IR Evidence for the Generation of $(C_5H_5)Mn(CO)_2(N_2O)$ in Near-Critical N_2O at Room Temperature and in Polyethylene Matrices at Low Temperature

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UV photolysis of $CpMn(CO)_3$ (Cp = C_5H_5) in near critical liquid N_2O at room temperature in both static and flow reactors leads to the formation of $CpMn(CO)_2(N_2O)$ identified via ν(C–O) and $\nu(N_2O)$ IR bands, the latter being recorded in low temperature polyethylene (PE) experiments. $CpMn(CO)_2(N_2O)$ has a lifetime of ca. 5 min at room temperature in near-critical N_2O and appears to have two decay pathways one of which leads to $CpMn(CO)_2(N_2)$, possibly via *O*-transfer.

Despite a considerable amount of research into N_2O-complexes, only one complex, $[Ru(NH_3)_5(N_2O)]^{2+}$ containing coordinated N_2O has ever been isolated.[1–3] Subsequently, a number of N_2O complexes have been identified either by low temperature techniques or by time resolved IR spectroscopy.[4–6]

Supercritical fluids (SCFs) have already proved quite successful for the synthesis (and sometimes isolation) of complexes containing weakly coordinated ligands, such as H_2, N_2, alkene and CO_2. The advantage of SCFs is that it is often possible to obtain a very high concentration of the weak ligand by using the supercritical ligand (e.g., C_2H_4, CO_2, etc.) as both reactant and solvent. The area has been reviewed recently in some detail.[7] N_2O has a critical temperature (T_c = 36.6 °C, P_c = 71.5 atm) slightly above that CO_2 (T_c = 31.1 °C, P_c = 72.8 atm). In this paper, we demonstrate how $CpMn(CO)_2(N_2O)$ can be generated by UV photolysis of $CpMn(CO)_3$ in near-critical N_2O, ncN_2O. Experiments at low temperature in polyethylene (PE) film provide direct IR evidence for coordinated N_2O.

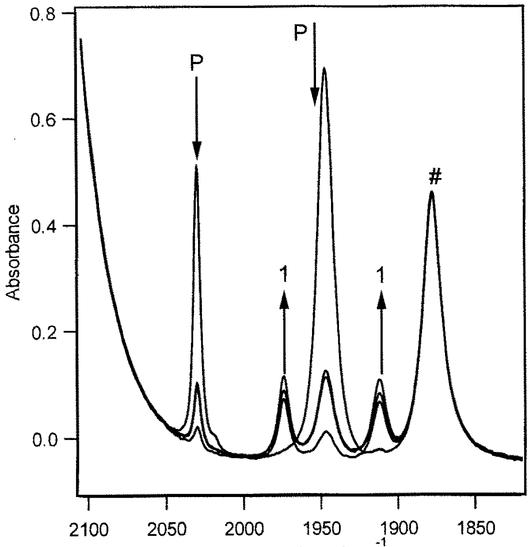


Figure 1. FTIR spectra obtained following photolysis of $CpMn(CO)_3$ (P) in ncN_2O at 298 K showing formation of $CpMn(CO)_2(N_2O)$ (1). The peak marked # due to ncN_2O is unaffected by photolysis. Prolonged photolysis leads to the complete disappearance of all bands in the ν(C-O) region.

Figure 1 shows IR spectra obtained following UV irradiation (unfiltered Xe arc) of $CpMn(CO)_3$ dissolved in ncN_2O. From the spectra, it can be seen that (1) a new compound is generated, having two ν(C–O) bands; (2) these bands are shifted to lower wavenumbers relative to the bands of $CpMn(CO)_3$; (3) the wavenumbers of the new bands indicate the formation of a $CpMn(CO)_2L$ complex (a' + a") but the precise values (see Table 1) are different from those of $CpMn(CO)_2(N_2)$ or $CpMn(CO)_2(CO_2)$. These observations are consistent with the formation $CpMn(CO)_2(N_2O)$ where coordination of N_2O does not alter the oxidation state of the Mn center.

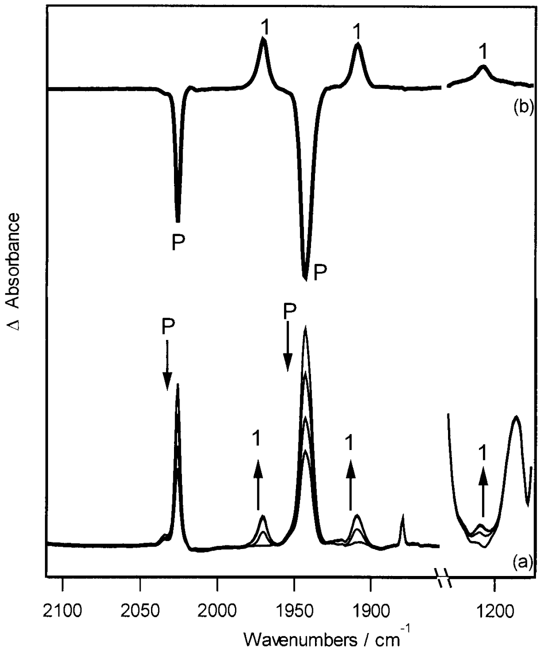


Figure 2. (a) FTIR spectra and (b) FTIR difference spectrum obtained after photolysis of $CpMn(CO)_3$ (P) in PE under N_2O (80 psi) at 220 K showing formation of $CpMn(CO)_2(N_2O)$ (1).

We have previously described a high pressure/low temperature cell for carrying out photochemical reaction of organometallic compounds impregnated into a PE film.[8,9] Figure 2 shows IR spectra obtained following UV irradiation of $CpMn(CO)_3$ in PE film at 220 K in the presence of N_2O. The spectra show the growth of the same ν(C–O) bands as were observed in ncN_2O, together with a third absorption centered at 1215 cm^{-1}. This band grows and decays in intensity at exactly at the same rate as the two ν(C–O) bands and therefore can be assigned to the same compound (this region of spectrum is obscured in the experiment with ncN_2O by the absorption of the N_2O solvent itself). IR data are available for a number of salts of $[Ru(NH_3)_5(N_2O)]^{2+}$. All of these show bands in the region 1250–1150 cm^{-1} and the BF_4^- salt[2] has a band at 1210 cm^{-1} almost coincident with that observed for our new complex in the PE film. This strongly suggests that the $CpMn(CO)_2$ complex has an N_2O ligand coordinated in a manner similar to that in $[Ru(NH_3)_5(N_2O)]^{2+}$ and, in these complexes, vibrational spectroscopy was interpreted to suggest that this mode involves coordination via the terminal N rather than the O atom.[10] The BF_4^- salt also has a band at 2275 cm^{-1}, however we were unable to observe this band in our studies because this region of the IR spectrum was obscured by absorptions due to excess N_2O.

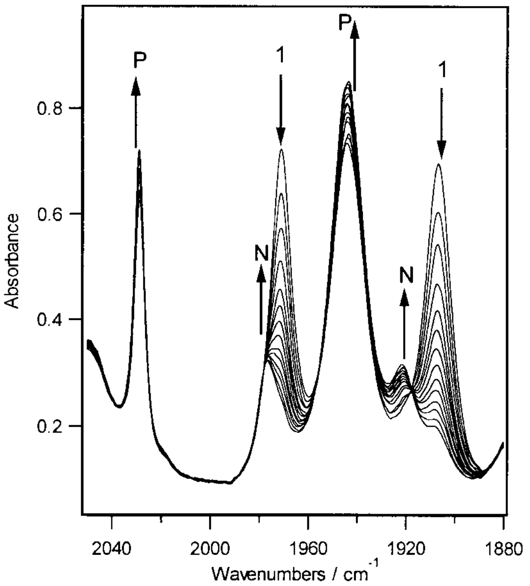


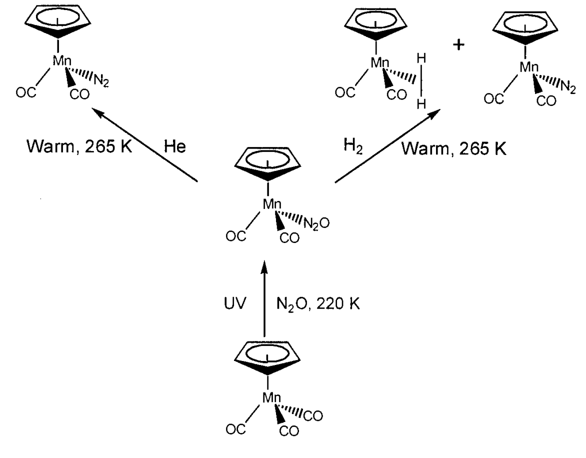
Figure 3. FTIR spectra showing the decay of $CpMn(CO)_2(N_2O)$ (1) and the growth of $CpMn(CO)_2(N_2)$ (N) in ncN_2O at 298 K over a period of ca. 20 minutes. Some parent compound (P) is regenerated over this time period.

Table 1. IR bands positions (cm^{-1}) of $CpMn(CO)_2(L)$ (L = CO, N_2O or N_2) in PE at 220 K and ncN_2O at 298 K.

Compound	PE, 220 K	ncN_2O, RT	Assignment
$CpMn(CO)_3$	2026.0	2029.1	a_1
	1943.2	1945.7	e
$CpMn(CO)_2(N_2O)$	1970.6	1971.9	a'
	1909.3	1908.2	a''
	1212.5	obscured	$\nu(N_2O)$
$CpMn(CO)_2(N_2)$	1975.6	1977.4	a_1
	1923.4	1922.7	b_1

$CpMn(CO)_2(N_2O)$ is thermally more stable than $W(CO)_5(N_2O)$.[5,11] Nevertheless, standing at room temperature in ncN_2O, or heating in PE film after venting of the N_2O pressure leads to decomposition of $CpMn(CO)_2(N_2O)$ both with formation of $CpMn(CO)_2(N_2)$ and with the regeneration of $CpMn(CO)_3$ (see Figure 3). $CpMn(CO)_2(N_2)$ was identified by photolysis of $CpMn(CO)_3$ in the presence of N_2.

By using $scCO_2$, the concentration of N_2O can be varied. The lifetime of $CpMn(CO)_2(N_2O)$ was increased by increasing concentrations of N_2O. In ncN_2O, lowering the temperature can also extend the lifetime (i.e. the lifetime is increased from ca. 5 min at 298 K to 20 min at 273 K). This behaviour is consistent with dissociative loss of the N_2O ligand. However, loss of N_2O cannot be the sole pathway to $CpMn(CO)_2(N_2)$ because, under a high pressure of H_2 in PE film, regeneration of $CpMn(CO)_3$ is suppressed (and $CpMn(CO)_2(H_2)$ is formed) but formation of $CpMn(CO)_2(N_2)$ is largely unaffected (Scheme 1). Therefore, we have the intriguing possibility that $CpMn(CO)_2(N_2)$ is formed by *O*-transfer from N_2O. Indeed a similar formation of N_2 complexes was observed previously [12] with $[Ru(NH_3)_5(N_2O)]^{2+}$.



Scheme 1. Reactions observed following photolysis of $CpMn(CO)_3$ in PE matrices at low temperature.

We have had some success in isolating unstable organometallic compounds generated in continuous or semi-continuous reactors by rapid expansion of supercritical and near critical fluids.[13,14] In this case, we have also generated $CpMn(CO)_2(N_2O)$ by UV photolysis of $CpMn(CO)_3$ in ncN_2O in a flow reactor with up to 50% conversion. Unfortunately, the compound has proved to be too unstable to be isolated under current conditions. However, we believe that it should be possible to isolate this compound from N_2O in the near future and there is clearly more to learn about the use of N_2O in atom transfer reactions.

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