170 Hz) and δ 3.24 ppm (dt, $J(CH)$ 141 Hz), respectively.

We also observe that ^{13}CO can be incorporated into $Ru(CO)_4(PPh_3)$ in benzene at room temperature in the absence of light. Interestingly, $RuH_2(CO)_3$-(PPh_3) is not formed by placing a C_6D_6 solution of $Ru(CO)_4(PPh_3)$ under a hydrogen atmosphere. However, photolysis of this mixture yields a doublet in the ^1H NMR spectrum at δ −6.69 ppm with 23 Hz coupling and two new bands in the infrared spectrum, a sharp band at 2078 and a broad band at 2018 cm^{-1}. We believe this species is $RuH_2(CO)_3(PPh_3)$. Whyman has reported that heating a heptane solution to 100°C under 550 atm. of H_2 generates new bands in the infrared at 2080 and 2021 cm^{-1} with a shoulder at 2010 which he attributes to $RuH_2(CO)_3(PPh_3)$ [8]. Our infrared data are consistent with this. This dihydride species is not very stable, reverting primarily to $Ru(CO)_4(PPh_3)$ within 24 h at room temperature under the hydrogen atmosphere [9].

Based on these observations, we propose the mechanism shown in Scheme 1 for the photochemically promoted hydroformylation in which $Ru(CO)_4(PPh_3)$ serves as the active catalyst precursor. This mechanism is closely related to that put forward by Wilkinson et al., for $Ru(CO)_3(PPh_3)_2$. In Scheme 1 the photochemical step is proposed to be CO dissociation to generate $Ru(CO)_3(PPh_3)$. This photodissociation has in fact been observed by Wrighton and co-workers [10, 11]. A second photochemical cycle involving the bis-phosphine species $Ru(CO)_3(PPh_3)_2$ and $RuH_2(CO)_2(PPh_3)_2$ probably exists as well during stages of the photolysis when $Ru(CO)_3(PPh_3)_2$ is present in solution in significant amounts. In Scheme 1 hydrogenation products result from reductive elimination of alkane from the alkyl hydride intermediate which occurs competitively with CO insertion. There are at least two other possibilities that we have been unable to rule out. These possibilities are product formation via a Ru^{IV} species or via bimolecular H-transfer. The feasibility of these possibilities is demonstrated by the observation that when a solution of $Ru(CO)_4(PPh_3)$ under H_2 + D_2 is photolyzed, substantial amounts of HD form rapidly as seen by the 1/1/1 triplet of HD at δ 4.42 ppm in the ^1H NMR spectrum. Also, when CO + H_2 + D_2 is the gas mixture used for hydroformylation, HD forms sufficiently rapidly relative to product formation that it precludes a determination of whether reductive elimination or another process is involved in product formation.
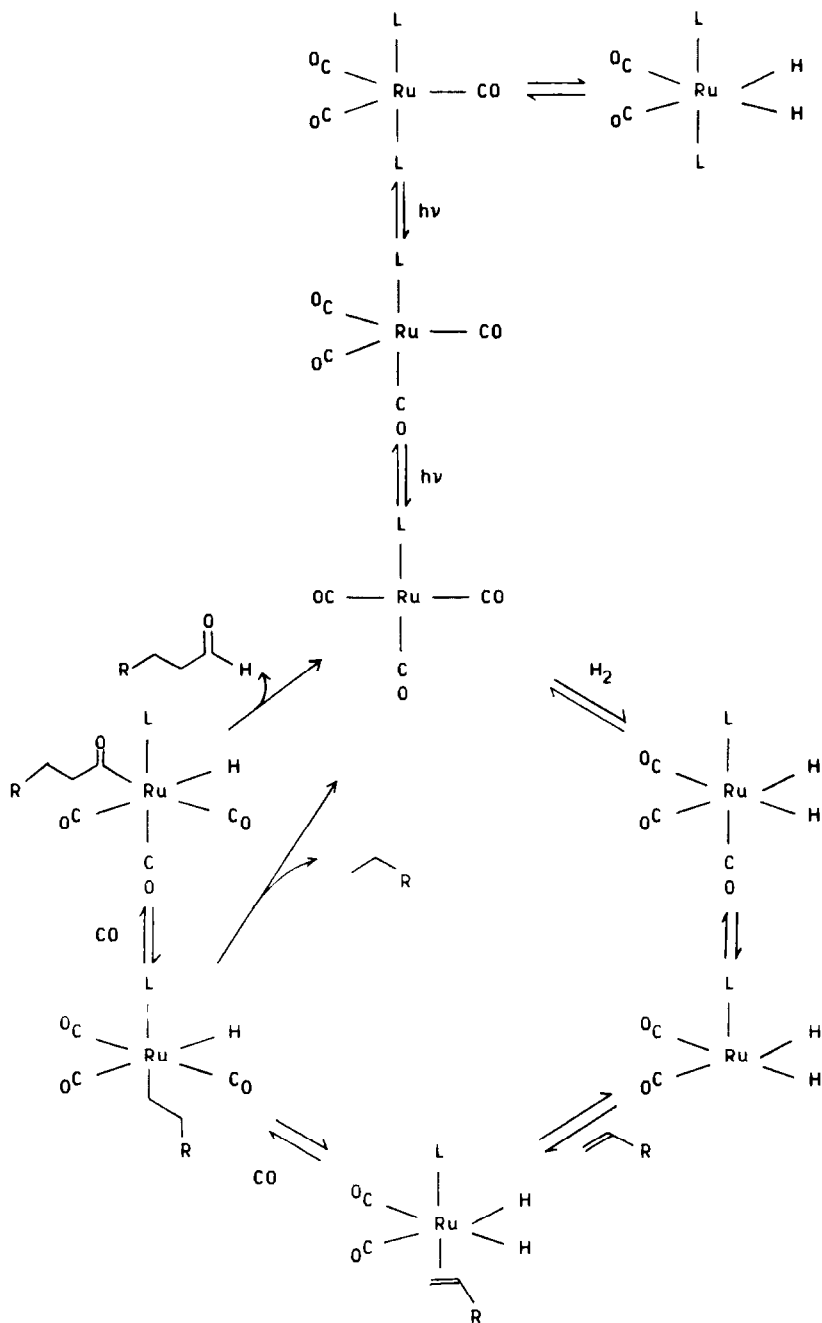
SCHEME 1

The product evolution pattern in the observed catalysis is consistent with the formation of alcohols occurring by hydrogenation of the aldehydes produced by hydroformylation. In a separate experiment, we observe that propionaldehyde is hydrogenated to 1-propanol by photolysis of a benzene solution of propionaldehyde and $Ru(CO)_3(PPh_3)_2$ or $Ru(CO)_4(PPh_3)$ under H_2. When D_2

is used instead of H_2, the 1-propanol produced shows a C(1) methylene proton resonance which integrates relative to the protons on C(2) and C(3) as 1/2/3. If oxidative addition were occurring, greater deuterium incorporation at the C(1) position would be observed. This leads us to propose that the hydrogenation occurs via coordination of the aldehyde through the oxygen rather than the oxidative addition of the aldehydic C—H bond to the catalyst center.

While further mechanistic details remain to be elucidated, this work demonstrates that light can be an effective means for promoting hydroformylation catalysis using Ru complexes under very mild pressure and temperature conditions.

References and notes

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