

It was found<sup>19</sup> that NaBH<sub>4</sub> gives a 2:1 diastereomer ratio whereas LiBEt<sub>3</sub>H gives only one diastereomer. If the proposed formyl species were a true intermediate, the stereochemical outcome of the reaction should not depend on the hydride source. However, this would not be the case if the borane product (BEt<sub>3</sub>) or other electrophilic species (Li<sup>+</sup>) were associated with the carbonyl oxygen and thereby able to influence the subsequent migration, whether from a M(CHO) or M(CO)(H) intermediate.

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**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **9** (4 pages); listings of observed and calculated structure factors for **9** (9 pages). Ordering information is given on any current masthead page.

## Organometallic Chemistry in Supercritical Fluids: The Generation and Detection of Dinitrogen and Nonclassical Dihydrogen Complexes of Group 6, 7, and 8 Transition Metals at Room Temperature

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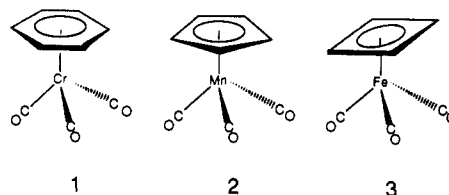
**Abstract:** The complete miscibility of N<sub>2</sub> and H<sub>2</sub> with supercritical fluids is used to stabilize unstable, and previously unknown, dinitrogen and dihydrogen complexes which would normally decay rapidly at ambient temperatures. UV photolysis of a series of (C<sub>n</sub>R<sub>n</sub>)M(CO)<sub>3</sub> compounds [M = Fe, Mn, Re or Cr; R = H for n = 4; R = H or Me for n = 5 or 6] dissolved in supercritical Xenon (scXe) under a high pressure of N<sub>2</sub> or H<sub>2</sub> leads to the formation of (C<sub>n</sub>R<sub>n</sub>)M(CO)<sub>2</sub>(N<sub>2</sub>) and (C<sub>n</sub>R<sub>n</sub>)M(CO)<sub>2</sub>(H<sub>2</sub>) complexes at room temperature. Re and Fe undergo facile substitution of more than one CO group by N<sub>2</sub>, while Cr and Mn do not. For all elements except Re, the spectroscopic evidence suggests that the (C<sub>n</sub>R<sub>n</sub>)M(CO)<sub>2</sub>(H<sub>2</sub>) complexes contain the "nonclassical" η<sup>2</sup>-H<sub>2</sub> ligand. No IR bands directly associated with η<sup>2</sup>-H<sub>2</sub> in these compounds have been observed, but the experiments were sufficiently sensitive to detect the ν(H-H) band of W(CO)<sub>5</sub>(H<sub>2</sub>) under similar conditions. Most of these dihydrogen complexes decompose by reaction with CO to regenerate the (C<sub>n</sub>R<sub>n</sub>)M(CO)<sub>3</sub> starting material, but significant amounts of Fe(CO)<sub>5</sub> are formed in the decay of (C<sub>6</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>(H<sub>2</sub>). Kinetic measurements between 11 and 80 °C show that (C<sub>6</sub>H<sub>5</sub>Me)Cr(CO)<sub>2</sub>(H<sub>2</sub>) reacts with CO with an activation energy of 70 ± 5 kJ mol<sup>-1</sup>, which may correspond to the Cr-(η<sup>2</sup>-H<sub>2</sub>) bond dissociation energy.

There is continuing interest in transition-metal complexes containing the η<sup>2</sup>-H<sub>2</sub> ligand, so-called "nonclassical" dihydrogen compounds.<sup>1</sup> The first example was isolated<sup>2</sup> only in 1984, but, since then, a large number of compounds have been found to be nonclassical. Although the existence of these compounds has stimulated several theoretical studies,<sup>3</sup> it is still far from clear precisely which factors are the most important in determining whether a particular dihydrogen ligand is classical or nonclassical. Nevertheless, several useful analogies have emerged.

There are similarities between the bonding in dinitrogen and dihydrogen complexes, and, for a given ML<sub>n</sub> fragment, the corresponding ML<sub>n</sub>(H<sub>2</sub>) and ML<sub>n</sub>(N<sub>2</sub>) complexes often have similar properties.<sup>4</sup> Indeed, it has been suggested<sup>5</sup> that, for d<sup>6</sup> centers at least, the wavenumber of the ν(N-N) IR band of ML<sub>n</sub>(N<sub>2</sub>)

is one indicator of classical/nonclassical behavior in the corresponding ML<sub>n</sub>H<sub>2</sub> species. Equally, there are strong similarities between η<sup>2</sup>-H<sub>2</sub> ligands and the "arrested" oxidative addition of HSiR<sub>3</sub> to d<sup>6</sup> centers.<sup>6</sup>

Such analogies have prompted us to search for previously unknown<sup>7</sup> dihydrogen complexes derived from the half-sandwich complexes, 1-3, because these (C<sub>n</sub>H<sub>n</sub>)M(CO)<sub>2</sub> moieties are known



to undergo arrested oxidative addition<sup>6,8</sup> and to form relatively stable dinitrogen complexes.<sup>9</sup> Furthermore, if the dihydrogen

(1) For recent reviews of "nonclassical" dihydrogen complexes, see: (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Ginsburg, A. G.; Bagaturyants, A. A. *Metalloorganicheskaya. Khim.* **1989**, *2*, 249.

(2) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P.; Wasserman, H. J. *Am. Chem. Soc.* **1984**, *106*, 451.

(3) See, e.g.: (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705. (b) Rabaa, H.; Saillard, J.-Y.; Schubert, H. J. *Organomet. Chem.* **1987**, *330*, 397. (c) Saillard, J.-Y.; Hoffmann, R. J. *Am. Chem. Soc.* **1984**, *106*, 2006. (d) Burdett, J. K.; Phillips, J. R.; Poliakoff, M.; Pourian, M.; Turner, J. J.; Upmacis, R. K. *Inorg. Chem.* **1987**, *26*, 3054. (e) Kober, E. M.; Hay, P. J. *The Challenge of d and f Electrons*; Salahub, D. R., Zerner, M. C., Eds.; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989; p 92. (f) Pacchiani, J. *Am. Chem. Soc.* **1990**, *112*, 80.

(4) Crabtree, R. H. *Inorg. Chim. Acta* **1986**, *125*, L7. Jackson, S. A.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J.; Burdett, J. K.; Grevels, F.-W. *J. Chem. Soc., Chem. Commun.* **1987**, 678. Joshi, A. M.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1785.

(5) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowich, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674.

(6) For a recent review of such compounds, see: Schubert, U. *Adv. Organomet. Chem.* In press.

(7) There was, before we started this work, evidence for an unstable, partly characterized compound formed on protonation of [CpMn(CO)<sub>2</sub>]<sup>2-</sup> in low-temperature solutions (Leong, V. S.; Cooper, N. J. *Organometallics* **1988**, *7*, 2080). Allowing for solvent shifts in the IR, it can be seen that this compound was probably the same species as CpMn(CO)<sub>2</sub>(H<sub>2</sub>) observed in scXe in this paper.

(8) (a) Hill, R. H.; Wrighton, M. S. *Organometallics* **1985**, *4*, 413; **1987**, *6*, 632. (b) Young, K. M.; Wrighton, M. S. *Ibid.* **1989**, *8*, 1063.

(9) (a) Sellmann, D.; Maisel, G. Z. *Naturforsch.* **1972**, *27b*, 465. (b) Sellmann, D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 919. (c) Sellmann, D. *J. Organomet. Chem.* **1972**, *36*, C27. (d) Cusanelli, A.; Sutton, D. J. *Chem. Soc., Chem. Commun.* **1989**, 1719. (e) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

complexes could be formed by direct substitution of CO by H<sub>2</sub> (eq 1), there would be considerable scope for varying both the metal center and the ring substituents and for investigating how these factors affect the stability of the dihydrogen complexes.<sup>10</sup>

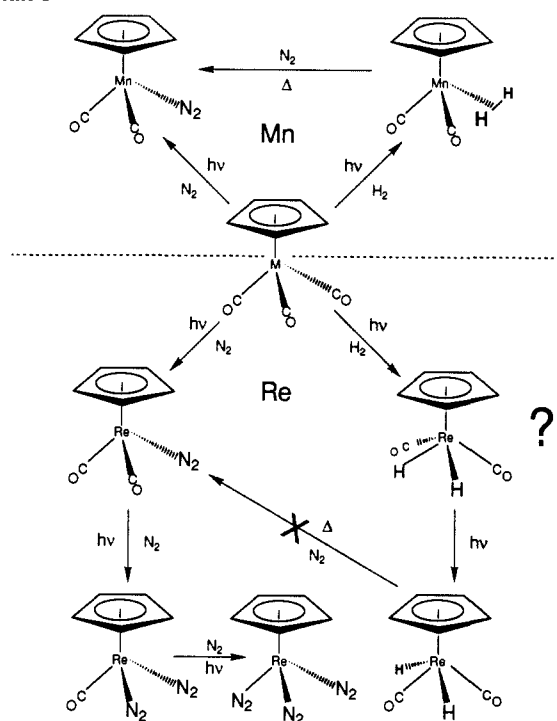


We have already shown<sup>11,12</sup> that a wide range of nonclassical dihydrogen complexes can be generated by the photolysis of an appropriate metal carbonyl precursor dissolved in liquid xenon, LXe, doped with H<sub>2</sub>. The low temperatures associated with LXe can stabilize even quite labile dihydrogen complexes, and its optical transparency has allowed us to detect the relatively weak  $\nu(H-H)$  IR bands of the  $\eta^2-H_2$  group in many of these complexes.<sup>13</sup> More recently, Bergman and co-workers have extended the applications of LXe by using it as an inert solvent for activating alkanes on a preparative scale.<sup>14</sup>

Unfortunately, LXe has a number of disadvantages for our present study. The maximum usable temperature in our LXe apparatus<sup>12a,15</sup> is inconveniently low for studying relatively stable dihydrogen complexes and, more importantly, some of the carbonyl precursors (e.g., (C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub>) are virtually insoluble in LXe, even at the relatively high temperature of -40 °C. Although more conventional solvents (e.g. *n*-heptane) do not suffer from these problems, they have a number of equally serious limitations. In particular, H<sub>2</sub> has a low solubility in such solvents at room temperature, and the detection of all but the most stable dihydrogen compounds requires very bulky high pressure cells<sup>12b</sup> or sophisticated time-resolved spectrometers.<sup>12c,16</sup>

The limitations of both liquid noble gas and conventional solvents can be overcome by the use of supercritical solvents, particularly supercritical xenon, scXe. Organometallic compounds are much more soluble in scXe than in LXe, and, in our miniature cell,<sup>17,18</sup> scXe can be used to study reactions up to 100 °C. H<sub>2</sub> is completely miscible with scXe so that, for a given pressure of H<sub>2</sub>, one can achieve an effective concentration of H<sub>2</sub> which is nearly an order of magnitude greater than that in a hydrocarbon solvent.<sup>19</sup> Furthermore, the concentration of gas dissolved in a conventional solvent varies with temperature, while the quantity

Scheme I



of gas mixed with a supercritical fluid remains constant. In addition, scXe is the only room-temperature solvent which is totally transparent throughout the IR and UV regions. IR is particularly useful for identifying the nonclassical nature of dihydrogen ligands in complexes which also contain carbonyl groups. Even if the  $\nu(H-H)$  band is not detectable, the  $\nu(C-O)$  bands can give a precise indication of the oxidation state of the metal center.<sup>12</sup> All of these properties of scXe are exploited in this paper to study the formation and behavior of dihydrogen and dinitrogen complexes.

We have already reported briefly<sup>17,18</sup> how high pressures of H<sub>2</sub> can be used to generate and stabilize nonclassical dihydrogen complexes in scXe at room temperature. In particular, we used IR spectroscopy to show that UV photolysis of CpMn(CO)<sub>3</sub> [Cp = C<sub>5</sub>H<sub>5</sub>] in the presence of H<sub>2</sub> led to the formation of the nonclassical complex, CpMn(CO)<sub>2</sub>(H<sub>2</sub>). By contrast, photolysis of CpRe(CO)<sub>3</sub> and H<sub>2</sub> proved to be a new route to the known<sup>20</sup> classical dihydride compound, *trans*-CpRe(CO)<sub>2</sub>H<sub>2</sub>. Under these supercritical conditions, CpMn(CO)<sub>2</sub>(H<sub>2</sub>) was surprisingly unreactive, with a half-life of ca. 12 h. In fact, it was possible to vent the pressure of H<sub>2</sub>, to refill the cell with N<sub>2</sub>, and to monitor the thermal reaction of CpMn(CO)<sub>2</sub>(H<sub>2</sub>) with N<sub>2</sub> to form CpMn(CO)<sub>2</sub>(N<sub>2</sub>). This known dinitrogen complex<sup>9b</sup> could also be generated directly by UV photolysis of CpMn(CO)<sub>3</sub> in scXe doped with N<sub>2</sub>. Photolysis of CpRe(CO)<sub>3</sub> under similar conditions<sup>21</sup> led to the sequential substitution of all three CO groups by N<sub>2</sub> with the ultimate formation of CpRe(N<sub>2</sub>)<sub>3</sub>.

It is the purpose of this paper to extend these preliminary experiments, summarized in Scheme I, to a wider range of (C<sub>n</sub>R<sub>n</sub>)M(CO)<sub>3</sub> complexes (M = Cr, Mn, and Fe) and, for each metal, to compare the stability of dinitrogen and dihydrogen complexes. We show that scXe provides an excellent medium for the systematic generation and spectroscopic characterization of such species at room temperature.

## Experimental Section

The nature of supercritical fluids means that all experiments have to be carried out under high pressure. We have, therefore, designed miniature cells to study these reactions on a small scale. The cells are much

(10) There is evidence that the related d<sup>4</sup> compound, CpMo(H)(CO)<sub>3</sub>, reacts with H<sub>2</sub> to form a nonclassical dihydrogen complex on photolysis in low-temperature matrices. (Sweany, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 6986.)

(11) For an excellent review of spectroscopy in liquified noble gases, see: Kimelfeld, Ya. M. *Usp. Khim.* **1988**, *57*, 1273; *Russ. Chem. Rev.* **1988**, *57*, 731.

(12) (a) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645. (b) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27. (c) Hodges, P. M.; Jackson, S. A.; Jacke, J.; Poliakoff, M.; Turner, J. J.; Grevels, F.-W. *Ibid.* **1990**, *112*, 1234. (d) Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547.

(13) Recently,  $\nu(H-H)$  bands have also been detected in low-temperature matrices. (Sweany, R. L.; Moroz, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 3577.)

(14) Sponsler, M. B.; Weiller, B. H.; Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 6841.

(15) (a) Our LXe cell (see: Maier, W. B.; Poliakoff, M.; Simpson, M. B.; Turner, J. J. *J. Mol. Struct.* **1982**, *80*, 83.) has maximum operating pressure of ca. 20 atm, which limits its use to temperatures below -30 °C. (b) Turner, J. J.; Poliakoff, M.; Howdle, S. M.; Jackson, S. A.; McLaughlin, J. G. *Faraday Disc.* **1988**, *86*, 271.

(16) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30.

(17) Poliakoff, M.; Howdle, S. M.; Healy, M. A.; Whalley, J. M. *Proceedings of the International Symposium on Supercritical Fluids*; Perrut, M., Ed.; Soc. Fr. Chim. **1988**; p 967. This contains a preliminary account of experiments with (C<sub>6</sub>H<sub>5</sub>Me)Cr(CO)<sub>3</sub>.

(18) Howdle, S. M.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1099.

(19) (a) H<sub>2</sub> has a relatively low solubility in organic solvents (e.g., 3.8 × 10<sup>-3</sup> M in cyclohexane for an overpressure of 1 atm).<sup>16</sup> By contrast, H<sub>2</sub> gas at 1 atm of pressure has a "concentration" of 4 × 10<sup>-2</sup> M, an order of magnitude greater. In practice, the difference may well be more marked because the scXe/H<sub>2</sub> mixture will not behave ideally. The difference could be further accentuated because, with higher gas pressures, it is often difficult to ensure that the H<sub>2</sub> is properly equilibrated with the organic solvent. (b) Howdle, S. M. Ph.D. Thesis, University of Nottingham, UK, 1989.

(20) Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783.

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**Table I.** Wavenumbers,  $\text{cm}^{-1}$ , of  $\nu(\text{C-O})$  and  $\nu(\text{N-N})$  IR Bands of (arene) $\text{Cr}(\text{CO})_3$  Compounds and Their Dihydrogen and Dinitrogen Derivatives in Supercritical Xe at 25 °C

( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_3$	( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_2(\text{H}_2)$	( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_2(\text{N}_2)^b$
1987.5 $a_1$	1947.7 $a'$	2150.9 $\nu(\text{N-N})$
1920.9 e	1895.7 $a''$	1947.3 $a'$
1978.1 $\nu(^{13}\text{C-O})$		1905.4 $a''$
1887.6 $\nu(^{13}\text{C-O})$		
( $\text{C}_6\text{H}_5\text{Me}$ ) $\text{Cr}(\text{CO})_3^c$	( $\text{C}_6\text{H}_5\text{Me}$ ) $\text{Cr}(\text{CO})_2(\text{H}_2)$	( $\text{C}_6\text{H}_5\text{Me}$ ) $\text{Cr}(\text{CO})_2(\text{N}_2)$
1984.8 $a'$	1944.9 $a'$	2150.2, 2141.4 $\nu(\text{N-N})$
1918.4 $a'/a''$	1895.7 $a''$	1944.7 $a'$
1975.0 $\nu(^{13}\text{C-O})$		1900.3 $a''$
1884.5 $\nu(^{13}\text{C-O})$		
( $\text{C}_6\text{Me}_6$ ) $\text{Cr}(\text{CO})_3$	( $\text{C}_6\text{Me}_6$ ) $\text{Cr}(\text{CO})_2(\text{H}_2)$	( $\text{C}_6\text{Me}_6$ ) $\text{Cr}(\text{CO})_2(\text{N}_2)^d$
1961.8 $a_1$	1917.2 $a'$	2115.5 $\nu(\text{N-N})$
1891.3 e	1867.9 $a''$	1917.8 $a'$
		1876.7 $a''$

<sup>a</sup> IR data  $\pm 0.2 \text{ cm}^{-1}$ . <sup>b</sup> Reported values:<sup>9a</sup> 2145, 1940, and 1898  $\text{cm}^{-1}$  in hexane. <sup>c</sup> In LXe at  $-90^\circ\text{C}$ : ( $\text{C}_6\text{H}_5\text{Me}$ ) $\text{Cr}(\text{CO})_3$ , 1980.5, 1913.3, and 1910.8  $\text{cm}^{-1}$ ; ( $\text{C}_6\text{H}_5\text{Me}$ ) $\text{Cr}(\text{CO})_2(\text{H}_2)$  1939.5 and 1887.5  $\text{cm}^{-1}$ ; ( $\text{C}_6\text{H}_5\text{Me}$ ) $\text{Cr}(\text{CO})_2(\text{N}_2)$  2144.8, 2136.8  $\text{cm}^{-1}$  and 1940.5, 1938.2 and 1898.0, 1895.8  $\text{cm}^{-1}$ . <sup>d</sup> Reported values:<sup>9a</sup> 2105, 1892, and 1845  $\text{cm}^{-1}$  in hexane.

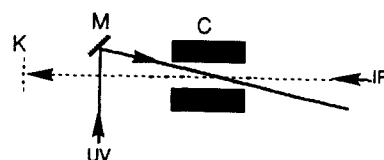
smaller than those used for conventional solvents because the low viscosity and absence of surface tension allow supercritical fluids to flow through very narrow bore tubing and orifices. **Safety Note: Care is needed when working with high-pressure fluids.**

The design of our cell has already been described in some detail.<sup>17,19</sup> Briefly, it is constructed from stainless steel with an internal volume of ca. 2.8 mL. It is designed to operate safely up to 100 °C and 4000 psi (ca. 270 atm) and has a single pair of  $\text{CaF}_2$  windows<sup>22</sup> both for IR spectroscopy and for UV photolysis (see below). The cell is fitted with a pressure transducer (RDP Electronics Model-A105 Sub-miniature, Flush diaphragm, 5000 psi max), a Chromel/Alumel thermocouple, and a magnetic agitator of our own design. There is a stainless steel cold-finger, the volume of which constitutes most of the volume of the cell. The cold-finger is used to condense Xe into the cell so that the cell can be pressurized without the aid of an external pump. When required, the cell is wrapped with heating tape, and the temperature is maintained within  $\pm 0.5^\circ\text{C}$  with a platinum resistance probe (RS 158-244) and a proportional feedback temperature controller (RS 344-603).

IR spectra were recorded either with a Nicolet MX-3600 or with a Nicolet Model 730 (HgCdTe detector) Fourier transform interferometer (16K data points, 2  $\text{cm}^{-1}$  resolution). All spectra were recorded at 25 °C unless otherwise stated. Kinetic data for (toluene) $\text{Cr}(\text{CO})_2(\text{H}_2)$  were recorded on a Perkin-Elmer Model 580B dispersive IR spectrometer set at fixed wavelength (Integrated Scan Mode 5) and running in "Time Drive". Traces were recorded on time scales between 15 s and 1 h and were measured by hand. Either a Philips HPK 125W medium pressure Hg arc or a Cermax 300W Xe arc lamp was used for UV photolysis. The Cermax lamp, which was far more intense than the Hg arc, was filtered with a Cermax OP2 mirror assembly to give wavelengths from 200 to 400 nm. We were able to record IR spectra during and immediately after UV photolysis by using the optical arrangement illustrated in Figure 1.

In a typical experiment, 1–3 mg of carbonyl complex were loaded into the cell. For most of the compounds described in this paper, this quantity gave a solution, suitable for IR spectroscopy, which was generally less than saturated. The cell was then evacuated, gaseous Xe was condensed into the cold-finger with using liquid  $\text{N}_2$ ; and the cell was pressurized with  $\text{H}_2$  or  $\text{N}_2$  gas, while the Xe was still solid.<sup>23</sup> On warming up to 25 °C, the total pressure in the cell was typically 2650 psi (i.e., 1150 psi Xe without added  $\text{H}_2$ ). The critical pressure of Xe,  $P_c$ , is ca. 880 psi (59 atm), and the critical temperature,  $T_c$ , is 16.8 °C. The small quantities of dissolved organometallics do not affect  $T_c$  appreciably, but the addition of  $\text{H}_2$  (or  $\text{N}_2$ ) in the quantities used here lowers  $T_c$  significantly (i.e., by 10–20 °C).<sup>19b</sup> Thus, all of our experiments have been performed under supercritical conditions.

Xe,  $\text{H}_2$ , and  $\text{N}_2$  (BOC Research Grade) were used without further purification. ( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_3$ , ( $\text{C}_6\text{H}_5\text{Me}$ ) $\text{Cr}(\text{CO})_3$ , and ( $\text{C}_6\text{Me}_6$ ) $\text{Cr}(\text{CO})_3$  were prepared by standard methods.<sup>24</sup>  $\text{CpMn}(\text{CO})_3$  and ( $\text{C}_5\text{Me}_5$ )Mn-



**Figure 1.** Schematic plan view of the optical arrangement used for UV irradiation of the miniature high pressure cell in the sample compartment of an IR spectrometer (or interferometer). The components are labeled as follows: C, the cell; M, a small front silvered mirror; K, a piece of KRS-5 (TlBrI), which filters out the stray UV light. For an alternative irradiation geometry, see ref 12c.

( $\text{CO}$ )<sub>3</sub> (Strem Chemicals) were used as supplied. We are grateful for gifts of  $\text{CpRe}(\text{CO})_3$  and ( $\text{C}_5\text{Me}_5$ ) $\text{Re}(\text{CO})_3$  from Dr. R. N. Perutz and of ( $\text{C}_4\text{H}_9$ ) $\text{Fe}(\text{CO})_3$  from Dr. F.-W. Grevels.

## Results and Discussion

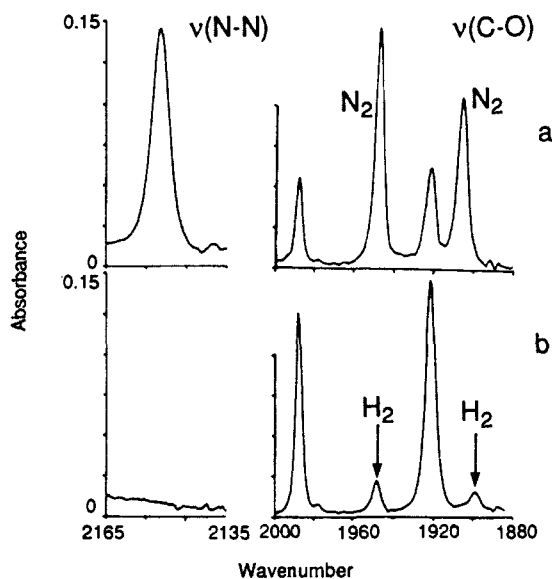
**Reactions of (arene) $\text{Cr}(\text{CO})_3$  with  $\text{N}_2$  and  $\text{H}_2$  in scXe.** Although ( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_3$  is insoluble in LXe, it is sparingly soluble in scXe at room temperature. UV photolysis of the scXe solution in the absence of added reactant did not give rise to any detectable products. By contrast, UV photolysis of ( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_3$  in the presence of  $\text{N}_2$  resulted in  $>75\%$  conversion to ( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{C-O})_2(\text{N}_2)$  with an IR spectrum,  $\nu(\text{N-N})$  and two  $\nu(\text{C-O})$  ( $a'$  +  $a''$ ), similar to that reported for conventional solvents,<sup>9a</sup> see Figure 2a. ( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_2(\text{N}_2)$  was not completely stable under these conditions, and, as in other solvents, it decomposed slowly even in the dark.

UV photolysis of ( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_3$  in the presence of  $\text{H}_2$  gave a new product which had two  $\nu(\text{C-O})$  bands, arrowed in Figure 2b, very close in frequency to those of ( $\text{C}_6\text{H}_6$ ) $\text{Cr}(\text{CO})_2(\text{N}_2)$  but without a  $\nu(\text{N-N})$  band. This product was thermally less stable

(23) The approximate amount of Xe condensed can be established by weighing the cell before the  $\text{H}_2$  is added. Typical weights were in the range 3–3.5 g, which correspond to 23–27 mmol of Xe in the cell. In the absence of Xe,  $\text{H}_2$  at a pressure of 1500 psi and 25 °C would give 11.5 mmol in the cell. The pressure of  $\text{H}_2$  used to fill the cell can be measured precisely, and, unless otherwise stated, it is this pressure of  $\text{H}_2$  which is quoted in this paper. Although these pressures are quite reproducible, it is difficult to quantitate the relative concentrations of  $\text{H}_2$  and Xe, because there is uncertainty in the precise volume of the cell occupied by the solid Xe (while frozen down) and in the exact temperature of the  $\text{H}_2$  gas when the cell is being pressurized with the cold-finger in liquid  $\text{N}_2$ . (In the case of  $\text{N}_2$ , care was required to avoid too much  $\text{N}_2$  condensing into the cell because this led to excessive pressures when the cell was warmed to room temperature.) Two further parameters, which can be measured are (i) the pressure of Xe when the cell is warmed up without any other gas added and (ii) the total gas pressure after the second gas has been added. However, these are also awkward to convert to relative concentrations of  $\text{H}_2$  and Xe because of the nonideal behavior of the mixtures. These problems do not arise when small quantities of gas (e.g., CO) are added before the Xe. Thus 5 psi pressure of CO gives 0.12 mmol on the cell.

(24) Strohmeier, W. *Chem. Ber.* 1961, 94, 2490.

(22) The windows are 15-mm diameter and 10-mm thick with an unsupported area 7 mm in diameter. The windows are sealed to the cell body with Oxford Instruments M5 low-temperature epoxy resin. The maximum operating pressure predicted for these windows is 9000 psi (600 bar). For details of calculations, see: Whyman, R. In *Laboratory Methods in Vibrational Spectroscopy*; Willis, H. A., Van Der Maas, J. H., Miller, R. G. J., Eds.; John Wiley: London, 1987; p 281.



**Figure 2.** A comparison of the  $\nu(\text{N-N})$  and  $\nu(\text{C-O})$  regions of the IR spectra of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{N}_2)$  and  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$  generated photochemically from  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$  in scXe. (a) After 100 s UV photolysis (medium pressure Hg arc) in the presence of  $\text{N}_2$  (700 psi); bands labeled "N<sub>2</sub>" are due to  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{N}_2)$ . (b) After 30 s UV photolysis in the presence of  $\text{H}_2$  (700 psi); bands labeled "H<sub>2</sub>" and arrowed are assigned to  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$ . In both spectra, the unlabeled  $\nu(\text{C-O})$  bands belong to unreacted  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$ .

than  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{N}_2)$ , decaying more slowly as the pressure of  $\text{H}_2$  was increased. The wavenumbers and relative intensities of the  $\nu(\text{C-O})$  bands are consistent with a  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2\text{L}$  species, and, since the product was not generated in the absence of  $\text{H}_2$ , L is most probably  $\text{H}_2$ .

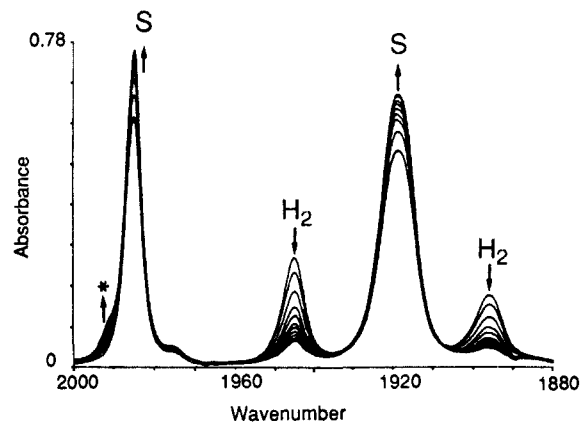
Analogous results were obtained upon photolysis of  $(\text{C}_6\text{H}_5)_3\text{Cr}(\text{CO})_3$  and  $(\text{C}_6\text{Me}_6)_3\text{Cr}(\text{CO})_3$  in scXe doped with  $\text{N}_2$  or  $\text{H}_2$ . In the case of  $\text{N}_2$ , the products could easily be identified as  $(\text{arene})\text{Cr}(\text{CO})_2(\text{N}_2)$  compounds from the IR data,<sup>25</sup> see Table I. The greater electron-donating power of the  $\text{C}_6\text{Me}_6$  ring causes the  $\nu(\text{C-O})$  and  $\nu(\text{N-N})$  bands to shift ca.  $35\text{ cm}^{-1}$  to lower wavenumber compared to the other arene species. In the case of  $\text{H}_2$ , the photoproducts were species with  $\nu(\text{C-O})$  bands very close to those of the corresponding  $(\text{arene})\text{Cr}(\text{CO})_2(\text{N}_2)$  compound. Although there was no positive spectroscopic evidence for coordinated hydrogen, both the route by which these compounds were generated, and the  $\nu(\text{C-O})$  spectra indicate that they are  $(\text{arene})\text{Cr}(\text{CO})_2(\text{H}_2)$  compounds. Are these dihydrogen species classical or nonclassical?

If one compares the  $\nu(\text{C-O})$  bands of a classical dihydride,  $\text{ML}_n\text{H}_2$ , and its dinitrogen analogue,  $\text{ML}_n\text{N}_2$ , the oxidation of the metal center in the dihydride produces a significant shift to higher wavenumber<sup>26</sup> (as in the case<sup>18</sup> of  $\text{CpRe}(\text{CO})_2(\text{H}_2)$ ). On the other hand, the metal center in a "nonclassical" dihydrogen complex has the same oxidation state as in a dinitrogen complex and so the two compounds have  $\nu(\text{C-O})$  bands at similar wavenumbers. Thus, the IR data in Table I indicate that all three  $(\text{arene})\text{Cr}(\text{CO})_2(\text{H}_2)$  complexes are nonclassical.

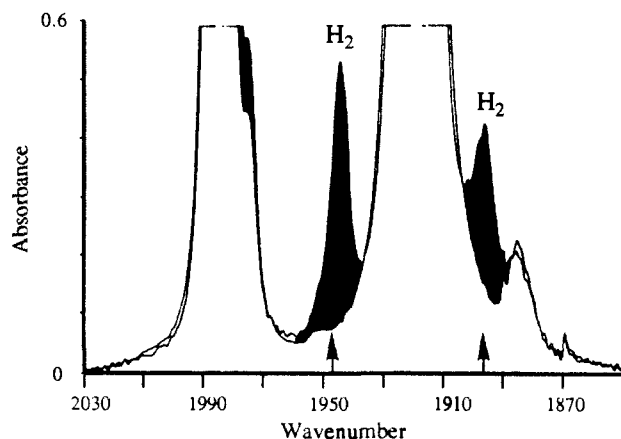
$(\text{C}_6\text{H}_5)_3\text{Cr}(\text{CO})_3$  is considerably more soluble in scXe than either  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$  or  $(\text{C}_6\text{Me}_6)_3\text{Cr}(\text{CO})_3$ . As with the other dihydrogen species,  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$  is thermally unstable

(25) In the case of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{N}_2)$ , there are two bands in the  $\nu(\text{N-N})$  region with relative intensities ca. 2:1, both of which were clearly due to  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{N}_2)$ —i.e., the relative intensity of two bands remained constant throughout the thermal decay of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{N}_2)$ . By contrast there were only two  $\nu(\text{C-O})$  bands observable in scXe at room temperature. However, when the experiment was repeated in cryogenic LXe at  $-80^\circ\text{C}$ , the  $\nu(\text{C-O})$  bands were also found to be slightly split (see Table I). The splittings are therefore assigned to rotamers, a consequence of the relatively low symmetry of the  $\text{C}_6\text{H}_5$  ring. No comparable splitting of the  $\nu(\text{C-O})$  bands of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$  were observed in LXe.

(26) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

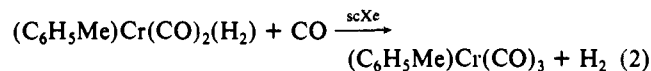


**Figure 3.** A series of IR spectra illustrating the changes which occur in the  $\nu(\text{C-O})$  region during the thermal decay of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$ , generated by UV photolysis of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$  in scXe under 1200 psi pressure of  $\text{H}_2$ . Under these conditions,  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$  decays with  $t_{1/2}$  of ca. 3 min at  $25^\circ\text{C}$ . The first spectrum was recorded immediately after blocking the UV lamp, and subsequent spectra were taken at intervals of ca. 50 s. The bands are assigned as follows:  $\text{H}_2$ ,  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$ ; S,  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$ , which is regenerated during the decay; and \*, trace quantities of  $\text{Cr}(\text{CO})_6$ .

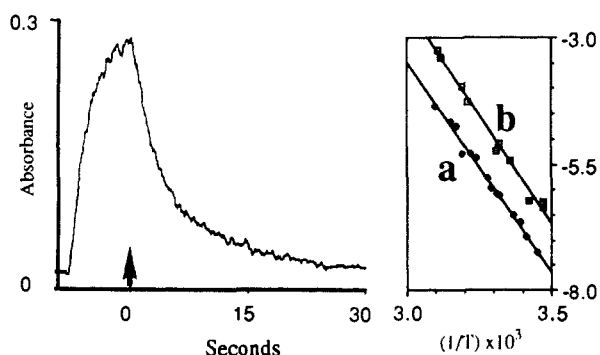


**Figure 4.** IR spectra recorded under similar conditions to those in Figure 3 but with a much higher concentration of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$  in the cell. The colored regions show the differences between spectra recorded with and without UV irradiation (medium pressure Hg arc). The bands are assigned as follows:  $\text{H}_2$ ,  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$ ; unmarked, unreacted  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$ . The arrows show the IR wavenumbers used for kinetic measurements (see, e.g., Figure 5). Note that the overall conversion to  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$  is not much greater than in Figure 3 but that, under these conditions, its formation is almost completely reversible.

in scXe, decaying when the UV irradiation is stopped. The spectra in Figure 3 show that the predominant process in the decay of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{H}_2)$  is regeneration of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$ , eq 2, although traces of  $\text{Cr}(\text{CO})_6$  are also formed.<sup>27</sup>



(27)  $\text{Cr}(\text{CO})_6$  has a particularly high extinction in the IR so even small traces are easily detected in the  $\nu(\text{C-O})$  region of the spectrum. With more concentrated solutions of  $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$ , the formation of  $\text{Cr}(\text{CO})_6$  was confirmed by recovering a small quantity of white residue which was left in the cell after prolonged (e.g., several hours) UV photolysis. This material dissolved in *n*-heptane, giving the characteristic IR spectrum of  $\text{Cr}(\text{CO})_6$ . Under these conditions, there was also a thin film of metal deposited on the  $\text{CaF}_2$  window through which the UV radiation entered the cell. The photochemical loss of the arene group from  $(\text{arene})\text{Cr}(\text{CO})_3$  and the subsequent formation of  $\text{Cr}(\text{CO})_6$  has been the subject of several studies which suggest that a polynuclear intermediate may be involved. E.g., Bamford, C. H.; Al-Lamee, K. D.; Konstantinov, C. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1406. Domogatskaya, E. A.; Sektina, V. N.; Baranetskaya, N. K.; Trembovler, V. N.; Yavorskii, B. M.; Shteinshneider, A. Ya.; Petrovskii, P. V. *J. Organomet. Chem.* **1983**, *248*, 161.



**Figure 5.** An IR kinetic trace (recorded at  $1945\text{ cm}^{-1}$ , Perkin-Elmer 580B spectrometer) showing the growth of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  during UV irradiation of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_3$  and  $\text{H}_2$  (1500 psi) in scXe and its subsequent thermal decay when the lamp was switched off at the point indicated by the arrow. The trace was recorded at  $70^\circ\text{C}$ , and the rate of the decay follows first-order kinetics. Inset: Arrhenius plots for the thermal decay of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  in scXe. The data in this figure are shown over the temperature range  $14\text{--}50^\circ\text{C}$  (a) in the absence of added CO and (b) in the presence of 5 psi (ca.  $1.5 \times 10^{-3}\text{ M}$ ) added CO. The gradients of the two traces give activation energies of (a)  $69 \pm 2\text{ kJ mol}^{-1}$  and (b)  $71.5 \pm 3.5\text{ kJ mol}^{-1}$ , respectively.

A kinetic analysis of the bands of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  in Figure 3 shows that the decay is definitely not a first-order process under these conditions. If, however, a very much more concentrated solution of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_3$  is used (see Figure 4), the formation of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  becomes effectively reversible. The  $\nu(\text{C}\text{--}\text{O})$  IR bands of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  decay exponentially (i.e., by a pseudo-first-order process) over several half-lives,<sup>28</sup> and we have used a dispersive IR spectrometer to monitor the kinetics of this process (see Figure 5). The kinetic problems are similar to those presented by the reaction of CO with  $\text{Ni}(\text{CO})_3(\text{N}_2)$  in liquid krypton,<sup>29</sup> where the leaving group,  $\text{N}_2$ , was in a great excess over the entering group, CO. Although uncertainties in reactant concentrations<sup>23</sup> mean that our measurements for  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  in scXe are less quantitative than were those for  $\text{Ni}(\text{CO})_3(\text{N}_2)$ , several conclusions can be drawn.

(i)  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  decays more slowly as the pressure of  $\text{H}_2$  in the cell is increased. This suggests that the reaction with CO cannot be a purely *dissociative* process, because the rate of such a process should not depend<sup>29</sup> on the concentration of  $\text{H}_2$ .

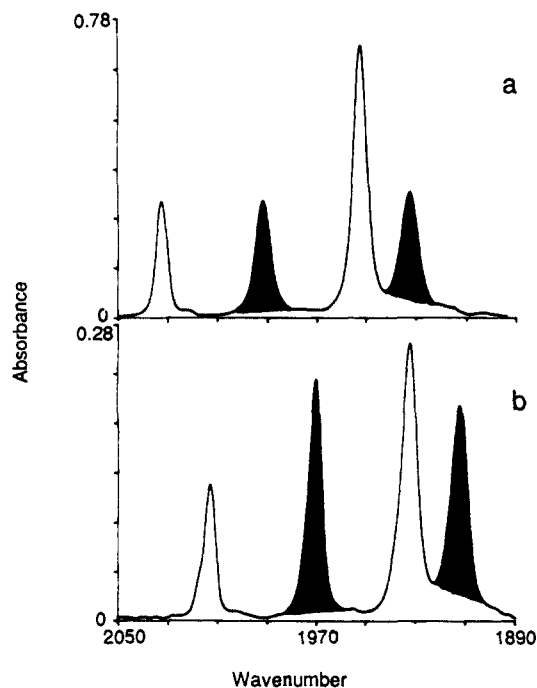
(ii) The rate of the reaction is increased by the addition of free CO to the scXe. Given (i), this observation is consistent with either a *dissociative* process or a combination of associative and dissociative pathways. It does not rule out the possibility that the decay of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  involves the formation of a transient dinuclear species via reaction with  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_3$ .

(iii) Over the temperature range  $11^\circ\text{C}$  (room temperature!) to  $80^\circ\text{C}$ , the decay of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  has an activation energy of  $70 \pm 5\text{ kJ mol}^{-1}$ . Within experimental error, this value is independent of the amount of CO or  $\text{H}_2$  present in the cell at the start of the experiment, see Figure 5. This observation is particularly significant. Relatively few reactions have been studied under supercritical conditions, and the properties of such fluids are known to show considerable anomalies near the critical point.<sup>30</sup>

(28) At higher temperatures, the rate of decay became comparable to the time required for the supercritical fluid to diffuse out of the irradiated volume of the cell. In these circumstances, the "decay" of the IR signal was initially very rapid but then became first-order as soon as the contents of the cell had equilibrated. Although there was clearly some decomposition of the sample (see ref 27), this did not appear to affect the reaction rates significantly. At a given temperature, the rate of decay of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$  remained unchanged within experimental error even after several days of UV irradiation.

(29) Turner, J. J.; Simpson, M. B.; Poliakov, M.; Maier, W. B., II *J. Am. Chem. Soc.* **1983**, *105*, 3898.

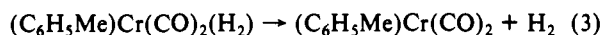
(30) This behavior may well be similar to that observed for solubility in some supercritical fluids. A plot of  $\ln(\text{solubility})$  vs  $1/T$  can give a straight line when measured at constant density although it may not be so "well-behaved" when measured at constant pressure because of the temperature-dependent compressibility of a supercritical fluid. See: Johnston, K. P.; Barry, S. E.; Read, N. K.; Holcomb, T. R. *Ind. Eng. Chem. Res.* **1987**, *26*, 2372.



**Figure 6.** IR spectra, comparing the  $\nu(\text{C}\text{--}\text{O})$  bands of the photoproducts obtained by photolysis of  $(\text{C}_5\text{R}_5)\text{Mn}(\text{CO})_3$  compounds in scXe under 1500 psi  $\text{H}_2$  at  $25^\circ\text{C}$ : (a) after 3-min UV irradiation (medium pressure Hg arc) of  $\text{CpMn}(\text{CO})_3$ , and (b) after 2-min UV irradiation (Cermax Xe arc) of  $\text{Cp}^*\text{Mn}(\text{CO})_3$ . In both spectra, the bands of the photoproducts are colored black, and those of unreacted starting material are unlabeled.

It is, therefore, gratifying to find that reactions can still show "classical" Arrhenius behavior in these circumstances. In fact, supercritical conditions have an added advantage. Unlike an experiment with conventional solvents, all of the reactants were in a single phase, and their concentrations did not vary with temperature. Thus, we do not have to adjust the value of the activation energy for varying solubility of the reactant gases.

These observations do not provide sufficient evidence to construct a complete mechanism for the reaction. It is nevertheless tempting to equate the activation energy with a rate-determining step which involves breaking the  $\text{Cr}\text{--}(\eta^2\text{--}\text{H}_2)$  bond. (eq 3).<sup>31</sup> The



value,  $70\text{ kJ mol}^{-1}$  is consistent with the elegant thermochemical measurements on Kubas's compounds,<sup>32</sup> and, indeed, it is almost identical with that predicted for the strength of the  $\text{W}\text{--}(\eta^2\text{--}\text{H}_2)$  bond.<sup>3a</sup>

Given the large number of nonclassical dihydrogen complexes of Group 6 metals, the formation of these (arene) $\text{Cr}(\text{CO})_2(\text{H}_2)$  complexes is not unexpected. What is surprising, however, is the thermal stability of the compounds. Our experiments indicate that the (arene) $\text{Cr}(\text{CO})_2(\text{H}_2)$  complexes are only slightly more

(31) The assumptions necessary for identifying an activation energy with a bond dissociation energy in this type of reaction have been discussed at length.<sup>29</sup> There are additional problems in the present case. Working in a closed cell means that these measurements are made at constant volume and, hence, at constant density rather than at constant pressure. Given the anomalous compressibility of a supercritical fluid,<sup>30</sup> it is not entirely clear how much the value of  $E_a$  will be affected. Two other factors suggest that one should be cautious in equating the activation and bond dissociation energies in our experiment. (i)  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2\text{Xe}$  may be formed at least transiently because Xe is known to interact significantly with coordinatively unsaturated intermediates (Simpson, M. B.; Poliakov, M.; Turner, J. J.; Maier, W. B., II; McLaughlin, J. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1355; Weiller, B. H.; Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; Pimentel, G. C. *J. Am. Chem. Soc.* **1989**, *111*, 8288.) (ii) We obtained an almost identical value for the activation energy in the thermal decomposition of  $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{N}_2)$ . Of course, this may merely be the consequence of similar strengths of  $\text{Cr}\text{--}(\eta^2\text{--}\text{H}_2)$  and  $\text{Cr}\text{--}\text{N}_2$  bonds, because the thermochemical measurements on tungsten complexes also gave similar values for dihydrogen and dinitrogen complexes.<sup>32</sup>

Table II. Wavenumbers,  $\text{cm}^{-1}$ , of  $\nu(\text{C-O})$  and  $\nu(\text{N-N})$  IR bands of  $\text{CpM}(\text{CO})_3$  and  $\text{Cp}^*\text{M}(\text{CO})_3$  [ $\text{M} = \text{Mn}$  and  $\text{Re}$ ] and Their Dihydrogen and Dinitrogen Derivatives in Supercritical Xe at 25 °C

$\text{CpMn}(\text{CO})_3^b$	$\text{CpMn}(\text{CO})_2(\text{H}_2)$	$\text{CpMn}(\text{CO})_2(\text{N}_2)^c$	
		2171.3 $\nu(\text{N-N})^d$	
2032.8 $a_1$	1991.9 (92.3) $^f a'$	1985.0 $a'$	
1952.3 $e$	1932.5 (31.4) $^f a''$	1934.0 $a''$	
2021.5	$g$	$g$ $\nu(^{13}\text{C-O})$	
1917.3	1903.8 (01.5) $^f$	1904.3 $\nu(^{13}\text{C-O})$	
$\text{Cp}^*\text{Mn}(\text{CO})_3$	$\text{Cp}^*\text{Mn}(\text{CO})_2(\text{H}_2)$		
2012.8 $a_1$		1970.4 $a'$	
1932.0 $e$		1912.2 $a''$	
2001.8 $\nu(^{13}\text{C-O})$		$g$	
1897.9 $\nu(^{13}\text{C-O})$		$g$	
$\text{CpRe}(\text{CO})_3$	$\text{CpRe}(\text{CO})_2(\text{N}_2)^h$	$\text{CpRe}(\text{CO})(\text{N}_2)_2$	$\text{CpRe}(\text{N}_2)_3$
	2146.8 $a' \nu(\text{N-N})$	2142.0 $a' \nu(\text{N-N})$	2135.9 $a_1 \nu(\text{N-N})$
2035.0 $a_1$	1978.4 $a'$	2095.1 $a'' \nu(\text{N-N})$	2069.0 $e \nu(\text{N-N})$
1946.9 $e$	1925.8 $a''$	1929 $a'$	
2023.9 $\nu(^{13}\text{C-O})$	$g$		
1912.1 $\nu(^{13}\text{C-O})$	$g$		
$\text{Cp}^*\text{Re}(\text{CO})_3$	$\text{Cp}^*\text{Re}(\text{CO})_2(\text{N}_2)^j$	$\text{Cp}^*\text{Re}(\text{CO})(\text{N}_2)_2$	$\text{Cp}^*\text{Re}(\text{N}_2)_3$
	2128.0 $a' \nu(\text{N-N})$	2123.8 $a' \nu(\text{N-N})$	2117.2 $a_1 \nu(\text{N-N})$
2018.0 $a_1$	1959.3 $a'$	2073.9 $a'' \nu(\text{N-N})$	2049.2 $e \nu(\text{N-N})$
1929.4 $e$	1907.8 $a''$	1906 $a'$	
2006.3 $\nu(^{13}\text{C-O})$	$g$		
1894.8 $\nu(^{13}\text{C-O})$	$g$		

<sup>a</sup> IR data  $\pm 0.2 \text{ cm}^{-1}$ . <sup>b</sup> Ca. 40 other IR bands (fundamentals, overtones, etc.) due to  $\text{CpMn}(\text{CO})_3$  could be observed in the range 5000–1100  $\text{cm}^{-1}$ . <sup>c</sup> Reported values:<sup>9b</sup> 2169, 1980, and 1923  $\text{cm}^{-1}$  in hexane. <sup>d</sup> 2137.2  $\text{cm}^{-1}$   $\nu(^{14}\text{N}-^{15}\text{N})$  satellite, natural isotopic abundance. <sup>e</sup> Values in parentheses for  $\text{CpMn}(\text{CO})_2(\text{D}_2)$ . <sup>f</sup> The region where  $\nu(^{13}\text{C-O})$  satellites are predicted is obscured by other bands. <sup>g</sup> Reported values:<sup>9c</sup> 2141, 1970 and 1915  $\text{cm}^{-1}$  in hexane. <sup>h</sup> Reported values:<sup>9c</sup> 2124, 1953, and 1901  $\text{cm}^{-1}$  in hexane.

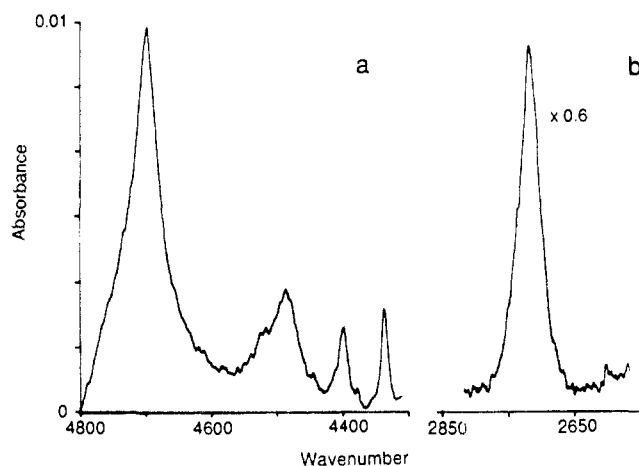


Figure 7. IR bands due to (a) pressure induced absorptions of molecular  $\text{H}_2$  dissolved in  $\text{scXe}$  and (b) the  $\nu(\text{H-H})$  vibration of  $\eta^2\text{-H}_2$  in  $\text{W}(\text{C-O})_3(\text{H}_2)$ . Both regions of the spectrum were recorded in the same experiment at 27 °C with a total pressure ( $\text{H}_2 + \text{scXe}$ ) 2460 psi and 1.8 mm optical pathlength. Under these conditions,  $\text{W}(\text{CO})_3(\text{H}_2)$  decays with  $t_{1/2}$  of only 20 s, and the IR spectra were recorded, while the sample was being irradiated with UV light. The spectrum in (a) has been digitally smoothed, whereas spectrum (b) is as recorded but plotted with 0.6 reduction in the Absorbance scale.

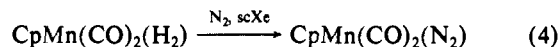
labile than the corresponding dinitrogen complexes, which were first isolated on a preparative scale over 20 years ago.<sup>9a</sup> The thermal stability of  $\text{CpMn}(\text{CO})_2(\text{H}_2)$ , described in the next section, is even more striking.

**Reaction of  $(\text{C}_5\text{R}_5)\text{Mn}(\text{CO})_3$  [ $\text{R} = \text{H}$  or  $\text{Me}$ ] with  $\text{H}_2$  in  $\text{scXe}$ .** The reactions of Group 7 metal complexes with  $\text{H}_2$  are particularly interesting because Mn and Re appear to be on opposite sides of the nonclassical/classical divide. As explained in Scheme I, photolysis<sup>18</sup> of  $\text{CpMn}(\text{CO})_3$  with  $\text{H}_2$  in  $\text{scXe}$  leads to nonclassical  $\text{CpMn}(\text{CO})_2(\text{H}_2)$ , while photolysis of  $\text{CpRe}(\text{CO})_3$  under similar conditions leads to the dihydride  $\text{CpRe}(\text{CO})_2\text{H}_2$ . One possible rationalization of this behavior, reminiscent of that observed for the  $\text{MH}_4\text{L}_3$  complexes of the Group 8 metals,<sup>1b</sup> is that the Re-H

bond strength is greater than the Mn-H. Alternatively, back-bonding from the metal center, which leads to rupture of the H-H bond in the coordinated  $\text{H}_2$ , is more facile for the larger Re atom. The electron density on the Mn center can be increased by use of the  $\text{C}_5\text{Me}_5$ ,  $\text{Cp}^*$ , ligand. How does  $\text{Cp}^*\text{Mn}(\text{CO})_3$  react with  $\text{H}_2$ ?

Figure 6 compares the IR spectra, in the  $\nu(\text{C-O})$  region, obtained by UV photolysis of (a)  $\text{CpMn}(\text{CO})_3$  and (b)  $\text{Cp}^*\text{Mn}(\text{CO})_3$  in the presence of  $\text{H}_2$ . The spectra show that, qualitatively, the behavior of the two compounds is identical.<sup>33</sup> In each case, a photoproduct is generated with  $\nu(\text{C-O})$  bands, colored black in Figure 6, shifted down in wavenumber relative to those of the parent tricarbonyl species. The positions of these bands indicate the formation of nonclassical dihydrogen complexes,  $(\text{C}_5\text{R}_5)\text{Mn}(\text{CO})_2(\text{H}_2)$ . The IR data are summarized in Table II. Thus, substitution of Cp by  $\text{Cp}^*$  does not affect the metal center sufficiently to promote the formation of a classical dihydride.

The difference in behavior of Mn and Re gives us considerable confidence in the use of  $\nu(\text{C-O})$  bands for distinguishing between classical and nonclassical complexes. Nevertheless, we have attempted to get further evidence for the presence of  $\eta^2\text{-H}_2$  in  $\text{CpMn}(\text{CO})_2(\text{H}_2)$ . The compound is sufficiently stable for  $\text{N}_2$  to be added to the cell after the photolysis and for the thermal reaction with  $\text{N}_2$  to be followed,<sup>18</sup> eq 4. Displacement of  $\text{H}_2$  by



$\text{N}_2$  is one of the characteristic reactions of nonclassical dihydrogen complexes,<sup>2b,12a,c</sup> but, unfortunately, it was not possible to make detailed kinetic measurements on this reaction.<sup>34</sup>

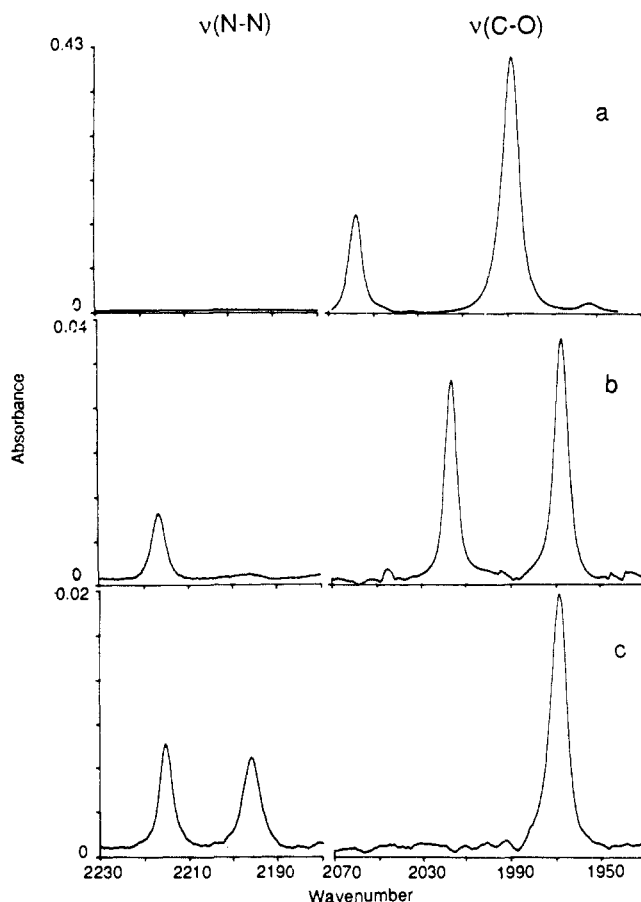
(32) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; Vega, R. L.; Mukherjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallic* 1988, 7, 2429. Gonzalez, A. A.; Hoff, C. D. *Inorg. Chem.* 1989, 28, 4295.

(33) Mass spectra of our sample of  $\text{Cp}^*\text{Mn}(\text{CO})_3$  showed that it was contaminated with a trace impurity of  $(\text{C}_5\text{Me}_4\text{H})\text{Mn}(\text{CO})_3$ . Although the IR bands of the two compounds are close in wavenumber, they can be resolved adequately under the conditions of our experiment. Thus, the impurity was not removed and, in fact, led to formation of detectable amounts of  $(\text{C}_5\text{Me}_4\text{H})\text{Mn}(\text{CO})_2(\text{H}_2)$ .

Even though sufficient  $\text{CpMn}(\text{CO})_2(\text{H}_2)$  was generated in our cell for us to detect overtones and combinations of the  $\nu(\text{C}-\text{O})$  vibrations, no IR band assignable to the  $\nu(\text{H}-\text{H})$  vibration of coordinated  $\text{H}_2$  could be observed. It is unlikely that this was due to an inherent lack of sensitivity in our experiment. As shown in Figure 7, we were able to observe the  $\nu(\text{H}-\text{H})$  band of  $\text{W}(\text{C}-\text{O})_5(\text{H}_2)$  under similar conditions<sup>35</sup> as well as some of the IR bands of uncomplexed  $\text{H}_2$  dissolved in  $\text{scXe}$ .<sup>36</sup> It is possible that the  $\nu(\text{H}-\text{H})$  band of  $\text{CpMn}(\text{CO})_2(\text{H}_2)$  could have been obscured by the  $\nu(\text{C}-\text{H})$  absorptions of the Cp ligand (ca.  $3000\text{ cm}^{-1}$ ), but, in that case, one might have expected to detect the  $\nu(\text{D}-\text{D})$  band of  $\text{CpMn}(\text{CO})_2(\text{D}_2)$ , which should have been shifted to lower wavenumber.<sup>37</sup> Most probably, the  $\nu(\text{H}-\text{H})$  band of  $\text{CpMn}(\text{CO})_2(\text{H}_2)$  is just very weak and rather broad,<sup>38</sup> making it difficult to locate. Crabtree has pointed out<sup>2b</sup> that it is much easier to observe the  $\nu(\text{H}-\text{H})$  bands of nonclassical dihydrogen complexes which also contain CO groups than of those which do not. It is a reasonable extrapolation to suggest that it will become progressively harder to locate the  $\nu(\text{H}-\text{H})$  band as one reduces the number of CO groups in a particular compound. Thus, with only two CO groups in the molecule, the  $\nu(\text{H}-\text{H})$  band of  $\text{CpMn}(\text{CO})_2(\text{H}_2)$  may well be undetectable among the forest of weak overtone and combination bands which congest this region of the spectrum.<sup>18,19b</sup>

**Reactions of  $\text{CpM}(\text{CO})_3$  [ $\text{M} = \text{Mn}$  and  $\text{Re}$ ] with  $\text{N}_2$  in  $\text{scXe}$ .** We have already reported<sup>18</sup> that UV photolysis of  $\text{CpMn}(\text{CO})_3$  and  $\text{N}_2$  in  $\text{scXe}$  leads to the formation of  $\text{CpMn}(\text{CO})_2(\text{N}_2)$ . After prolonged photolysis, traces of a secondary photoproduct can be observed with a weak  $\nu(\text{N}-\text{N})$  band at  $2121.9\text{ cm}^{-1}$ . This band disappears completely within 30 s of the UV lamp being switched off. The band may be one of the two  $\nu(\text{N}-\text{N})$  bands expected for  $\text{CpMn}(\text{CO})(\text{N}_2)_2$  ( $a' + a''$ ), but it is so weak that the assignment can only be tentative.<sup>39</sup> Thus, if substitution of more than one CO group does occur, it must be a relatively minor process for  $\text{CpMn}(\text{CO})_3$  under these conditions.

Multiple substitution does occur in the reaction of  $\text{CpRe}(\text{CO})_3$  with  $\text{N}_2$  in  $\text{scXe}$ .<sup>21</sup> see Scheme I. The spectroscopic identification of the various  $\text{CpRe}(\text{CO})_{3-x}(\text{N}_2)_x$  species ( $x = 1-3$ ) was supported by matrix isolation experiments, which included a full  $^{14}\text{N}_2/^{15}\text{N}_2$  isotopic analysis.<sup>21</sup> The matrix experiments had an additional significance because they confirmed that all of the species generated under these conditions in  $\text{scXe}$  were mononuclear. In fact, we have not observed the formation of any dinuclear species in our experiments in  $\text{scXe}$ . Nevertheless,  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  has been known for many years.<sup>40a</sup> and the Mn analogue has been observed



**Figure 8.** IR spectra in the  $\nu(\text{N}-\text{N})$  and  $\nu(\text{C}-\text{O})$  regions of (a)  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ , (b)  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$ , and (c)  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})(\text{N}_2)_2$  dissolved in  $\text{scXe}$  under 1200 psi pressure of  $\text{N}_2$ . The dinitrogen species were generated by UV photolysis (Cermox Xe arc) of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ . Spectra (b) and (c) have been obtained by computer subtraction of spectra similar to those in Figure 9, to remove the effects of overlap between the bands of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$  and  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})(\text{N}_2)_2$ .

both at low temperatures in LXe solution<sup>40b</sup> and transiently at room temperature by time-resolved IR in conventional solvents.<sup>40c</sup> These dinuclear species are formed by the reaction of coordinatively unsaturated intermediates and unphotolyzed starting material,<sup>40c</sup> eq 5. Formation of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  is competitive with



the reaction with  $\text{N}_2$ , and, presumably, the concentration of  $\text{N}_2$  in the  $\text{scXe}$  solution is sufficiently high to suppress the formation of dinuclear species.

We have now extended these experiments with  $\text{N}_2$  to generate the analogous  $\text{Cp}^*\text{Re}(\text{CO})_{3-x}(\text{N}_2)_x$  compounds in  $\text{scXe}$ , see Table II. The  $\text{Cp}^*$  compounds were more difficult to generate than the corresponding Cp species, and the ultimate concentration of  $\text{Cp}^*\text{Re}(\text{N}_2)_3$  was rather lower than could be achieved with  $\text{CpRe}(\text{N}_2)_3$ . Probably, this reflects minor differences in quantum yield between the two systems. Both the Cp and  $\text{Cp}^*$  dinitrogen compounds were surprisingly stable at room temperature, and the thermal reaction with added CO was quite slow. Indeed, traces of  $\text{CpRe}(\text{CO})(\text{N}_2)_2$  survived 2 weeks exposure to air.<sup>21</sup>

**Reaction of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  with  $\text{N}_2$  in  $\text{scXe}$ .** Although  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  is formally isoelectronic with the  $(\text{C}_n\text{R}_n)\text{M}(\text{CO})_3$  compounds discussed above, it differs from them in a number of important ways: (i) There is some uncertainty<sup>8,41</sup> whether the Fe should be considered to be a  $d^6$  center as in the other

(34) The problem is that an indeterminate amount of  $\text{H}_2$  is left in the cell after the bulk of  $\text{H}_2$  has been vented. The Xe is frozen with liquid nitrogen before the  $\text{H}_2$  is vented, and some of the  $\text{H}_2$  becomes trapped in the solid and is not released even under vacuum. Nevertheless, one can see that  $\text{CpMn}(\text{CO})_2(\text{H}_2)$  is thermally much less labile than the (arene) $\text{Cr}(\text{CO})_2(\text{H}_2)$  complexes. For the Cr case, low level impurities of  $\text{N}_2$  (300 ppm) in the  $\text{H}_2$  gas will give rise to detectable quantities of (arene) $\text{Cr}(\text{CO})_2(\text{N}_2)$ , while for Mn, the formation of  $\text{CpMn}(\text{CO})_2(\text{N}_2)$  is relatively slow,<sup>18</sup> even under a substantial pressure of added  $\text{N}_2$ .

(35) The  $\nu(\text{H}-\text{H})$  band of  $\text{W}(\text{CO})_5(\text{H}_2)$  is rather broad, and possible origins of this breadth have been discussed at some length.<sup>15b</sup> It is particularly surprising that the width of the band seems to be quite independent of temperature and solvent density. The band has exactly the same width (ca.  $40\text{ cm}^{-1}$  FWHM) at  $25\text{ }^\circ\text{C}$  in  $\text{scXe}$  (density  $1.1\text{ g/mL}$ ) as at  $-90\text{ }^\circ\text{C}$  in LXe (density ca.  $3\text{ g/mL}$ ).

(36) The assignment of the IR bands of dissolved  $\text{H}_2$  and  $\text{D}_2$  have been given elsewhere: LXe solution (in the supplementary data to ref 12d) and liquid Ne (Ewing, G. E.; Trajmar, S. J. *Chem. Phys.* **1965**, *42*, 4038.)

(37) The use of  $\text{D}_2$  causes a definite shift in the wavenumber of the  $\nu(\text{C}-\text{O})$  bands<sup>18</sup> (Table II). This indicates that the complex must contain hydrogen (or deuterium), but it does not show whether they are classical or not.

(38) Preliminary results show that, in LXe solution,  $\text{CpV}(\text{CO})_3(\text{H}_2)$  has a  $\nu(\text{H}-\text{H})$  band which is nearly three times the width of that of  $\text{W}(\text{CO})_5(\text{H}_2)$  (Howard, M. T.; George, M. W.; Howdle, S. M.; Poliakov, M. *Early Transition Metal Conference*; Brighton, UK, 1989; Abstr. No. 79; To be published).

(39) There is no evidence, in our  $\text{scXe}$  experiments, for formation of the dinuclear complex,  $(\text{CpMn}(\text{CO})_2)_2(\text{N}_2)$ . This compound was originally synthesized by using diazoethane, and it has been stated that this species is unlikely to be formed by direct reaction with  $\text{N}_2$ . (Ziegler, M. A.; Weidenhammer, K.; Zeiner, H.; Skell, P. S.; Herrmann, W. A. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 695.

(40) (a) Foust, A. S.; Hoyano, J.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65. (b) Howard, M. T.; Poliakov, M. Unpublished results. (c) Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakov, M. *Organometallics* **1987**, *6*, 2600.

(41) Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401.



Table III. Wavenumbers,<sup>a</sup> cm<sup>-1</sup>, of  $\nu(\text{C-O})$  and  $\nu(\text{N-N})$  IR Bands of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  and Its Dihydrogen and Dinitrogen Derivatives in Supercritical Xe at 25 °C

$(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$	$(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{H}_2)$	$(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)^b$	$(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})(\text{N}_2)_2^c$	$\text{Fe}(\text{CO})_5$	$\text{H}_2\text{Fe}(\text{CO})_4^d$
		2203.4 a' $\nu(\text{N-N})$	2201.0 a' $\nu(\text{N-N})$ 2161.7 a'' $\nu(\text{N-N})$		
2056.9 a <sub>1</sub> 1985.0 e 2046.4 $\nu(^{13}\text{C-O})$ 1950.5 $\nu(^{13}\text{C-O})$	2023.5 a' 1967.9 a''	2016.3 a' 1967.0 a''	1969.1 a'	2025.9 a <sub>2</sub> '' 2004.0 e'	2120.1 2051.8 2042.2

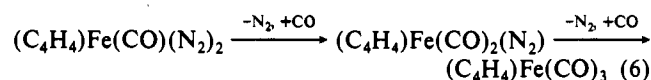
<sup>a</sup> IR data  $\pm 0.2$  cm<sup>-1</sup>. <sup>b</sup> Reported values:<sup>44a</sup> 2206.8, 2013.6, and 1961.0 cm<sup>-1</sup> in N<sub>2</sub> matrix at 20 K. <sup>c</sup> Reported values:<sup>44a</sup> 2170 and 1967 cm<sup>-1</sup> in N<sub>2</sub> matrix at 20 K. <sup>d</sup> Reported values:<sup>46</sup> 2122, 2051, 2043 cm<sup>-1</sup> in Ar matrix at 8 K.

$(\text{C}_n\text{R}_n)\text{M}(\text{CO})_3$  species or d<sup>8</sup> as in (butadiene)Fe(CO)<sub>3</sub>. (ii) Many iron carbonyl species are relatively active catalysts for the hydrogenation of olefins and dienes.<sup>42</sup> (iii) The dinitrogen complex,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$ , has not been isolated.<sup>43</sup> There is evidence for formation of both  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$  and  $(\text{C}_4\text{H}_4)\text{Fe}(\text{C-O})(\text{N}_2)_2$  in low-temperature matrices<sup>44,45</sup> and circumstantial evidence that (butadiene)Fe(CO)<sub>2</sub>(N<sub>2</sub>) may be relatively stable at temperatures near ambient.<sup>46</sup> These factors make the reactions of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  with N<sub>2</sub> and H<sub>2</sub> in scXe particularly interesting.

Figure 8a illustrates the IR spectrum of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  dissolved in scXe doped with N<sub>2</sub>. Photolysis of this solution caused depletion of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  and the generation of a product with three IR bands, one  $\nu(\text{N-N})$  and two  $\nu(\text{C-O})$ , Figure 8b and Table III. The positions and relative intensities of these bands agree well with those of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$  previously observed in rare gas matrices.<sup>44,45</sup> When the lamp was blocked off,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$  decayed with  $t_{1/2}$  ca. 90 min.

Prolonged photolysis of the solution resulted in the appearance of a second photoproduct with two  $\nu(\text{N-N})$  bands and only one  $\nu(\text{C-O})$  band, see Figure 8c and Table III. This photoproduct appeared to be formed at the expense of the primary photoproduct  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$ . The IR bands of this species are quite close in frequency (allowing for solvent shifts) to those of the secondary photoproduct observed in matrices.<sup>44,45</sup> By analogy with the behavior of CpRe(CO)<sub>3</sub>/N<sub>2</sub> (see above), this secondary photoproduct can be assigned to the bis(dinitrogen) species,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})(\text{N}_2)_2$ . The higher frequency  $\nu(\text{N-N})$  band of this species is actually partially overlapped by the  $\nu(\text{N-N})$  band of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$ , which probably explains why this band was not observed in matrices.<sup>45</sup>

Although  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})(\text{N}_2)_2$  was considerably more labile than  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$ , significant concentrations of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})(\text{N}_2)_2$  were formed during photolysis. However, as soon as the UV lamp was blocked off, the compound decayed thermally with  $t_{1/2}$  of 5 min, Figure 9. The figure indicates that the decay was the reverse of the photolysis, sequential loss of N<sub>2</sub>, and the reaction with CO, eq 6. There was no evidence that the C<sub>4</sub>H<sub>4</sub> ring could be lost through UV irradiation under these conditions. Even after prolonged photolysis, no trace of Fe(CO)<sub>5</sub> could be detected.



(42) For a general review of this photocatalytic hydrogenation reaction, see: Moggi, L.; Juris, A.; Sandrini, D.; Manfrin, M. F. *Rev. Chem. Intermed.* 1981, 4, 171.

(43) Von Gustorf and co-workers (Fischler, I.; Hildebrand, K.; Von Gustorf, E. A. K. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 55.) attempted to prepare  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$ , by photolysis in THF solution at -40 °C. However, they actually produced a dinuclear species  $[(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})]_2(\mu\text{-CO})$  with a bridging CO group and, since the species proved to be diamagnetic, a postulated metal-metal triple bond. A similar dinuclear compound has been isolated and characterized crystallographically. (Murahashi, S. I.; Mizoguchi, T.; Hosokawa, T.; Moritani, I. *J. Chem. Soc., Chem. Commun.* 1974, 563.)

(44) Rest, A. J.; Sodeau, J. R.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* 1978, 652.

(45) Fitzpatrick, N. J.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* 1979, 351.

(46) Poliakov, M.; Gadd, G. E.; Simpson, M. B.; Turner, J. J.; Upmacis, R. K. *Proceedings of the 4th International Symposium on Homogeneous Catalysis*; Gordon and Breach: 1985; pp 873-8.

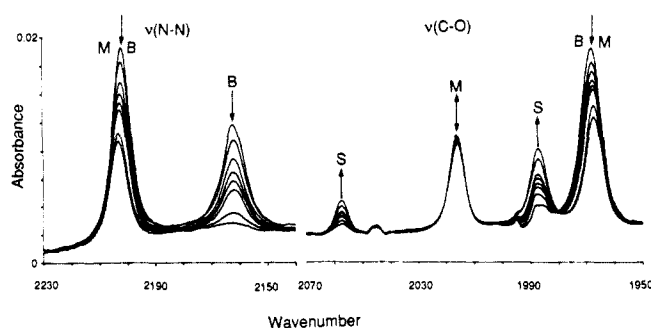


Figure 9. IR spectra in the  $\nu(\text{N-N})$  and  $\nu(\text{C-O})$  regions showing the result of prolonged UV photolysis (ca. 20 min) of an scXe solution of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  and N<sub>2</sub> (1200 psi). The first spectrum was recorded immediately after blocking off the UV lamp, and subsequent spectra were taken at ca. 1-min intervals. The bands are labeled as follows: B,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$ ; M,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})(\text{N}_2)_2$ ; and S,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ . The decay or growth of each IR band is indicated by the direction of the arrows.  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$  decays with  $t_{1/2}$  of 5 min into  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ , which decays relatively little on this time scale ( $t_{1/2}$  = 90 min). Note that some of the growth in intensity of the bands of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  is due to diffusion from the "dark" regions of the cell.

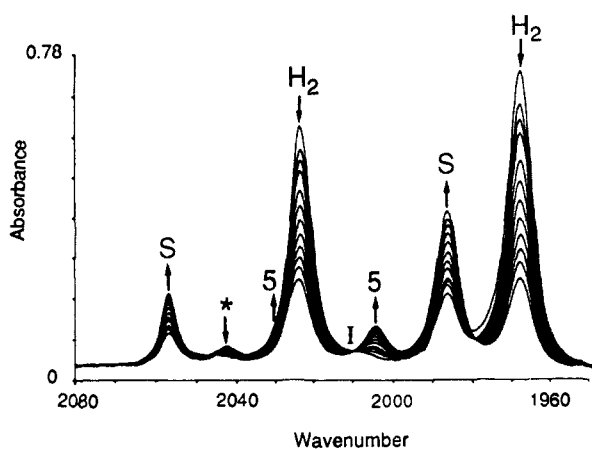
By analogy with the CpRe(CO)<sub>3</sub>/N<sub>2</sub> system, one might have expected that  $(\text{C}_4\text{H}_4)\text{Fe}(\text{N}_2)_3$  would be formed on prolonged photolysis. In fact, a very weak  $\nu(\text{N-N})$  band, 2128 cm<sup>-1</sup>, could be observed when IR spectra were recorded during UV photolysis. The species responsible for this absorption was extremely unstable, decaying completely in less than 20 s. Two  $\nu(\text{N-N})$  bands are predicted for  $(\text{C}_4\text{H}_4)\text{Fe}(\text{N}_2)_3$ , ( $a_1 + e$ ). Thus, if this band were assigned to  $(\text{C}_4\text{H}_4)\text{Fe}(\text{N}_2)_3$ , one would have to assume that the second  $\nu(\text{N-N})$  band was obscured by the stronger absorptions of the mono- and bis(dinitrogen) species. This is not unreasonable, given the observed wavenumbers of the corresponding Re species, see Table II.

Thus, we have an unusual situation. Although  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$  is thermally less stable than the corresponding  $(\text{C}_n\text{R}_n)\text{M}(\text{CO})_2(\text{N}_2)$  compounds of Cr and Mn, it is nevertheless possible to generate significant quantities of the bis(dinitrogen) complex,  $(\text{C}_n\text{R}_n)\text{M}(\text{CO})(\text{N}_2)_2$ , for Fe but not for the other two metals.

**Reaction of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  with H<sub>2</sub> in scXe.** UV photolysis of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  in scXe under a pressure of H<sub>2</sub> led to the formation of a new species with two  $\nu(\text{C-O})$  bands, similar in wavenumber to those of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{N}_2)$ , Table III. This behavior is analogous to our observations with the other  $(\text{C}_n\text{R}_n)\text{M}(\text{CO})_3$  compounds (qv), where photolysis in the presence of H<sub>2</sub> generated nonclassical dihydrogen compounds with IR spectra similar to those of the corresponding dinitrogen complexes. Thus, the most probable assignment of the bands is to the non-classical dihydrogen complex,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{H}_2)$ .

Like the Mn and Cr dihydrogen complexes,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{H}_2)$  was thermally unstable. Under 1500 psi pressure of H<sub>2</sub>, it decayed with a half-life of ca. 10 min, Figure 10. This decay appeared to proceed via two different pathways: the first led to regeneration of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ , while the second involved the formation of appreciable quantities of Fe(CO)<sub>5</sub>, peaks labeled "5" in Figure 10. The fact that the Fe(CO)<sub>5</sub> was formed directly from the decay of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{H}_2)$  is suggested by the presence of an isosbestic point, arrowed in Figure 10, between the bands of the two compounds.





**Figure 10.** A series of IR spectra illustrating the changes occurring in the  $\nu(\text{C-O})$  region during the thermal decay of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{H}_2)$ , generated by UV photolysis of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  in *sc*Xe under 1200 psi pressure of  $\text{H}_2$ . The bands are labeled as follows:  $\text{H}_2$ ,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{C-O})_2(\text{H}_2)$ ; S,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ ; 5,  $\text{Fe}(\text{CO})_5$ ; and \*, trace amounts of  $\text{H}_2\text{-Fe}(\text{CO})_4$ , formed by photolysis of  $\text{Fe}(\text{CO})_5$ . (Later in the experiment  $\text{H}_2\text{Fe}(\text{CO})_4$  becomes the predominant species in solution.) The first spectrum was recorded immediately after blocking off the Cermox Xe arc (after 3-min photolysis), and subsequent spectra were taken at ca. 2.5-min intervals. The decay or growth of each IR band is indicated by the direction of the arrows, and "I" indicates an isobestic point between the bands of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{H}_2)$  and  $\text{Fe}(\text{CO})_5$ .

As described above, extended UV photolysis of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  and  $\text{N}_2$  led to the formation of a bis(dinitrogen) compound,  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})(\text{N}_2)_2$ . However, there was no evidence for the formation of the corresponding bis(dihydrogen) species. Instead, prolonged UV photolysis in the presence of  $\text{H}_2$  resulted in almost total destruction of the  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  starting material and the formation of the known dihydride,<sup>47</sup>  $\text{H}_2\text{Fe}(\text{CO})_4$ , which itself decayed completely over a period of 70 min, with the regeneration of  $\text{Fe}(\text{CO})_5$  (not illustrated).

The loss of the organic ring during photolysis in the presence of  $\text{H}_2$  represents a significant difference between  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  and the other  $(\text{C}_n\text{R}_n)\text{M}(\text{CO})_3$  compounds considered in this paper. For the Cr compounds, loss of the organic moiety was only a very minor process, and it was not observed at all for Mn. This behavior is consistent with the known catalytic properties of the metal centers: iron carbonyl complexes are highly efficient hydrogenation catalysts by comparison with Cr or Mn species.<sup>42</sup> Furthermore, loss of the organic ligand via hydrogenation would explain why  $\text{Fe}(\text{CO})_5$  was not formed when  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$  was photolyzed under a pressure of  $\text{N}_2$  (see Figure 9).

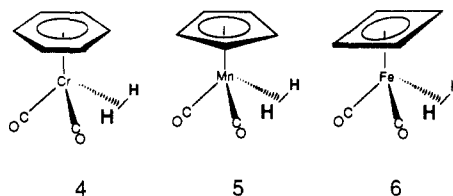
Initially, it seems surprising that a compound which contains both a diene and dihydrogen bound to the same Fe center should be moderately stable. However, the result can be understood because the  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2$  fragment is isolobal and isoelectronic with the other  $(\text{C}_n\text{R}_n)\text{M}(\text{CO})_2$  fragments,<sup>3b</sup> which we have already shown to form nonclassical dihydrogen complexes. What the experiments do show is that changing the metal center from Mn to Fe does not perturb the energies of the relevant orbitals sufficiently to affect the mode of binding of  $\text{H}_2$ . Indeed, it may be that most, or even all, (diene) $\text{Fe}(\text{CO})_2$  fragments form dihydrogen complexes and that the lifetime of the resulting (diene) $\text{Fe}(\text{CO})_2(\text{H}_2)$  complexes is determined by the ease of hydrogenation of the diene. In these circumstances, the relative stability of  $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2(\text{H}_2)$  would be attributed to a higher activation barrier for the hydrogenation of  $\text{C}_4\text{H}_4$  than that for the hydrogenation of other dienes.<sup>48</sup>

## Conclusions

These experiments show that organometallic chemistry of the type normally associated with matrix isolation or cryogenic solvents is possible at room temperature. We have exploited the complete miscibility of  $\text{H}_2$  and  $\text{N}_2$  with supercritical solvents to generate dinitrogen and dihydrogen half-sandwich complexes of transition metals in Groups 6, 7, and 8. High pressures of  $\text{N}_2$  or  $\text{H}_2$  can be used to stabilize, at room temperature, a range of compounds which were previously unknown or only detected under cryogenic conditions.

Multiple substitution of CO groups leads to complexes with two and even three dinitrogen ligands on the same metal center. In particular, the complexes  $(\text{C}_5\text{R}_5)\text{Re}(\text{CO})(\text{N}_2)_2$  and  $(\text{C}_5\text{R}_5)\text{-Re}(\text{N}_2)_3$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ) appear to be sufficiently stable, even after the pressure of  $\text{N}_2$  has been vented, that they can probably be isolated.

The use of a supercritical solvent has provided a general route to a new class of dihydrogen complexes,  $(\text{C}_n\text{R}_n)\text{M}(\text{CO})_2(\text{H}_2)$ , 4-6, which can be generated in spectroscopic quantities. Our results



confirm the presence of hydrogen in these compounds, and the spectroscopic data point to a nonclassical  $\eta^2\text{-H}_2$  ligand. All of these compounds, especially  $\text{CpMn}(\text{CO})_2(\text{H}_2)$ , have significant thermal stability under these conditions.  $\text{CpMn}(\text{CO})_2(\text{H}_2)$  and its  $\text{Cp}^*$  analogue are the first nonclassical dihydrogen complexes of Manganese.

Although frequent analogies have been drawn<sup>3,5</sup> between the bonding of  $\eta^2\text{-H}_2$ ,  $\text{N}_2$ , and  $\eta^2\text{-HSiEt}_3$ , there are few occasions on which these three ligands can be compared experimentally. Since  $\text{CpMn}(\text{CO})_2(\text{N}_2)^{9b}$  and  $\text{CpMn}(\text{CO})_2(\text{HSiR}_3)^6$  are well-characterized compounds, the observation of  $\text{CpMn}(\text{CO})_2(\text{H}_2)$  provides a unique opportunity to compare  $\eta^2\text{-H}_2$ ,  $\text{N}_2$ , and  $\eta^2\text{-HSiEt}_3$ , bonded to identical metal centers. Furthermore, by combining our results with previously published data for oxidative addition,<sup>8</sup> we can extend this comparison to three metal centers, Fe, Mn, and Cr.

The  $\nu(\text{C-O})$  IR data for the compounds of all three metals are summarized in Table IV. These data can be used in several ways. We shall consider just two: the wavenumbers of the bands give an indication of the electron density at the metal center, and, for a particular compound, the relative intensities of the two bands provide an estimate of the C-M-C bond angle.<sup>49</sup> We have already pointed out that the positions of the  $\nu(\text{C-O})$  bands of each dihydrogen complex are very close to those of the corresponding dinitrogen complex. It can now be seen from Table IV that the bands of these compounds are higher in wavenumber than the bands of their  $\eta^2\text{-HSiEt}_3$  analogues, even after allowing for differences in solvent. This indicates that the electron density on the metal center is higher for the  $\eta^2\text{-HSiEt}_3$  complexes than for the  $\eta^2\text{-H}_2$  and  $\text{N}_2$  species. The data do not, of course, show whether the difference is due to greater donor power of the  $\eta^2\text{-HSiEt}_3$  group or better acceptor properties of  $\text{H}_2$  and  $\text{N}_2$ . However, a similar analysis of the IR spectra of  $\text{W}(\text{CO})_5(\text{H}_2)$ , where the high symmetry allows more precise conclusions, suggested that  $\eta^2\text{-H}_2$  is a relatively strong  $\pi$ -acceptor.<sup>50</sup>

Detailed structural information is difficult to obtain for unstable compounds. In these  $(\text{C}_n\text{H}_n)\text{M}(\text{CO})_2\text{L}$  species, IR band intensities can provide at least a rough indication of C-M-C bond angles.

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(48) Slight support is given by very tentative spectroscopic evidence that UV photolysis of (butadiene) $\text{Fe}(\text{CO})_3$  in LXe doped with  $\text{H}_2$  at  $-80^\circ\text{C}$  gives rise to a short-lived species, possibly (butadiene) $\text{Fe}(\text{CO})_2(\text{H}_2)$ , with  $\nu(\text{C-O})$  IR bands similar to those of (butadiene) $\text{Fe}(\text{CO})_2(\text{N}_2)$ . Gadd, G. E. Ph. D. Thesis, University of Nottingham, U.K., 1985.

(49) For a dicarbonyl species with symmetric and antisymmetric  $\nu(\text{C-O})$  vibrations, the C-M-C bond angle,  $\theta$ , and the band intensities, I, are related by  $\tan^2 \theta/2 = (I_{\text{antisym}}/I_{\text{sym}})$ . Such calculations involve a number of assumptions (see, e.g., Burdett, J. K.; Poliakoff, M.; Turner, J. J.; Dubost, H. *Adv. Infrared Raman Spectrosc.* **1976**, *3*, 1.) which should be valid in cases such as this where a number of closely related species are being compared.

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**Table IV.** Comparison of the Wavenumbers,<sup>a</sup> cm<sup>-1</sup>, of  $\nu(\text{C-O})$  bands, Their Relative Intensities,<sup>b</sup> and Calculated C-M-C Bond Angles<sup>c</sup> for  $(\text{C}_n\text{H}_n)\text{M}(\text{CO})_2\text{L}$  Species [L = H<sub>2</sub>, N<sub>2</sub>, and HSiEt<sub>3</sub>]

$(\text{C}_n\text{H}_n)\text{M}(\text{CO})_2$	H <sub>2</sub>	N <sub>2</sub>	HSiEt <sub>3</sub>
$(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2$	2023.5 (1.0) 1967.9 (1.22)	2016.3 (1.0) 1967.0 (1.25)	2010 (1.0) <sup>d</sup> 1950 (1.0) <sup>d</sup>
<b>angle</b>	<b>95 ± 2.5°</b>	<b>96 ± 2.5°</b>	<b>90 ± 3°</b>
$(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2$	1992.1 (1.0) 1932.7 (1.0)	1985.0 (1.0) 1934.0 (1.1)	1978.3 (1.09) <sup>e</sup> 1915.5 (1.0) <sup>f</sup>
<b>angle</b>	<b>90 ± 2.5°</b>	<b>92 ± 2.5°</b>	<b>87.5 ± 2.5°</b>
$(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_2$	1947.7 (1.7) 1895.7 (1.0)	1947.3 (1.43) 1905.4 (1.0)	1921 (1.2) <sup>g</sup> 1821 (1.0) <sup>g,h</sup>
<b>angle</b>	<b>75° (83 ± 5°)<sup>i</sup></b>	<b>80 ± 2.5°</b>	<b>85 ± 3°</b>

<sup>a</sup>Unless otherwise stated the IR data is for scXe at 25 °C from this work,  $\pm 0.2$  cm<sup>-1</sup>. <sup>b</sup>Intensity data in parentheses; the values used are the peak absorbance with the weaker of the two bands arbitrarily set to 1.0. In all cases, the symmetric  $\nu(\text{C-O})$  stretch is the higher wavenumber band. The error in the intensity data is  $\pm 10\%$ . <sup>c</sup>For details of calculations see ref 49. <sup>d</sup>Data from ref 8: methylcyclohexane, 100 K,  $\pm 2$  cm<sup>-1</sup>. <sup>e</sup>*n*-Heptane solution, 25 °C; as an indication of the solvent shift, the bands of  $(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  are shifted ca. 5 cm<sup>-1</sup> to lower wavenumber in this solvent than in scXe. <sup>f</sup>These bands have significantly different half-widths: 1947.7 is 3/4 the width of 1895.7. The angle in parentheses is calculated by using ( $I = \text{absorbance} \times \text{peak width}$ ). <sup>g</sup>Data from ref 8: HSiEt<sub>3</sub>, 100 K,  $\pm 2$  cm<sup>-1</sup>. <sup>h</sup>The wavenumber reported for this band seems anomalously low compared to data from our own work: e.g.,  $(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$ , 1890 and 1841 cm<sup>-1</sup>, *n*-heptane -20 °C;  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{HSiEt}_3)$  in *n*-heptane at -40 °C 1931.3 and 1925.1 (two bands, partly resolved, intensity 1.0) and 1872.2 cm<sup>-1</sup> (intensity 1.2). The two bands have a combined width (FWHM) 1.4 times that of the lower frequency band. Thus, the angle calculated by using ( $I = \text{absorbance} \times \text{peak width}$ ) is 85.5°.

see Table IV. Although such calculations are difficult to verify in detail, the values for the HSiEt<sub>3</sub> compounds of Mn and Cr are similar to the values found in the crystal structures of less labile silane complexes.<sup>51</sup> In addition, the calculations indicate that,

for a particular ligand L, the C-M-C angle in  $(\text{C}_n\text{H}_n)\text{M}(\text{CO})_2\text{L}$  decreases from Fe to Cr. This is consistent with crystallographic studies<sup>52</sup> on the unsubstituted  $(\text{C}_n\text{H}_n)\text{M}(\text{CO})_3$  where a similar trend is found. The calculations also suggest that, for a given metal, the  $\eta^2\text{-H}_2$  complex has a larger angle than the HSiEt<sub>3</sub> compound. However, the differences are small, and one is probably justified in concluding that steric effects play a relatively minor role in determining the geometry at the metal center in these compounds.

Although the work described in this paper has been carried out in scXe (largely for spectroscopic reasons), less exotic supercritical fluids could also be used as solvents for such reactions. Preliminary experiments<sup>53</sup> indicate that the same compounds can be generated in supercritical CO<sub>2</sub> or ethane. Our experiments have taken advantage of just one specific property of supercritical fluids, their miscibility with H<sub>2</sub> and N<sub>2</sub>. Work is now in progress in our laboratory applying some of the other unusual properties of supercritical fluids to organometallic chemistry.

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## Synthesis and Structural Studies of Some New Rhenium Phosphine Heptahydride Complexes. Evidence for Classical Structures in Solution

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**Abstract:** A series of new rhenium phosphine heptahydride complexes  $\text{ReH}_7\text{L}_2$  ( $\text{L}_2 =$  a chelating bidentate phosphine) have been synthesized and characterized by IR and <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectroscopy. The hydride resonances of  $\text{ReH}_7(\text{dppf})$  (1, dppf = 1,1'-bis(diphenylphosphino)ferrocene),  $\text{ReH}_7(\text{dppb})$  (2, dppb = 1,4-bis(diphenylphosphino)butane), and  $\text{ReH}_7((+)\text{-diop})$  (3, (+)-diop = (4*S*,5*S*)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane) undergo decoalescence upon cooling. The low-temperature hydride patterns suggest classical 9-coordinate tricapped trigonal prismatic structures. Consistent with the classical structures, <sup>1</sup>H NMR spectra of deuterated  $\text{ReH}_7\text{L}_2$  complexes show very small and temperature-independent upfield isotope shifts in the hydride region and no change in <sup>2</sup>*J*<sub>HP</sub>. Sequential treatment of 1, 2, and 3 with NaH and Me<sub>2</sub>SO<sub>4</sub> in the presence of Ph<sub>3</sub>SiH leads to  $\text{ReH}_6(\text{SiPh}_3)\text{L}_2$  ( $\text{L}_2 =$  dppf, dppb, (+)-diop). Variable-temperature <sup>1</sup>H NMR studies of these silyl derivatives provide further support for the classical formulation of their parent heptahydrides. Theoretical *T*<sub>1</sub>(min) values are calculated for some polyhydrides on the basis of different structural models and are compared with the experimental numbers. Precautions to be taken in interpreting *T*<sub>1</sub> data are discussed.

Transition-metal dihydrogen complexes<sup>1</sup> have attracted much recent attention. Their structural characterization is a particularly challenging problem for which we have previously developed a solution <sup>1</sup>H NMR *T*<sub>1</sub> method.<sup>2,3</sup> The method is based on the fact

that the dipole-dipole mechanism dominates spin-lattice relaxation in small diamagnetic molecules in which the protons are close together (<2 Å). By this mechanism the relaxation rate, i.e. *T*<sub>1</sub><sup>-1</sup>, increases with the inverse sixth power of the H...H distance. The *T*<sub>1</sub> value is dependent on temperature and spectrometer field

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