Photochemical Generation of Chlorohydridotristriphenylphosphineruthenium, $[RuHCl(PPh_3)_3]$

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Summary Ultraviolet irradiation of $[RuHCl(CO)(PPh_3)_3]$ solutions results in loss of carbon monoxide and generation of $[RuHCl(PPh_3)_3]$, a known efficient hydrogenation catalyst.

$[RuHCl(PPh_3)_3]$ has been shown to be an effective catalyst for the homogeneous hydrogenation of olefins,[1] anhydrides,[2] ketones, aldehydes, and nitriles.[3] It is reported[1] to be the most efficient of all known homogeneous catalysts for hydrogenating terminal olefins and is at least 10 times as active as $[RhCl(PPh_3)_3]$ under comparable conditions. Nevertheless, $[RuHCl(PPh_3)_3]$ has not gained wide usage or attention, presumably because it is extremely air-sensitive and relatively difficult to prepare. Its sensitivity to air (solid samples decompose over several hours and solutions turn brown and are deactivated immediately upon exposure) has hampered accurate kinetic measurements, and quite variable rate data[1,4] have been reported for its catalytic reactions. Although the synthesis is straightforward and results in high yields,[5] it requires lengthy inert-atmosphere and vacuum-line manipulations. We now report a simple and convenient method for generating $[RuHCl(PPh_3)_3]$ *via* the photoinduced decarbonylation of $[RuHCl(CO)(PPh_3)_3]$ [equation (1)].

$$[RuHCl(CO)(PPh_3)_3] \xrightarrow{h\nu} [RuHCl(PPh_3)_3] + CO \qquad (1)$$

$[RuHCl(CO)(PPh_3)_3]$ is easily prepared by the reaction of $RuCl_3{\cdot}3H_2O$ with HCHO and PPh_3 in refluxing 2-methoxyethanol.[6] Solid samples are air-stable, although solutions slowly turn brown upon exposure to air. Irradiation of a thoroughly degassed 1×10^{-3}M benzene solution of $[RuHCl(CO)(PPh_3)_3]$ with 366 nm light results in changes in the electronic absorption spectrum. As the irradiation proceeds the colour changes from yellow to purple and new absorption bands appear and increase in intensity at 520 and 470 nm. The spectrum recorded after 7 min irradiation is identical to that of an authentic sample of $[RuHCl(PPh_3)_3]$ prepared by the reaction of $[RuCl_2(PPh_3)_4]$ with H_2 and Et_3N.[5] The photochemical reaction can be followed in the i.r. spectral region, and irradiation of a CH_2Cl_2 solution leads to a decrease in intensity of the carbonyl stretch of $[RuHCl(CO)(PPh_3)_3]$ at 1920 cm^{-1} and the simultaneous appearance of the metal–hydride stretch of $[RuHCl(PPh_3)_3]$ at 2020 cm^{-1}. The maintenance of the isosbestic point at 374 nm during the electronic spectral changes indicates a clean conversion, and the quantum yield of formation of $[RuHCl(PPh_3)_3]$ measured at 313 nm is 0·06 ± 0·02. Solid samples of $[RuHCl(PPh_3)_3]$ can be isolated from irradiated solutions, although they are normally contaminated with small amounts of the starting complex and $[RuHCl(CO)_2(PPh_3)_2]$, formed from the reaction of $[RuHCl(CO)(PPh_3)_3]$ with photoreleased CO.

Further confirmation of the course of reaction (1) comes from a catalytic hydrogenation experiment. Deaerated solutions of hex-1-ene and $[RuHCl(CO)(PPh_3)_3]$ in benzene show no tendency to take up hydrogen. When irradiated, however, solutions turn purple and hydrogen uptake commences at a rate comparable to that of $[RuHCl(PPh_3)_3]$ solutions under similar conditions.

Although we have demonstrated that the catalyst can be conveniently generated photochemically from a relatively air-stable precursor, attempts to reverse reaction (1) by adding CO have failed because of the irreversible formation of $[RuHCl(CO)_2(PPh_3)_2]$. We have been unable to induce CO loss photochemically from $[RuHCl(CO)_2(PPh_3)_2]$, although i.r. and electronic absorption spectral changes indicate that the complex undergoes a reversible isomerization, similar to that reported for $[RuCl_2(CO)_2(PPh_3)_2]$[7] and $[RuI_2(CO)_2(PPh_3)_2]$.[8]

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