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Thermal Exchange Reactions of (η^5-C_5R_5)Mn(CO)$_2$(^wL) Compounds (^wL = Weakly-Bound Ligand) in Supercritical Fluid Solution and the Isolation of (η^5-C_5R_5)Mn(CO)$_2$(η^2-H_2) Using High-Pressure Flow and Semiflow Reactors

Peter D. Lee, Jennifer L. King, Steffen Seebald, and Martyn Poliakoff*

Department of Chemistry, University of Nottingham, Nottingham, England NG7 2RD

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Supercritical fluids offer unrivaled opportunities for manipulating compounds with labile ligands. This paper reports a study of ligand-exchange reactions in supercritical solution aimed at evaluating compounds as precursors for the thermal synthesis of CpMn(CO)$_2$(η^2-H_2) in supercritical CO_2 (scCO_2). A series of (η^5-C_5R_5)Mn(CO)$_2$(^wL) compounds have been prepared, where ^wL is a weakly-bound ligand (i.e., ^{n}PrCN, η^2-$H_2C{=}CHOEt$ (EVE), and η^2-H-SiEt$_3$), and their reactions with C_2H_4, N_2, and H_2 have been studied in supercritical solution. This is the first time that the EVE ligand has been used with the (η^5-C_5R_5)Mn(CO)$_2$ moiety. We describe flow and semiflow reactors for carrying out these thermal reactions in supercritical solution. Both of these reactors exploit rapid expansion of the supercritical fluid to enable these labile complexes to be isolated from supercritical solution without loss of the labile ligand. The reaction of Cp*Mn(CO)$_2$(η^2-HSiEt$_3$) with H_2 is found to be the best route for the thermal synthesis of Cp*Mn(CO)$_2$(η^2-H_2), both in terms of purity and convenience. There are clear opportunities for scale-up. We find that exchange between these ligands is so facile that conditions in supercritical solution can be varied sufficiently to favor the interchange between almost any pair of the labile ligands. This ease of interchange has important implications for homogeneous catalysis in supercritical solution.

Introduction

Supercritical CO_2 (scCO_2) is becoming increasingly attractive as an environmentally-acceptable replacement for conventional solvents in the "cleaner synthesis" of chemicals.[1] However, scCO_2 offers additional opportunities for chemical synthesis and reactions which would be difficult to carry out in other media.[2] Striking organometallic examples include the synthesis[3] of CpRe(N_2)$_3$ from CpRe(CO)$_3$ and N_2, the hugely increased efficiency[4] in the catalytic hydrogenation of scCO_2, and the isolation of the first nonclassical dihydrogen compound of manganese,[5] CpMn(CO)$_2$(η^2-H_2). All three of these examples exploit the fact that scCO_2 is completely miscible with permanent gases such as N_2 or H_2 so that the effective concentration of "dissolved" gas can be nearly an order of magnitude higher than would be obtained in a conventional organic solvent under similar conditions.[3] These high concentrations of gas can stabilize dinitrogen and dihydrogen compounds in supercritical solution. Although the first observation of CpMn(CO)$_2$(η^2-H_2) was in THF solution,[6] the isolation of such compounds from conventional solvents is difficult because the labile η^2-H_2 ligand is lost together with the evaporating solvent. By contrast, they can be isolated from supercritical solution by expansion through a valve or back-pressure regulator, which precipitate solid material very rapidly from solution while maintaining the high concentration of the dissolved gas until the very last moment before isolation.

Although the use of supercritical fluids involves high pressures and specialized equipment, many of the problems can be minimized by using continuous flow reactors which allow relatively large amounts of material to be processed in apparatus with a very small volume. Recently, we showed how miniature flow reactors can be applied to organometallic synthesis. Two photochemical flow reactors were described in detail, one for the photochemical generation[5,7] of Cr(CO)$_5$(C_2H_4)

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* Author to whom correspondence should be addressed.. E-mail: Martyn.Poliakoff@nottingham.ac.uk. http://www.nottingham.ac.uk/supercritical/.

[1] For an excellent general introduction to supercritical fluids, see: McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth-Heinemann: Boston, 1994.

[2] For a recent review of reactions in supercritical fluids, see: Savage, P. E.; Gopaian, S.; Mizan, T. I.; Martino, C. J.; Brock, E. E. *A. Inst. Chem. Eng. J.* **1995**, *41*, 1725. Eckert, C. A.; Knutson, B. L.; Debendetti, P. G. *Nature* **1996**, *383*, 313.

[3] (a) Howdle, S. M.; Grebenik, P.; Perutz, R. N.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1517. (b) Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804.

[4] Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231. Jessop, P. G.; Hsiano, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344.

[5] Banister, J. A.; Lee, P. D.; Poliakoff, M. *Organometallics* **1995**, *14*, 3876.

[6] Leong, V. S.; Cooper, N. J. *Organometallics* **1988**, *7*, 2080.

[7] Banister, J. A.; Howdle, S. M.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1814.

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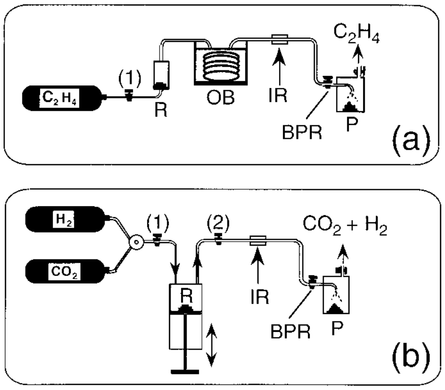

Figure 1. Schematic diagrams of the flow reactors for the supercritical synthesis of (a) $(C_5R_5)Mn(CO)_2(C_2H_4)$ in scC_2H_4 and (b) $(C_5R_5)Mn(CO)_2(\eta^2\text{-}H_2)$ in $scCO_2/H_2$. The components of the two reactors are labeled as follows (from left to right): R, reservoir of solid reactant; OB, oil bath; IR, spectroscopic cell for monitoring the reaction; BPR, back-pressure regulator for reducing the pressure and precipitating the solid product, P. Part (a) shows a continuous thermal flow reactor where the precursor compound is dissolved in scC_2H_4 and flowed through a coil in the oil bath to undergo thermal reaction. The semiflow reactor shown in part (b) differs from the flow reactor in part (a) because the reservoir, R, now acts as a batch reactor. Again, the precursor is dissolved in a supercritical solution ($scCO_2/H_2$) by opening valve 1. The thermal reaction then takes place within R, allowing longer residence times at lower operating temperatures. Opening 2 allows small aliquots of the reacting solution to be withdrawn for monitoring. Once the reaction reaches completion, the piston in R is used to push the solution through BPR where the fluid expands, precipitating the dry solid. The full layouts of these reactors are shown in Figures 8 and 9, respectively.

from the reaction of $Cr(CO)_6$ with supercritical C_2H_4 and the other reactor[5] for the synthesis of $CpMn(CO)_2(\eta^2\text{-}H_2)$ from $CpMn(CO)_3$ and H_2 in $scCO_2$. This was the first time that either compound had been isolated as a solid, and both were found to be thermally less labile than had been anticipated.

A photochemical route to such compounds has the advantage that the whole synthesis can be carried out at relatively low temperatures, thereby minimizing the decomposition of the labile products. However, photochemical routes do have significant limitations: (i) photochemistry in a flow reactor is only appropriate for reactions with high quantum yields; thus, the approach would not be appropriate for photochemical C−H activation,[8] (ii) there is the possibility of secondary photolysis and formation of unwanted side products; for example, *trans*-$Cr(CO)_4(C_2H_4)_2$ is formed during the synthesis of $Cr(CO)_5(C_2H_4)$, and (iii) the high intensity of the UV light needed for rapid reaction can lead to a build-up of opaque decomposition products on the photolysis window and, hence, to a limit on the amount of product which can be prepared in a particular reactor.

Thermal reactions in a flow system do not suffer from the same limitations as photochemical reactions. Therefore, this paper investigates thermal routes for the synthesis of $CpMn(CO)_2(\eta^2\text{-}H_2)$ and related compounds in supercritical fluid solution. In the first part, we outline the overall strategy for thermal synthesis and then we evaluate possible starting compounds and report their behavior in a thermal flow reactor. In the second part, we explain why thermal reactions are more effectively carried out in a *semiflow* reactor and describe a range of reactions and preparations using this approach. Finally, we highlight the key chemical results and show that these results have significant implications for future chemical reactions in supercritical fluids.[9]

Results and Discussion

Synthetic Strategy. The target molecules $(C_5R_5)Mn(CO)_2(\eta^2\text{-}H_2)$, R = H or Me, are extremely labile. By contrast, the simplest starting materials, $(C_5R_5)Mn(CO)_3$, are some of the most thermally stable transition metal carbonyl compounds. This means that even a "thermal" route will necessarily have to involve a photochemical step to create the $(C_5R_5)Mn(CO)_2$ moiety. However, this photochemical step can be carried out under conventional conditions prior to the high-pressure supercritical reactions. Our strategy, therefore, is to prepare a precursor compound with a weakly-bound ligand, ^wL, which can subsequently be displaced by H_2 to form the $(C_5R_5)Mn(CO)_2(\eta^2\text{-}H_2)$ target compound, eq 1. The first stage is carried out in conventional preparative photochemical apparatus (see Experimental Section), and we have developed reactors for the supercritical stage, which are shown schematically in Figure 1. They differ in the method of carrying out the thermal reaction, either as continuous or batch processes. The continuous reactor is based on the photochemical flow reactors which have been described in our previous paper.[5] The continuous and batch methods each have their advantages and limitations, as described below.

$$(C_5R_5)Mn(CO)_3 \xrightarrow{h\nu,\ {}^wL} (C_5R_5)Mn(CO)_2{}^wL \xrightarrow{scCO_2 + H_2} (C_5R_5)Mn(CO)_2(\eta^2\text{-}H_2) \quad (1)$$

Both reactors exploit rapid expansion of the supercritical fluid to isolate the solid products. This places some constraints on the synthetic route because rapid expansion of $scCO_2$ precipitates *all* solid materials dissolved in the fluid, and subsequent purification of the solids is extremely difficult. Therefore, if a pure product is to be isolated, the *precursor* → *product* conversion must be both clean and as quantitative as possible. In addition, reaction with H_2 necessarily liberates free ^wL which, if solid, will be precipitated with the product.

Initially, we tried to eliminate the problems of free ^wL being precipitated by using a ligand which was bound to a polymer. The precursor compound would then be generated *in situ* in the polymer, and the starting material and free ligand would, therefore, be completely insoluble in $scCO_2$. Reaction with H_2 would take place within the polymer matrix, and once formed, $(C_5R_5)Mn(CO)_2(\eta^2\text{-}H_2)$ could be flushed out of the poly-

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[8] Banister, J. A.; Cooper, A. I.; Howdle, S. M.; Jobling, M.; Poliakoff, M. *Organometallics* **1996** *15*, 1804.

[9] Preliminary accounts of this work have been presented, see: Lee, P. D.; King, J. L.; Seebald S.; Poliakoff, M. *International Conference of Organometallic Chemistry*, Brisbane, Australia, July 1996. King, J. L. Lecture at RSC Predoctoral Symposium, Brunel University, U.K., Sept. 1996.

mer by the $scCO_2$. Problems of separating the reactant and products would be eliminated. Previous work[10] in our laboratory had shown that $(C_5R_5)Mn(CO)_2(C{=}C)_{polymer}$ could be formed by photochemical reaction of $(C_5R_5)Mn(CO)_3$ with the residual C=C groups in low-density polyethylene (LDPE) and that $(C_5R_5)Mn(CO)_2(C{=}C)_{polymer}$ would indeed react thermally with H_2. Although this approach initially appeared promising, commercial LDPE proved to have an insufficient concentration of olefinic groups to make the reaction viable on a preparative scale.[11] We, therefore, decided to focus on ligands ^wL which were volatile liquids in their free state and were, therefore, unlikely to be precipitated or trapped during the rapid expansion of the $scCO_2$. If successful, such an approach would provide an effective and "solvent-free" synthetic route to labile organometallic complexes.

Reactions in a Thermal Flow Reactor. THF Complexes. The conventional route to $(C_5R_5)Mn(CO)_2L$ complexes is via $(C_5R_5)Mn(CO)_2(THF)$, generated photochemically from $(C_5R_5)Mn(CO)_3$ in THF solution. Thus, THF seemed to be an obvious choice for ^wL. Unfortunately, $(C_5R_5)Mn(CO)_2(THF)$ cannot be easily separated from excess THF, but nevertheless, we tried experiments with $Cp'Mn(CO)_2(THF)$ ($Cp' = C_5H_4Me$) *in THF solution*. Initially, the reaction was carried out in the flow reactor, Figures 1a and 8. A solution of $Cp'Mn(CO)_2(THF)$, held at *ca.* 0 °C, was slowly bled into $scCO_2/H_2$ or scC_2H_6/H_2 already flowing through the reactor at 2480 psi. Under these conditions, $Cp'Mn(CO)_2(THF)$ was highly reactive. No $Cp'Mn(CO)_2(THF)$ was detectable by on-line FTIR, even when the oil bath was completely bypassed. Only $Cp'Mn(CO)_3$ and a small amount of $Cp'Mn(CO)_2(\eta^2\text{-}H_2)$ could be detected. However, the recovery of these products proved to be impossible because they were precipitated as a concentrated THF solution. The apparatus was modified to allow the solution of $Cp'Mn(CO)_2(THF)$ to be pumped with a cooled HPLC pump (Gilson model 305), but again, reaction occurred instantaneously and on-line FTIR showed a 1:1 ratio of $Cp'Mn(CO)_2(\eta^2\text{-}H_2)$ and $Cp'Mn(CO)_3$. The formation of $Cp'Mn(CO)_3$ was almost certainly due to phase separation between the THF and the scC_2H_6/H_2 phases. As soon as the phases separate, the advantages of supercritical fluids are lost. $Cp'Mn(CO)_3$ is formed by the decomposition of $Cp'Mn(CO)_2(THF)$ in the THF phase in the virtual absence of H_2. Unfortunately, it proved almost impossible to adjust the relative flow rates of THF and scC_2H_6/H_2 in the apparatus to give simultaneously a single phase and a reasonable output of $Cp'Mn(CO)_2(\eta^2\text{-}H_2)$. These difficulties convinced us to find more amenable starting materials (i.e., those which could be isolated as solids).

N-Donor Ligands. The first compound which we investigated, $Cp'Mn(CO)_2(pyr)$, proved to be insoluble in both $scCO_2/H_2$ and scC_2H_6/H_2. Therefore, a heterogeneous reaction was attempted by a procedure similar to that used for the reaction of $CpMn(CO)_2(LDPE)$ powder with H_2. Powdered $Cp'Mn(CO)_2(pyr)$ was loaded into an extraction vessel and warmed under flowing scC_2H_6/H_2 to 78 °C. Previous experiments with polyethylene had already shown that $Cp'Mn(CO)_2(\eta^2\text{-}H_2)$ was unstable above this temperature. The hope was that solid $Cp'Mn(CO)_2(pyr)$ would react with the H_2 to give $Cp'Mn(CO)_2(\eta^2\text{-}H_2)$, which is soluble in scC_2H_6/H_2. However, no $Cp'Mn(CO)_2(\eta^2\text{-}H_2)$ was detectable by on-line FTIR.

Alkyl substituents are well-known to improve the solubility of pyridine complexes,[12] and we found that $Cp'Mn(CO)_2(tbp)$ (tbp = tertiary isobutylpyridine) and $Cp'Mn(CO)_2(bpp)$ (bpp = 4-(1-butylpentyl)pyridine) were indeed soluble in $scCO_2/H_2$. $Cp'Mn(CO)_2(bpp)$ was an air-sensitive liquid, which proved very difficult to separate from excess bpp (bp = 265 °C) after its synthesis. FTIR was used to monitor the effects of heating these compounds under $scCO_2/H_2$ in a static cell. Both compounds were thermally too stable to react at <70 °C.

The butyronitrile complex, $Cp'Mn(CO)_2(NC_4H_7)$, was also rather thermally stable and reacted no better in $scCO_2/H_2$ than did the pyridine complexes. We, therefore, decided to switch to Cp* ($Cp^* = C_5Me_5$) derivatives because the greater electron-donating power of Cp* might increase the thermal stability of the dihydrogen complex and, thus, permit reactions to be carried out at higher temperatures without decomposition. The on-line FTIR spectra showed that the thermal reaction of $Cp^*Mn(CO)_2(NC_4H_7)$ with H_2 did indeed generate detectable amounts of $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$, but there was an additional strong IR band at 1785 cm^{-1}. Furthermore, the precipitated product was green (the dihydrogen compound is pale yellow). It was quickly realized that the reaction was generating $Cp^*_2Mn_2(\mu\text{-}CO)_3$, a green compound first isolated[13] by Herrmann and coworkers by evaporation of a THF solution of $Cp^*Mn(CO)_2(THF)$.

Given the problems of generating $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$ in the thermal flow reactor, it was decided to attempt

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[10] Clarke, M. J.; Howdle, S. M.; Jobling, M.; Poliakoff, M. *J. Am. Chem. Soc.* **1994**, *116*, 8621.

[11] The work in ref 10 was carried out with thin hot-pressed films of LDPE. We have shown that similar impregnation/photolysis experiments can be carried out using powdered LDPE, which would be needed for preparative-scale experiments in a flow reactor (Lee, P. D. Ph.D. Thesis, University of Nottingham, U.K., 1996). Preliminary experiments showed that similar reactions were possible with polybutadiene, which has a much greater concentration of C=C bonds than LDPE. However, polybutadiene is a rubbery material, and although possible, preparing powdered polybutadiene was too lengthy a process to make this a viable route to $(C_5R_5)Mn(CO)_2(\eta^2\text{-}H_2)$.

[12] Fluorination is also known to increase the solubility in $scCO_2$, and $Cp'Mn(CO)_2$(fluoropyridine) was synthesized. However, it proved to be too pyrophoric to be useful in these reactions. For a recent review of the solubility of chelating ligands and metal-containing compounds in $scCO_2$, see: Smart, N. G.; Carleson, T.; Kast, T.; Clifford, A. A.; Burford, M. D.; Wai, C. M. *Talanta* **1997**, *44*, 137.

[13] Herrmann, W. A.; Serrano, R.; Weichmann, J. *J. Organomet. Chem.* **1983**, *246*, C57.

[14] We also tried to synthesize $Cp^*_2Mn_2(CO)_3$ in the flow reactor using $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$ as a labile intermediate The flow reactor was modified to incorporate a UV photolysis cell similar to that used in ref 5 prior to the heated tube. It was, therefore, possible to perform successive photochemical and thermal reactions in the same run. We intended to synthesize $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$ from $Cp^*Mn(CO)_3$ and $scCO_2/H_2$ and then to immediately decompose it thermally in the oil bath to yield $Cp^*_2Mn_2(CO)_3$. On-line FTIR spectra confirmed that near 100% conversion to $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$ could be achieved, but when the flow was diverted through a 1 mL coil in the oil bath at 101 °C, very little $Cp^*_2Mn_2(CO)_3$ was produced; instead, the major decomposition product was $Cp^*Mn(CO)_3$. The problem appeared to be that the CO liberated during the photochemical synthesis of $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$ was still present in the solution when it was heated in the oil bath. Therefore, $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$ reacted with CO to regenerate $Cp^*Mn(CO)_3$. By contrast, the reaction of $Cp^*Mn(CO)_2(NC_4H_7)$ with H_2 in the flow reactor produced $Cp^*_2Mn_2(CO)_3$ because there was no excess CO in the system (the same applies to Herrmann's original synthesis[13] of the dimer from $Cp^*Mn(CO)_2(THF)$).

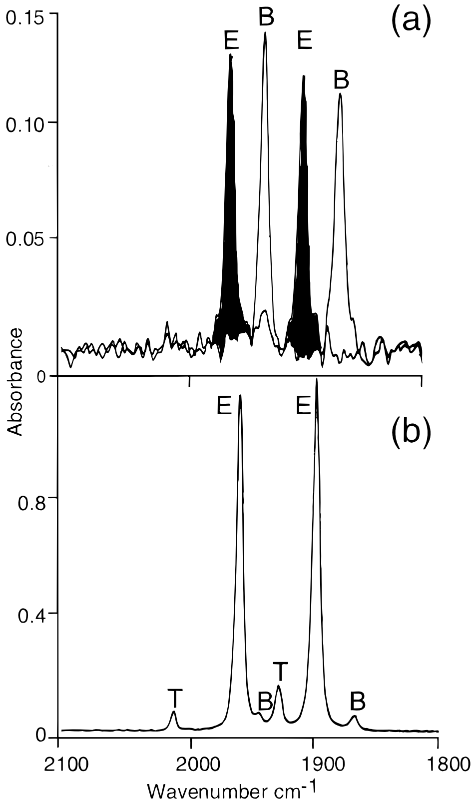
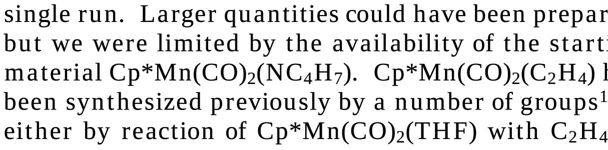


Figure 2. IR spectra illustrating the generation of Cp*Mn(CO)$_2$(C_2H_4) (E) from the butyronitrile complex Cp*Mn(CO)$_2$(NC_4H_7) (B). (a) Two superimposed traces recorded in scC_2H_4 prior to and after reaction at 100 °C in the continuous flow reactor (see Figures 1a and 8). Thermal reaction causes the almost complete disappearance of the bands of B and a corresponding growth of E. (b) IR spectrum of the solid product isolated from the reactor and redissolved in *n*-pentane saturated with C_2H_4. Bands marked T are due to Cp*Mn(CO)$_3$.

the synthesis of a more stable complex Cp*Mn(CO)$_2$(C_2H_4) in scC_2H_4, eq 2. Cp*Mn(CO)$_2$(C_2H_4) was synthesized in good yield by this route. Figure 2 shows the spectrum of the isolated product as well as those recorded during the on-line monitoring of the reaction. Up to 150 mg of Cp*Mn(CO)$_2$(C_2H_4) was produced in a single run. Larger quantities could have been prepared, but we were limited by the availability of the starting material Cp*Mn(CO)$_2$(NC_4H_7). Cp*Mn(CO)$_2$(C_2H_4) has been synthesized previously by a number of groups[15,16] either by reaction of Cp*Mn(CO)$_2$(THF) with C_2H_4 or by photolysis of Cp*Mn(CO)$_3$ in pentane doped with C_2H_4. Our preparation proved that the thermal reactor does indeed work and, even without optimization, can produce relatively pure compounds without further workup. However, our overall conclusion was that, in general, N-donor ligands are too strongly-bound to be good starting materials for the synthesis of Cp*Mn(CO)$_2$(η^2-H_2).



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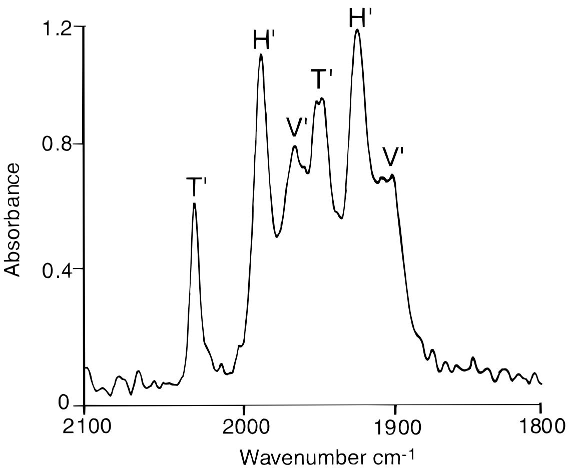

Figure 3. On-line IR spectrum recorded during the thermal reaction of Cp′Mn(CO)$_2$(EVE) in scCO_2/H_2 at 56 °C in the continuous thermal reactor (see Figures 1a and 8). The bands are labeled as follows: H′, Cp′Mn(CO)$_2$(η^2-H_2); V′, Cp′Mn(CO)$_2$(EVE); T′, Cp′Mn(CO)$_3$.

Alkene Ligands. Cp*Mn(CO)$_2$(C_2H_4) was found to be stable in scCO_2 and reluctant to exchange C_2H_4 thermally for other ligands (e.g., HSiEt$_3$), even at 70 °C. However, Cp*Mn(CO)$_2$(HSiEt$_3$) could be formed rapidly when Cp*Mn(CO)$_2$(C_2H_4) was photolyzed in scCO_2/HSiEt$_3$ at room temperature. Therefore, it was clear that if alkene complexes were to be useful starting materials for thermal reactions, the alkene would have to be less strongly bound than C_2H_4. Our search for suitable ligands led to a report[16] by Herberhold and coworkers that the methyl vinyl ether complex CpMn(CO)$_2$(C_2H_3OMe) decomposed at 22 °C. Unfortunately, C_2H_3OMe is a gas at room temperature, thereby complicating the preparation of CpMn(CO)$_2$(C_2H_3OMe). By contrast, ethyl vinyl ether (EVE), C_2H_3OEt, is a liquid under ambient conditions. We have, therefore, synthesized two new compounds, Cp$^\pm$Mn(CO)$_2$(EVE) (Cp$^\pm$ = Cp* or Cp′), see Experimental Section.

Cp′Mn(CO)$_2$(EVE) was passed through the thermal flow reactor with scCO_2/H_2. With the oil bath at 50 °C, bands of Cp′Mn(CO)$_2$(η^2-H_2) were apparent in the online FTIR spectra. At 56 °C, the ν(C−O) bands of Cp′Mn(CO)$_2$(η^2-H_2) were more intense than those of either Cp′Mn(CO)$_2$(EVE) or Cp′Mn(CO)$_3$, see Figure 3. Heating to higher temperatures reduced the yield of Cp′Mn(CO)$_2$(η^2-H_2), and little improvement could be achieved by varying any of the other reactor parameters.

The reason for this poor conversion can be understood from the spectra in Figure 4, which were recorded for reactions in a static cell. Figure 4a shows the results from the reaction of Cp*Mn(CO)$_2$(EVE) with H_2 in scCO_2. Unlike the reaction in the flow reactor, the reaction in the cell went almost to completion. At 38 °C, the conversion to Cp*Mn(CO)$_2$(η^2-H_2) was almost quantitative with formation of only small amounts of Cp*Mn(CO)$_3$. Moreover, the presence of the two isos-

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(15) Kögler, H. P.; Fischer, E. O. *Z. Naturforsch., B* **1960**, *15*, 676. Alt, H.; Herberhold, M.; Kreiter, C. G.; Strack, H. *J. Organomet. Chem.* **1974**, *77*, 353.

(16) Herberhold, M.; Wiedersatz, G. O.; Kreiter, C. G. *J. Organomet. Chem.* **1976**, *104*, 209.

(17) Spectra are recorded in a spectroscopic cell, previously placed in a glovebox to allow 1−2 mg of the EVE complex to be added, then pressurized with N_2 (500 psi) and CO_2 to give a total pressure of 3000 psi.

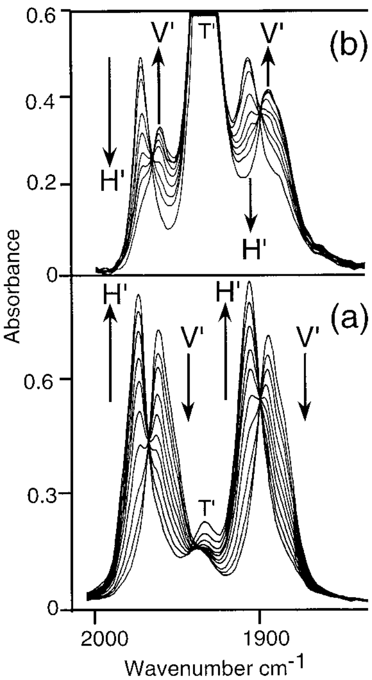
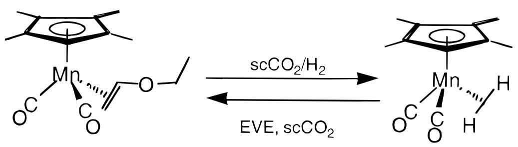


Figure 4. IR spectra illustrating the reversibility of the reaction between Cp′Mn(CO)$_2$(EVE) and H$_2$. (a) (lower part of figure) Spectra recorded over a period of 255 min, showing the thermal conversion of Cp′Mn(CO)$_2$(EVE), V′, to Cp′Mn(CO)$_2$(η^2-H$_2$), H′, at 38 °C in scCO$_2$/H$_2$. The reaction is almost quantitative, with only a small amount of Cp′Mn(CO)$_3$, T′, formed at the end of the reaction. (b) Spectra illustrating the reverse reaction, Cp′Mn(CO)$_2$(η^2-H$_2$) + EVE at 18 °C. (This temperature is below T_c for CO$_2$, but at the pressure used (*ca.* 2000 psi), the cell will be filled entirely with *liquid* CO$_2$.) Again, the reaction is almost quantitative, as shown by the isosbestic points. The band of Cp′Mn(CO)$_3$, T′, is much stronger in this case because Cp′Mn(CO)$_2$(η^2-H$_2$) was generated *in situ* by photolysis of Cp′Mn(CO)$_3$ in an scCO$_2$/H$_2$ mixture, prior to monitoring the reaction with EVE.

bestic points in the spectra suggests that little decomposition of the η^2-H$_2$ product was occurring. By contrast, the spectra in Figure 4b show that the *reverse reaction* proceeds equally smoothly but at a lower temperature. At only 18 °C, Cp*Mn(CO)$_2$(η^2-H$_2$) reacts with EVE to generate Cp*Mn(CO)$_2$(EVE) almost quantitatively, again with isosbestic points in the spectra. Thus, although the η^2-H$_2$ complex is somewhat more reactive toward EVE than the EVE complex is toward H$_2$, the EVE and dihydrogen compounds are effectively in equilibrium, eq 3. Under the conditions of Figure 4a,



(3)

the equilibrium favors the dihydrogen complex merely because H$_2$ is in great excess. In the thermal flow reactor, the reactants only spend a short period of time in the heated region. Thus, high rates of reaction are required if all the starting material is to react before it leaves the heated coil. The problem is that the EVE compound is thermodynamically more stable than the η^2-H$_2$ compound. This means that rapid formation of the η^2-H$_2$ compound requires a relatively high temperature, conditions under which the decomposition rate of the η^2-H$_2$ compound is also high. Thus, it is unlikely that the conditions in our simple flow reactor could be optimized for quantitative formation of Cp′Mn(CO)$_2$(η^2-H$_2$). Our conclusion was that it might be better to carry out the reaction in a *semiflow reactor* where the residence time could be much longer, and consequently, the reaction temperature much lower than in the flow reactor. The reaction would take longer, but the thermal decomposition of the η^2-H$_2$ product would be reduced or even eliminated.

Reactions in Semiflow Reactors. Vinyl Ether Precursors. Traditionally, most high-pressure reactions are run as batch processes in autoclaves or similar vessels. Our approach has to differ because we need to recover the products by *controlled* rapid expansion of the fluid at the end of the reaction. The principle of our semiflow reactor is shown in Figure 1b. The design is based on our method[8] previously used for recovering the products of photochemical C−H activation of scC$_2$H$_6$ by Cp*Ir(CO)$_2$. The major development has been to carry out the reaction in a variable-volume view cell[18,19] fitted with a piston which drives the supercritical solution through the expansion valve at the end of the reaction. Although the supercritical solution can be observed through the window of the view cell in the semiflow reactor, currently it is not possible to record FTIR spectra in situ. However, the piston in the cell can be used to drive small aliquots at regular intervals into an on-line high-pressure FTIR cell so that the progress of the reaction can be monitored. Thus, the semiflow reactor allows us to combine the flexible reaction time of a batch reactor with the monitoring and rapid product recovery of a flow system.

Our initial test of the semiflow reactor involved the synthesis of Cp*Mn(CO)$_2$(N$_2$). Although the Mn dinitrogen complexes are more thermally stable than the corresponding dihydrogen compounds, they are conventionally prepared by a multistage route.[20] The closely related CpMn(CO)$_2$(N$_2$) was the first stable carbonyl dinitrogen compound to be isolated,[20] and we have since prepared it photochemically in a supercritical flow reactor.[5] Figure 5a shows a series of spectra monitoring the reaction of Cp*Mn(CO)$_2$(EVE) with N$_2$ in scCO$_2$, and Figure 5b shows the spectrum of the recovered solid, which is largely Cp*Mn(CO)$_2$(N$_2$). The only impurities are residual Cp*Mn(CO)$_2$(EVE) and a small amount of Cp*Mn(CO)$_3$, which was probably a contaminant in the starting material.

The reaction of Cp*Mn(CO)$_2$(EVE) with N$_2$ was reversible. At 18 °C, Cp*Mn(CO)$_2$(N$_2$) reacts almost quantitatively with EVE in scCO$_2$ (not illustrated). Thus, as with the dihydrogen complex, the EVE and dinitrogen complexes are so close in energy that the equilibrium between them can be manipulated at will

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(18) The design of this cell is described in detail in ref 1, p 92.

(19) The same vessel had already been used as a reservoir in our flow reactor, see Experimental Section. The view cell can be safely cooled to well below 0 °C and can be conveniently used as a “stainless-steel Schlenk tube” to transfer material from the conventional reaction to the supercritical apparatus.

(20) Sellmann, D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 919.

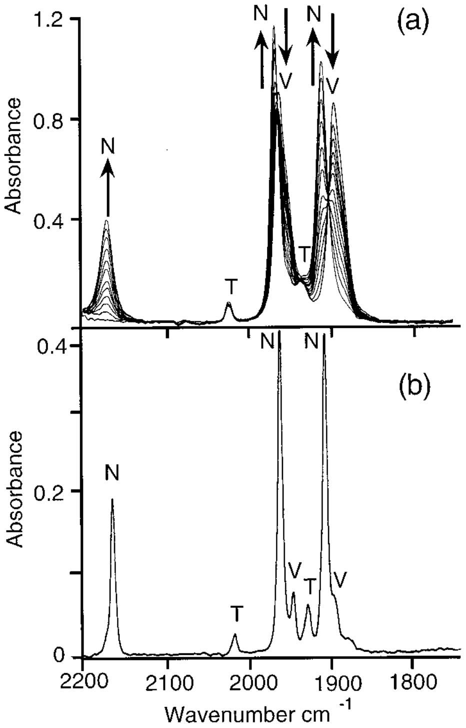
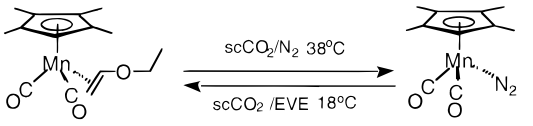


Figure 5. (a) Continuous FTIR monitoring in the ν(C−O) region, illustrating the thermal batch reaction of Cp*Mn(CO)$_2$(EVE) with an scCO$_2$/N$_2$ solution at 38 °C in a spectroscopic cell.[17] FTIR spectra were recorded at 10 min intervals over a period of 300 min. The bands are labeled as follows: N, Cp*Mn(CO)$_2$(N$_2$); V, Cp*Mn(CO)$_2$(EVE); and T, Cp*Mn(CO)$_3$. Wavenumbers are given in Table 1. (b) IR spectrum of the solid product isolated from the same reaction, carried out in the semiflow reactor (see Figures 1b and 9) and redissolved in *n*-pentane at room temperature.

in scCO$_2$, eq 4. By contrast, the reaction of Cp*Mn(CO)$_2$(EVE) with H$_2$ in the batch reactor was not as clean as the reaction with N$_2$, presumably because the dihydrogen complex is more labile than the dinitrogen complexes. Cp*Mn(CO)$_2$(η^2-H$_2$) is pale yellow, but the solid reaction product was *green* and its spectrum, Figure 6a, showed disappointing amounts of residual starting material, Cp*Mn(CO)$_3$ and Cp*$_2$Mn$_2$(μ-CO)$_3$. Therefore, there was still a need to find a more effective starting material for the preparation of the η^2-H$_2$ complex.



(4)

Dinitrogen/Dihydrogen Ligand Exchange. Recent work at Nottingham has involved the use of high-pressure photoacoustic calorimetry to estimate M−L bond strengths in dihydrogen and dinitrogen complexes.[21] Experiments in heptane[21b] indicated that the Cr−(η^2-H$_2$) (60 ± 4 kJ mol^{-1}) and Cr−N$_2$ (66 ± 4 kJ mol^{-1}) bond strengths in (η^6-C$_6$H$_6$)Cr(CO)$_2$L) were surprisingly similar. These results suggested that Cp*Mn(CO)$_2$(N$_2$) might react with H$_2$ in scCO$_2$ to form Cp*Mn(CO)$_2$(η^2-H$_2$). Such ligand exchange would have obvious potential as a room temperature synthesis of Cp*Mn(CO)$_2$(η^2-H$_2$).

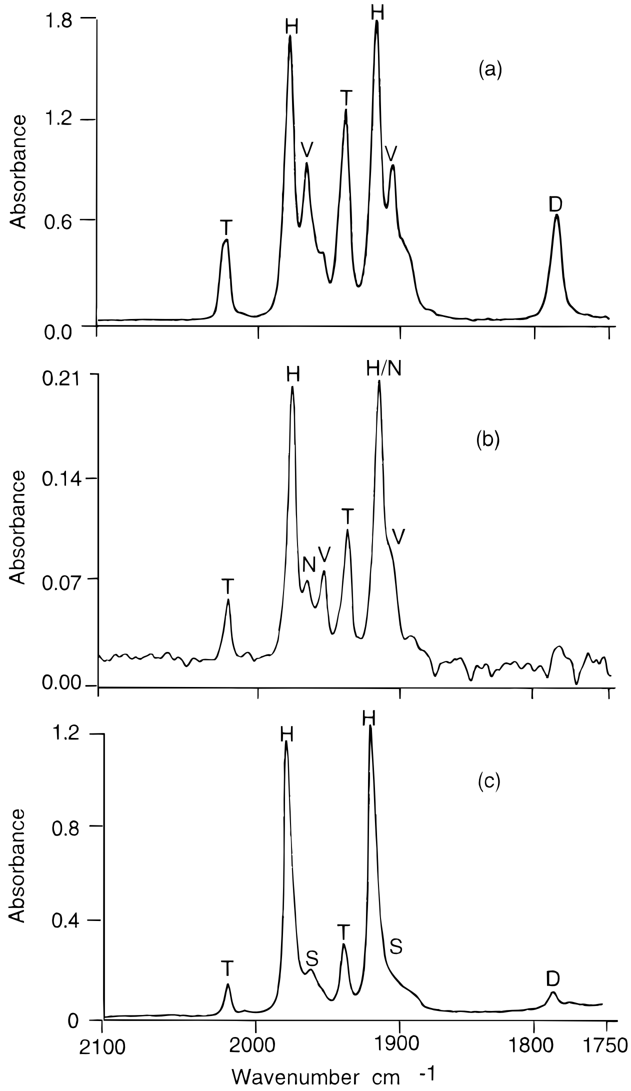


Figure 6. IR spectra (*n*-pentane solution) comparing the purity of the products isolated from different synthetic routes to Cp*Mn(CO)$_2$(η^2-H$_2$). In all spectra, bands are assigned as follows: V, Cp*Mn(CO)$_2$(EVE); H, Cp*Mn(CO)$_2$(η^2-H$_2$); T, Cp*Mn(CO)$_3$; D, Cp$_2$*Mn$_2$(CO)$_3$. (a) Products formed in the semiflow reactor from Cp*Mn(CO)$_2$(EVE) in scCO$_2$/H$_2$. (b) IR spectrum of the products formed from the sequential reaction of Cp*Mn(CO)$_2$(EVE) with scCO$_2$/N$_2$ as in Figure 5a followed by reaction of Cp*Mn(CO)$_2$(N$_2$) with scCO$_2$/H$_2$ at room temperature for 4 h. Note that high pressures of H$_2$ depress T_c for CO$_2$/H$_2$ mixtures below room temperature. (c) IR spectrum of the products formed from the thermal reaction of Cp*Mn(CO)$_2$(η^2-H-SiEt$_3$), S, with scCO$_2$/H$_2$ over a period of 4 h. Comparison of the spectra shows that (c) is by far the most successful route for the synthesis and isolation of Cp*Mn(CO)$_2$(η^2-H$_2$).

There are only a few examples of the thermal reaction of a dinitrogen complex with dihydrogen.[22] The converse reaction of dihydrogen compounds with N$_2$ is far more common. Indeed, we have shown[5,21] that Cp*Mn(CO)$_2$(η^2-H$_2$) reacts with N$_2$ in scXe and scCO$_2$. N$_2$ will

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[21] (a) Walsh, E. F.; Popov, V. K.; George, M. W.; Poliakoff, M. *J. Phys. Chem.* **1995**, *99*, 12016. (b) Walsh, E. F.; George, M. W.; Goff, S. E. J.; Nikiforov, S. M.; Popov, V. K.; Sun, X. Z.; Poliakoff, M. *Ibid.* **1996**, *100*, 19425.

[22] Gonzalez, A. A.; Hoff, C. D. *Inorg. Chem.* **1989**, *28*, 4295. Cooper, A. I.; Poliakoff, M. *Chem. Phys. Lett.* **1993**, *212*, 611. Albertin, G.; Antoniutti, S.; Baldan, D.; Bordignon, E. *Inorg. Chem.* **1995**, *34*, 6205.

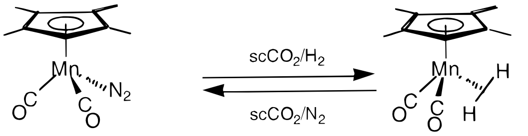
Table 1. Wavenumbers (cm^{-1}) of ν(C−O) Bands of the Cp*MnCO)$_2$^{w}L and Related Complexes Discussed in This Paper

compound		solvent		
ring	L	THF	pentane	supercritical[a]
Cp′	THF	1924.7, 1847.6		
Cp′	pyr	1920.2, 1849.3	ns	
Cp′	tbp	1918.8, 1847.5	ns	
Cp′	bpp	1919.0, 1847.5	ns	
Cp′	η^2-H_2	1971.5, 1903.7	1982.8, 1922.5	1980.5, 1917.1
Cp*	η^2-H_2		1963.2, 1897.7	1967.0, 1907.1
Cp*	C_2H_4		1958.5, 1898.9	1959.5,[c] 1899.9[c]
Cp*	THF	1906.2, 1832.7		
Cp*	NC_4H_7		1928.5, 1868.9	1931.1,[c] 1869.6[c]
Cp*	η^2-N_2		2146.5 ν(N−N), 1958.0, 1909.2	2152.1[b] ν(N−N), 1959.6,[b] 1907.2[b]
Cp*	EVE		1955.0, 1896.0	1953.7, 1892.0
Cp*	η^2-H−$SiEt_3$		1951.9, 1893	1948.2, 1886.1

[a] Unless otherwise stated, $scCO_2/H_2$ was 3000 psi total. Precise wavenumbers of bands show a modest *ca.* 1 cm^{-1} shift, dependent on temperature and pressure. [b] $scCO_2/N_2$. [c] scC_2H_4; ns = not soluble. Note: The corresponding ν(C−O) bands in LDPE for Cp′Mn(CO)$_2$(pendant C=C) 1956.7, 1897.4 cm^{-1}; Cp′Mn(CO)$_2$(terminal) 1960.8, 1902.7 cm^{-1}; see also ref 10.

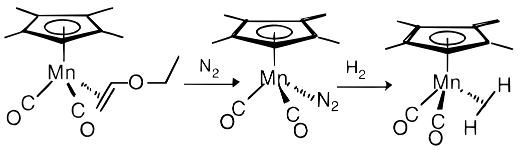
always be a stronger ligand than η^2-H_2 on purely enthalpic considerations, but in some circumstances, η^2-H_2 can be preferred from an entropic point of view. Therefore, the difference in the stability of the two types of complex can be less than expected.

The reaction between Cp*Mn(CO)$_2$(N_2) and H_2 had not been previously investigated in supercritical solution. A sample of Cp*Mn(CO)$_2$(N_2) was prepared in the semiflow reactor and was precipitated directly into a high-pressure IR cell. Once 1−2 mg of the complex had been deposited in the cell, it was filled with 1000 psi of H_2 and then to 3000 psi using CO_2. FTIR spectra (not illustrated) were recorded at 10 min intervals, and the reaction was monitored at room temperature by the disappearance of the ν(C−O) a′ and ν(N−N) stretching bands of Cp*Mn(CO)$_2$(N_2) and the concurrent growth of the ν(C−O) a′ stretch of Cp*Mn(CO)$_2$(η^2-H_2), see Table 1 for wavenumbers. There was good conversion to the dihydrogen complex, although the formation of some Cp*Mn(CO)$_3$ was observed during the later stages of the reaction. Thus, as in the case of the EVE complex, we can use the relative concentrations of H_2 and N_2 in $scCO_2$ to manipulate the equilibrium between Cp*Mn(CO)$_2$(N_2) and Cp*Mn(CO)$_2$(η^2-H_2), eq 5.



(5)

Two-Stage Synthesis of Cp*Mn(CO)$_2$(η^2-H_2). The conversions of Cp*Mn(CO)$_2$(EVE) into Cp*Mn(CO)$_2$(N_2) and of Cp*Mn(CO)$_2$(N_2) into Cp*Mn(CO)$_2$(η^2-H_2) both appeared to be quantitative on a small scale in our high-pressure IR cells. This prompted us to attempt a two-stage synthesis of Cp*Mn(CO)$_2$(η^2-H_2) on a larger scale in the semiflow reactor. The overall reaction is shown in eq 6. Cp*Mn(CO)$_2$(N_2) was prepared in the view cell



(6)

by reaction of Cp*Mn(CO)$_2$(EVE) with N_2 in $scCO_2$, but the compound was not vented by expansion at the end of the reaction. Instead, the $scCO_2/N_2$ mixture was slowly vented with care being taken to minimize the loss of material. The cell was immediately re-pressurized with H_2 (800 psi) and CO_2 (2480 psi) and was then left at room temperature while the reaction proceeded to Cp*Mn(CO)$_2$(η^2-H_2). The reaction was monitored at regular intervals by FTIR. Once the reaction was complete, the total contents of the cell were expanded rapidly and the solid material collected in an argon-filled Schlenk tube. The solid was dissolved in degassed pentane and analyzed by FTIR.

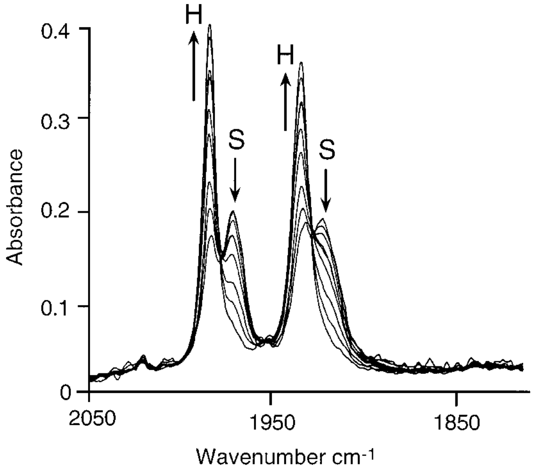
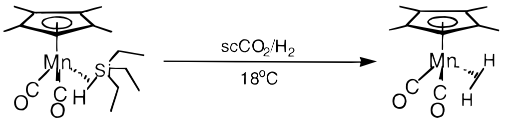


Figure 7. IR spectra of Cp*Mn(CO)$_2$(η^2-H-$SiEt_3$), S, in $scCO_2/H_2$ recorded during the room temperature reaction to form Cp*Mn(CO)$_2$(η^2-H_2), H. A small sample of the reaction mixture was pushed into the on-line FTIR cell (see Figure 9) to allow the continuous monitoring of the reaction, essential to avoid formation of the stable complex Cp*Mn(CO)$_3$ in the later stages of the reaction. The reaction took *ca.* 4 h to reach completion.

This route is successful in principle. Figure 6b shows a typical spectrum of the products; the ν(CO) bands of Cp*Mn(CO)$_2$(η^2-H_2) are indeed the most intense, and there is no trace of Cp*$_2$Mn$_2$(CO)$_3$. On the other hand, there are significantly intense bands of Cp*Mn(CO)$_3$, Cp*Mn(CO)$_2$(N_2), and Cp*Mn(CO)$_2$(EVE). The problem was that all of the steps in the synthesis are carried out in the same vessel and that none of these steps go to 100% completion. Hence, all of the impurities from each stage accumulate to contaminate the final product. The greatest drawback, however, was that the overall process was extremely time consuming, typically three whole days from the preparation of Cp*Mn(CO)$_2$(EVE) to the isolation of the final solid. Probably, one could make a larger amount of Cp*Mn(CO)$_2$(η^2-H_2) by running our original photochemical flow reactor[5] continuously over the same period, even allowing for clean up of the windows at regular intervals! Thus, we continued to search for a better precursor which would react directly with H_2.

Silane Complexes. Previous attempts to isolate Cp*Mn(CO)$_2$(η^2-HSiEt$_3$) have demonstrated the thermal lability of this complex.[23] We have found that the compound can be prepared as a dark orange oil which is readily soluble in CO_2. A small-scale test reaction of Cp*Mn(CO)$_2$(η^2-HSiEt$_3$) with H_2/scCO$_2$ was carried out in an FTIR cell. The reaction was relatively fast, taking only 50 min at 18 °C, eq 7. However, it was again noticed that decomposition of Cp*Mn(CO)$_2$(η^2-H_2) began soon *after* completion of the reaction. The precise reaction time in the semiflow reactor proved to be surprisingly sensitive to the exact conditions, so that on-line FTIR monitoring was essential, Figure 7. Typically, the reaction was complete within 3 h. Figure 6c shows the spectrum of the product isolated from a reaction in the semiflow reactor. The purity is considerably better than that obtained from the reaction of Cp*Mn(CO)$_2$(EVE), but the sample clearly contains some Cp*$_2$Mn$_2$(CO)$_3$. This is consistent with the greenish tinge of the precipitated solid.



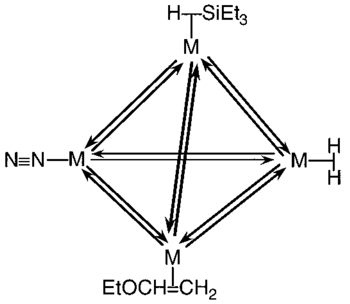
(7)

Conclusions

Cp*Mn(CO)$_2$(η^2-H_2) is one of the simplest dihydrogen complexes yet it is one of the more stable. We have shown that Cp*Mn(CO)$_2$(η^2-HSiEt$_3$) is clearly the best precursor for the thermal synthesis of Cp*Mn(CO)$_2$(η^2-H_2), both in terms of purity and convenience. There are no obvious chemical reasons why the procedure should not be scaled up, and larger variable-volume view cells are available. Thus, the route via Cp*Mn(CO)$_2$(η^2-HSiEt$_3$) should provide more widespread access to this interesting dihydrogen compound.

However, our experiments have wider implications for supercritical chemistry. The four principal ligands considered in this paper, η^2-H$_2$C=CHOEt (EVE), η^2-H−SiEt$_3$, N_2, and H_2, all bind weakly to the Mn center in the CpMn(CO)$_2$ moiety. We have shown that, within a supercritical solution, the compounds of these ligands are effectively in equilibrium. Furthermore, the properties of the supercritical solvent allow conditions to be sufficiently varied widely that the position of the equilibria can be manipulated to force exchange between any pair of these ligands and, hence, to favor the formation of a particular compound, see Scheme 1. Such manipulation of gaseous ligands like N_2 and H_2 would be difficult if not impossible in more conventional solvents, where the solubility of gases is limited. Our observations, therefore, have potentially significant implications for reactions involving gases and homogeneous organometallic catalysts (e.g., hydrogenation, carbonylation, or hydroformylation). Supercritical solvents permit the relative concentrations of the components in these reactions to be varied much more widely than in conventional conditions. Although there have been a number of important studies on homogeneous catalysis in supercritical media,[24] many chemists may not have appreciated that the supercritical environment can provide a substantial increase in the range of reaction conditions. The possibilities are waiting to be explored.

Scheme 1. Schematic Representation of the Facile Interchange of the Ligands in Cp*Mn(CO)$_2$^{w}L Complexes in scCO$_2$ Solution[a]



[a] In this scheme M represents the Cp*Mn(CO)$_2$ moiety. See text for conditions of reactions. In principle, this tetrahedron could be extended to include other weakly-bound ligands, e.g., THF, which also undergo facile exchange.

Experimental Section

Conventional Synthesis of Starting Materials. All reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Solvents were distilled under N_2 with the appropriate drying agents. Cp*Mn(CO)$_3$ was prepared by Dr. S. Seebald. For a typical procedure, see ref 25. Reactants were purchased from Aldrich and used without further purification. IR spectra were recorded on a Nicolet 205 FTIR spectrometer.

General Procedure for Reaction of Cp′Mn(CO)$_3$ and Cp*Mn(CO)$_3$ with ^{w}L. The procedure described here proved suitable for Cp*Mn(CO)$_2$(C$_2$H$_3$OEt), referred to as Cp*Mn(CO)$_2$(EVE), Cp′Mn(CO)$_2$(pyr), Cp′Mn(CO)$_2$(tbp), Cp′Mn(CO)$_2$(bpp), and Cp*Mn(CO)$_2$(NC$_4$H$_7$) and will not be repeated in detail for each case. Where the starting material Cp*Mn(CO)$_3$ is used, the solid is added to the quartz irradiation vessel prior to evacuation. In each case, the same volume of THF solvent is added in order to ensure complete coverage of the Hg lamp inside the vessel. The quantity of the starting material used for each complex varied slightly, and hence, differing reaction times were needed to achieve complete conversion as indicated by regular FTIR solution spectrum analysis.

Preparation of Cp*Mn(CO)$_2$(EVE). An 80 mg portion of Cp*Mn(CO)$_3$ was added to an evacuated and argon-filled two-necked quartz irradiation vessel. A 150 mL portion of degassed and freshly-distilled THF was added to the vessel by cannula. With a gentle stream of argon bubbling through the solution and magnetic stirring, the solution was irradiated with a 120 W Hg UV lamp for 1 h. To prevent thermal

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[23] Hill, R. H.; Wrighton, M. S. *Organometallics* **1987**, *6*, 632.

[24] Rathke, J. W.; Klingler, R. J.; Krause, T. R. *Organometallics* **1991**, *10*, 1350. Burk, M. J.; Feng, S.; Gross, M. F.; Tumas, W. *J. Am. Chem. Soc.* **1995**, *117*, 827. Kainz, S.; Koch, D.; Baumann, W.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1628.

[25] Calabro, D. C.; Hubbard, J. L.; Belvins, C. H.; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839.

decomposition of the product, an ice bath is placed around the vessel and an EtOH/H_2O cooling mixture is flowed through the internal double walls of the vessel using an Endocol RTE-9B refrigerated circulating bath set at 3 °C. After 1 h, the lamp is switched off and the reaction mixture shows a color change from yellow to bright red. An FTIR solution spectrum is taken to confirm complete conversion to $Cp^*Mn(CO)_2(THF)$. A 5-fold excess of ethyl vinyl ether is added to the vessel by syringe. The ice bath is removed, and with a continual argon purge and stirring, the reaction mixture is allowed to reach room temperature in the dark. Regular solution FTIR spectra are recorded to monitor the extent of reaction, and after *ca.* 4 h, the conversion to $Cp^*Mn(CO)_2(EVE)$ is complete. A further color change from red to orange is observed. The $Cp^*Mn(CO)_2$(EVE) solution is transferred by cannula into an evacuated and argon-filled Schlenk tube, where the THF is removed by vacuum to yield the orange solid $Cp^*Mn(CO)_2(EVE)$. No further work-up was attempted, and each complex was used as isolated. (Yields were close to quantitative with purity greater than 95%, as measured by FTIR spectroscopy.)

Preparation of $Cp^*Mn(CO)_2(HSiEt_3)$. Using the same apparatus, 81 mg of $Cp^*Mn(CO)_3$ was dissolved in 25 mL of triethylsilane and 100 mL of degassed, freshly distilled pentane. After 30 min of irradiation, a FTIR solution spectrum shows complete conversion to $Cp^*Mn(CO)_2(HSiEt_3)$. The excess triethylsilane and pentane solvent are removed by vacuum to give a dark orange oil. The oil was transferred directly to the supercritical apparatus, see below, and the purity was estimated from the FTIR spectrum (>95%). FTIR analysis confirms this to be $Cp^*Mn(CO)_2(HSiEt_3)$ by comparison of the ν(CO) band positions with those previously reported in the literature.[23]

Safety Hazard! *The experiments described in this paper involve the use of relatively high pressures and require equipment with the appropriate pressure rating. It is the responsibility of individual researchers to verify that their particular apparatus meets the necessary safety requirements. The individual components which were described in our previous paper[5] work well, but they are not necessarily the only equipment of this type available nor the most suitable for the purpose.*

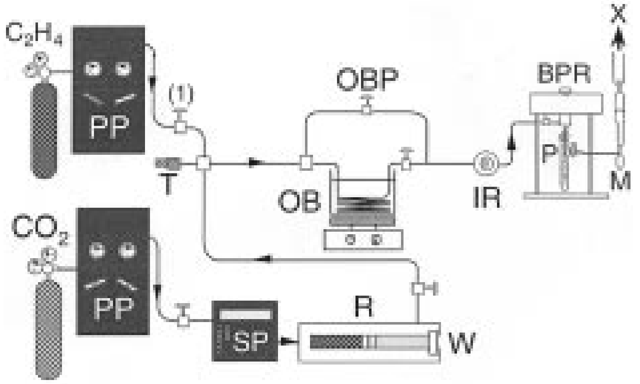

Figure 8. Layout of the continuous thermal flow reactor for the synthesis and subsequent isolation of $Cp^*Mn(CO)_2(C_2H_4)$ in scC_2H_4. The components are labeled as follows (alphabetically): BPR, back-pressure regulator (Jasco model 880-81); C_2H_4, ethene cylinder; CO_2, carbon dioxide cylinder; IR, infrared cell; M, soap-film flow meter; OB, oil bath; OBP, oil bath bypass; P, solid product, $Cp^*Mn(CO)_2(C_2H_4)$; PP, pneumatic pump (NWA model PM101); R, reservoir for supercritical solution, in this case a variable-volume cell is used, the volume of which is altered by means of a piston; SP, syringe pump (Brownlee Lab Microgradient) containing $scCO_2$ to drive the piston of the variable-volume cell; T, pressure transducer (RDP Electronics); W, sapphire window of the variable-volume cell; X, exhaust vent. 1 denotes the main control valve in the reactor, which is used to both fill and dissolve the contents of R and dilute the solution as required. A slight modification of this layout to include H_2 (not illustrated) was made for the reaction of $Cp'Mn(CO)_2$-EVE with $scCO_2/H_2$, as in Figure 3. (Note that this figure is not drawn to scale.)

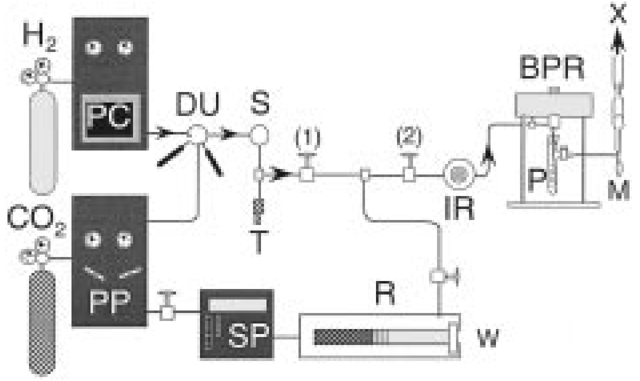

Figure 9. Layout of the semiflow reactor for the synthesis and isolation of $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$ from $Cp^*Mn(CO)_2{}^{w}L$ (^{w}L = labile ligand) and H_2 in $scCO_2$. The reactor is very similar to that shown in Figure 8 but without the oil bath. Here we use the variable-volume, two-compartment reservoir, R, as a thermal reactor. Furthermore, the gas-handling stage now includes two pumps and a mixing unit. The components are labeled as in Figure 8 in addition to DU, gas dosage unit (NWA); H_2, hydrogen cylinder; PC, pneumatic compressor (NWA model CU105); S, mixer with magnetic stirrer (Kontron M491). 1 and 2 denote the main control valves in the reactor. With 1 open and 2 closed, the contents of the variable-volume cell can be dissolved in an $scCO_2/H_2$ mixture. R can be placed in an oven if elevated temperatures are required. With 1 closed and 2 open, SP can be used to push a small sample into the on-line FTIR cell for monitoring. (Note that this figure is not drawn to scale.)

The Thermal Flow Reactor. Preparation of $Cp^*Mn(CO)_2(C_2H_4)$. The flow reactor apparatus is set up as illustrated in Figure 8 but without the collection vessel between the BPR and bubble meter, M. $Cp^*Mn(CO)_2(NC_4H_7)$ was prepared by the method described above. scC_2H_4 (150 atm) was flowed through both the oil bath and through the bypass in order to ensure that residual air was removed from the system. A "background" FTIR spectrum was recorded at the operating pressure of the system, in this case 150 atm. The variable-volume, two-compartment cell, R, was evacuated and Ar-filled on a Schlenk line. A 200 mg sample of $Cp^*Mn(CO)_2(NC_4H_7)$, dissolved in a minimum of freshly distilled and degassed pentane, was added into the front compartment of R by cannula. The solvent was removed by vacuum, and R was left under Ar. R was plumbed into the reactor and pressurized to 150 atm (set by the BPR) to give a solution of $Cp^*Mn(CO)_2(NC_4H_7)$ in C_2H_4. The control valve was then adjusted to give a flow rate of 200 mL of gas per min at atmospheric pressure, as measured by M. With scC_2H_4 flowing via the bypass, the oil bath was switched on and allowed to warm up to 100 °C. The back compartment of R was slowly pressurized with CO_2 (from the syringe pump, SP) until the piston began to move forward, forcing the solution of $Cp^*Mn(CO)_2(NC_4H_7)$ into the stream of flowing scC_2H_4. The concentration of $Cp^*Mn(CO)_2(NC_4H_7)$ in the flowing scC_2H_4 depends upon the speed at which the piston moves, and the intensity of the ν(CO) bands in the on-line FTIR spectra is used as a guide in adjusting the speed of the piston. The SP setting is usually between 100 and 300 $\mu L\ min^{-1}$. Once the spectra indicated a constant concentration of $Cp^*Mn(CO)_2(NC_4H_7)$, the flow was diverted through the coil (1 mL in volume) in the oil bath. Almost immediately, on-line FTIR spectra show complete conversion to Cp*Mn(CO)$_2$(C_2H_4) with no indication of any decomposition products. The flow reactor was temporarily stopped while a glass collection vessel (purged free of air and Ar-filled on a Schlenk line) was fitted to the BPR then restarted. A yellow solid was deposited continually for approximately 2 h, after which the flow was stopped and the glass collection vessel removed. In a flow reactor, the product yield depended on the flow rate and run times. Typically, this reactor gave 40−50 mg/h at >90% purity.

The Semiflow Reactor. The procedure described below is applicable for reaction of both Cp*Mn(CO)$_2$(EVE) and Cp*Mn(CO)$_2$(HSiEt$_3$) (see above). The only difference was the temperature at which the reaction is carried out. The triethylsilane complex was reacted at room temperature (20 °C), whereas the EVE complex reacted in a vessel heated in a Carlo-Erba GC oven (38 °C). Full details are given only for the synthesis of Cp*Mn(CO)$_2$(η^2-H_2) from Cp*Mn(CO)$_2$(HSiEt$_3$).

Preparation of Cp*Mn(CO)$_2$(η^2-H_2) from Cp*Mn(CO)$_2$(η^2-H-SiEt$_3$). The modified apparatus is shown in Figure 9. Using a scCO$_2$/H_2 flow, the flow system was purged and a background FTIR spectrum recorded. A 70 mg amount of Cp*Mn(CO)$_2$(HSiEt$_3$) was added to the front compartment of R, as described above. With the BPR controlling the overall reactor pressure (180 kg cm^{-2}), the CO_2 pump, PP, and H_2 compressor, PC, were both set at 210 atm. The switching rate of the dosage unit, DU, only controlled the rate at which R was filled, so its setting was arbitrary (in this instance it was set at 1 Hz). The front compartment of R was pressurized to 180 atm with scCO$_2$/H_2. SP was used to pressurize the back compartment of R so that small aliquots of the solution could be pushed into the on-line FTIR cell. Regular scanning allowed the extent of reaction to be monitored at room temperature. As soon as the reaction reached completion, an Ar-filled glass collection vessel was attached to the BPR and the contents of R were rapidly pushed through the reactor and isolated as a yellow solid (typically 40 mg, *ca*. 80% yield).

Note Added in Proof. Since the submission of this article, a paper has been published (Linehan, J. C.; Wallen, S. L.; Yonker, C. R.; Bitterwolf, T. E.; Bays, J. T. *J. Am. Chem. Soc.* **1997**, *119*, 10170) which reports elegant ^{1}H NMR experiments on Cp′Mn(CO)$_2$(C_2H_4) and Cp′Mn(CO)$_2$(η^2-H_2), photochemically generated from Cp′Mn(CO)$_3$ and C_2H_4 or H_2 in supercritical fluid solution. However, the paper reports a much lower photochemical conversion of Cp′Mn(CO)$_3$ to Cp′Mn(CO)$_2$(η^2-H_2) than was found in our earlier results.[5] The authors attributed these differences to the fact that the experiments in ref 5 were in a flow system, whereas theirs were carried out in a sealed NMR apparatus, where the photoejected CO could not diffuse away. We believe that this explanation is unlikely, given the reactivity found in the thermal reactions of the dihydrogen compounds described above and the fact that we have observed almost *quantitative* conversion to CpMn(CO)$_2$(η^2-H_2) in *sealed* FTIR cells.[5] More plausible causes of the low yield in the NMR experiments are (i) the NMR experiments used monochromatic light for photolysis while the preparative experiments involved broad-band UV and (ii) *higher* concentrations of Cp′Mn(CO)$_3$ and *lower* concentrations of H_2 appear to have been used in the NMR than in the preparative experiments.[5]

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