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Preliminary communication

PHOTOCATALYSIS OF HYDROGENATION AND ISOMERIZATION OF ALKENES BY *cis*-$HMn(CO)_4PPh_3$

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Summary

Photolysis of *cis*-$HMn(CO)_4PPh_3$ in the presence of H_2 and 1-alkene results in catalytic hydrogenation and isomerization of the alkene. The isomerization leads to *cis*- and *trans*-2-alkene in the presence or absence of H_2. Catalytic hydrogenation also occurs when *cis*-$CH_3Mn(CO)_4PPh_3$ is irradiated in the presence of H_2; use of D_2 leads exclusively to CH_3D. The possible mechanism of the hydrogenation is discussed.

The individual steps of which catalytic reactions are composed have been frequently studied in model complexes [1—3]. However, interception of the intermediates in actual catalytic reactions has seldom been possible. Photolytic activation of a complex which is thermally inert offers a possible route to trap intermediates [4]. The photocatalytic behavior of such a complex, *cis*-$HMn(CO)_4PPh_3$, is the subject of this communication.

Photocatalysis by metal carbonyl complexes has been the subject of several reports [4]. Most studies have centered on the Group VI complexes [5—13], although $Fe(CO)_5$ has been investigated [14—17] as have the $M_3(CO)_{12}$, M = Fe, Ru, Os, complexes [17—19]. There do not appear to have been any studies of the photocatalytic behavior of metal carbonyl hydride complexes [4].

The photochemical behavior of metal carbonyl hydrides could lead to either M—CO bond cleavage or M—H bond homolysis [20—22]. The relative contributions of the two paths have been in some dispute. Recent matrix isolation experiments on $HMn(CO)_5$ showed CO loss to be the primary photochemical act, although M—H cleavage was also observed [21,22]. Either path could lead to

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catalytic behavior. To explore the potential for photocatalysis by metal carbonyl hydride complexes we have examined the reaction of *cis*-$HMn(CO)_4PPh_3$ with several simple alkenes in the presence or absence of H_2.

Preparations. *cis*-$HMn(CO)_4PPh_3$ was prepared according to literature procedures [23]. The product was purified by column chromatography (alumina/toluene) and recrystallized from toluene/hexane. The spectroscopic properties of the yellow product (IR: 2064(m), 1982(s), 1966(s) and 1956(m) cm^{-1}; NMR: hydride doublet (–6.9 ppm, *J*(P—H) 34 Hz)) were in good agreement with previously recorded values [23].

The rhenium analogue, *cis*-$HRe(CO)_4PPh_3$, was prepared by literature procedures [24]. Purification was effected by column chromatography (alumina/hexane) and recrystallization from toluene/hexane producing white, air-stable crystals. The infrared spectrum (2081(m), 1993(s), 1978(vs) and 1966(s) cm^{-1}) and NMR spectrum (hydride, doublet at –4.3 ppm, *J*(P—H) 22 Hz) were in agreement with previous data [24].

cis-$CH_3Mn(CO)_4PPh_3$ was prepared from reaction of $CH_3Mn(CO)_5$ with PPh_3 as described previously [25]. Purification was achieved by recrystallizations from hexane. Spectroscopic properties were in agreement with literature values [25].

Photolysis. Alkenes and solvents were dried and degassed prior to use in the photocatalytic reactions. Typically 10 mg of catalyst would be placed in an evacuated pyrex tube, 0.5 ml of the alkene would be distilled into the tube and 1 atmosphere of H_2 would be added. This tube would be photolyzed (Ace-Hanovia High Pressure Mercury Vapor Lamp, 100 watts) for a specified period of time. The tube would then be placed on a vacuum line for analysis of gaseous, volatile and solid products. Isomerized and hydrogenated alkenes were quantitatively analyzed by gas chromatography on 12′ carbowax columns at 75—100°C. Methane, from reactions of *cis*-$CH_3Mn(CO)_4PPh_3$, was analyzed on a Poropak Q column and by GC-MS with the assistance of Dr. Tim Wachs of Cornell University.

When *cis*-$HMn(CO)_4PPh_3$ is dissolved in 1-octene in the presence of H_2 and photolyzed, hydrogenation and isomerization to *cis*- and *trans*-2-octene occurs:

$$\text{1-octene} + H_2 \xrightarrow{cis\text{-}HMn(CO)_4PPh_3} \text{octane} + cis\text{- and } trans\text{-2-octene}$$

The hydrogenation occurs at a rate of 10 turnovers per hour with slow loss of activity during time. In the absence of photolysis no reaction occurs. The isomerization occurs in the absence of added H_2 (22 turnovers per hour) and during the hydrogenation (30 turnovers per hour), also with some loss of activity during photolysis. The solution becomes orange and an orange product may be isolated, which decomposes rapidly to *cis*-$HMn(CO)_4PPh_3$ and 1-octene. A similar product may be isolated from the photolytic reaction of *cis*-$HMn(CO)_4PPh_3$ with cyclohexene, a reaction which does not lead to cyclohexane if conducted under hydrogen. It seemed most likely that the orange product was (alkyl)$Mn(CO)_4$-PPh_3 or HMn(alkene)$(CO)_3PPh_3$. The reaction of $LiMn(CO)_4PPh_3$ and $CH_3(CH_2)_6CH_2Cl$ was accomplished to attempt to prepare $(n\text{-}C_8H_{17})Mn(CO)_4PPh_3$, one of the possibilities from the photolytic reaction of *cis*-$HMn(CO)_4PPh_3$ with 1-octene.

$$LiMn(CO)_4PPh_3 + CH_3(CH_2)_6CH_2Cl \xrightarrow[RT]{THF} HMn(CO)_4PPh_3 + \text{1-octene} + LiCl$$

At room temperature in the dark the only manganese product observed is *cis*-$HMn(CO)_4PPh_3$. Thus the decomposition observed for the orange product is consistent with that for $(n\text{-}C_8H_{17})Mn(CO)_4PPh_3$. Bromination of the orange product led to a mixture which included $Mn(CO)_4PPh_3Br$, $C_8H_{17}Br$ and $C_8H_{16}Br_2$.

The reaction of C_2H_4 with *cis*-$HMn(CO)_4PPh_3$ was investigated under a hydrogen atmosphere in a sealed NMR tube. The spectrum after short irradiation times contains a triplet at δ 1.00 ppm and a broad resonance centered at δ 2.00 ppm, consistent with $C_2H_5Mn(CO)_4PPh_3$. Continued irradiation led to an increase in the resonance absorptions but all coupling was lost, presumably due to formation of paramagnetic species or precipitation [21,22].

The catalytic cycle can also be entered by use of *cis*-$CH_3Mn(CO)_4PPh_3$ with only slightly reduced turnovers for catalytic hydrogenations (7 turnovers per hour). Concomitant with the catalytic hydrogenation is the formation of CH_4 with about 67% of the CH_4 eliminated after 1 hour. Use of D_2 leads to CH_3D exclusively.

The rhenium analogue, *cis*-$HRe(CO)_4PPh_3$, is not active as a catalyst for hydrogenation and isomerization. The photochemical reactions of this species appear to be quite different from *cis*-$HMn(CO)_4PPh_3$ [26].

The photochemical reactions reported herein have shown:

$$cis\text{-}HMn(CO)_4PPh_3 + \text{alkene} \rightleftarrows (\text{alkyl})Mn(CO)_4PPh_3$$

$$(\text{alkyl})Mn(CO)_4PPh_3 + H_2 \rightarrow cis\text{-}HMn(CO)_4PPh_3 + \text{alkane}$$

Of the primary intermediates in a sequence which involves CO dissociation, only $HMn(CO)_3(\text{alkene})PPh_3$ cannot be detected. Apparently the alkene insertion occurs too rapidly for this product to be detected at ambient conditions. Alt and coworkers have suggested a CO dissociative mechanism for the photochemical reaction of $HMCp(CO)_3$ with alkenes [27].

It is impossible to determine from the results thus far the role of H—Mn bond cleavage. CO dissociation is the primary photoprocess upon irradiation of $HMn(CO)_5$ [21,22]. The loss of coupling and broadening of the NMR absorption suggest that some H—Mn bond cleavage occurs for $HMn(CO)_4PPh_3$; The formation of CH_3D which occurred in the reaction of *cis*-$CH_3Mn(CO)_4PPh_3$ with D_2 is inconsistent with CH_3—Mn bond cleavage for this reaction. Completely sorting out the role of CO dissociation and Mn—H bond homolysis will require further work.

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