

Preliminary communication

PHOTOCATALYSIS OF HYDROGENATION AND ISOMERIZATION OF ALKENES BY *cis*-HMn(CO)₄PPh₃

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Summary

Photolysis of *cis*-HMn(CO)₄PPh₃ in the presence of H₂ 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 H₂. Catalytic hydrogenation also occurs when *cis*-CH₃Mn(CO)₄PPh₃ is irradiated in the presence of H₂; use of D₂ leads exclusively to CH₃D. 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)₄PPh₃, 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 M₃(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)₄PPh₃ with several simple alkenes in the presence or absence of H₂.

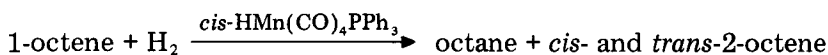
Preparations. *cis*-HMn(CO)₄PPh₃ was prepared according to literature procedures [23]. The product was purified by column chromatography (alumina/toluene) and recrystallized from toluene/hexane. The spectroscopic properties of the yellow product (IR: 2064(m), 1982(s), 1966(s) and 1956(m) cm⁻¹; NMR: hydride doublet (-6.9 ppm, *J*(P-H) 34 Hz)) were in good agreement with previously recorded values [23].

The rhenium analogue, *cis*-HRe(CO)₄PPh₃, 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].

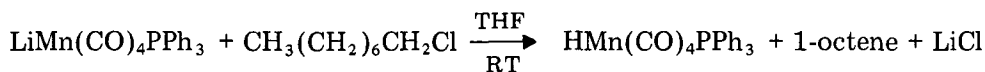
cis-CH₃Mn(CO)₄PPh₃ was prepared from reaction of CH₃Mn(CO)₅ with PPh₃ as described previously [25]. Purification was achieved by recrystallizations from hexane. Spectroscopic properties were in agreement with literature values [25].

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 H₂ 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*-CH₃Mn(CO)₄PPh₃, 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)₄PPh₃ is dissolved in 1-octene in the presence of H₂ and photolyzed, hydrogenation and isomerization to *cis*- and *trans*-2-octene occurs:



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 H₂ (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)₄PPh₃ and 1-octene. A similar product may be isolated from the photolytic reaction of *cis*-HMn(CO)₄PPh₃ 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-PPh₃ or HMn(alkene)(CO)₃PPh₃. The reaction of LiMn(CO)₄PPh₃ and CH₃(CH₂)₆CH₂Cl was accomplished to attempt to prepare (n-C₈H₁₇)Mn(CO)₄PPh₃, one of the possibilities from the photolytic reaction of *cis*-HMn(CO)₄PPh₃ with 1-octene.



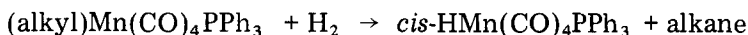
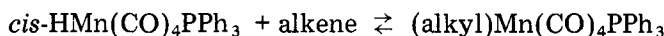
At room temperature in the dark the only manganese product observed is *cis*-HMn(CO)₄PPh₃. Thus the decomposition observed for the orange product is consistent with that for (n-C₈H₁₇)Mn(CO)₄PPh₃. Bromination of the orange product led to a mixture which included Mn(CO)₄PPh₃Br, C₈H₁₇Br and C₈H₁₆Br₂.

The reaction of C₂H₄ with *cis*-HMn(CO)₄PPh₃ 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 C₂H₅Mn(CO)₄PPh₃. 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*-CH₃Mn(CO)₄PPh₃ with only slightly reduced turnovers for catalytic hydrogenations (7 turnovers per hour). Concomitant with the catalytic hydrogenation is the formation of CH₄ with about 67% of the CH₄ eliminated after 1 hour. Use of D₂ leads to CH₃D exclusively.

The rhenium analogue, *cis*-HRe(CO)₄PPh₃, 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)₄PPh₃ [26].

The photochemical reactions reported herein have shown:



Of the primary intermediates in a sequence which involves CO dissociation, only HMn(CO)₃(alkene)PPh₃ 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)₄PPh₃; The formation of CH₃D which occurred in the reaction of *cis*-CH₃Mn(CO)₄PPh₃ with D₂ is inconsistent with CH₃—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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