Journal of Organometallic Chemistry 724 (2013) 1–6

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Stoichiometric H_2 production from H_2O upon $Mn_2(CO)_{10}$ photolysis

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ARTICLE INFO

Article history:
Received 18 July 2012
Received in revised form
10 October 2012
Accepted 19 October 2012

Keywords:
Manganese
Photochemistry
Water activation
Hydride

ABSTRACT

Photolysis of $Mn_2(CO)_{10}$ in an alkane/water biphasic system has resulted in the generation of 1.80 ± 0.16 mol of hydrogen per mol of $Mn_2(CO)_{10}$. Various studies including deuteration have indeed shown water to be the H_2 source while kinetic studies have indicated a strong correlation between the concentration of the key intermediate $MnH(CO)_5$ with the production rate of H_2. Some of the oxygen atoms of water have been incorporated into a white solid assigned to $MnCO_3$. A mechanism accounting for $MnH(CO)_5$ formation from $Mn_2(CO)_{10}$ photolysis and subsequently H_2 production from $MnH(CO)_5$ has been proposed.

1. Introduction

Hydrogen production from water upon photolysis of transition metal complexes has generated considerable interest as a cleaner source of energy to replace fossil fuels. In recent years, several examples of metal complexes containing platinum [1,2], cobalt in cobaloximes [3,4], iron in hydrogenase mimics [5–9], ruthenium [10], molybdenum [11] and [12] manganese have been reported to catalytically activate water. Oxidative addition of water to a metal centre which forms an essential part of the reaction pathway has been discussed in a recent review [13]. Apart from catalysis, understanding O–H bond activation of water is also of much importance. In a previous study by Byers et al. [14], photolysis of $Mn_2(CO)_8L_2$ (L = CO, $P(OEt)_3$ and PBu_3) and HCl afforded $MnH(CO)_4L$ and $MnCl(CO)_4L$ along with traces of H_2. Recently, our group has demonstrated stoichiometric photoactivation of water by cyclopentadienyl manganese tricarbonyl $CpMn(CO)_3$ to produce hydrogen and hydrogen peroxide [15]. However, more examples and extensive studies are still required to understand the various photopathways, both stoichiometric and catalytic, leading to H_2 generation from water especially under ambient conditions.

In this paper, we report the stoichiometric hydrogen production upon photolysis of commercially-available dimanganese decacarbonyl $Mn_2(CO)_{10}$ in a biphasic mixture of alkane and water. Although $Mn_2(CO)_{10}$ is known to produce H_2 upon reaction with HCl [14], our study demonstrates that the system still works with water. The key intermediate has been identified as $MnH(CO)_5$ and a mechanism has been proposed to account for the general features of the experimental data.

2. Results and discussion

Broadband irradiation (300–800 nm) of $Mn_2(CO)_{10}$ in a cyclohexane/water biphasic system resulted in the disappearance of its ν_{CO} bands (2045, 2013, 2002 and 1983 cm^{-1}) and the concomitant appearance of two new peaks at 2015 cm^{-1} and 2007 cm^{-1} (Fig. 1a). The corresponding ^1H NMR spectrum of the sample recorded in C_6D_6 solvent showed a signal at −7.9 ppm. These spectroscopic assignments could be matched closely to previously reported data for $MnH(CO)_5$ [16]. At the same time, the gas phase IR spectrum (Fig. 1b) of the headspace above the solution showed the production of CO, CO_2 and $MnH(CO)_5$ vapour [17]. The presence of $MnH(CO)_5$ was further confirmed upon formation of $MnH(CO)_4PPh_3$ [18] in the presence of triphenylphosphine (PPh_3) under mild heating.

A series of control experiments has been carried out to understand how $MnH(CO)_5$ is generated. Photolysis of $Mn_2(CO)_{10}$ in anhydrous cyclohexane or its thermal heating (up to 100 °C) in wet cyclohexane resulted in much slower decomposition of $Mn_2(CO)_{10}$ and negligible signals of $MnH(CO)_5$. In a series of deuteration experiments, $Mn_2(CO)_{10}$ photolysis in d_{12}-cyclohexane/H_2O yielded $MnH(CO)_5$ while the corresponding photolysis in cyclohexane/D_2O mixture afforded carbonyl signals which could be matched to the literature values for $MnD(CO)_5$ [16] (ν_{CO} = 2015 cm^{-1} and 2006 cm^{-1}) (Fig. 2). The involvement of a cationic $Mn(CO)_5^+$ or $Mn(CO)_6^+$ intermediate

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http://dx.doi.org/10.1016/j.jorganchem.2012.10.034

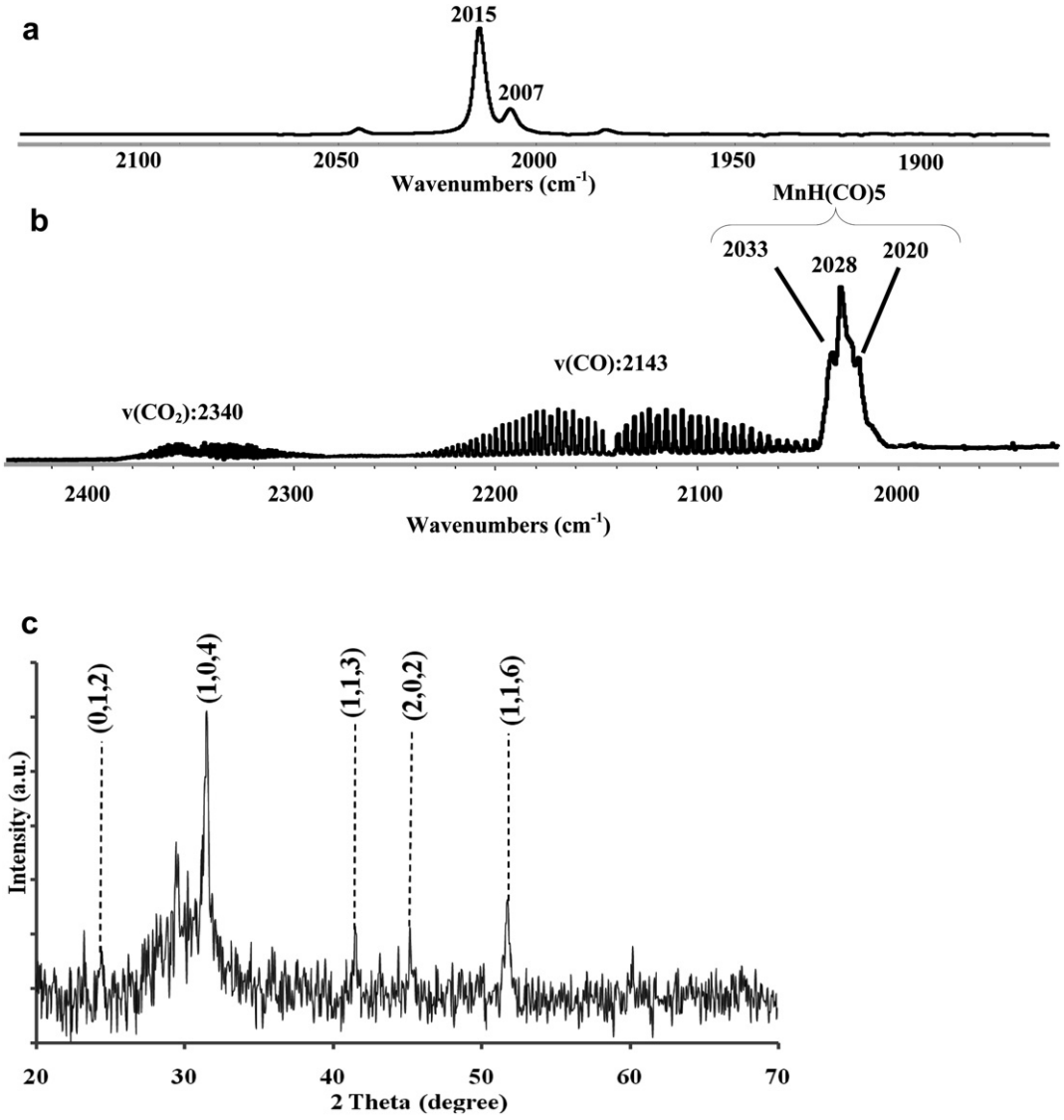

Fig. 1. FTIR spectra recorded after a 2-h broadband irradiation of $Mn_2(CO)_{10}$ in biphasic cyclohexane/water. (a) The production of $MnH(CO)_5$ (2015 and 2007 cm^{-1}) taken in the cyclohexane layer (b) the production of CO ($\nu_o = 2143$ cm^{-1}), CO_2 ($\nu_o = 2340$ cm^{-1}) and $MnH(CO)_5$ ($\nu_{CO} = 2033$, 2028 and 2020 cm^{-1}) in the headspace above the reaction mixture. (c) XRD analysis of the white precipitate $MnCO_3$.

has been ruled out as the photolysis of $Mn_2(CO)_{10}$ with tetra-*n*-butylammonium bromide did not give $MnBr(CO)_5$. In the presence of tetrafluoroboric acid HBF_4 in the aqueous layer, both rates of $Mn_2(CO)_{10}$ decomposition and $MnH(CO)_5$ formation were not affected significantly as the pH is decreased from 6 to 2, suggesting that H^+ ions do not have a significant role in the formation of $MnH(CO)_5$. From these data, it is evident that only light and water but no additives are required for $MnH(CO)_5$ formation.

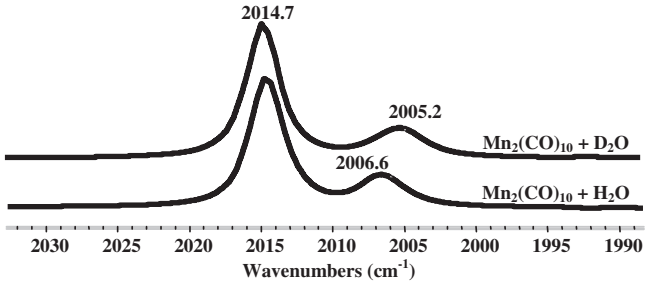

Fig. 2. FTIR spectrum of $MnH(CO)_5$ (2014.7 cm^{-1} and 2006.6 cm^{-1}) or $MnD(CO)_5$ (2014.7 cm^{-1} and 2005.2 cm^{-1}) recorded at 0.5 cm^{-1} resolution after a 2-h broadband irradiation of $Mn_2(CO)_{10}$ in a biphasic cyclohexane/H_2O or cyclohexane/D_2O respectively.

Upon prolonged photolysis (>6 h) of the reaction mixture, a white solid has been obtained in 5–10% yield. The solid shows alkaline behaviour as it requires two equivalents of H^+ (from HCl aqueous solution) for neutralization. An XRD (X-ray powder diffraction) analysis of the solid in Fig. 1c confirms its identity to be manganese carbonate $MnCO_3$ (JCPDS Card No.: 83-1763) [19–21].

Along with the $MnH(CO)_5$ formation, H_2 evolution has been observed throughout the photolysis until all the $Mn_2(CO)_{10}$ and $MnH(CO)_5$ have decomposed. The headspace mass spectrum indicated the production of H_2 at 1.80 ± 0.16 mol per mol of $Mn_2(CO)_{10}$ used. D_2 was also detected at 1.40 ± 0.10 mol per mol of $Mn_2(CO)_{10}$ for D_2O. The time profile of the H_2 evolution has been shown together with those of the respective IR signals of $MnH(CO)_5$ and $Mn_2(CO)_{10}$ in Fig. 3. The quantification of H_2 production is carried out relative to the amount of $Mn_2(CO)_{10}$ used since the latter could be weighed accurately, rather than based on the IR absorbance of