Journal of Organometallic Chemistry, 429 (1992) 345–368
Elsevier Sequoia S.A., Lausanne
JOM 22476

Formation of a manganese alkyl complex as an intermediate in the ring-opening hydroformylation of α-cyclopropylstyrene by $HMn(CO)_5$

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(Received August 5, 1991)

Abstract

The reaction of α-cyclopropylstyrene (CPS) with $HMn(CO)_5$ can result in either hydrogenation or hydroformylation. The hydrogenation occurs by a previously established pathway involving sequential hydrogen atom transfers from the metal hydride to the organic substrate, and is the predominant reaction observed with samples of $HMn(CO)_5$ that have been thoroughly dried and purified using P_2O_5. With samples of $HMn(CO)_5$ that have been not been treated with P_2O_5, the reaction that occurs with CPS is ring-opening hydroformylation, leading to the isolation of $Mn_2(CO)_9(\eta^1$-$HCOCH_2CH_2CH$=$C(Ph)CH_3)$. The detailed procedures for preparation and handling of $HMn(CO)_5$ that are reported in this paper enable the hydroformylation reaction to be reproducibly observed as the predominant reaction. An induction period of a few hours is typically observed in the hydroformylation, but addition of $Mn_2(CO)_9(\eta^1$-tolualdehyde) eliminates the induction period. The hydroformylation reaction is inhibited by CO (1 atm). The manganese alkyl complex $(CO)_5MnCH_2CH_2CH$=$C(Ph)CH_3$ is an intermediate in the hydroformylation. The details of the mechanism of formation of this alkyl complex from CPS and $HMn(CO)_5$ are not completely understood, but several mechanistic possibilities are considered.

Introduction

Hydrogenation and hydroformylation of alkenes are two of the most thoroughly studied catalytic reactions involving transition metal hydrides. In the hydroformylation [1] of alkenes to give aldehydes, hydrogenation of alkenes to give alkanes is frequently observed as a competitive side-reaction. Only small amounts of hydrogenation products are typically observed in the hydroformylation of simple alkenes such as propylene. On the other hand, with substituted styrenes and other unsaturated substrates capable of forming stabilized benzylic radicals, substantial amounts of hydrogenation products are observed under some conditions.

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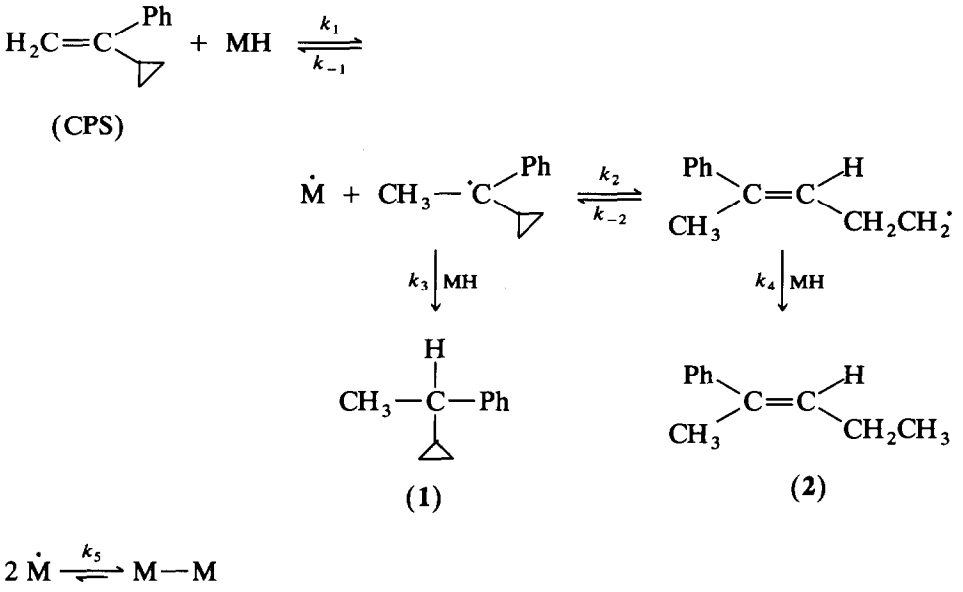


(CPS)

(1)

(2)

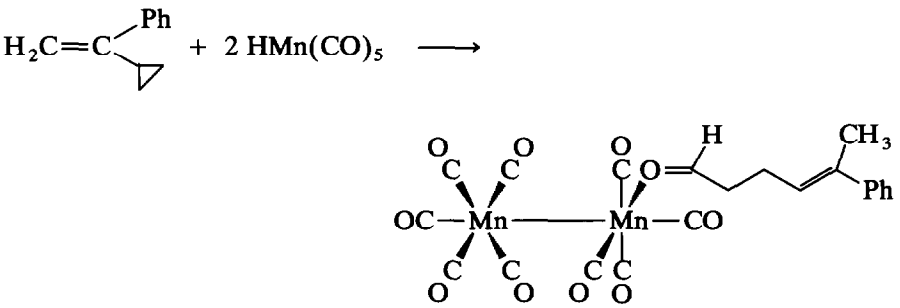
Scheme 1.

We have reported [2] a kinetic and mechanistic study of the hydrogenation of α-cyclopropylstyrene (CPS) by transition metal hydride complexes. Metal hydrides such as $HM(CO)_3(C_5H_5)$ (M = Cr, Mo, W), $HMn(CO)_4PPh_3$ and $HFe(CO)_2(C_5H_5)$ react with CPS to give a mixture of the unrearranged hydrogenation product (**1**) and the rearranged hydrogenation product (**2**). The mechanism for this reaction involves hydrogenation of the CPS by sequential hydrogen atom transfers from the metal hydride, as shown in Scheme 1. The relative rates at which a variety of metal hydrides can serve as hydrogen atom donors to the carbon-centered radical intermediate were established by evaluation of the unrearranged/rearranged product ratio as a function of metal hydride concentration. The reaction of rigorously purified (see below) $HMn(CO)_5$ with CPS gives almost exclusively the unrearranged product **1**. As reported earlier [3], the kinetics of this hydrogenation reaction were determined by ^1H NMR spectroscopy at 25°C and conform to the rate law $-d[CPS]/dt = k[HMn(CO)_5][CPS]$. The rate constant determined for tubes sealed off under vacuum is similar to the rate constant obtained for tubes sealed under 1 atm CO, and an inverse kinetic isotope effect [4] was observed using $DMn(CO)_5$ ($k_{HMn}/k_{DMn} \sim 0.4$). These kinetics results are analogous to those observed [2] with the other metal hydrides, indicating that the mechanism of hydrogenation of CPS by all of these hydrides (including pure $HMn(CO)_5$) is that shown in Scheme 1.

In a preliminary communication, we reported [3] that under some conditions, the reaction of α-cyclopropylstyrene with $HMn(CO)_5$ can result in hydroformylation rather than hydrogenation as the predominant pathway. Some of the factors that influence selectivity for hydroformylation *versus* hydrogenation have been elucidated, and a full account of this work is given here.

Results

In contrast to the well-behaved hydrogenation observed with thoroughly purified samples of $HMn(CO)_5$, other (ostensibly similar) samples of this hydride reacted with CPS to give predominantly the ring-opening hydroformylation reaction (eq. 1) instead of hydrogenation. The organometallic product of the hydroformylation is the manganese aldehyde complex $Mn_2(CO)_9(\eta^1\text{-}HCOCH_2CH_2CH{=}C(Ph)CH_3)$ (**3**) which has been fully characterized by spectroscopic data



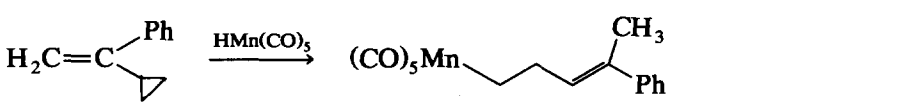
(1)

(**3**)

[5] as well as a single crystal X-ray diffraction study [3]. The stoichiometry for the hydrogenation and hydroformylation is identical, requiring two equivalents of $HMn(CO)_5$ and one CPS, with no added CO being required for the stoichiometric hydroformylation. The preference for hydroformylation over hydrogenation is very sensitive to the purification procedures utilized for the $HMn(CO)_5$, as will be discussed in detail later. In addition to the sensitivity of the reaction to the purity of $HMn(CO)_5$, our study of the ring-opening hydroformylation reaction was complicated by the fact that the hydroformylation reaction exhibits an induction period. Using the procedures given, however, the hydroformylation reaction is readily reproducible, and it is possible to observe either hydrogenation or hydroformylation as the major reaction.

Formation of $(CO)_5MnCH_2CH_2CH{=}C(Ph)CH_3$ from $HMn(CO)_5$ and CPS

The ring-opening/hydroformylation of cyclopropylstyrene by $HMn(CO)_5$ (eq. 1) is an unprecedented reaction that involves ring-opening of the cyclopropyl ring, formation of an aldehyde, and coordination of the aldehyde to the manganese. The manganese alkyl complex $(CO)_5MnCH_2CH_2CH{=}C(Ph)CH_3$ (**4**) has been conclusively identified as an intermediate in the formation of **3** from CPS and $HMn(CO)_5$ (eq. 2). The kinetics of formation of manganese aldehyde complex **3** from the reaction of manganese alkyl complex **4** with $HMn(CO)_5$ (eq. 3) were recently reported [5].



(2)

CPS (**4**)

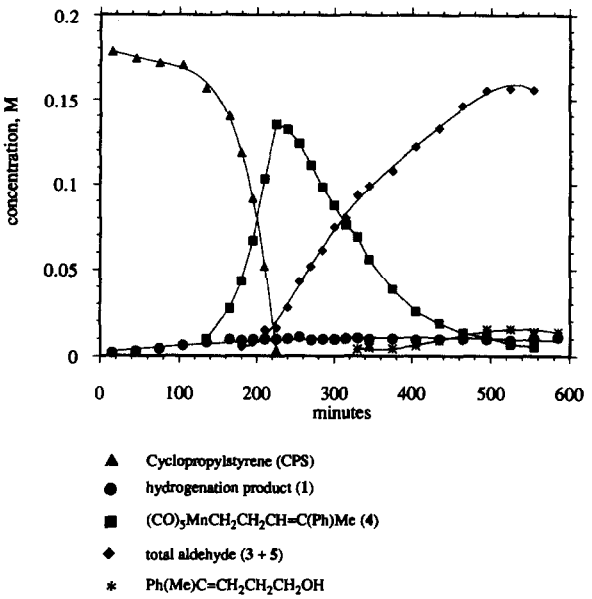
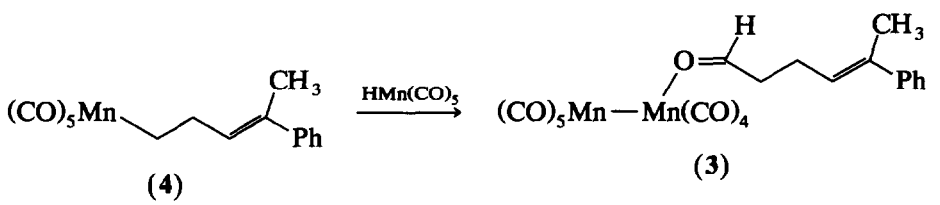


Fig. 1. Time-dependence of concentrations of CPS and products from the reaction of $HMn(CO)_5$ (1.5 *M*) and CPS (0.18 *M*) at 22°C in C_6D_6.



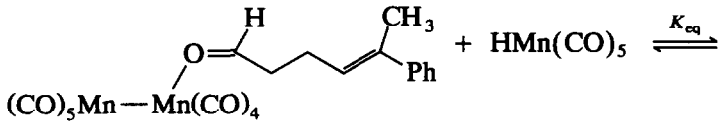
(4) (3)

(3)

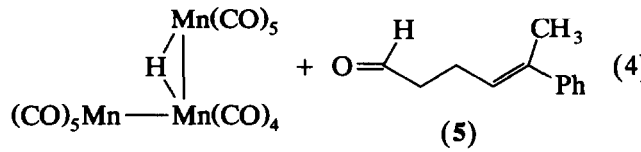
Evidence for the generality of formation of manganese aldehyde complexes from reactions of this type comes from the isolation of $Mn_2(CO)_9(\eta^1$-tolualdehyde) from the reaction of $(CO)_5Mn(p\text{-}CH_3C_6H_4)$ with $HMn(CO)_5$ and the analogous formation of $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ from $(CO)_5MnCH_3$ and $HMn(CO)_5$ [5]. We now report our results on the perplexing ring-opening reaction (eq. 2) that converts $HMn(CO)_5$ and CPS to manganese alkyl complex **4**.

Figure 1 shows the time profile for a typical reaction of $HMn(CO)_5$ (initial concentration 1.5 *M*) and CPS (initial concentration 0.18 *M*) at 22°C in C_6D_6. ^1H NMR spectra taken at 15 or 30 min intervals were integrated *versus* an internal integration standard (bibenzyl). During the first 100 min, the only observable reaction is hydrogenation of CPS to give the unrearranged hydrogenation product **1**. Following this relatively slow consumption of CPS by hydrogenation is a comparatively rapid depletion of the CPS and a corresponding production of the manganese alkyl complex **4**. Only ~ 5% CPS is consumed in the first 100 min, but once the induction period is over, the concentration of CPS drops from 0.17 *M* to nearly zero in 120 min. The maximum concentration of manganese alkyl complex **4** (observed at $t = 225$ min) is 0.13 *M*, which is 72% of the initial CPS concentration. A pseudo-first-order disappearance of **4** is observed as it is converted to the

aldehyde. The pseudo-first-order rate constant determined from the concentrations of **4** from $t = 225$ min to the end of the reaction is $k = 1.8 \times 10^{-4}$ s^{-1}. This rate constant is similar to those reported earlier in our study of the kinetics of eq. 3, in which isolated samples of **4** were used. Thus the conversion of **4** to **3** is well-behaved in all cases, using either isolated **4** or solutions of **4** generated by the unusual route of eq. 2. The hydrogenation reaction essentially stops when the hydroformylation begins, due to the rapid consumption of the CPS in its conversion to **4**. Figure 1 displays the total aldehyde formed, the sum of complexed aldehyde **3** and the free aldehyde $CH_3(Ph)C{=}CHCH_2CH_2CHO$ (**5**). The free aldehyde **5** is normally observed prior to observation of resonances for the complexed aldehyde **3**, but its concentration levels out while the concentration of **3** continues to increase until the end of the reaction. At the end of the reaction shown in Fig. 1, the ratio of **3**:**5** was about 3:1. Our previously reported study of eq. 3 established that the changes in the free to complexed ratio of aldehydes as the reaction proceeds is accounted for by the equilibrium shown in eq. 4.



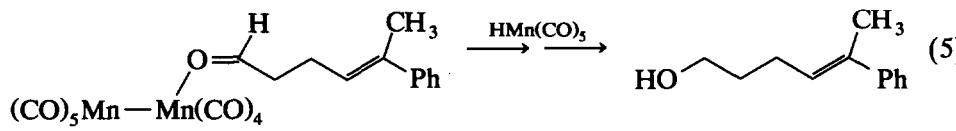
(**3**)



(**5**)

The equilibrium constant for eq. 4 was established to be $K_{eq} = 1.2 \times 10^{-2}$ at 22°C, indicating that $HMn(CO)_5$ is even more weakly bound to the $Mn_2(CO)_9$ moiety than is the aldehyde.

Although complexed aldehyde **3** and free aldehyde **5** are the initially formed hydroformylation products, a small amount of further hydrogenation of the aldehyde to the alcohol has been observed (eq. 5).



Preparation and purification of $HMn(CO)_5$ and the resultant effect on the reaction

The observation of predominant hydroformylation from some batches of $HMn(CO)_5$ and hydrogenation from other preparations prompted us to carefully examine how the preference for hydrogenation versus hydroformylation varied with the way in which the $HMn(CO)_5$ had been prepared and purified. Time profiles similar to that shown in Fig. 1 have been observed for reactions of CPS with $HMn(CO)_5$ that was prepared by either of the methods shown in eqs. 6 and 7.

$$Mn_2(CO)_{10} \xrightarrow{NaK} K^+Mn(CO)_5^- \xrightarrow[\text{tetraglyme}]{H_3PO_4} HMn(CO)_5 \qquad (6)$$

$$BrMn(CO)_5 + Zn \xrightarrow[\text{tetraglyme}]{H_3PO_4} HMn(CO)_5 \qquad (7)$$

Both of these methods provided high yields of $HMn(CO)_5$ which gave good activity for hydroformylation of CPS. Normal procedures involved in the purification of $HMn(CO)_5$ are drying over P_2O_5, and collecting the $HMn(CO)_5$ in a trap at low temperature. These purification procedures, however, can lead to a substantial loss in activity for hydroformylation. We first discovered the ring-opening hydroformylation reaction using $HMn(CO)_5$ which had been dried over P_2O_5. In other experiments, however, treating the $HMn(CO)_5$ with P_2O_5 caused it to give low activity for hydroformylation, so subsequent experiments avoided P_2O_5 in order to insure the reproducibility of the hydroformylation reaction. Erratic results were also obtained with $HMn(CO)_5$ which had been trapped in a U-tube at either $-40°C$ or at $-78°C$; in some cases this had little effect on the hydroformylation while in other cases it rendered the $HMn(CO)_5$ much less active.

We have found that most of the water in $HMn(CO)_5$ can be readily removed without the use of chemical desiccants such as P_2O_5. When $HMn(CO)_5$ (prepared by either eq. 6 or eq. 7) is stored under vacuum in a glass tube at $-20°C$, most of the water separates from the hydride and crystallizes near the top of the tube, making it possible to remove the liquid $HMn(CO)_5$ from the bottom of the tube by syringe. $HMn(CO)_5$ purified in this manner *reproducibly* reacted with CPS to give the ring-opening hydroformylation reaction, and yet was freed from most of the water present in the crude hydride. Conversely, the hydrogenation reaction is favored, and the competing hydroformylation minimized, by thoroughly purifying the hydride by repeated treatment with P_2O_5. Complete details of the preparation and purification procedures for $HMn(CO)_5$ are provided in the Experimental section.

Normally, the use of P_2O_5 in the purification of $HMn(CO)_5$ is carried out in order to remove the water that is present in the aqueous H_3PO_4 used in the synthesis of the hydride. Since thorough treatment of $HMn(CO)_5$ with P_2O_5 leads to deactivation of the hydride for the hydroformylation reaction, one possibility is that water is the reagent causing the hydroformylation to occur at the expense of the hydrogenation reaction. In the preliminary communication of this work, we reported [3] that "wet" $HMn(CO)_5$ gives the hydroformylation reaction, while "dry" $HMn(CO)_5$ results in hydrogenation. Further experiments reported herein indicate that it is not *simply* water that makes the hydroformylation occur. The effect of adding water to the reaction was studied by preparing a C_6D_6 solution of CPS (0.2 *M*) and dry $HMn(CO)_5$ (0.6 *M*). The solution was divided equally between two NMR tubes. One of the tubes was kept dry and the other was treated with 1 μL H_2O ($\sim$ 0.6 equiv. based on CPS). After 3 days at room temperature, the NMR spectra of both tubes indicated that the hydrogenated product was being formed, but $< 5\%$ yield of hydroformylation products was observed for either tube. While this experiment makes it clear that it is not *simply* water which causes the reaction to occur, other experiments to be discussed later made it difficult to rule out *some* role for water in the hydroformylation reaction.

There is apparently some impurity formed in the preparation of the $HMn(CO)_5$ which is required for the ring-opening hydroformylation reaction to occur. Clearly, this impurity can be removed by treatment with P_2O_5. It also appears to be somewhat more volatile than the $HMn(CO)_5$, since collecting the $HMn(CO)_5$ in a U-tube at $-40°C$ (or at $-78°C$) in some cases rendered the $HMn(CO)_5$ less active for ring-opening hydroformylation. Further evidence that this impurity is volatile

comes from a consideration of the way in which we handled the $HMn(CO)_5$; it was stored in a freezer at $-20°C$, and each time it was used, it was removed from the storage tube by vacuum transfer. Therefore, any non-volatile impurities or decomposition products would have been left behind. We considered the possibility that the alleged impurity reacted with $HMn(CO)_5$ to give the active species which was not volatile, so that the presence of the induction period might have been caused by our method of handling the hydride. To test this conjecture, $HMn(CO)_5$ was vacuum transferred into an NMR tube and allowed to stand at room temperature for 4 h before adding the C_6D_6 solution of CPS. An induction period was still observed, suggesting that the hydride and the impurity and CPS were all required in order to form the species that promoted the hydroformylation.

Effect of added reagents on the hydroformylation reaction

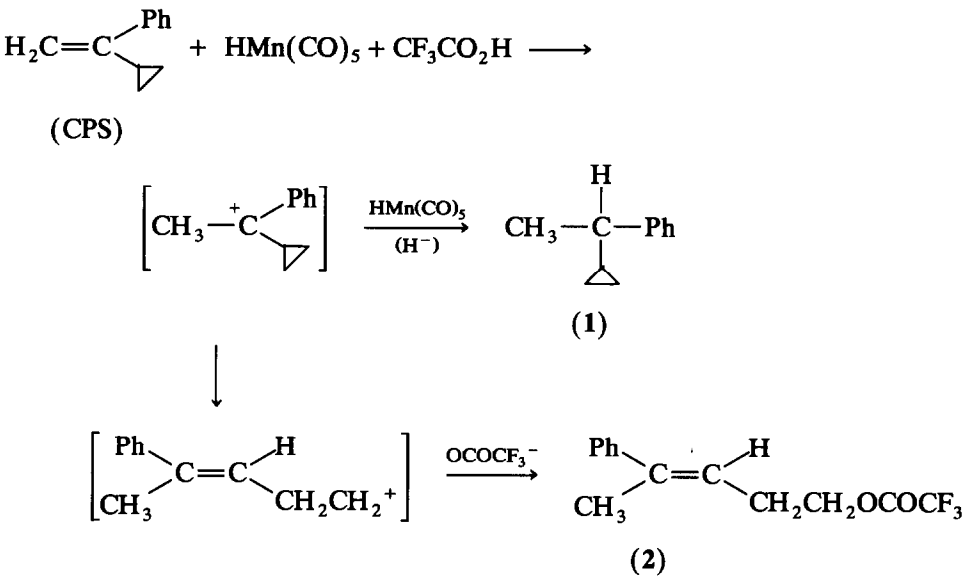
The effect of several reagents on the ring-opening hydroformylation reaction was examined. Most of these experiments were carried out in NMR tubes using ~ 0.2 *M* CPS in C_6D_6 with an excess (~ 5–10 equiv.) of $HMn(CO)_5$, but the ring-opening hydroformylation has also been successfully carried out using a lower concentration of CPS (0.03 *M*). One purpose of these experiments was to determine which reagents might inhibit the hydroformylation reaction and divert the reaction path back to hydrogenation; another was to see whether any reagents might eliminate the induction period characteristically observed in the hydroformylation reaction.

No differences were noted between experiments carried out under an argon atmosphere compared to those carried out in solutions which were degassed by several freeze-pump-thaw cycles. Intentional addition of air (150 μL air $\approx$ 1.2 μmol O_2) to a solution of CPS (0.13 mmol) in C_6D_6 (0.4 mL) containing a large excess of $HMn(CO)_5$ resulted in a yellow solution (due to $Mn_2(CO)_{10}$ formed from decomposition of $HMn(CO)_5$). This addition of air did not prevent the hydroformylation, nor did it eliminate the induction period observed prior to the onset of the hydroformylation.

Although the hydroformylation proceeds similarly under argon or under vacuum, carrying out the reaction under CO inhibits the hydroformylation. The reaction of CPS (0.18 *M*) with excess $HMn(CO)_5$ (1.35 *M*) in C_6D_6 under 1 atm CO resulted in hydrogenation, with a 92% yield of hydrogenation product and only $\sim 5\%$ free aldehyde product detected after 11 days at room temperature. A similar inhibition of the hydroformylation was found upon addition of pyridine (0.5 equiv. based on CPS) to the reaction of CPS and $HMn(CO)_5$.

The inhibition of hydroformylation under CO suggested that a vacant coordination site was required. Since phosphine oxides have been shown to be effective at labilizing CO from metal carbonyl complexes [6], we examined the effect of $Ph_3P{=}O$ (0.15 equiv. based on CPS) on the reaction. However, the presence of the phosphine oxide not only failed to accelerate the hydroformylation, it essentially prevented the hydroformylation. The hydrogenation of CPS still occurred in the presence of the phosphine oxide.

In an attempt to assess the possible influence of acidic impurities, the reaction of $HMn(CO)_5$ and CPS was carried out in the presence of CF_3CO_2H (~ 2 equiv. based on CPS). A rapid reaction occurred at room temperature, giving the hydrogenation product **1** along with the ring-opened trifluoroacetate. The mecha-



(CPS)

(1)

(2)

Scheme 2.

nism of formation of these products (Scheme 2) involves protonation of CPS by the acid to give a tertiary carbocation. Rearrangement of this initially formed carbocation gives a primary carbocation which can be trapped by trifluoroacetate to give the observed ester. As implied in Scheme 2, the formation of the trifluoroacetate ester requires no $HMn(CO)_5$ but only CPS and acid. It has been previously reported [7] that the reaction of either acetic acid or trifluoroacetic acid with CPS (and other vinylcyclopropanes) leads to the formation of acetate or trifluoroacetate esters. The unrearranged hydrogenation product **1** which formed in this reaction is identical to that formed by sequential hydrogen atom transfers from metal hydrides as shown in Scheme 1. It is formed by an ionic route here, however, with $HMn(CO)_5$ serving as a hydride (H^-) donor to the carbocation. This type of very rapid ionic hydrogenation of olefins, using acids and metal hydrides, has been developed further and was published elsewhere [8]. For purposes of this investigation, these results indicate that acidic impurities are unlikely to contribute to the ring-opening hydroformylation pathway.

Although $Mn_2(CO)_{10}$ is the predominant organometallic product formed when $HMn(CO)_5$ decomposes, we investigated the possible effect that Mn metal decomposition products might have on the reaction. Addition of small amounts of Mn metal to C_6D_6 solutions of CPS and $HMn(CO)_5$ had no pronounced effect on the reaction; the metal neither prevented the hydroformylation reaction, nor eliminated the induction period.

During the induction period, there was apparently some reaction occurring that caused the ring-opening hydroformylation reaction. However, the only reaction *known* to be taking place was the hydrogenation of CPS by $HMn(CO)_5$ to give hydrogenation product **1** and $Mn_2(CO)_{10}$. While it was not obvious how either of these might form the unknown species that was causing the hydroformylation, it

was straightforward to rule out this possibility. Separate experiments showed that neither of these reagents had any notable effect on the induction period or on the progress of the hydroformylation reaction.

The manganese aldehyde complex **3** is dark orange, allowing the color change from pale yellow to dark orange to be used as a qualitative indication formation of the aldehyde complex. When the reaction was carried out in NMR tubes, an unusual characteristic was observed: the solution in the lower part of the tube became orange first, while the top part of the solution remained yellow. This peculiar feature led us to consider the possibility that some insoluble heterogeneous material at the bottom of the tube (or possibly a colloid) was responsible for the hydroformylation activity. No insoluble particles were seen in any of these tubes, but visual indications are insufficient to rule out the presence of a heterogeneous reaction component. One established test for the presence of heterogeneous catalysts is to run the reaction in the presence of liquid Hg, which can selectively poison heterogeneous catalysts [9]. As shown in Table 1 (entry 1), the hydroformylation reaction proceeded smoothly in the presence of Hg.

Most of the ring-opening hydroformylation experiments were carried out at room temperature, but the reaction was also observed to occur at higher (50°C) and lower (3°C) temperatures (entries 2 and 3 in Table 1). A labeling experiment was performed by adding $^{18}OH_2$ to a C_6D_6 solution of $HMn(CO)_5$ and CPS. After the hydroformylation reaction was complete, CO was added to convert the **3** to $Mn_2(CO)_{10}$ and **5**. Analysis by GC/MS showed no incorporation of ^{18}O in either the aldehyde or $Mn_2(CO)_{10}$ products.

In spite of the fact that simple addition of water to solutions of CPS and purified $HMn(CO)_5$ did not cause the hydrogenation to be diverted to the hydroformylation pathway, other results indicated that the role of water could not be completely dismissed. As noted above, repeated treatment of the $HMn(CO)_5$ with P_2O_5 is required to minimize the hydroformylation. However, when $HMn(CO)_5$ purified in this manner is stirred with water, the amount of hydroformylation resulting from this "rewetted" hydride is increased. Entry 4 of Table 1 shows the time profile of products formed from reaction of CPS with $HMn(CO)_5$ which was stirred with water (25 mol% based on $HMn(CO)_5$) for 1 day at room temperature.

Most of the experiments reported here used C_6D_6 (for ^1H NMR experiments) or hexane (for preparative experiments). Although CPS has low solubility in water, the ring-opening hydroformylation did occur in an experiment carried out in D_2O. Use of THF-d_8 or CD_3CN as solvents resulted in predominant hydrogenation, with only traces of hydroformylation products being formed. No aldehyde was formed in reactions carried out in CD_2Cl_2 or CD_3OD.

An unexpected result was obtained when the reaction of CPS and $HMn(CO)_5$ was carried out in the presence of ethylene (1 atm). In contrast to the reactions carried out in the presence of other ligands (e.g. CO) which inhibit the hydroformylation, carrying out the reaction at room temperature with added ethylene not only led to the formation of hydroformylation products from reaction with CPS, it also resulted in the hydrogenation of ethylene. After all of the CPS was consumed, more ethylene was added, but negligible further hydrogenation of ethylene was detected after 18 h. The yield of ethane was not accurately determined due to uncertainties concerning its partitioning between solution and the gas phase, but a conservative lower limit indicates that 0.2 equiv. of ethane were

Table 1. Time profiles and product yields for reaction of CPS and $HMn(CO)_5$ under different conditions [a].

Entry	$[CPS]_0$ (M)	$[HMn(CO)_5]_0$ (M)	Conditions	Time	CPS remaining (%)	4 (%) $(CO)_5MnR$	3 (%) $Mn_2(RCHO)$	5 (%) free RCHO	1 (%) (hydrogenated product)	Alcohol (%)
1	0.18	1.9	Hg added [b]	3.5 h	17	65	3	7	7	0
				7.5 h	0	2	58	24	7	8
2	0.20	1.3	50°C	20 min	2	17	48	17	5	6
				60 min	0	0	37	26	5	28
3	0.20	1.0	3°C	2 weeks	0	0	60	18	8	10
4	0.18	1.3	"Rewetted" $HMn(CO)_5$ [b]	4.5 h	50	13	12	12	9	0
				10 h	42	0	24	16	11	0
				21 h	29	0	20	19	19	8
				56 h	15	0	12	18	33	17
				94 h	8	0	4	14	39	27
				141 h	5	0	0	12	42	36
5			0.1 M $Mn_2(CO)_{10}$ (dark)	3.75	74	20	0	0	5	0
			cf. entry 6	5.0 h	0	62	17	12	5	0
				8.0 h	0	4	66	19	5	4
6	0.19	1.2 M	0.1 M $Mn_2(CO)_{10}$ ($h\nu$, 366 nm)	3.75 h	30	54	5	0	6	0
			cf. entry 5	5.0 h	0	43	33	14	6	0
				8.0 h	0	0	67	20	6	0
7	0.19	1.1	[c]	3.5 h	11	58	7	11	6	0
				7.5 h	0	0	63	28	6	0
8	0.19	1.0	0.03 M Mn_2(tol-CHO) added [c]	15 min	67	26	0	0	< 2	0
				45 min	14	69	6	8	< 2	0
				2.0 h	0	23	53	19	< 2	0

[a] All experiments were carried out in the dark in C_6D_6 solvent at 22°C, unless noted otherwise. [b] See Experimental section for additional experimental details. [c] The experiments in entries 7 and 8 were parallel runs using the same batch of $HMn(CO)_5$; entry 7 had no added aldehyde complex and entry 8 was carried out with 0.03 M $Mn_2(CO)_9(\eta^1$-tolualdehyde) added.

formed per equivalent of CPS consumed (see Experimental section for complete details). Along with the ^1H NMR resonance for the aldehydic hydrogen of **3** at δ 8.43, another aldehyde resonance (δ 8.27, ~25% yield) was observed in this reaction and is tentatively assigned to $Mn_2(CO)_9(\eta^1\text{-}CH_3CH_2CHO)$. This aldehyde product would result from hydroformylation of ethylene. Supporting this assignment is the observation of small amounts of CH_3CH_2CHO and $CH_3CH_2CH_2OH$ in the volatile products resulting after the reaction mixture was treated with CO. The identity of these two organic products was also confirmed by GC/MS.

In order to test whether the induction period could be eliminated photochemically, a solution of CPS and $HMn(CO)_5$ was divided into two equal portions. One tube was photolyzed at 366 nm for 30 min, and the other tube was kept in the dark. No difference in the induction period was noted, nor was there any difference in the progress of the hydroformylation reaction. NMR integrations for the two tubes agreed within $\pm 5\%$ for all product resonances. Another photochemical experiment was carried out in order to test for the possibility of a radical chain reaction involving photochemically generated $(CO)_5Mn\cdot$ radicals [10]. A solution of CPS and excess $HMn(CO)_5$ containing $Mn_2(CO)_{10}$ (0.5 equiv. based on CPS) was divided into two portions. One tube was photolyzed at 366 nm for 30 min, while the other tube was stored in the dark. Results are tabulated in entries 5 and 6 of Table 1.

In all of the above reactions, the onset of the hydroformylation reaction was not observed until after an induction period that typically lasted 2–3 h. We have found that addition of $Mn_2(CO)_9(\eta^1$-tolualdehyde) (0.1–0.2 equiv. based on CPS) results in the elimination of the induction period. Whereas the alkyl complex is not normally seen until at least 2 h after the start of the reaction, reactions to which $Mn_2(CO)_9(\eta^1$-tolualdehyde) has been added show conversion of CPS to the alkyl complex within minutes. The acceleration of the reaction by the added aldehyde complex can be evaluated by comparing the reaction of CPS and $HMn(CO)_5$ with and without added aldehyde complex (entries 7 and 8 of Table 1). Since the hydrogenation product **1** is normally generated during the induction period, the use of the aldehyde complex to eliminate the induction period also prevents the formation of significant amounts of **1**, and > 95% total aldehyde yield can be obtained.

It was mentioned above that $HMn(CO)_5$ subjected to standard purification procedures is sometimes rendered significantly less active for hydroformylation of CPS. Although the $HMn(CO)_5$ purified in this manner showed relatively weak activity for hydroformylation, the reaction could be "catalyzed" using $Mn_2(CO)_9(\eta^1$-tolualdehyde), but the rate of this reaction was still significantly slower than the rate observed with $HMn(CO)_5$ which had not been partially deactivated by treatment with P_2O_5.

Consideration of the effect of trace impurities on the reaction

The induction period observed in this reaction, along with the variable results obtained with different purification methods used for the $HMn(CO)_5$, raised questions about impurities that could be causing the hydrogenation reaction to be diverted to the hydroformylation pathway. IR spectra of $HMn(CO)_5$ (see Experimental section for details) were in good agreement with literature reports. Simi-

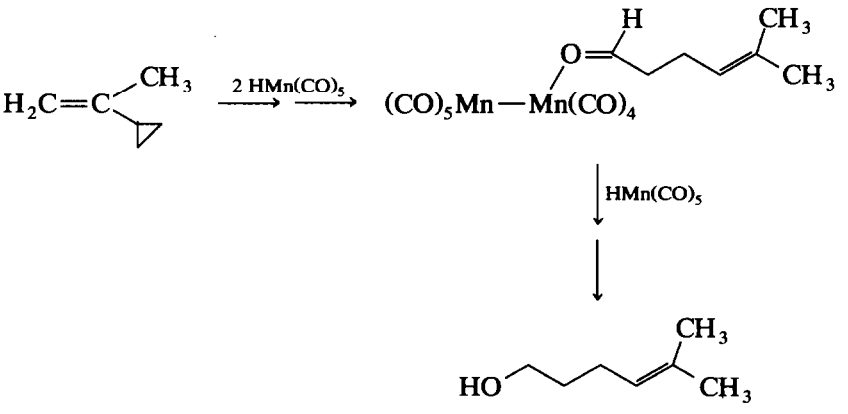
larly, ^1H NMR spectra of concentrated (10–30% by vol.) C_6D_6 solutions of $HMn(CO)_5$ were also recorded. In neither the IR nor NMR spectra were any differences observed in the preparations of hydride which gave good hydroformylation activity compared to those which gave predominantly hydrogenation.

Since most of the hydroformylation reactions were carried out on samples of $HMn(CO)_5$ prepared using aqueous phosphoric acid and tetraglyme solvent, experiments were carried out to assess the possibility that some volatile impurity in one of these might be causing the hydroformylation. Two preparations of $HMn(CO)_5$ were carried out in the absence of any solvent, by reacting solid $NEt_4Mn(CO)_5$ with either H_3PO_4 or H_2SO_4, and collecting the volatile hydride in a U-tube at -196°C. Both of these batches of $HMn(CO)_5$ gave aldehyde upon reaction with CPS, thus ruling out impurities in the tetraglyme from further consideration. Note that the use of sulfuric rather than phosphoric acid also ruled out the possibility that an impurity in the phosphoric acid caused the reaction.

Reaction of $HMn(CO)_5$ with other cyclopropyl compounds

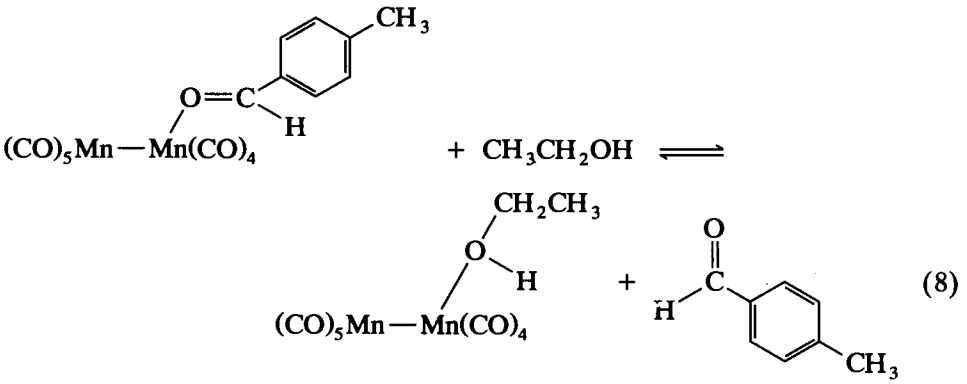
A few experiments were carried out to briefly assess the reactivity of $HMn(CO)_5$ with other organic compounds containing cyclopropyl rings. When a C_6D_6 solution of **1** (0.15 *M*) and $HMn(CO)_5$ (1.6 *M*) was heated at 62°C for 5 days, the solution turned yellow due to decomposition of the hydride and formation of $Mn_2(CO)_{10}$. Half of the hydride had decomposed, and a singlet at δ 4.51 was observed due to H_2, but no change in **1** was detected by ^1H NMR.

Although no reaction was observed with **1**, it was possible that the reaction would occur with other vinylcyclopropanes besides CPS. The reaction of $HMn(CO)_5$ with 2-cyclopropylpropene has been studied less extensively than that of CPS, but preliminary experiments suggest analogous behavior, as shown in Scheme 3. Thus reaction of 2-cyclopropylpropene with $HMn(CO)_5$ at room temperature gave a dark wine-red solution characteristic of the formation of an $Mn_2(CO)_9(\eta^1$-aldehyde) complex. Aldehyde resonances for free (δ 9.29) and complexed (δ 8.45) aldehydes were similar to those observed in the analogous reaction with CPS. Further hydrogenation of the aldehyde to alcohol was found to be somewhat faster in this system relative to CPS, since after 3 days at room temperature all of the aldehyde was consumed, giving a mixture of the alcohol complex $Mn_2(CO)_9(\eta^1$-



Scheme 3.

$HO(CH_2)_3CH{=}C(CH_3)_2$) along with the free alcohol. We have previously established the exchange of aldehyde and alcohol ligands on $Mn_2(CO)_9$ complexes as shown in eq. 8, but the alcohol complexes have not been isolated.



(8)

Carbonylation with 1 atm CO releases the free alcohol $HO(CH_2)_3CH{=}C(CH_3)_2$ and produces $Mn_2(CO)_{10}$ as the organometallic product.

Discussion

Dichotomous reactivity of $HMn(CO)_5$ with CPS: hydrogenation versus *hydroformylation*

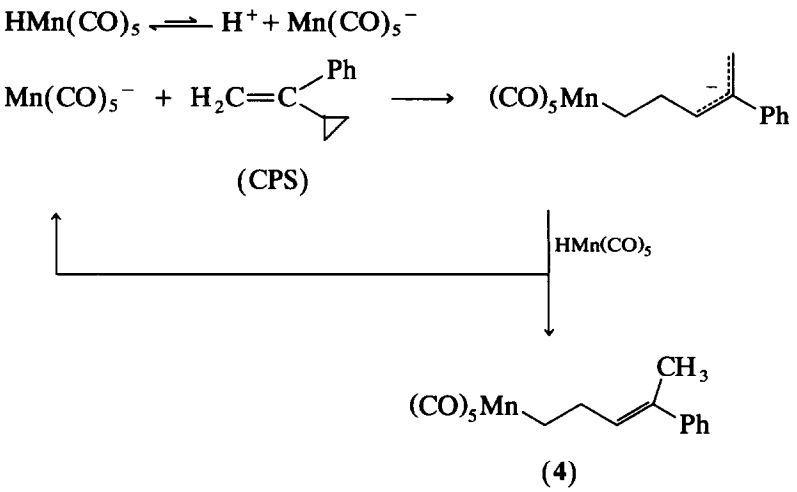
Competition between hydrogenation and hydroformylation is commonly observed in catalytic [1] and stoichiometric [11] hydroformylation reactions. Formation of considerable amounts of hydrogenation products is especially prevalent in hydroformylation of substituted styrenes and other substrates capable of undergoing a free-radical hydrogenation. The competition described here between hydrogenation and hydroformylation is fundamentally different, however. Normally, the hydrogenation and hydroformylation reactions proceed in competitive, parallel pathways. In this paper, we have reported conditions where the hydrogenation and hydroformylation can be observed sequentially, since the relatively slow hydrogenation occurs during the induction period that precedes the onset of the comparatively rapid hydroformylation reaction.

Influence of water on the reaction

The possible role of water in the reaction was carefully considered since collective evidence from several experiments strongly implied that water had a real (though apparently not readily interpretable) effect. Two prominent observations suggesting that water had a role in this chemistry were the fact that thorough treatment of the $HMn(CO)_5$ with P_2O_5 suppressed most of its activity for the hydroformylation reaction, and rewetting of dry, purified $HMn(CO)_5$ caused it to regain some of its activity for the hydroformylation reaction. On the other hand, addition of water to a solution containing CPS and thoroughly purified $HMn(CO)_5$ did not cause the hydroformylation, and no incorporation of ^{18}O was found in the aldehyde or organometallic product when $^{18}OH_2$ was used.

Consideration of ionic pathways

Since $HMn(CO)_5$ is moderately acidic ($pK_a = 14.1$ in CH_3CN, $pK_a \sim 7.1$ in H_2O) [12], we considered mechanisms initiated by heterolysis of the H–Mn bond.



Scheme 4.

One such pathway would involve attack of the $Mn(CO)_5^-$ anion at the cyclopropyl ring to give a substituted allyl anion. This stabilized anion could then form the manganese alkyl complex **4** by proton transfer from $HMn(CO)_5$ as shown in Scheme 4. Note that this mechanism is catalytic in $Mn(CO)_5^-$, since the anion is regenerated by the proton transfer. Although nucleophilic ring-opening of cyclopropyl rings is far less common than electrophilic ring-opening reactions [13], there is evidence [14,15] that it can occur with sufficiently nucleophilic anions, such as Bu_3Sn^-. Although this mechanism has some appealing features, it fails to accommodate either the observed induction period or the inhibition of the reaction by CO. Additional evidence against this mechanism comes from the failure to observe significant amounts of hydroformylation products from the reaction of CPS and purified $HMn(CO)_5$ in the presence of added $NEt_4Mn(CO)_5$ and H_2O. Furthermore, this ionic mechanism should be more favorable in high polarity solvents such as acetonitrile, but we see little hydroformylation in CD_3CN compared to reactions in C_6D_6.

The other type of ionic pathway, initiated by proton transfer from $HMn(CO)_5$ to CPS (cf. Scheme 2), would lead to hydrogenation product **1**, and was ruled out above.

Evidence for requirement of a vacant coordination site

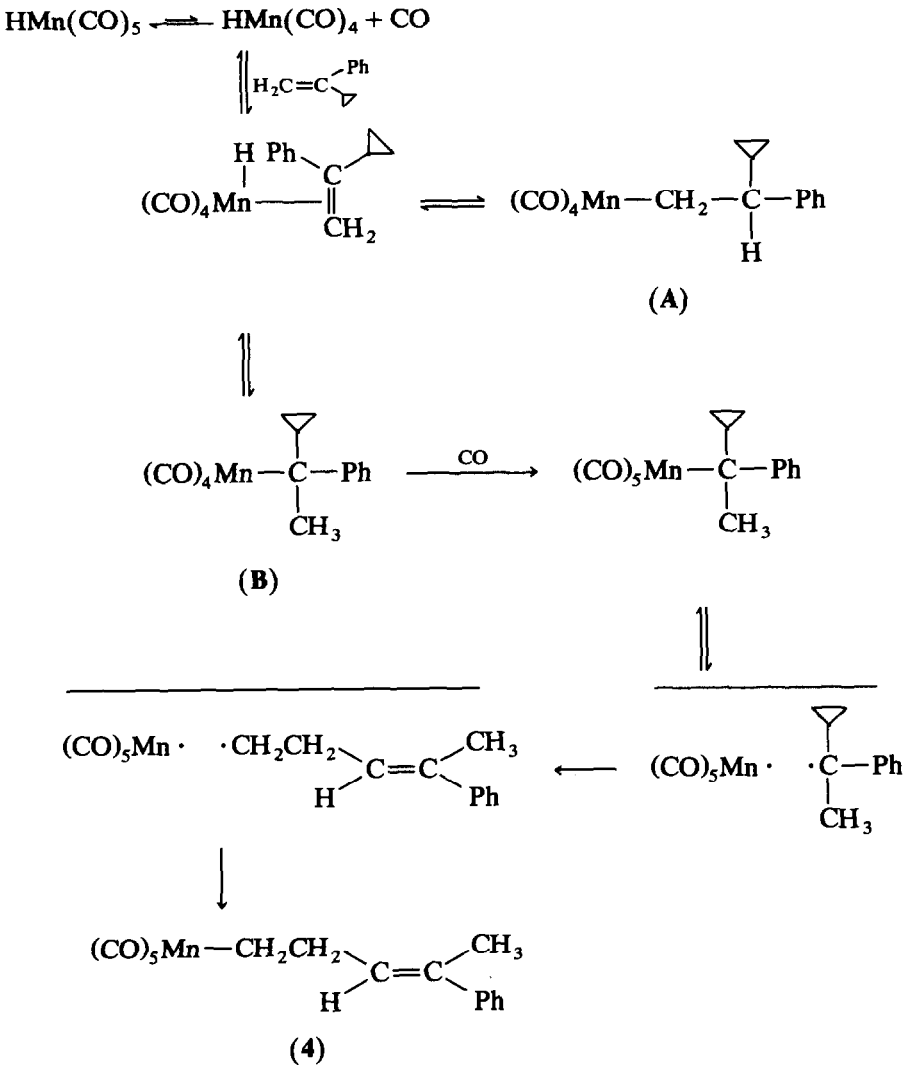
The observation of substantially diminished hydroformylation activity in donor solvents (CH_3CN and THF) or in the presence of potential donor ligands (CO, pyridine, $Ph_3P{=}O$) suggests that a vacant coordination site is required for the hydroformylation reaction to proceed. Since the aldehyde ligand is readily displaced by other ligands which are better donors [5], and since some of these same coordinating ligands inhibit the hydroformylation reaction, it is possible that the elimination of the induction period caused by addition of $Mn_2(CO)_9(\eta^1$-tolualdehyde) at the start of the reaction is due to a scavenging of traces of inhibitors (e.g. CO) which prevent the reaction from occurring. This possibility provides a plausi-

ble explanation for the induction period, but does not provide a comprehensive explanation of all of the observations because it does little to explain why the reaction actually occurs after the induction period is over.

Consideration of radical pathways

The hydrogenation of CPS using thoroughly purified $HMn(CO)_5$ has been established to occur by the radical pathway shown in Scheme 1. There are several intriguing features of the comparison of the hydrogenation pathway previously established, and the hydroformylation pathway under consideration here. Note that, in principle, the manganese alkyl complex **4** can be generated from combination of the rearranged carbon-centered radical $[Ph(CH_3)C{=}CHCH_2CH_2\cdot]$ with the organometallic radical $[(CO)_5Mn^{\cdot}]$. While both of these are indeed present in the hydrogenation of CPS by $HMn(CO)_5$, mechanistic evidence reported earlier [2] in the study of the hydrogenation reaction strongly argues against the formation of **4** by simple combination of these two free radicals. Due to the high concentrations of $HMn(CO)_5$ used in the hydroformylation experiments, $k_3[HMn(CO)_5] \gg k_2$ in Scheme 1. As a result, the unrearranged product **1** is the predominant hydrogenation product formed, and negligible formation of rearranged product **2** is observed. An alternative mechanism which would produce **4** is given in Scheme 5. The first step of this mechanism, reversible loss of CO to give a coordinatively unsaturated intermediate, would account for the observation that little hydroformylation occurs under 1 atm CO. Coordination of the CPS to manganese could be followed by insertion of the olefin into the Mn–H bond. While the primary alkyl complex **A** would be favored sterically, β-hydride elimination could occur to regenerate the alkene-hydride complex. Insertion in the other direction would produce a sterically encumbered tertiary alkyl complex **B**, which could react with CO to give a coordinatively saturated alkyl complex. Homolysis of the Mn–C bond would produce a caged radical pair containing a metal-centered radical and a carbon-centered radical. Ring-opening rearrangement of this radical would produce the metal-centered radical and the rearranged carbon-centered radical in a cage. Combination of these radicals would produce the manganese alkyl complex **4**.

Several variants of the mechanism shown in Scheme 5 can be envisioned. For example, the point at which CO is reassociated to the coordinatively unsaturated manganese alkyl complex could be different than shown. The mechanism shown in Scheme 5 involves π-coordination of CPS to a coordinatively unsaturated manganese center, with the site of coordination being produced by CO dissociation. Another mechanism that would involve generation of a vacant coordination site on manganese is formation of a manganese formyl complex, $(CO)_4MnCHO$. In their studies of the reaction of $HMn(CO)_5$ with phosphines, Byers and Brown [16] suggested the possible intermediacy of this formyl complex, but it was not possible to obtain conclusive evidence for its involvement. Regardless of whether CO loss or generation of a formyl complex is used as a means of production of a vacant coordination site, the key steps of this mechanism involve coordination of CPS to the metal in even-electron steps, prior to the odd-electron steps involving manganese-carbon bond homolysis. An attractive feature of the mechanism shown in Scheme 5 is that the formation of manganese alkyl complex **4** occurs by a pathway initiated by CO loss, which would account for the inhibition of the reaction under CO. On the other hand, the mechanism as shown would require an extremely



Scheme 5.

efficient radical cage [17], and it is difficult to conceive of any factors which would make the cage so efficient to prevent escape and trapping of some free radicals. Diffusive cage escape of the free radical [$Ph(CH_3)C{=}CHCH_2CH_2\cdot$] would undoubtedly be followed by conversion of this radical to rearranged hydrogenation product **2** by a fast hydrogen atom transfer from $HMn(CO)_5$. The lack of observation of any significant quantities of **2** in hydroformylation of CPS, coupled with the requirement for an extremely efficient cage, make this mechanism appear untenable.

Ligand substitution in several metal carbonyl hydrides has been established to proceed by a radical chain mechanism initiated by hydrogen atom abstraction from the metal hydride to give a 17-electron metal radical as the chain-carrying species.

An induction period and irreproducible kinetics often characterize these reactions. It is known that trace amounts of air can serve as an initiator, while larger amounts of oxygen can inhibit radical chain reactions. Norton and co-workers [18] reported that intentional addition of trace amounts of air accelerated CO substitution by PPh_3 in $(CO)_4Os(CH_3)H$, whereas Byers and Brown [19] found that oxygen inhibited substitution in $HRe(CO)_5$. We found that intentional addition of a small amount of oxygen to a solution of CPS and $HMn(CO)_5$ did not prevent the hydroformylation from occurring. This indicates that the air did not destroy the species responsible for causing the hydroformylation. This experiment alone, however, is inconclusive regarding the possible radical chain behavior for the ring-opening hydroformylation. Unlike $HRe(CO)_5$, the manganese hydride $HMn(CO)_5$ is very air-sensitive, so most of the oxygen was probably consumed through decomposition of the manganese hydride. A more decisive test for possible radical chain behavior is to generate metal-centered radicals photochemically. Brown and co-workers [19,20] have successfully used photolysis of metal dimers to produce chain-carrying metal radicals, which are capable of producing large rate enhancements in chain reactions. The modest increase in the rate of hydroformylation observed when solutions of CPS/$HMn(CO)_5$/$Mn_2(CO)_{10}$ were photolyzed is probably due to slight heating of the photolyzed tube compared to the dark tube. It is clear that the small acceleration observed here is far less than that observed in radical chain reactions that are initiated by photochemical generation of metal radicals.

Potential relevance to other systems

Our studies of the unusual ring-opening hydroformylation reactivity reported herein have thus far been limited to the reaction of $HMn(CO)_5$ with vinylcyclopropane substrates, CPS and 2-cyclopropylpropene. Despite this limited generality and the peculiar features of this reaction, there are certain aspects which are strikingly similar to earlier studies of manganese carbonyl complexes. Dombek [21] reported the reaction of the manganese complex $(CO)_5MnCH_2OC(=O)^tBu$ with H_2 (65 psi) at 75°C in sulfolane solvent (eq. (9)). The observed formation of an aldehyde, followed by further hydrogenation to an alcohol, parallels the reactivity we observed, although hydrogenation of aldehyde to alcohol was comparatively faster in their reaction than ours.

$$(CO)_5Mn-CH_2O\overset{O}{\overset{\|}{C}}CMe_3 \xrightarrow{H_2} HC\overset{O}{\overset{\|}{C}}H_2O\overset{O}{\overset{\|}{C}}CMe_3 \xrightarrow{H_2} HOCH_2CH_2O\overset{O}{\overset{\|}{C}}CMe_3 \quad (9)$$

The fact that they observed an induction period prior to autocatalytic formation of products in eq. 9 is quite intriguing, since we also observe an induction period. Another similarity between our observations and their system is that they also report inhibition of their reaction by CO. While there are some differences in the two systems, it is interesting to note that Dombek suggested that "complexed aldehyde is an intermediate in the conversion into alcohol".

Conclusion

The ring-opening hydroformylation reaction of α-cyclopropylstyrene by $HMn(CO)_5$ is an unusual reaction that involves conversion of a cyclopropyl-containing organic compound into a ring-opened η^1-aldehyde complex of $Mn_2(CO)_9$. This reaction is readily reproducible using specific procedures reported herein for the preparation and handling of $HMn(CO)_5$. If the $HMn(CO)_5$ is subjected to thorough treatment with P_2O_5, the activity for hydroformylation is greatly diminished, and hydrogenation of α-cyclopropylstyrene occurs instead, by a previously established free-radical mechanism. The hydroformylation of CPS was observed from more than 10 separate batches of $HMn(CO)_5$, and control experiments have ruled out sources of contamination from solvent, acid, or CPS as being responsible for the differences in hydrogenation *versus* hydroformylation activity. Key features that have been unambiguously established for the hydroformylation reaction are that it has an induction period, and that it proceeds through an intermediate manganese alkyl complex. It is inhibited by CO, and occurs to an appreciable extent only in non-polar, non-donor solvents (e.g., hexane or benzene). Despite the absence of conclusive spectroscopic data indicative of an impurity in the $HMn(CO)_5$ which promotes the hydroformylation, collective evidence strongly supports this contention. Several mechanistic possibilities have been considered, but since none of them provide a totally comprehensive explanation of all of the experimental observations, some details of the reaction remain enigmatic.

Experimental section

General

All manipulations were carried out under an atmosphere of nitrogen or argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz for ^1H). IR spectra were recorded on a Mattson Polaris FTIR spectrometer or a Nicolet MX-1 spectrometer, using CaF_2 cells. Toluene, THF, Et_2O, and hexane were distilled under nitrogen from Na/benzophenone. C_6D_6 was dried over NaK, stored over $(Cp_2TiCl)_2ZnCl_2$ [22], and vacuum transferred prior to use. $HMn(CO)_5$ was stored under vacuum at $-20°C$ in the dark, and vacuum transferred immediately prior to each use. $Mn_2(CO)_{10}$ was purchased from Strem and used as received. $Ph_3P{=}O$ was recrystallized from absolute ethanol and dried under vacuum. Tetraglyme (tetraethylene glycol dimethyl ether) was purchased from Aldrich and vacuum distilled from NaH immediately prior to use. α-Cyclopropylstyrene (CPS) was prepared by a published procedure [23].

Preparation of $HMn(CO)_5$

Method A. NaK alloy [24] (3 mL) was added to a solution of $Mn_2(CO)_{10}$ (4.00 g, 0.013 mol) in THF (60 mL) at room temperature, and the mixture was stirred at room temperature for 1 h. The solution was initially yellow but turned red, then green. An IR spectrum taken after 1 h (ν(CO) 1896, 1863, 1831 cm^{-1}) agreed with the literature report [24] and indicated conversion to $KMn(CO)_5$. The mixture was filtered twice through Celite in a drybox using a medium frit, and the THF was evaporated. Tetraglyme (20 mL) was added, and the solution was pumped on a

vacuum line for 2 h. Then 85% H_3PO_4 (2 mL) was added to the solution, and the volatile products were collected in a U-tube cooled to −196°C on a vacuum line. The product was vacuum transferred to a glass tube, and was stored overnight in a freezer at −20°C. The glass container was cooled to −78°C, and the $HMn(CO)_5$ present at the bottom of the tube was removed by syringe, leaving the ice at the upper part of the tube. The $HMn(CO)_5$ was yellow-orange due to a small amount of air oxidation during the syringe transfer. It was vacuum transferred to another glass bulb to give $HMn(CO)_5$ as a very pale yellow liquid. Yield 3.247 g (81%).

Method B. This preparation is similar to that above, with the main differences being in the reducing agent used to prepare the metal anion, and the purification procedure for the hydride. This method of preparation of $HMn(CO)_5$ is a minor modification of a previously reported procedure [25]. A mixture of $Mn_2(CO)_{10}$ (4.017 g, 1.030×10^{-2} mol) and KH [26] (0.977 g, 2.44×10^{-2} mol) in THF (100 mL) was stirred for 4.5 h and filtered through Celite on a medium frit. The solvent was evaporated, and freshly distilled tetraglyme (25 mL) was added. This solution of $KMn(CO)_5$ was connected to a vacuum line, and was pumped overnight to remove residual THF. Aqueous 85% H_3PO_4 (1.5 mL) was added to the solution, and the volatile products were collected in a U-tube cooled to −196°C on a vacuum line. The product was vacuum transferred to a flask containing a small amount of P_2O_5, and was then vacuum transferred into a glass storage bulb. Yield 2.92 g (72%). The liquid was still slightly cloudy, so it was condensed onto another portion of P_2O_5, then recondensed into a glass storage bulb. (This batch of $HMn(CO)_5$ was effective at the hydroformylation reaction, despite having been dried with P_2O_5.) This preparation can also be successfully carried out using Na/Hg to reduce $Mn_2(CO)_{10}$ to $NaMn(CO)_5$.

Method C. This method for preparation of $HMn(CO)_5$ was briefly noted [27] for $HMn(CO)_5$ and has been described in detail for preparation of $HRe(CO)_5$ [28]. A mixture of $BrMn(CO)_5$ (2.50 g, 9.09×10^{-3} mol), Zn dust (1.2 g, 0.018 mol) and tetraglyme (15 mL) were placed into a Schlenk flask which was attached to a vacuum line, and aqueous 85% H_3PO_4 (1 mL) was added. The volatile components were collected in a U-tube at −196°C on the vacuum line. Yields of $HMn(CO)_5$ > 80% were routinely obtained using this procedure. Samples of $HMn(CO)_5$ prepared by this method still contain water. Removal of the water by drying over P_2O_5 is effective, but sometimes causes the resultant $HMn(CO)_5$ to lose much of its activity for hydroformylation of CPS. An alternative purification procedure described below has been found to reproducibly work well to remove most of the water and acetaldehyde (see below), and yet the $HMn(CO)_5$ purified in this way is still effective for hydroformylation of CPS. When the $HMn(CO)_5$ prepared as described above is stored under vacuum in a glass tube overnight in a freezer at −20°C, most of the water forms ice crystals near the top of the tube. The glass container is cooled to −78°C, in order to keep the ice from melting, and the $HMn(CO)_5$ can then be removed by syringe and transferred to another glass bulb.

^1H NMR spectra of $HMn(CO)_5$

^1H NMR spectra of several very concentrated (10–25% $HMn(CO)_5$ by vol.) C_6D_6 solutions of $HMn(CO)_5$ were recorded in an effort to detect any impurities that might be involved in causing the hydroformylation reaction. The resonance for $HMn(CO)_5$ in C_6D_6 appears at δ −7.85. Small amounts (typically < 2% relative to

$HMn(CO)_5$) of CH_3CHO (δ 9.16, q, $J = 2.8$ Hz, CHO; δ 1.42, d, $J = 2.8$ Hz, CH_3 in C_6D_6) were often observed in the preparations of $HMn(CO)_5$. The way in which the acetaldehyde is formed is unknown, but it must arise in some way from the tetraglyme solvent during the preparation of the $HMn(CO)_5$. No acetaldehyde was observed in preparations of $HMn(CO)_5$ carried out in the absence of any solvent (from reaction of solid $NEt_4Mn(CO)_5$ with either H_3PO_4 or H_2SO_4). The tetraglyme had been distilled from NaH, and was collected at room temperature using an air-cooled (as opposed to cold water) condenser. Thus any acetaldehyde formed in the purification of the solvent by distillation should not have been collected. Furthermore, any acetaldehyde formed in the distillation step by cleavage of the tetraglyme by NaH should have existed in the form of the enolate rather than free aldehyde. In any case, the small amount of acetaldehyde does not interfere with the reaction. It is much more volatile than the hydride and can be readily separated from it. The resonance for water dissolved in C_6D_6 appears as a sharp singlet δ 0.42, while the resonance for undissolved water is a broad resonance centered around δ 5.10. Along with these peaks identified for water and acetaldehyde, a few additional resonances were observed which were determined to be due to trace impurities in the solvent. No additional peaks were seen for trace impurities in samples of $HMn(CO)_5$ which were active for the hydroformylation reaction, compared to thoroughly dried samples which produced mainly hydrogenation upon reaction with CPS.

IR spectra of $HMn(CO)_5$

IR spectra of $HMn(CO)_5$ in hexane solution were recorded using CaF_2 cells. As in the case of the NMR spectra discussed above, no differences were observed between different batches of $HMn(CO)_5$. IR spectrum of $HMn(CO)_5$ (hexane): 2118.1w, 2037w, 2015.0vs, 2007.7vs, 1982.1m, 1967.2w cm^{-1}. This is in good agreement with the bands reported by Byers and Brown [16] in hexane (2117, 2043, 2015.5, 2007.5, 1981, 1966 cm^{-1}).

General procedure for reaction of CPS with $HMn(CO)_5$

Most of these experiments were carried out in 5 mm NMR tubes using the procedures described here. The NMR tubes used in these experiments were either joined to a stopcock so that they could be sealed off with a flame on the vacuum line, or were connected to a teflon valve directly on the top of the tube (NMR tubes with J. Young valves purchased from Wilmad Glass Company). In a drybox, α-cyclopropylstyrene (CPS) (15 μL, 9.95×10^{-5} mol) was added to an NMR tube using a 25 μL syringe. C_6D_6 (400 μL) and bibenzyl ($\sim$ 1 mg as an internal integration standard) were added, and the valve on the NMR tube was closed. The tube was connected to a vacuum line, and $HMn(CO)_5$ was then added by vacuum transfer. The tube was either flame-sealed or sealed by closing the teflon valve. The volume of the solution was calculated from the height of the solution in the NMR tube using a published formula [29]. The amounts of starting materials and products were determined by ^1H NMR over the course of the reaction by integration *versus* the bibenzyl internal standard. In most cases, the solutions in the NMR tubes were not shaken throughout the reaction. A control experiment was carried out in which identical solutions were separated into two tubes, one of which was left undisturbed, the other of which was mixed by turning it end over

end during the course of the reaction. No significant acceleration of rate (or diminution of the induction period) was observed for the agitated tube compared to the undisturbed tube.

Reaction of CPS with $HMn(CO)_5$ in the presence of Hg

Using the general procedure described above, CPS (15 μL, 9.95×10^{-5} mol), C_6D_6 (400 μL) and bibenzyl ($\sim$ 1 mg) were added to an NMR tube containing Hg (25 mg, 1.2×10^{-4} mol). Then $HMn(CO)_5$ (prepared by method C) was added by vacuum transfer, and the tube was sealed. The progress of the reaction was monitored by NMR, and the results are given in Table 1.

Reaction of CPS with $HMn(CO)_5$ in the presence of $Ph_3P{=}O$

Using the general procedure described above, the reaction of a solution of CPS (0.18 *M*), $HMn(CO)_5$ (1.6 *M*, prepared by method A), and $Ph_3P{=}O$ (4.2 mg, 0.027 *M*) in C_6D_6 was carried out at room temperature and monitored by ^1H NMR. The hydrogenation of CPS proceeded smoothly, with little of the hydroformylation products observed. After 11 days, the yields of products were 92% for the hydrogenation product **1** and 7% free aldehyde.

Reaction of CPS with $HMn(CO)_5$ in the presence of $H_2C{=}CH_2$

Using the general procedure described above, CPS (15 μL, 9.95×10^{-5} mol), C_6D_6 (400 μL) and bibenzyl ($\sim$ 1 mg) were added to an NMR tube in a drybox. Then $HMn(CO)_5$ (prepared by method A) was added by vacuum transfer. Ethylene was condensed into a U-tube on a vacuum line at -196°C, and was pumped under vacuum to remove any oxygen. Then the ethylene was allowed to warm up, giving 1 atm in the vacuum line and NMR tube. An NMR spectrum established initial concentrations as 0.18 *M* CPS and 1.4 *M* $HMn(CO)_5$. The total concentration of ethylene could not be precisely determined since part of it is in the gas phase, but integration of the amount in solution indicated $[C_2H_4]_{soln} = 0.099$ *M*. After 66 h at room temperature the solution had the characteristic dark orange-red color resulting from hydroformylation of CPS. The amount of ethylene in solution had decreased to 15% of its initial value. The concentration of ethane (δ 0.81) in solution was $[C_2H_6]_{soln} = 0.04$ *M*. More ethylene (1 atm) was added, but negligible further hydrogenation of ethylene to ethane was observed over the next 18 h at room temperature. Along with resonances for the normal expected products resulting from hydroformylation of CPS, an additional ^1H NMR resonance was observed at δ 8.27. This singlet is tentatively assigned as the aldehyde H of $Mn_2(CO)_9(\eta^1\text{-}CH_3CH_2CHO)$. Addition of CO (1 atm) caused a color change from dark orange-red to light orange. The volatile components from this reaction were transferred to another NMR tube by vacuum transfer. Along with the excess $HMn(CO)_5$, the presence of CH_3CH_2CHO and $CH_3CH_2CH_2OH$ were observed in the NMR spectrum. ^1H NMR of CH_3CH_2CHO (C_6D_6): δ 9.23 (br s, 1 H, CHO), 1.67 (q, $J = 7$ Hz, 2H, CH_2), 0.67 (t, $J = 7$ Hz, 3 H, CH_3). ^1H NMR of $CH_3CH_2CH_2OH$ (C_6D_6): δ 3.26 (t, $J = 6$ Hz, 2H, CH_2OH), 1.33 (sextet, $J = 7$ Hz, 2H, CH_3CH_2), 0.77 (t, $J = 7$ Hz, 3 H, CH_3), 0.54 (br s, 1 H, OH). These spectra agree with spectra of authentic samples of CH_3CH_2CHO and $CH_3CH_2CH_2OH$ except that the OH resonance of authentic CH_3CH_2OH appears at δ 0.91.

Thorough drying and rewetting of $HMn(CO)_5$

Samples of $HMn(CO)_5$ which are dried thoroughly over several grams of P_2O_5 result in predominant hydrogenation of CPS rather than the hydroformylation reaction. $HMn(CO)_5$ is a volatile (but very air-sensitive) liquid, so these manipulations are straightforwardly carried out on a vacuum line. In order to minimize the amount of hydroformylation, it is recommended that a sufficient quantity of P_2O_5 relative to the $HMn(CO)_5$ be used so that the hydride is completely in contact with the drying agent, with nearly all of the liquid hydride coated onto the P_2O_5. In most cases, some decomposition of the hydride occurs, leading to a pale yellow coloration of the P_2O_5 due to $Mn_2(CO)_{10}$. It is necessary to remove the hydrogen (formed as a by-product of the decomposition of $HMn(CO)_5$) by freeze-pump-thaw cycles, prior to vacuum transfer of the purified hydride to separate it from the P_2O_5. A sample of $HMn(CO)_5$ purified in this way was reacted with CPS using the standard procedures described above. After 5 days, $< 10\%$ of hydroformylation products were observed by NMR, and the hydrogenation product **1** was formed in $\sim 90\%$ yield. A sample of this same batch of purified, dried $HMn(CO)_5$ (1.18 g, 6.04 mmol) was "rewetted" by condensing it onto H_2O (27 μL, 1.50 mmol, 25 mol% based on $HMn(CO)_5$) and stirring the mixture for 1 day at room temperature. This "rewetted" sample of $HMn(CO)_5$ was then reacted with CPS; results are given in Table 1.

Dark and photochemical reactions of CPS with $HMn(CO)_5$ in the presence of $Mn_2(CO)_{10}$

A C_6D_6 solution of CPS (30 μL, 0.19 *M*), $HMn(CO)_5$ (1.2 *M*, prepared by method C) and $Mn_2(CO)_{10}$ (40 mg, 0.10 *M*) and bibenzyl internal integration standard was prepared using the general procedure described above. An initial NMR spectrum was taken in order to determine the amounts of CPS and $HMn(CO)_5$ relative to the internal standard. In a drybox, the solution was divided into two equal portions, and both tubes solutions were freeze-pump-thawed three times. One of the tubes was kept in the dark, and the other was photolyzed. The photolysis was carried out with a Photon Technology International (PTI) 100 W Hg-Xe lamp with a water-filled IR filter and grating monochromator (bandwidth 16 nm); the approximate light intensity determined by ferrioxalate actinometry was 10^{-7} einsteins/s. Results for the dark and photolyzed samples are provided in Table 1.

Reaction of CPS with $HMn(CO)_5$ in D_2O

CPS (20 μL) was added to an NMR tube in a drybox, then D_2O (0.4 mL) and an excess of $HMn(CO)_5$ (prepared by method B) were added to the tube by vacuum transfer. The tube was flame-sealed and shaken to give an immiscible mixture. After 2 h at 7°C, the organic phase was dark red-orange, indicating formation of the aldehyde complex. The volatile components were removed by evaporation, and the manganese aldehyde product **3** was identified by comparison of its IR spectrum with that of an authentic sample.

Preparation and isolation of $Mn_2(CO)_9(\eta^1\text{-}HCOCH_2CH_2CH{=}C(Ph)CH_3)$ (3)

A solution of CPS (0.177 g, 1.23 mmol) in hexane (3 mL) was degassed by three freeze-pump-thaw cycles, and $HMn(CO)_5$ (0.736 g, 3.76 mmol, prepared by method

B) was added by vacuum transfer. The solution was maintained at 7°C. After 16 h the color of the solution was dark orange-red. A red oil had formed after 26 h, but deep red-orange crystals were present after 44 h. The product was obtained in three crops from hexane, giving a total yield of 465 mg (70%) of **3**. Spectroscopic characterization [5] and the crystal structure [3] of this product were reported previously.

Reaction of 2-cyclopropylpropene with $HMn(CO)_5$

A C_6D_6 solution of 2-cyclopropylpropene (0.18 *M*) and $HMn(CO)_5$ (1.7 *M*, prepared by method A) was prepared using the general procedures described above for CPS. Negligible reaction was observed by ^1H NMR after 6.5 h at room temperature. After 24 h, the solution was dark wine-red, and NMR integration *versus* the bibenzyl internal standard indicated 58% of the initial concentration of 2-cyclopropylpropene remained. Resonances assigned to $Mn_2(CO)_9(\eta^1$-$HCOCH_2CH_2CH{=}C(CH_3)_2)$ (18% yield) were observed at δ 8.45 (singlet, aldehyde H) and δ 4.57 (multiplet, vinyl H). The free aldehyde $HCOCH_2CH_2CH{=}C(CH_3)_2$ was observed in 13% yield (δ 9.29, s, aldehyde H; δ 4.92, multiplet, vinyl H). A vinyl resonance (7% yield) at δ 5.22 (apparent triplet of quintets, $J = 7.1$ Hz, 1.4 Hz) is tentatively assigned to the manganese alkyl complex $(CO)_5MnCH_2CH_2CH{=}C(CH_3)_2$. After another 4 h, the amount of 2-cyclopropylpropene had dropped to 29%, while the yields of free and complexed aldehydes had increased to 20% and 40%, respectively. After a total of 47 h, only 8% of the 2-cyclopropylpropene remained. The decreasing yields of free and complexed aldehydes (14% and 34%) were accompanied by the appearance of vinyl resonances at δ 5.07 (28% yield) and δ 4.89 (14%) assigned to $HO(CH_2)_3CH{=}C(CH_3)_2$ and $Mn_2(CO)_9(\eta^1$-$HO(CH_2)_3CH{=}C(CH_3)_2)$. The vinyl resonance assigned to the complexed aldehyde overlaps with the vinyl resonance of the free aldehyde, but the relative contributions can be ascertained, since the amount of aldehyde is readily determined from integration of the aldehyde CHO resonance. After a total of 72 h, all free and complexed aldehyde had been consumed, and the yields of free and complexed alcohol were 51% and 41%. Addition of CO (1 atm) to the solution caused a color change from dark wine-red to light orange within a few seconds, and the NMR spectrum of only free alcohol was observed. Resonances for the alcohol were all broadened somewhat, presumably due to small amounts of paramagnetic impurities or decomposition products, so an accurate determination of coupling constants was not obtained. ^1H NMR spectrum of $HO(CH_2)_3CH{=}C(CH_3)_2$ in C_6D_6: δ 5.11 (1 H, vinyl), 3.43 (2H, CH_2), 1.99 (2H, CH_2), 1.62 (3 H, CH_3), 1.47 (3 H, CH_3), 1.6–1.4 (broad, 3 H total, CH_2 and OH). Further confirmation of the identity of the free alcohol came from the GC/MS spectrum; high mass peaks listed as *m/e* (% of base peak, assignment): 114 (25%, M^+); 96 (31%, $M^+ - H_2O$); 81 (100%, $M^+ - H_2O - CH_3$).

Acknowledgements

This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH0016 with the US Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We thank Dr. Edward Samsel for preliminary experiments on this project, Professor Darrell Eyman (University of Iowa) for suggesting the mechanism in Scheme 4, Drs. Mark

Andrews and George Gould for helpful discussions, and Ms. Elinor Norton for GC/MS analyses.

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