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# Organometallic Synthesis as a Continuous Process: The Synthesis and Isolation of $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ and $(C_5R_5)Mn(CO)_2(\eta^2\text{-}C_3H_6)$ ($R = H$ and Me) from Superheated Liquid Propene

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$(C_5R_5)Mn(CO)_2(\eta^2\text{-}C_3H_6)$ ($R = H$ and Me) and $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ have been synthesized by UV photolysis of $CpMn(CO)_3$ and $Cr(CO)_6$ in liquid propene at 25 °C and 2100 psi pressure and by the thermal reaction of $Cp^*Mn(CO)_2(EVE)$ (EVE = ethyl vinyl ether) with propene. The propene complexes are precipitated by rapid expansion through a back pressure regulator. The precipitation leads to finely divided solid materials. Although these contain some residual starting materials, none of the compounds have previously been isolated as solids. All three compounds are significantly more stable in the solid state than in solution. The Cp* complex appears to be thermally less stable than the Cp analog.

## Introduction

There is continuing interest in $\eta^2$-propene complexes of transition metals.[1−3] This interest originates partly because they are the simplest complexes which can undergo $\beta$-hydride migration from $\eta^2$-alkene to $\eta^3$-allylhydrido complexes and partly because the $\eta^2$-propene ligand is often so weakly coordinated that the complexes are challenging to isolate.[4]

In this paper, we investigate the possibility of extending techniques[5,6] which have already been used successfully to isolate ethene complexes from supercritical $C_2H_4$, $scC_2H_4$, for the isolation of propene complexes from liquid or near-critical propene. The properties of propene are very different from those of $C_2H_4$ so it is not clear a priori whether the approach used with $scC_2H_4$ can be extended to *liquid* propene. A supercritical fluid (SCF) solvent enables very high concentrations of weak ligands such as $C_2H_4$ to be achieved,[5] and the same is obviously true for a liquid. Either the SCF can be used as both solvent and reactant (e.g., $scC_2H_4$ used as a solvent for preparation of $C_2H_4$ complexes[6−8]) or a chemically inert SCF can be used as a solvent for reactions with permanent gases (e.g., $H_2$, $N_2$, etc.) which are completely miscible with the SCF.[5,9−11] This miscibility gives rise to concentrations of dissolved gases up to 1 order of magnitude higher than in conventional solvents under similar pressures of the gas.[11] The high concentration of gases has led to the photochemical generation of a whole range of previously unknown $H_2$ and $N_2$ complexes.[9−11]

The solvent power of an SCF can be dramatically reduced by reducing the applied pressure and hence the density of the SCF. Thus, complexes can be isolated from an SCF by rapid precipitation, the so-called RESS technique (rapid expansion of the supercritical solution).[5,12,13] RESS has a number of advantages over conventional solvent removal. First, the isolation is rapid, reducing the time for the product compound to decompose.[6] Second, as the gas expands, the cooling effect gives additional stabilization. Finally, when the complex has been precipitated, there is a continuous stream of the reactant gas flowing over the solid. Thus, RESS involves neither heating nor use of vacuum (to remove a solvent), factors which normally render compounds with weak ligands so hard to isolate from solution. RESS has been used to isolate a whole range of unstable complexes, e.g., $CpMn(CO)_2(H_2)$,[5] $Cp^*Ir(CO)(H)Et$,[14] and, most relevant here, $Cr(CO)_5(\eta^2\text{-}C_2H_4)$, from the photochemical reaction of $Cr(CO)_6$ with $scC_2H_4$.[5,6]

Propene has a critical temperature, $T_c = 91.6$ °C, which is really too high for generating thermally labile propene complexes in scPropene. Therefore, this paper investigates the possibility of using rapid expansion to

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isolate propene complexes from room temperature *liquid* propene, superheated well above its normal boiling point ($T = -47.4$ °C). Rapid expansion of a pressurized liquid is quite a different physical process from the expansion of an SCF because the liquid has a nonzero latent heat of vaporization. Evaporation will therefore be noninstantaneous, and there is the possibility of forming an oil (i.e., a highly concentrated solution) rather than a dry powdered solid. Complexes with labile ligands are often stabilized in the solid state. Therefore, oils may be significantly less stable than dry solids.

None of our targets compounds, $C_5R_5Mn(CO)_2(\eta^2\text{-}C_3H_6)$ (R = H or Me) or $Cr(CO)_5(\eta^2\text{-}C_3H_6)$, have ever been isolated from conventional solvents, although it is well-known[2,15] that the photolysis of $CpM(CO)_3$ (M = Mn and Re) in hexane doped with propene solution leads to the formation of the corresponding $CpM(CO)_2(\eta^2\text{-}C_3H_6)$. However, although $CpMn(CO)_2(\eta^2\text{-}C_2H_4)$ is a stable complex,[16] $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$ displays low stability in solution and is highly air-sensitive, making its isolation difficult.[17] Similarly, $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ has been observed in low-temperature solutions, following the UV photolysis of $Cr(CO)_6$ and propene.[18] The analogous tungsten complexes, $W(CO)_5(\eta^2\text{-}C_3H_6)$ and *trans*-$W(CO)_2(\eta^2\text{-}C_3H_6)$, have been observed in solution but they also have proved difficult to isolate.[18]

We now describe the isolation of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$, its Cp* analog, and $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ from liquid propene in continuous reactors. In both cases, our strategy has been to optimize the reaction spectroscopically in a small static cell before scaling up to a continuous reactor.

$$CpMn(CO)_2 \xrightarrow[C_3H_6\ \text{liq}]{\text{UV}} CpMn(CO)_2(\eta^2\text{-}C_3H_6) + CO$$

$$Cr(CO)_6 \xrightarrow[C_3H_6\ \text{liq}]{\text{UV}} Cr(CO)_5(\eta^2\text{-}C_3H_6) + CO$$

## Results and Discussion

**Photolysis of $CpRe(CO)_3$ and $Cp^*Re(CO)_3$ in Liquid Propene.** As an initial test, we carried out the photolysis of the $CpRe(CO)_3$ and $Cp^*Re(CO)_3$ in liquid propene. Both of these complexes have previously been photolyzed in hexane solution[2] with propene bubbling through to remove the photoejected CO. Our experiments in liquid propene in a *closed vessel* (1−2 mg in 1 mL of $C_3H_6$ at 2100 psi) showed that high conversion to the corresponding propene complexes could be achieved with 60 s UV irradiation at 20 °C *without the removal of CO*. The IR bands of the propene complexes were close to the literature values,[2] see Table 1. An additional band observed at 1901.8 cm$^{-1}$ for the Cp* system is assigned to the allyl hydrido complex, *exo*-$Cp^*Re(CO)(H)(\eta^3\text{-}C_3H_5)$ by comparison with published data.[2] There was no obvious band corresponding to the *endo*-isomer, although, possibly, it was weak and obscured by other bands. After 24 h, no decomposition of the propene complex was apparent. Similar results were obtained for $CpRe(CO)_3$ except that there was a weak band assignable to *endo*-$CpRe(CO)(H)(\eta^3\text{-}C_3H_5)$, see Table 1. Furthermore, over 24 h, there was significant decomposition of both $CpRe(CO)_2(\eta^2\text{-}C_3H_6)$ and *exo*-$CpRe(CO)(H)(\eta^3\text{-}C_3H_5)$ with concomitant growth of the IR band of *endo*-$CpRe(CO)(H)(\eta^3\text{-}C_3H_5)$. These experiments show that photolysis in liquid propene is a viable route to propene complexes and that, given the excess of propene, there are no problems from photoejected CO. Also, as expected the Cp* propene complex is more stable than its Cp analog.

**Table 1. IR Wavenumbers of $\nu$(C−O) Bands (cm$^{-1}$) of the Photoproducts of the Reaction of $Cp^*Re(CO)_3$ with Liquid Propene and Their Cp Analogs**

| complex | liquid $C_3H_6$[a] | hexane solution[b] |
|---|---|---|
| $Cp^*Re(CO)_3$ | 2013.5 | |
| | 1921.8 | |
| $CpRe(CO)_3$ | 2029.6 | |
| | 1938.6 | |
| $Cp^*Re(CO)_2(\eta^2\text{-}C_3H_6)$ | 1959.5 | 1961 |
| | 1887.7 | 1890 |
| $CpRe(CO)_2(\eta^2\text{-}C_3H_6)$ | 1973.6 | |
| | 1925.8 | |
| *exo*-$Cp^*Re(CO)(H)(C_3H_5)$ | 1901.8 | 1904 |
| *endo*-$Cp^*Re(CO)(H)(C_3H_5)$ | not observed | 1912 |
| *exo*-$CpRe(CO)(H)(C_3H_5)$ | 1902.8 | |
| *endo*-$CpRe(CO)(H)(C_3H_5)$ | 1918.9 | |

[a] This work. [b] Reference 2.

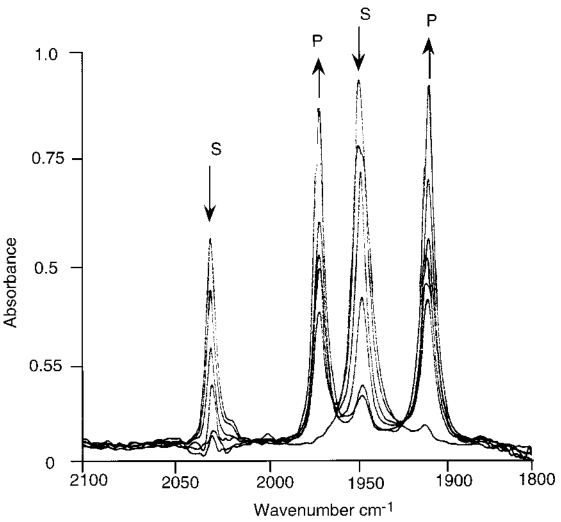

**Figure 1.** IR spectra recorded at intervals during the broad band UV photolysis (Cermax 300W Xe arc) of $CpMn(CO)_3$ in liquid $C_3H_6$, at 2100 psi and 20 °C. The bands are labeled as follows: S, $CpMn(CO)_3$; P, $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$. Note that the total photolysis time is only 8 s.

**Synthesis of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$.** Figure 1 shows the results of the photochemical reaction of $CpMn(CO)_3$ in liquid propene in a static cell. It can be seen that after only 8 s irradiation complete conversion from reactant to a new product was achieved. The product has two $\nu$(C−O) bands, assigned to the a′ and a″ $\nu$(C−O) vibrations of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$ by analogy with the spectrum of $CpMn(CO)_2(\eta^2\text{-}C_2H_4)$.[19] Although $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$ is unstable in hexane solution saturated with propene,[15] we found that unlike the Re complex the decomposition of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$ in liquid propene

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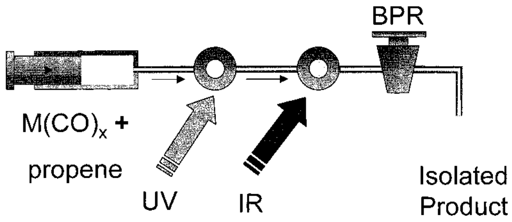

**Figure 2.** Schematic diagram of the continuous reactor for synthesis of propene complexes. A solution of metal carbonyl is pumped through the UV photolysis and IR spectroscopic cells before rapid expansion through a back pressure regulator (BPR) to precipitate the product.

**Table 2. IR Band Positions ($cm^{-1}$) of $CpMn(CO)_3$ and $(C_5R_5)Mn(CO)_2(\eta^2\text{-}C_3H_6)$ ($C_5R_5$ = H and Me) Recorded in Liquid Propene at 25 °C[a]**

| $C_5R_5Mn(CO)_3$ | | $C_5R_5Mn(CO)_2(\eta^2\text{-}C_3H_6)$ | |
|---|---|---|---|
| | | R = H | |
| 2028.3 | $a_1$ | 1969.2 | a′ |
| 1945.8 | e | 1909.6 | a″ |
| 4049 | 2 × $a_1$ | 3928 | 2 × a′ |
| 3958 | $a_1$ + e | 3852 | a′ + a″ |
| 3880 | 2 × e | 3804 | 2 × a″ |
| | | R = Me | |
| 2009.3 | $a_1$ | 1951.8 | a′ |
| 1927.7 | e | 1892.3 | a″ |

[a] $Cp^*Mn(CO)_2(EVE)$: $\nu(CO)$ bands at 1942.9 and 1884 $cm^{-1}$.

was negligible, even overnight. Thus, by using liquid propene both as solvent and reactant, we have reduced the lability of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$ in solution. The challenge is how to isolate the complex.

**Isolation of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$.** The principle of our continuous reactor is illustrated in Figure 2. A solution of $CpMn(CO)_3$ in liquid propene is pumped continuously from a reservoir through a UV irradiation cell and via an IR cell to an expansion valve (back pressure regulator) where the product is precipitated. The complete layout of the reactor is similar that used for SCF experiments and is shown in the Experimental Section, Figure 6. The IR cell is used to monitor the conversion of reactant to product and, hence, to optimize the conversion. On a preparative scale, the $\nu$(C−O) bands of the reactant and product proved too intense for convenient spectroscopic monitoring. Therefore, the reaction is monitored in the overtone and combination region, ca. 4000 $cm^{-1}$, see Table 2. Even though the S/N ratio is worse than that in the $\nu$(C−O) region, the spectra are sufficiently good to monitor the reaction.

Conditions in the reactor could be optimized to give nearly > 60% conversion, and rapid expansion of the solution gave a yellow solid which melted to a yellow oil at room temperature. (Under similar conditions, the starting material $CpMn(CO)_3$ appears as an off-white solid.) Using a simple adaptator,[20] the solid product was transferred to an NMR tube with minimum exposure to room temperature solvent or vacuum, both of which could cause rapid decomposition. The sample was analyzed by $^1H$, $^{13}C$, and C-DEPT NMR, which confirmed the presence of $\eta^2\text{-}C_3H_6$, see Table 3. No significant impurities other than $CpMn(CO)_3$ and free $C_3H_6$ were detected.

**Table 3. $^{13}C$ NMR Shifts of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$, $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$, and $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ (in ppm)**

| | CH | $CH_2$ | $CH_3$ |
|---|---|---|---|
| $CpMn(CO)_2(\eta^2\text{−}C_3H_6)$[a] | 54 | 40 | 19.8 |
| $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$[b] | 56.8 | 45.2 | 22.9 |
| $Cr(CO)_5(\eta^2\text{-}C_3H_6)$[c] | 90.7 | 67.6 | 19.6 |
| free $C_3H_6$[c] | 133.9 | 115.4 | 22 |

[a] $C_6D_5CD_3$, 273 K, the Cp group shift is 83.6 ppm. [b] $C_6D_5CD_3$, 273 K, the $C_5Me_5$ group shift is 9.4 ppm. [c] $C_6D_5CD_3$, 230 K, $CO_{ax}$ 224.1 and $CO_{eq}$ 216.1 ppm.

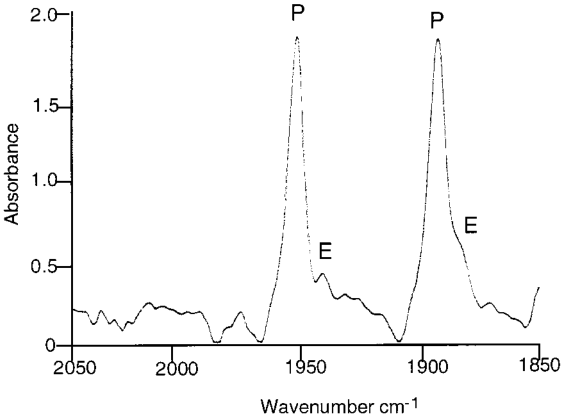

**Figure 3.** On-line IR spectrum of a liquid $C_3H_6$ solution (2100 psi) recorded at 20 °C after a 48 h thermal reaction of $Cp^*Mn(CO)_2(EVE)$, bands labeled E, with $C_3H_6$. The bands labeled P are due to $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$.

**Isolation of $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$ by a *Thermal* Route.** Our previous work[16] with $scC_2H_4$ has shown that $Cp^*Mn(CO)_2(EVE)$ (EVE = ethyl vinyl ether) can be used as a precursor in the thermal synthesis of alkene complexes at room temperature. The reaction between $Cp^*Mn(CO)_2(EVE)$ and liquid propene was monitored on a small scale in a spectroscopic cell. Initially, the reaction occurred rapidly and was monitored overnight, but even after 12 h at 20 °C, some of the EVE complex remained. A heating block was then used to heat the cell to 45 °C, and after 30 min, the reaction reached completion with almost no $Cp^*Mn(CO)_2(EVE)$ detectable by IR. Once $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$ was formed in liquid propene, no decomposition was observed over 48 h.

The reaction was therefore scaled up using the reactor in Figure 6 in a semiflow mode at room temperature, see Experimental Section. The on-line IR spectra in Figure 3 showed the almost complete conversion of $Cp^*Mn(CO)_2(EVE)$ to $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$ under these conditions. A solid material was then isolated by rapid expansion of the propene solution through the back-pressure regulator. The other product, free EVE, is highly volatile and should not condense under these conditions. $^1H$ and $^{13}C$ NMR spectra of the redissolved solid confirmed the formation of $Cp^*Mn(CO)_2(\eta^2\text{-propene})$ (Table 3), but an almost equal concentration of $Cp^*Mn(CO)_2(EVE)$ was also present in solution. Since the on-line IR analysis indicated a very high product conversion, significant decomposition of the labile propene complex appears to have occurred on precipitation and redissolving. Furthermore, the EVE complex does not decompose under these conditions,[16] yet the NMR spectrum shows it to be a major component rather than

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a residual trace in the mixture in solution. Therefore, from the IR and NMR data, it can be estimated that almost 90% of $Cp^*Mn(CO)_2(\eta^2$-propene) decomposes during precipitation and subsequent dissolution. This is much *higher* than the decomposition observed for $CpMn(CO)_2(\eta^2$-propene) on precipitation. This result is intriguing because, as with Re, the Cp* group usually confers stability to $\eta^2$-coordinated ligands through enhanced back-donation. However, due to the size of the Cp* group, this interaction may be sterically hindered for Mn, thus making $Cp^*Mn(CO)_2(\eta^2$-propene) less stable than its Cp counterpart. Nevertheless, despite the decomposition, we believe that this is the first isolation of $Cp^*Mn(CO)_2(\eta^2$-propene) as a solid.

**Synthesis and Isolation of $Cr(CO)_5(\eta^2\text{-}C_3H_6)$.** As with $CpMn(CO)_3$, the reaction of $Cr(CO)_6$ with propene was initially studied on a small scale. Since $Cr(CO)_6$ has rather low solubility in liquid $C_3H_6$, a small quantity of $Cr(CO)_6$ was photolyzed in $scCO_2$, doped with $C_3H_6$. The resulting spectra indicated the formation of $Cr(CO)_5(\eta^2\text{-}C_3H_6)$, identified by comparison with the $\nu$(C−O) bands of $W(CO)_5(\eta^2\text{-}C_3H_6)$.[6] However, the broadness of the bands in $scCO_2$ made it difficult to eliminate the possibility that traces of *trans*-$Cr(CO)_4(C_3H_6)_2$ were also formed. No decomposition of the $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ was apparent after 40 min, but almost all of the complex decomposed with regeneration of $Cr(CO)_6$ over a 12 h period. This means that $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ is rather less stable than $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$ under these conditions, and pure liquefied $C_3H_6$ was used the solvent in the larger scale preparation of $Cr(CO)_5(\eta^2\text{-}C_3H_6)$, despite the sparing solubility of $Cr(CO)_6$.

Figure 4a shows IR spectra recorded during the continuous reaction of $Cr(CO)_6$ with $C_3H_6$; the bands (Table 4) were assigned by analogy with those obtained in $scC_2H_4$.[5,12] The photochemical reactor, Figure 6, is similar to that used for the synthesis of $Cr(CO)_5(\eta^2\text{-}C_2H_4)$ in supercritical $C_2H_4$.[8] As before, the FTIR spectrum, Figure 4a, was used to optimize the conversion of reactant to product, which was isolated by rapid expansion. Figure 4b shows the FTIR spectrum of the isolated yellow product, redissolved in pentane saturated with $C_3H_6$. NMR spectra were recorded in $d_8$-toluene at 230 K to minimize thermal decomposition. No further purification was required since, fortuitously, excess $Cr(CO)_6$ precipitates out under these conditions. The $^{13}C$ and C-DEPT 135 NMR spectra identify the product as $Cr(CO)_5(\eta^2\text{-}C_3H_6)$, Figure 5, Table 3. The upfield shift of the coordinated propene signals is consistent with the partial rehybridization of the alkene C atoms.

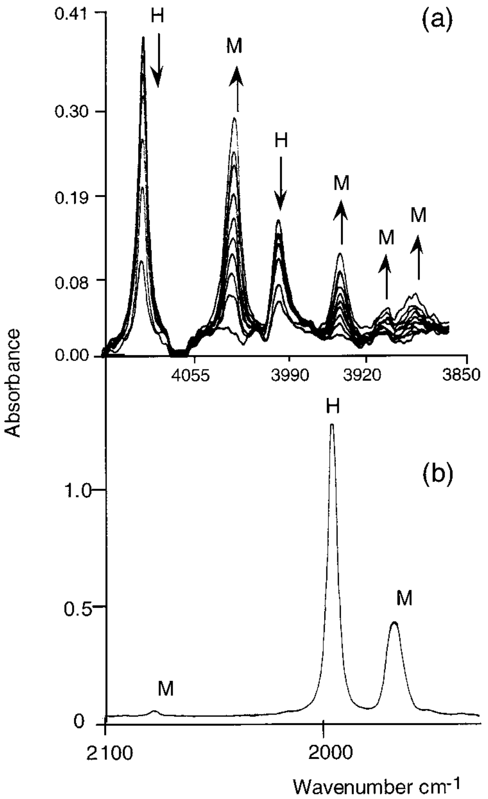

**Figure 4.** (a) FTIR spectra recorded on-line while the reaction of $Cr(CO)_6$ with $C_3H_6$ was being optimized. (b) Spectrum of the solid product redissolved in pentane. In both spectra, bands are labeled as follows: H, $Cr(CO)_6$; M, $Cr(CO)_5(\eta^2\text{-}C_3H_6)$.

**Table 4. IR Band Positions ($cm^{-1}$) of $Cr(CO)_6$ and $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ in Liquid Propene and Pentane**

| $Cr(CO)_6$ | | $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ | | $Cr(CO)_5(\eta^2\text{-}C_2H_4)^a$ |
|---|---|---|---|---|
| liquid $C_3H_6$ | pentane | liquid $C_3H_6$ | pentane | $scC_2H_4$ |
| | | 4022 | | 4035 $a_1 + b_2$ |
| 4099 $a_{1g} + t_{1u}$ | | 3940 | | 3955 $a_2 + a_1/b_2$ |
| 3994 $e_g + t_{1u}$ | | 3904 | | 3905 $2 \times b$ |
| | | 3882 | | |
| | | 2075.2 | 2077 | 2082.7 $a_1$ |
| 1990 | 1995 $t_{1u}$ | | | (2003.7 $a_2$)$^b$ |
| | | 1959.3 | 1967 | 1964.5 $a_1/b_2$ |

$^a$ Data taken from ref 5. $^b$ Raman active only.

**Reactions of $Cr(CO)_5(\eta^2\text{-}C_3H_6)$.** As a start to exploring the reactions of $Cr(CO)_5(\eta^2\text{-}C_3H_6)$, we have briefly investigated its photochemical reactions with $N_2$ and $H_2$. The products were likely to be even more labile than the starting material so the reactions were carried out at low temperature in polyethylene (PE) matrices. We have previously described our high pressure/low-temperature cell, which can be used to react gases with organometallic compounds impregnated into a PE film.[21,22] The use of PE matrices was pioneered by Rest and co-workers.[23] The novelty of our cell is that the PE film can be surrounded by a pressure of gas which can be changed at will during the course of the experiment. In these experiments, $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ was generated in situ in PE film (a stack of 5 × 50 $\mu$m disks) by UV photolysis of $Cr(CO)_6$ in the presence of propene (80 psi, 120K). In addition to $Cr(CO)_5(\eta^2\text{-}C_3H_6)$, the reaction generated *cis*-$Cr(CO)_4(\eta^2\text{-}C_3H_6)_2$, identified by comparing its IR spectrum with the reported IR data[24,25] for *cis*-$Cr(CO)_4(\eta^2\text{-}C_2H_4)_2$, see Table 4. The film was then heated to room temperature to vent as much residual propene as possible from the film and to destroy *cis*-$Cr(CO)_4(\eta^2\text{-}C_3H_6)_2$, which is thermally much less stable than $Cr(CO)_5(\eta^2\text{-}C_3H_6)$. The cell was then recooled and pressurized with either $H_2$ (1500 psi, 120 K) or $N_2$ (1400

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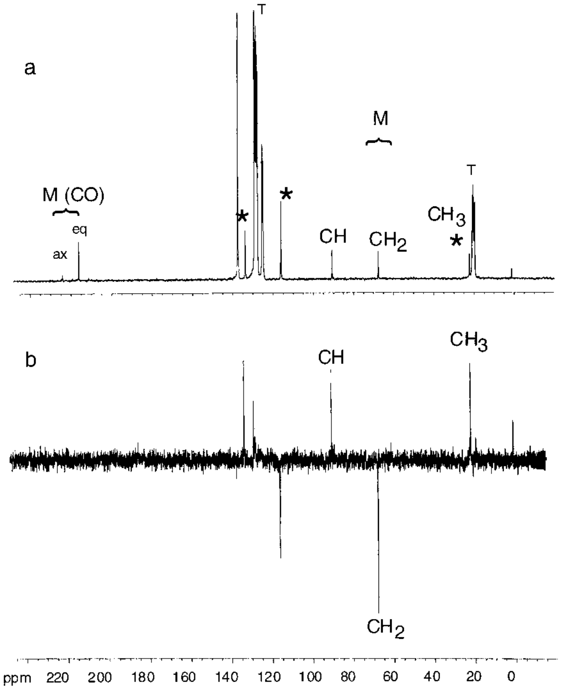

**Figure 5.** $^{13}C$ NMR spectra ($^1H$ decoupled) of $Cr(CO)_6$ and reaction products in $d_8$-toluene (T) at 230 K. (a) $^{13}C$ spectrum; *, free $C_3H_6$; M, resonances of $Cr(CO)_5(\eta^2\text{-}C_3H_6)$. (b) C-DEPT 135 spectrum of the same solution ($C_6D_5CD_3$, 75.5 MHz, 230 K). The resonances labeled T are due to $C_6D_5CD_3$.

**Table 5. IR Bands Positions[a] ($cm^{-1}$) for $C_3H_6$ and $C_2H_4$ Complexes in Polyethylene Film at Low Temperature**

| | R = $C_3H_6$ | R[b] = $C_2H_4$ |
|---|---|---|
| $Cr(CO)_5(R)$ | 2083.4 | 2077.6 (2078.9)[c] |
| | 1947.3 | 1966.1 (1967.4)[c] |
| | | 1960.4 (1960.4)[c] |
| *cis*-$Cr(CO)_4(R)_2$ | 2027.4 | (2036.8)[c] |
| | 1931.4 | (1949.3)[c] |
| | 1895.5 | (1913.4)[c] |
| *cis*-$Cr(CO)_4(R)(N_2)$[e] | 2222.0 | (2223.4)[d] |
| | 2038.0 | (2043.1)[d] |
| | 1946 | |
| | 1920.6 | (1929.7)[d] |
| *cis*-$Cr(CO)_4(R)(\eta^2\text{-}H_2)$[f] | 2043.8 | (2049.2)[d] |
| | 1939.1 | |
| | 1914.8 | (1925.1)[d] |

[a] Data in parentheses for liquid Xe solution. [b] Values for PE from ref 25. [c] Liquid Xe ref 24. [d] Liquid Xe .[26] [e] 160 K. [f] 120 K.

psi, 160 K) and photolyzed with a medium-pressure Hg arc. The IR spectra of the product mixtures were quite complicated, but the more important bands are summarized in Table 5. The experiments showed that, on photolysis, $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ can lose either $C_3H_6$ to generate the known complexes $Cr(CO)_5X_2$ (X = N or H) or CO to form the previously unobserved *cis*-$Cr(CO)_4(\eta^2\text{-}C_3H_6)(N_2)$ and *cis*-$Cr(CO)_4(\eta^2\text{-}C_3H_6)(\eta^2\text{-}H_2)$. Both these complexes were identified by comparison with the spectra of the $C_2H_4$ analogs.[26,27] The propene complexes were thermally stable at 160 K ($N_2$) and 120 K ($H_2$) but rapidly decomposed on further warming.

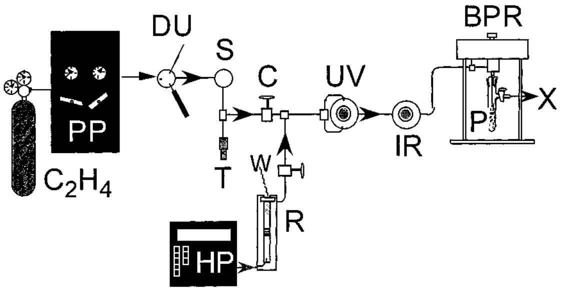

**Figure 6.** Diagram of the continuous reactor used in these experiments. The components are labeled as follows (in alphabetical order): BPR, back pressure regulator (Jasco model 880-81); $C_3H_6$, cylinder of propene; IR, high-pressure cell for FTIR spectroscopy ($CaF_2$ windows); HP, high-pressure liquid pump (Gilson model 303); P, precipitated product; PP, pneumatic pump (NWA PM101); R, variable volume reservoir cell with piston and window, W; T, pressure transducer (RDP Electronics); UV, photolysis cell ($CaF_2$ window, Cermax 300 UV photolysis lamp).

## Experimental Section

**Chemicals.** $Cr(CO)_6$ 99.9% and $CpMn(CO)_3$, Aldrich, were used as starting materials. Propene (BOC 99.5% purity) was used without further purification.

**Equipment. Safety note**: *These experiments involve high pressures of inflammable gases. The equipment described here is not necessarily the best for this purpose, and it is the responsibility of each researcher to establish the safety of their equipment.*

Figure 6 shows the layout of the equipment used for these reactions. It is derived from the $scC_2H_4$ flow reactor which has been described in great detail previously.[5,16,20] The major simplification is that the piston in the two compartment view-cell, R, is pressurized using a liquid, cyclohexane, and a conventional HPLC pump (Gilson model 303) rather than using supercritical $CO_2$. This makes the reactor both more compact and simpler to operate. It is important to stress that, although the reactor described here can only produce ≤ 20 mg/h, more product can be obtained merely by running the reactor for longer. Furthermore, the reactor could easily be scaled up by using a more powerful UV lamp.

**Synthesis and Isolation of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$ on a Preparative Scale.** The whole flow system was purged with $C_3H_6$ for 1 h, and a background FTIR spectrum was recorded with the $C_3H_6$ pressure at 2100 psi. Then, 350 mg of $CpMn(CO)_3$ was loaded into the front compartment of the cell, R, and pressurized with $C_3H_6$ to the same pressure. The $CpMn(CO)_3$ was allowed to dissolve for 1 h. With the back pressure regulator (BPR) set to 2175 psi, the solution of $CpMn(CO)_3$ was fed into the reactor by the HPLC pump (HP). The flow rate of HP was varied between 100 and 500 $\mu$L $min^{-1}$. Ice packs were placed around the UV irradiation cell to minimize thermal decomposition of $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$ and the solution was photolyzed. The flow rate was varied between 100 and 500 $\mu$L $min^{-1}$ and the reaction was monitored (3 mm path length). The maximum conversion (60%) from reactant to product was obtained at 150 $\mu$L $min^{-1}$, with the BPR at 150 kg $cm^{-2}$ to give a reactor pressure of 2100 psi (IR, Table 1, and NMR, Table 3), typical yield 10 mg $h^{-1}$. The $^1H$ NMR spectrum of the isolated $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$ contains a single resonance for the Cp protons at 3.72 ppm, with a multiplet at 2.90 ppm and doublets at 2.22, 1.70, and 1.42 ppm.

**$Cp^*Mn(CO)_2(\eta^2$-propene).** $Cp^*Mn(CO)_2$(EVE) was synthesized as described previously,[16] and the isolated yellow solid was redissolved in minimum of pentane. The solution was transferred to the front compartment of the variable volume cell, the solvent was removed, and ca. 20 mg of the EVE

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complex was left under an Ar atmosphere. The cell was attached to the flow reactor, pressurized to 2100 psi with $C_3H_6$, and maintained at 20 °C. After 1 h, a sample was driven out into the on-line IR cell, and the reaction was then monitored at regular intervals at room temperature. After 12 h, the most intense IR bands were those of $Cp^*Mn(CO)_2(\eta^2$-propene) with a small shoulder band corresponding to $Cp^*Mn(CO)_2(EVE)$. After a total of 48 h reaction time, the conversion to $Cp^*Mn(CO)_2(\eta^2$-propene) was essentially complete (see Figure 3). The remaining contents of the cell were then precipitated via the BPR and were collected for NMR analysis. The $^1H$ NMR spectrum of $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$ displayed a singlet (Cp* protons) at 1.5 ppm, with a multiplet at 2.2 ppm (CH) and doublets at 2.0 (*cis*-$CH_2$), 1.8 (*trans*-$CH_2$) and 1.42 ppm ($CH_3$).

**Synthesis of $Cr(CO)_5(C_3H_6)$.** The reactor is flushed with $C_3H_6$ as for $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$, but $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ is more air-sensitive than the Mn compounds. Therefore, in a typical experiment, $Cr(CO)_6$ (ca. 300 mg) was loaded into the front compartment of R, which was then purged by repeated evacuation and Ar filling on a Schlenk line, before being connected to the flow system and pressurized to 1450 psi with $C_3H_6$. Because of the poor solubility of $Cr(CO)_6$ in liquid $C_3H_6$, the solution was left overnight to ensure that $Cr(CO)_6$ was fully dissolved.

Once the pressure in R has reached that of the system, the pressure of the cyclohexane pump, HP, is increased further and the solution flows through the UV and IR cells. When the IR bands are of constant intensity, the UV lamp is switched on. By continuously monitoring the FTIR spectrum, the flow rate of the solution could be adjusted with the cyclohexane pump to ensure optimum conversion from $Cr(CO)_6$ to $Cr(CO)_5(\eta^2\text{-}C_3H_6)$. Optimum conditions were found: $Cr(CO)_6$ 220 mg; BPR 100 kg $cm^{-2}$; reactor pressure 1370 psi; HPLC pump 50 $\mu L\ min^{-1}$. Yields were similar to those for $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$.

## Conclusion

In this paper, we have demonstrated how techniques originally developed for supercritical fluids[5,6,16] can be extended to liquefied gases. In particular, we have shown that rapid expansion can also be used as an effective isolation method from superheated liquids. We have isolated $CpMn(CO)_2(\eta^2\text{-}C_3H_6)$, $Cp^*Mn(CO)_2(\eta^2\text{-}C_3H_6)$, and $Cr(CO)_5(\eta^2\text{-}C_3H_6)$ for the first time. Although none of the compounds was obtained completely free of starting material, all of them were thermally more stable as solids than they were in solution. Most interestingly, the Cp* complex appears to be less stable than the Cp compound, the opposite of what has been observed for the Re analogs.

Our results demonstrate the possibilities of continuous reactors for the isolation of highly labile organometallic complexes. The extension of these techniques from supercritical fluids to liquefied gases greatly increases the scope of such experiments. We believe that a similar approach can be used to prepare a whole range of other alkene complexes and compounds containing other labile ligands, and experiments are currently in progress in our laboratory.

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