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“Solvent-Free” Photochemical Activation of CH_4, C_2H_4, and C_2H_6 by $(C_5Me_5)Ir(CO)_2$ in Supercritical Fluid Solution

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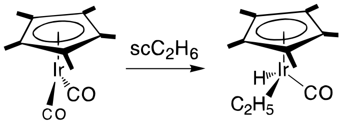
We report the activation of H_2 and light hydrocarbons (CH_4, C_2H_4, and C_2H_6) by $Cp^*Ir(CO)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) in supercritical fluid solution. The reactions have been carried out both in the presence of a supercritical solvent ($scCO_2$, scXe, or $scCHF_3$) or “solvent-free” in the pure supercritical hydrocarbon ($scCH_4$, scC_2H_4, or scC_2H_6). As far as we are aware, this is the first use of $scCH_4$ as a solvent for photochemical reactions. The presence of H_2 in scC_2H_6 greatly enhances the effectiveness of the C−H activation, but even in the presence of D_2, Cp*Ir(CO)(H)Et and not Cp*Ir(CO)(D)Et is formed. Reaction of $Cp^*Ir(CO)_2$ with H_2 occurs efficiently in CHF_3, but C−H activation of C_2H_6 is almost suppressed in this mixed scC_2H_6/$scCHF_3$ fluid, possibly through H-bonding to the metal center. A technique for recovering the products from milligram-scale reactions is described.

Introduction

Research into the activation of C−H bonds by transition-metal centers has seen an almost explosive growth in recent years. Much of this research, however, has avoided the lighter alkanes (e.g. CH_4, C_2H_6, etc.) because of the problems of finding suitable solvents for these reactions. In a few cases, such as the recent example from Perutz and co-workers,[1] the activation of the alkane is so selective that the problem of solvents does not arise; in their work, $Os(H)_2(P(CH_2CH_2PPh_2)_3)$ was found to activate CH_4 in almost complete preference to the cyclohexane solvent. Generally, however, it is necessary to find a solvent which cannot undergo C−H activation or any other unwanted reaction. To this end, Graham and co-workers have used perfluoroalkanes as solvents[2] for studying the activation of CH_4 by $Cp^*Ir(CO)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$). Lees and Marx[3] used C_6F_6 which, although aprotic, was subsequently shown by Perutz and co-workers to form isolable $\eta^2\text{-}C_6F_6$ complexes under these conditions.[4] In a somewhat different approach, Bergman and his group have exploited the inertness of liquid noble gases at cryogenic temperatures for both preparative-scale[5] and spectroscopic studies of C−H activation.[6] It has been known for some time that liquid and supercritical CO_2 ($scCO_2$) show a surprising lack of reactivity toward unsaturated metal centers,[7] and recently we described how this lack of reactivity can be exploited by using $scCO_2$ as an inert solvent for C−H activation of C_2H_6 by $Cp^*Ir(CO)_2$ at ambient temperatures.[7]

Scheme 1



However, the simplest and most elegant method of resolving the problem of solvents for C−H activation is to eliminate the use of solvents entirely. Such elimination was achieved by Graham and Rest,[8] who used solid CH_4 matrices at ca. 20 K, to observe the photochemical activation CH_4 by $CpIr(CO)_2$. Other similar experiments in CH_4 matrices have since been reported,[9,10] but the small scale of these low-temperature experiments effectively precludes the recovery of the reaction products. Recently, we described a somewhat different approach to solvent-free C−H activation,[7] the use of supercritical C_2H_6 (scC_2H_6), where the fluid is both the reactant and the solvent for the photochemical activation of C_2H_6 by $Cp^*Ir(CO)_2$ (Scheme 1).

The efficiency of this reaction was strikingly enhanced by addition of H_2 to the reaction mixture.[7] The reaction then proceeds via $Cp^*Ir(CO)H_2$, which is generated more easily than $Cp^*Ir(CO)(H)C_2H_5$ from $Cp^*Ir(CO)_2$. These observations are reminiscent of those of Bloyce et al.,[9] who reported that $CpIr(CO)H_2$ is highly efficient at activation in cryogenic CH_4 matrices. The effect in scC_2H_6 is particularly dramatic, because the the gaslike nature of scC_2H_6 leads to complete miscibility with H_2, with concentrations of “dissolved” H_2 almost an order of magnitude higher than those in a conventional sol-

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Scheme 2

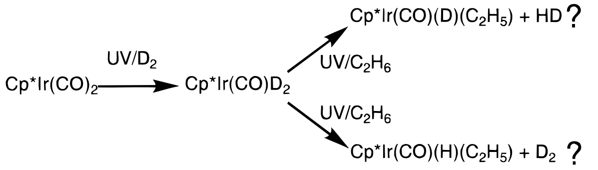

Table 1. Critical Data for Selected Substances[a]

substance	T_c/K	P_c/MPa	ρ_c/(g/mL)
CH_4	190.5	4.604	0.162
C_2H_4	282.3	5.041	0.214
Xe	289.7	5.84	1.110
CHF_3	299.3	4.858	0.528
CO_2	304.1	7.375	0.468
C_2H_6	305.4	4.884	0.203

[a] For critical data for other substances, see the excellent compilation by Reid et al.[44]

vent under similar conditions. This high concentration of H_2 has already been exploited in the generation of new dihydrogen complexes,[11] for hydroformylation,[12] and, most recently, for the hydrogenation of CO_2 itself.[13]

Although the general course of the $Cp^*Ir(CO)_2/H_2/scC_2H_6$ reaction is clear from our original experiments, the precise role of $Cp^*Ir(CO)H_2$ cannot be determined without isotopic tracers. In this paper, therefore, we describe more extensive experiments, with H_2 and D_2, aimed at establishing whether D is incorporated during the C−H activation of C_2H_6 (see Scheme 2). Then, we extend the concept of "solvent-free" C−H activation to the reactions of $Cp^*Ir(CO)_2$ with $scCH_4$ and scC_2H_4 as well as show that such reactions can be carried out in $scCO_2$, scXe, and $scCHF_3$, although the efficiency is very low in this last fluid.

Experimental Section

(a) Materials. The critical parameters of all of the fluids used here are listed in Table 1. Xe (BOC Research Grade), CO_2 (Air Products SFE grade), H_2 (Air Products), CH_4 (BOC), C_2H_4 and C_2H_6 (Air Products), and CHF_3 (Aldrich) were used without further purification. D_2 (BDH) was supplied in cylinders at a pressure lower than those required for many of these experiments. The gas was therefore compressed with use of a manual pump (High Pressure Equipment Co. pressure generator, Model 62-6-10). $Cp^*Ir(CO)_2$ was synthesized by literature procedures.[14]

(b) High-Pressure Cell. Our microscale apparatus for reaction chemistry in supercritical fluids has been described in some detail elsewhere.[15] Most of the reactions reported in this paper were carried out in the stainless steel cell shown schematically in Figure 1. Initially, the required quantity of solid $Cp^*Ir(CO)_2$, typically 1−2 mg, is added to the cell either by undoing the coupling at the end of the cold finger or by removing the window holder. The cell is then resealed and evacuated to remove air ($Cp^*Ir(CO)_2$ is sufficiently involatile to be unaffected by this evacuation). Once the cell is evacuated, the fluid is added. Although the cold finger of the cell normally points vertically upward, the cell is inverted during the filling procedure, the cold finger is cooled using liquid nitrogen, and the fluid is condensed into the cold finger which is then warmed to room temperature. Alternatively, the cold finger can remain in liquid nitrogen while the cell is pressurized with H_2 gas over the frozen fluid. Once the cold finger has reached room temperature, the cell is allowed to equilibrate so that the fluid mixture throughout the cell/cold finger is homogeneous. The chemical outcome of the reactions was not sensitive to the precise quantity of $Cp^*Ir(CO)_2$ used, because in all of the experiments except $scCH_4$, the quantity of $Cp^*Ir(CO)_2$ was at least 1 order of magnitude less than that required for a saturated solution.

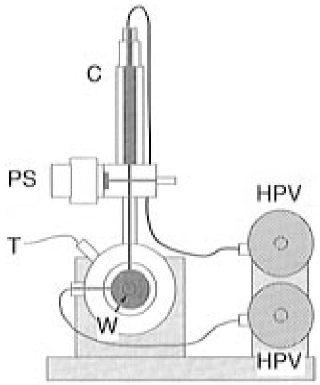

Figure 1. Schematic view of the high-pressure cell used for all of the supercritical experiments, apart from $scCH_4$. The important features are as follows: (C) the cold finger which not only allows the contents of the cell to be frozen down but also provides additional volume; (HPV) the two high-pressure valves which permit fluid to be flowed through the cell for product recovery (see Figure 2); (PS) the pressure sensor (RDP Electronics); (T) the thermocouple; (W) the CaF_2 windows (15 mm diameter, 10 mm thickness; such a window is calculated to have a maximum safe operating pressure of 9000 psi, 600 bar, for an unsupported area of 3.5 mm radius). These windows are used for both IR spectroscopy and UV excitation. In these experiments, the cell was used with an optical pathlength between 1 and 7 mm, depending on the amount of product to be generated. The dark gray shading indicates the region occupied by the bulk of the fluid in the cell.

(c) UV Photolysis and IR Spectroscopy. A Cermax 300 W UV lamp was used with an OP2 cold mirror to remove visible and near-IR radiation. A small front-silvered mirror was used so that the high-pressure cell could be irradiated *in situ* in the sample compartment of a Nicolet Model 730 FTIR interferometer and IR spectra could be collected at the same time (2 cm^{-1} resolution, 16K data points, 32K transform data points). Spectra were processed on a Nicolet Model 620 Data Station.

"Blank" experiments (i.e. photolysis of $Cp^*Ir(CO)_2$ in the appropriate fluid in the absence of added H_2, CH_4, etc.) have been carried out for all of the photochemical reactions described here. Prolonged UV irradiation of $Cp^*Ir(CO)_2$ in $scCO_2$ led to the appearance of weak IR bands at 1930 and 1759 cm^{-1} assignable to $[Cp^*_2Ir_2(CO)_3]$ from literature values[16] (1933, 1755 cm^{-1}, C_6D_6 solution) and 1690 cm^{-1} assignable to $[Cp^*_2Ir_2(CO)_2]$ from the reported value[14] (1702 cm^{-1}, hexane solu-

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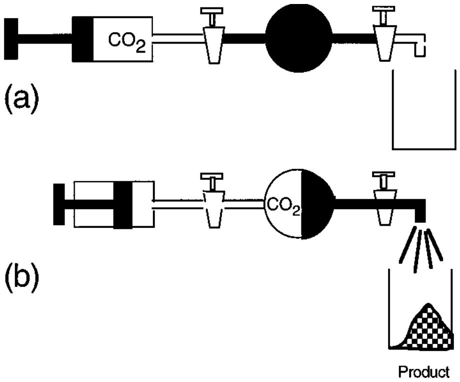

Figure 2. Schematic representation of the procedure for product retrieval from the cell shown in Figure 1. (a) At the end of the reaction, the inlet valve is attached to a Lee Scientific Model 501 syringe pump. (b) This pump forces $scCO_2$ through the cell and drives the reaction mixture (colored) out through a Jasco 880/881 back-pressure regulator. As the fluid passes through this regulator, the fluid is expanded in a controlled manner and any product dissolved in the fluid is deposited as shown. A key feature of this method is that high-pressure "stabilizing" conditions are maintained right up to the point of precipitation when the product is deposited by rapid expansion of the fluid.

tion). Apart from a gradual disappearance of $Cp^*Ir(CO)_2$ during prolonged irradiation, the other blank experiments did not lead to the growth of any new bands in the ν(C−O) or ν(Ir-H) regions of the IR spectrum.

The quantum yield for C−H activation is too low for use of the miniature flow reactor[11c,17] which we used to isolate $Cr(CO)_5(C_2H_4)$ or $CpMn(CO)_2(\eta^2\text{-}H_2)$. Thus, in the present case we used a sealed cell and recovered the product subsequently, as shown schematically in Figure 2. A variety of different techniques were used to collect the products, including deposition onto a spectroscopic plate (e.g. KBr) for immediate IR characterization of the solid or deposition directly into the cold finger of a second high-pressure cell, which was then repressurized with scXe.[18] Larger quantities of material were required for NMR analysis, and a number of trials showed that much of the product was lost when it was deposited directly into an NMR tube. More efficient collection was achieved by use of the stainless steel collection device[19] illustrated in Figure 4 of ref 11c. ^1H NMR data (293 K, Bruker 250 MHz) were obtained for products recovered in this way by dissolving the deposited solids in C_6D_6 (Aldrich): $Cp^*Ir(CO)(H)_2$, δ 1.76 (s, 15H, Cp*), −15.72 (s, 2H, Ir-H); $Cp^*Ir(CO)(H)(\eta^1\text{-}C_2H_3)$, δ 7.30, 6.70, 5.90 (3 × m, 3 × 1H, C_2H_3[20]), 1.64 (s, 15H, Cp*).

(d) Supercritical CH_4. Cooling the cold finger of the high-pressure cell is an effective means of filling, but on occasions such as our experiments with CH_4, it is desirable to cool an entire cell. It is extremely difficult to cool the cell shown in Figure 1 much below 0 °C without damaging the windows or the pressure seals. In contrast, Figure 3 shows a variable-temperature high-pressure cell which can be cooled as low as 20 K while still maintaining the integrity of the pressure seals. This cell was originally developed for experiments involving polymer films[15b,21] and was modified to provide an increased optical pathlength for use with $scCH_4$. In the present experiments, the cell was loaded with excess $Cp^*Ir(CO)_2$ (i.e. ca. 2−3 mg) and cooled, CH_4 was added, and the cell was warmed to the desired temperature for photochemical reaction. Alternatively, for studies of the solubility of $Cp^*Ir(CO)_2$ in $scCH_4$, CH_4 was condensed off-line into a high-pressure "bomb" cooled with liquid N_2 and, after it was warmed, this bomb was used as a source of high-pressure CH_4 to fill the cell directly at room temperature.

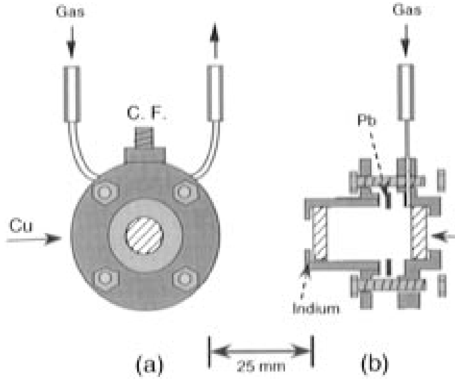

Figure 3. (a) External view and (b) cross-section of the miniature high-pressure IR cell used for the experiments with $scCH_4$. The cell is constructed from copper and is capable of being cooled to cryogenic temperatures. Parts are labelled as follows: (C. F.) mounting stud for cold finger of cryogenic cooler; (Indium) metal seals uniting the CaF_2 to the Cu cell body; (Pb) main lead seal between the halves of the cell; (↑ and ↓) gas fill ports. Note that this cell has an optical pathlength of ca. 25 mm, much longer than that in the cell shown in Figure 1.

Safety Hazard. *The experiments described in this paper involve the use of relatively high pressures and require equipment with the appropriate pressure rating. It is the responsibility of the individual researcher to verify that his or her particular apparatus meets the necessary safety requirements.*

Results

Addition of H_2 to scC_2H_6 has already been shown to enhance the C−H activation of C_2H_6 by $Cp^*Ir(CO)_2$. UV irradiation of $Cp^*Ir(CO)_2$ in H_2/scC_2H_6 produces a mixture of $Cp^*Ir(CO)H_2$ and Cp*Ir(CO)(H)Et, but the amount of Cp*Ir(CO)(H)Et is considerably greater than would have been generated from the same quantity of $Cp^*Ir(CO)_2$ under the same photolysis conditions but in the absence of H_2. Clearly, irradiation of $Cp^*Ir(CO)_2$ in an scC_2H_6/D_2 mixture will lead to formation of $Cp^*Ir(CO)D_2$ but, as explained above, the important questions are whether any $Cp^*Ir(CO)H_2$ will be formed and whether the other product will be Cp*Ir(CO)(H)Et or Cp*Ir(CO)(D)Et. Although NMR might seem to be the obvious means of analyzing such products, FTIR is both easier and more sensitive for these studies (see Experimental Section).

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[18] Comparison of spectra of the original solution and of the redissolved material showed that the precipitation process did not cause significant changes in the composition of the reaction mixture, nor did the precipitation itself promote any reactions.

[19] The efficiency of the collection vessel was tested using the Fischer carbene complex $W(CO)_5{=}CPh(OMe)$. This compound was selected because it has a solubility similar to that of $Cp^*Ir(CO)_2$ and also because and it is brightly colored (orange), so that one can see where the compound had been deposited. The carbene (35 mg) was placed in the supercritical cell and then flushed out through the back-pressure regulator and into the collection vessel, and it was found that >90% of the carbene could be collected.

[20] Assigned by analogy with published data (Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1734). The S/N for $Cp^*Ir(CO)(H)(\eta^1\text{-}C_2H_3)$ was insufficiently high to obtain conclusive evidence for the presence of a metal-hydride resonance. Although Cp*Ir(CO)(H)Et could be precipitated and satisfactorily redissolved for our IR experiments, it appeared to decompose during our NMR procedure and no satisfactory NMR data were obtained.

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Table 2. Wavenumbers[a] (cm^{-1}) of the ν(C−O) and ν(Ir−H) Bands of Cp*Ir$(CO)_2$ and its Reaction Products in Different Supercritical Fluids

compd	$scCO_2$	scXe	scC_2H_6	scC_2H_4	$scCH_4$	$scCHF_3$	assignt
Cp*Ir$(CO)_2$[b]	2019.9	2023.5	2024.0	2023.3	2026.8	2016.9	a′ ν(C−O)
	1951.2	1958.4	1959.2	1959.3	1963.7	1948.0	a″ ν(C−O)
Cp*Ir(CO)$(H)_2$	2140	2138.5	2140			2137	ν(Ir−H)[d]
	1996.9	2002.4	2004.0			1991.3	ν(C−O)
Cp*Ir(CO)$(D)_2$	1997.9	2003.1	2003.3				ν(C−O)
	1540.0	1538.3	*c*				ν(Ir−D)[d]
Cp*Ir(CO)(H)Me	2138[e]	2137			2142		ν(Ir−H)
	1990.4	1995.3			2000.1		ν(C−O)
Cp*Ir(CO)(H)Et	2142	2141	2142			2135	ν(Ir−H)
	1985.7	1990.9	1992.2			1976.4	ν(C−O)
Cp*Ir(CO)(η^2-C_2H_4)		1965.0	1967.1	1959			ν(Ir−H)
Cp*Ir(CO)(H)(η^1-C_2H_3)		2144	*c*	*c*			ν(Ir−H)
		2005.9	2001.6	2005.9			ν(C−O)
		1570.0					ν(C=C)[f]
		1263.3					δ(C−H)[f]
Cp*Ir(η^2-C_2H_4)$_2$		1180.6					δ(C−H)

[a] Spectra recorded at 2 cm^{-1} resolution, with error ± 0.2 cm^{-1}. The precise wavenumbers show some temperature and pressure dependence; see figure captions for typical conditions. [b] Cf. 2020 and 1953 cm^{-1} in hexane.[14] [c] Band obscured by absorptions of the fluid. [d] Unresolved bands due to overlapping symmetric and antisymmetric vibrations of Ir$(-H)_2$ or Ir$(-D)_2$ moieties.[22] [e] Band observed after computer subtraction. [f] Assignments made with reference to the corresponding CpIr(CO)(H)(η^1-C_2H_3) complex.[20]

We therefore describe a series of FTIR experiments with H_2, D_2, and scC_2H_6 to establish which species are formed.

(a) Reaction with C_2H_6 in the Presence of H_2 or D_2. Figure 4b shows the spectrum obtained after photolysis of Cp*Ir$(CO)_2$ and D_2 in $scCO_2$. The ν(C−O) region is similar to that observed with H_2 (Figure 4a), apart from a very small wavenumber shift in the position between the bands of Cp*Ir(CO)H_2 and Cp*Ir(CO)D_2 (see Table 2). This difference in wavenumber occurs because coupling between the ν(Ir−H) and ν(C−O) vibrations in Cp*Ir(CO)H_2 shifts the two bands apart; replacement of H by D will remove this coupling and cause a small shift of the ν(C−O) band to higher wavenumber compared to that of Cp*Ir(CO)H_2. A similar but slightly smaller shift[9] has been observed for CpIr(CO)H_2/D_2.

A more obvious difference between the H_2 and D_2 spectra is the absence of a ν(Ir-H) band,[22] noted by arrows in Figure 4a; instead, a weak band is observed for Cp*Ir(CO)D_2 at ca. 1540 cm^{-1}, as shown in Figure 4b. The wavenumber of the ν(Ir-H) band is shifted by isotopic substitution slightly less than would be predicted for an isolated Ir−H diatomic; ν(Ir−D)/ν(Ir−H) = 1.390 (observed), 1.414 (predicted). The shift is, however, similar to those observed for other dihydrides of third-row metals.[22] The inherent weakness of the ν(Ir−D) band and the presence of atmospheric water vapor conspire to make the signal/noise ratio (S/N) of the spectra very poor in this region of the IR spectrum compared to that achievable for the ν(Ir-H) band, recorded under similar conditions (Figure 4a). This poor S/N means that, in our experiments, direct detection of the ν(Ir−D) bands cannot be used quantitatively to investigate the outcome of reactions such as photolysis of Cp*Ir$(CO)_2$ in scC_2H_6/D_2 mixtures.

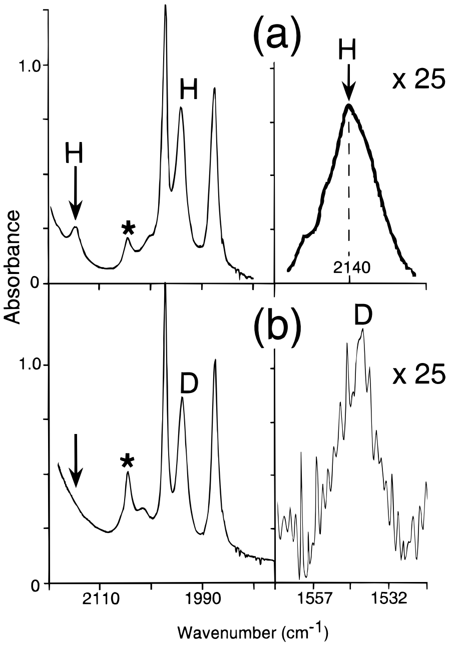

Figure 4. FTIR spectra showing the photochemical activation by Cp*Ir$(CO)_2$ of (a) H_2 and (b) D_2 in $scCO_2$ solution. (a) Spectrum recorded after 60 min of UV photolysis of Cp*Ir$(CO)_2$ in $scCO_2$ (115 atm) with H_2, added to give a total pressure of 270 atm. The unlabeled bands are due to unreacted Cp*Ir$(CO)_2$; the bands labeled H are due to Cp*Ir(CO)H_2, and that marked with an asterisk is a relatively weak absorption of $scCO_2$ itself. The slope in the base line toward higher wavenumbers is also due to absorption by $scCO_2$. (b) Spectrum recorded after 80 min of irradiation of Cp*Ir$(CO)_2$ in $scCO_2$ (67 atm) and D_2 (14 atm). The ν(C−O) band of Cp*Ir(CO)D_2 is labeled D. Note the absence of an ν(Ir−H) band at the wavenumber marked by an arrow in spectrum b and the appearance of a weak band at ca. 1540 cm^{-1} shown with expanded absorbance scale. The S/N in this region is rather poor, and this is emphasized by plotting an ν(Ir−H) band of *similar absorbance* to the ν(Ir−D) band immediately above in (a). Note that this ν(Ir−H) band was recorded in a separate experiment from the ν(C−O) spectrum.

The spectra shown in Figure 4 were recorded in $scCO_2$, where the ν(Ir−H) region is largely free of absorption by $scCO_2$. In scC_2H_6, there are even problems in monitoring the ν(Ir−H) region of the spectrum, because scC_2H_6 itself has a broad absorption in this region which causes the base line to slope to high wave-

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(22) Although *two* ν(Ir−H) vibrations, $a_1 + b_1$, might be expected for an IrH_2 moiety, only *one* IR band is observed in practice for dihydrides such as Cp*Ir(CO)H_2, because the vibrational coupling between the two Ir−H bonds is relatively small and the separation between the symmetric and antisymmetric vibrational modes is less than their line widths (see, e.g.: Duckett, S. B.; Haddleton, D. M.; Jackson, S. A.; Perutz, R. N.; Poliakoff, M.; Upmacis, R. K. *Organometallics* **1988**, *7*, 1526).

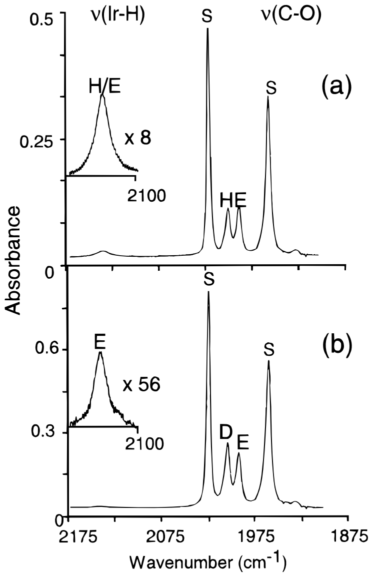

Figure 5. FTIR spectra recorded in scXe after UV irradiation of Cp*Ir(CO)$_2$ with (a) H_2 in scC_2H_6 and (b) D_2 in scC_2H_6. In both cases, the reaction products were flushed out of the cell into a second high-pressure cell, using the procedure shown in Figure 2. scXe was then condensed into this second cell, and the products were redissolved. The bands are labeled as follows: (D) Cp*Ir(CO)(D)$_2$; (E) Cp*Ir(CO)(H)(C_2H_5); (H) Cp*Ir(CO)H_2; (S) unreacted Cp*Ir(CO)$_2$. In both spectra the ν(Ir-H) region is shown as an inset with expanded absorbance scale.

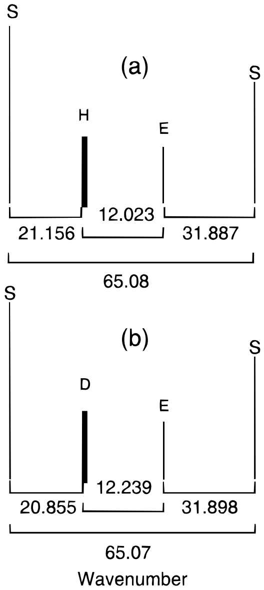

Figure 6. Schematic representation of the spectra in Figure 5, showing the separation (cm^{-1}) between the various ν(C−O) bands.

number. Although such a base line can easily be corrected by computer subtraction, it is somewhat unappealing to draw mechanistic conclusions from spectroscopic data, all of which have been manipulated by computer. Therefore, we decided to precipitate our reaction products from scC_2H_6 solution, using the procedure described in the Experimental Section. This precipitate is then redissolved in scXe, where there are no problems of solvent absorption.[23]

Thus, two separate experiments were carried out. Cp*Ir(CO)$_2$ was dissolved in scC_2H_6 containing either H_2 or D_2. Each mixture was irradiated with UV light and the products (together with any unreacted Cp*Ir(CO)$_2$) were deposited into a second high-pressure cell which was pressurized with scXe to redissolve the solids.[24] Photolysis conditions, gas pressures, etc. were kept as similar as possible in the two experiments. The resulting spectra are shown in Figure 5. The differences between the two spectra are not large, the most obvious being that the ν(Ir−H) band is much weaker, relative to the ν(C−O) bands in the D_2 experiment (Figure 5b). There is also a small but significant shift in wavenumber[25] of one (*and only one*) of the the ν(C−O) bands, as can be seen schematically in Figure 6. This shift is consistent with the formation of Cp*Ir(CO)D_2 rather than CpIr(CO)H_2 (see Figure 4 and Table 2).

Thus, the spectra confirm that Cp*Ir(CO)D_2 is formed during the photolysis of Cp*Ir(CO)$_2$ in scC_2H_6/D_2. Never theless, a weak ν(Ir-H) band is present in Figure 5b, but this can be assigned on the basis of the relative intensities of the ν(Ir−H) and ν(C−O) bands, as outlined in Figure 7. This analysis of the relative intensities indicates that the ν(Ir−H) band in Figure 5b can be attributed entirely to the formation of Cp*Ir(CO)(H)Et and that negligible amounts of Cp*Ir(CO)H_2 are formed in this reaction. Furthermore, the separation of the ν(C−O) band of Cp*Ir(CO)(H)Et and the low-wavenumber band of Cp*Ir(CO)$_2$ is unaltered within 0.01 cm^{-1} between the H_2 and D_2 experiments (Figure 6), which suggests that insignificant amounts of Cp*Ir(CO)(D)Et are generated.

There has been some argument over the effect of added CO on the efficiency of C−H activation by Cp*Ir(CO)$_2$. For example, Marx and Lees found that 1 atm pressure of CO did not alter the quantum yield for C−H activation[27] but their deductions of an *associative* mech-

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[23] For a general overview of liquid and supercritical Xe, see: *Molecular Cryospectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Advances in Spectroscopy 25; Wiley: London, 1994.

[24] All of these species, Cp*Ir(CO)$_2$, Cp*Ir(CO)H_2, and Cp*Ir(CO)D_2, are quite soluble in scXe, and under the conditions of our experiments, the concentrations of all solutions were substantially below saturation.

[25] The IR spectra were recorded at a nominal 2 cm^{-1} resolution, and the position of the "peak" absorbance was picked automatically using the Nicolet SX software. The wavelength calibration of such FTIR interferometers is based on a He/Ne laser, which gives very high precision and reproducibility to the measurements (e.g. 0.01 cm^{-1}, quoted in current Nicolet promotional literature). Of course, the data points in an spectrum are relatively sparse, typically 1 cm^{-1} apart in a 2 cm^{-1} resolution spectrum. However, the precision of the peak-picking algorithms is much higher, at least 10 times higher than the nominal resolution. The reproducibility of the *separation between well-resolved peaks*, such as those in our experiments, would be expected to be even higher (Mills, I. M. Personal communication, 1995). Thus, we have used the separation of the bands rather than their absolute wavenumbers, because the absolute values show some slight dependence on the precise pressure and temperature of the scXe, while the separations are insensitive to the small differences which inevitably occur between experiments.

[26] The presence of Cp*Ir(CO)H_2 would increase the intensity of the ν(Ir−H) band relative to that of the ν(C−O) band of Cp*Ir(CO)(H)Et, while the presence of Cp*Ir(CO)(D)Et would reduce the relative intensity. Therefore, if Cp*Ir(CO)H_2 and Cp*Ir(CO)(D)Et were present in the appropriate relative concentrations (i.e. [Cp*Ir(CO)H_2]:[Cp*Ir(CO)(H)Et] = 0.018:0.102 = 1:5.6), the two effects would cancel out and our analysis of the band intensities would fail to detect their presence. The chance of such a fortuitous cancellation occurring seems rather small. Similarly, our experiments do not definitively exclude the formation of some Cp*Ir(CO)(H)D but, if it were formed, another fortuitous cancellation would be required to explain the observed spectra. As far as we are aware, the wavenumber of the ν(C−O) bands of Cp*Ir(CO)(D)Et is unknown but, by analogy with Cp*Ir(CO)H_2/D_2, one would expect a small but significant shift from the ν(C−O) band of Cp*Ir(CO)(H)Et.

[27] Marx, D. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1121.

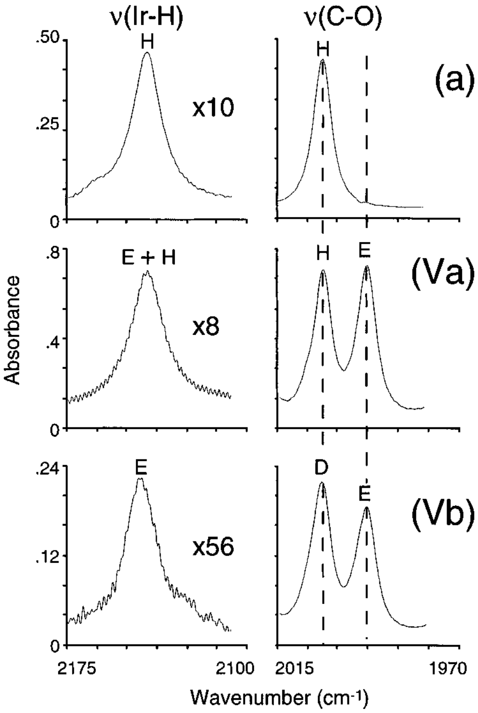

Figure 7. FTIR spectra covering the ν(Ir−H) and ν(C−O) bands of the products obtained from three different photolysis experiments, which can be used to calibrate the relative intensities of the bands of Cp*Ir(CO)H_2 and Cp*Ir(CO)(H)Et: (a) spectrum obtained after photolysis of Cp*Ir$(CO)_2$ in H_2/scXe; (Va and Vb) corresponding regions of parts a and b, respectively, of Figure 5. From (a), we can measure the absorbance of the ν(Ir−H) band of Cp*Ir(CO)H_2 to be 0.102 times that of the ν(C−O) band. In (Va), the ν(Ir-H) band has an absorbance which is 0.120 times that of the ν(C−O) band of Cp*Ir(CO)H_2, somewhat more intense than the value (0.102) measured from spectrum (a). Since the ν(Ir−H) bands of Cp*Ir(CO)H_2 and Cp*Ir(CO)(H)Et are so close in wavenumber that they are essentially superimposed, this "extra" intensity can be reasonably assigned to the ν(Ir−H) band of Cp*Ir(CO)(H)Et, which is therefore $0.120 - 0.102 = 0.018$ times the intensity of the ν(C−O) band. We can now apply these two values to assign the ν(Ir−H) band in spectrum Vb. The ν(C−O) band of Cp*Ir(CO)(H)Et in Vb has an absorbance of 0.17. If the band were due entirely to Cp*Ir(CO)(H)Et, we would expect the absorbance of the ν(Ir−H) band to be $0.018 \times 0.17 = 0.0306$. This value is within experimental error of the observed absorbance, 0.031. This shows that Cp*Ir(CO)(H)Et predominates and that little if any other products are formed,[26] i.e. Cp*Ir(CO)(D)Et or Cp*Ir(CO)H_2. Note that the absorbance scales all refer to the ν(C−O) region.

anism were contradicted by subsequent experiments with activation of Si-H bonds.[28] We investigated briefly the effects of added CO on the activation of scC_2H_6. We studied the photochemical reaction of Cp*Ir$(CO)_2$ in scC_2H_6 containing CO pressures of 7, 13, 23, 47, and 60 atm. Cp*Ir(CO)(H)Et was formed at all concentrations except the highest, where C_2H_6:CO reached ca. 2:1. The probable reason that eventual inhibition of the C−H activation of ethane was observed is probably related to the high concentration of CO gas attainable in a supercritical solution. Subsequent heating of a solution of Cp*Ir(CO)(H)Et in scC_2H_6 containing CO resulted in the regeneration of Cp*Ir$(CO)_2$.

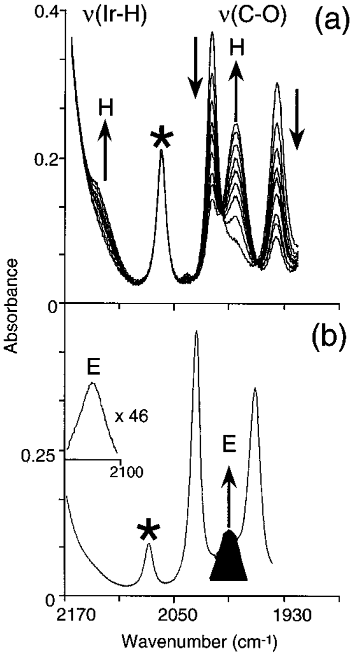

Figure 8. FTIR absorption spectra illustrating the activation of (a) H_2 and (b) C_2H_6 in scCHF_3. (a) Spectra recorded at 10 min intervals during UV irradiation of a solution containing Cp*Ir$(CO)_2$ and H_2 (100 atm) in scCHF_3 (total pressure 273 atm at 27.1 °C; see Table 1 for critical data). The bands are labeled as follows: (H) Cp*Ir(CO)H_2; and (*) scCHF_3 itself. (b) Spectrum obtained after 45 min of UV photolysis of a solution containing Cp*Ir$(CO)_2$ and C_2H_6 (130 atm) in scCHF_3 (total cell pressure 269 atm at 27.1 °C). Irradiation of the solution produced Cp*Ir(CO)(H)Et in relatively low yield, identified from the ν(C−O) band (labeled E) and from an extremely weak ν(Ir−H) band (inset), which could only be observed after performing a computer subtraction to remove the solvent absorption. Note that the ν(C−O) band, E, has been colored merely to aid visualization and the coloring does not necessarily represent the true area of the band.

(b) Reaction with H_2 and C_2H_6 in scCHF_3. UV photolysis of Cp*Ir$(CO)_2$/H_2 in scCHF_3 leads to formation of Cp*Ir(CO)H_2 with an efficiency comparable to that observed in scC_2H_6, scCO_2, or scXe (see Figure 8a). This is interesting because scCHF_3 is considerably more polar than the other fluids[29] but this polarity does not affect the reaction with H_2. However, the ν(Ir−H) band is somewhat broader in scCHF_3 than in the other media,[30] probably as the result of the greater polarity of the fluid. There is no evidence, however, for the C−H activation of CHF_3 in either the presence or absence of H_2.

In contrast, the photolysis of Cp*Ir$(CO)_2$ in a mixture of scC_2H_6 and scCHF_3 does lead to activation of C_2H_6 but the activation is extremely ineffective even compared to that in pure scC_2H_6; after 45 min of UV irradiation, only very weak bands assignable to Cp*Ir(CO)(H)Et could be observed (see Figure 8b and Table 2). This observation is quite surprising, given the relative ease of activation of H_2 in scCHF_3. Subsequent addition of H_2 to this scC_2H_6/scCHF_3 mixture and further photolysis generates Cp*Ir(CO)H_2, but unlike pure scC_2H_6, addition of H_2 does not appear to have any effect on the C−H activation of C_2H_6. On the other

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(28) Drolet, D. P.; Lees, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4186.

(29) Kazarian, S. G.; Poliakoff, M. *J. Phys. Chem.* **1995**, *99*, 8624.

(30) See Figure 6 of ref 15b.

hand, low-temperature experiments in polyethylene matrices[31] have shown that C−H activation of the polymer by Cp*Ir(CO)$_2$ is inhibited by H-bonding of $(CF_3)_3COH$ to the Ir center, although the precise mechanism of this inhibition was far from clear. The interaction F_3CH···Ir will, of course, be much weaker[32] than $(CF_3)_3COH$···Ir, because of the lower acidity of CHF_3. Nevertheless, it is possible that the H-bonding is sufficiently strong to influence the activation of C_2H_6 in scCHF_3.

(c) Reaction with scC_2H_4. In principle, the reaction of Cp*Ir(CO)$_2$ with C_2H_4 is more complicated than the activation of C_2H_6 because there are at least three possible products: Cp*Ir(CO)(H)(η^1-CH=CH$_2$), Cp*Ir(CO)(η^2-C_2H_4), and Cp*Ir(η^2-C_2H_4)$_2$. However, the IR spectra of these molecules are all well-documented through extensive studies of the activation of C_2H_4 with CpIr(CO)$_2$, particularly by Perutz and co-workers.[20,33]

As shown in Table 1, C_2H_4 has a critical temperature only slightly lower than that of C_2H_6, and we have already reported how scC_2H_4 can be used as a solvent for generating labile olefin complexes.[17] The chief disadvantage is that scC_2H_4 has much stronger IR absorptions than scC_2H_6 in the ν(C−O) region. As before, this problem can be overcome by replacing scC_2H_4 by scXe for spectroscopic analysis at the end of the reaction. Figure 9 shows spectra obtained in such an experiment, which demonstrate that FTIR can provide a *complete* characterization of Cp*Ir(CO)(H)(η^1-CH=CH$_2$). There are bands characteristic not only of the CO group but also of both the hydride and the vinyl groups. These spectra indicate that all three possible products are formed but that Cp*Ir(CO)(H)(η^1-CH=CH$_2$) predominates.

Perutz and co-workers[33] have shown that UV photolysis of CpIr(CO)(η^2-C_2H_4) can lead to the formation of CpIr(CO)(H)(η^1-CH=CH$_2$) in the absence of excess C_2H_4. In collaborative experiments with Perutz,[34] we have shown that a similar reaction can occur in scXe solution. In the present case, however, it is difficult to establish whether the formation of Cp*Ir(CO)(H)(η^1-CH=CH$_2$) occurs via Cp*Ir(CO)(η^2-C_2H_4), because (a) the ν(C−O) band of Cp*Ir(CO)(η^2-C_2H_4) is almost coincident with one of those of Cp*Ir(CO)$_2$ (Table 2) and (b) these overlapping bands are largely obscured by a broad IR absorption band of scC_2H_4.

We attempted to establish the relative efficiency of C−H activation of C_2H_6 and C_2H_4 by a competition experiment. Cp*Ir(CO)$_2$ was irradiated with UV light for a prolonged period in a mixture of scC_2H_6 and scC_2H_4. The results were not conclusive, but the yields of Cp*Ir(CO)(H)Et and Cp*Ir(CO)(H)(η^1-CH=CH$_2$) appeared to be broadly in proportion to the relative concentrations of C_2H_6 and C_2H_4 in the original mixture.[35]

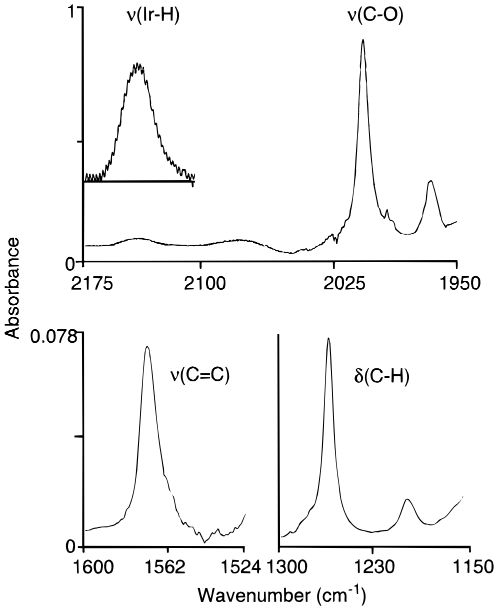

Figure 9. IR spectra, recorded in scXe, showing the bands of the products of UV irradiation of a solution containing Cp*Ir(CO)$_2$ in scC_2H_4. As before, the mixtures of products were flushed out of the supercritical cell (see Figure 2); the solids were collected and redissolved in scXe. Since the ν(C−O) bands of Cp*Ir(CO)$_2$ and Cp*Ir(CO)(η^2-C_2H_4) overlap, the ν(C−O) bands of unreacted Cp*Ir(CO)$_2$ have been removed from the spectra by scaled computer subtraction. The bands are assigned to Cp*Ir(CO)(η^2-C_2H_4), Cp*Ir(CO)(H)(η^1-CH=CH$_2$), and Cp*Ir(η^2-C_2H_4)$_2$, as listed in Table 2.

(d) Reaction with scCH_4. We have already reported[7] that Cp*Ir(CO)$_2$ can activate CH_4 in scCO_2 solution and a similar reaction can be observed in scXe (see Table 2). In both fluids, there is evidence for the formation of another unidentified photoproduct, which is rather labile and decays rapidly when the UV irradiation is stopped. CH_4 is normally considered to be a "real gas" because its critical temperature is *115 °C lower* than that of C_2H_6 (see Table 1). Thus, one would expect CH_4 to have a relatively low solvent power at ambient temperatures.[36] For spectroscopic experiments such as these, the low solvent power can be at least partially offset by the fact that CH_4 has almost no IR absorption in the ν(C−O) region. It is therefore feasible to use optical pathlengths far longer than those which would be practical with scC_2H_6 or scCO_2, both of which have combination bands in the ν(C−O) region.

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[31] Cooper, A. I.; Kazarian, S. G.; Poliakoff, M. *Chem. Phys. Lett.* **1993**, *206*, 175.

[32] Cp*(CO)$_2$Ir···H bonding has been detected for a number of highly acidic fluoro alcohols. The spectroscopic evidence is a shift to high wavenumber of the ν(C−O) bands: the stronger the interaction, the larger the shift (Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069). Any interaction with CHF_3 would be weak by comparison and therefore not easily detectable by this means. Indeed, the ν(C−O) bands of Cp*Ir(CO)$_2$ are observed at *lower* wavenumbers in scCHF_3 than in other supercritical solvents (see Table 2), presumably as a consequence of the higher polarity of scCHF_3.

[33] See: Bell, T. W.; Brough, S.-A.; Partridge, M. G.; Perutz, R. N.; Rooney, A. D. *Organometallics* **1993**, *12*, 2933 and references therein.

[34] Jobling, M.; Perutz, R. N.; Poliakoff, M. Unpublished results.

[35] One of the more intriguing facets of supercritical fluids is the transient solute−solvent clustering which occurs at temperatures not far above T_c and which can lead to altered selectivity in the course of chemical reactions. A striking example of this was recently reported in which the product distribution of the photo-Fries rearrangement of naphthyl acetate was changed by clustering in scCO_2 doped with 2-propanol (T_c = 235 °C) (Andrew, D.; Des Islet, B. T.; Margaritis, A.; Weedon, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 6132). In our case the values of T_c for C_2H_4 and C_2H_6 are quite close (see Table 1) and the mole fraction of C_2H_4 (ca. 0.5) sufficiently high that dramatic clustering effects are not anticipated and were not observed.

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

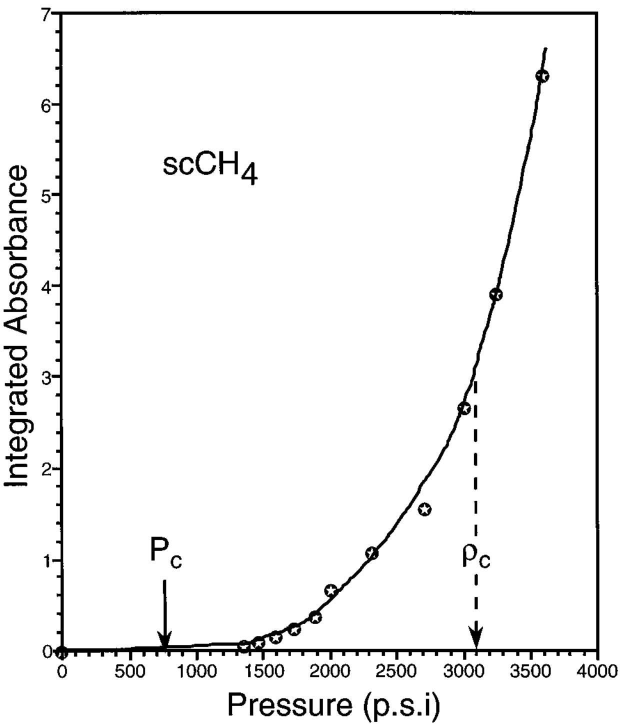


Figure 10. Plot showing the variation in solubility of $Cp^*Ir(CO)_2$ in CH_4 over a range of gas pressures at 275 K, as measured by the sum of the integrated IR absorbance (arbitrary units) of the two ν(C−O) bands of $Cp^*Ir(CO)_2$. The integrated rather than peak absorbance was used because the shapes of the bands change as the pressure is increased. Note that $Cp^*Ir(CO)_2$ is virtually insoluble at the critical pressure, P_c (669 psi), but that it increases rapidly when the density of the gas reaches its critical value, ρ_c (0.162 g/cm^3).

Figure 10 shows the results of our qualitative measurements on $Cp^*Ir(CO)_2$. As far as we are aware,[37] there have been no previous measurements of the solubility of organometallics in $scCH_4$. The compound only begins to dissolve in significant amounts when the density of CH_4 approaches the critical density, ρ_c (see Table 1). The dependence of solubility on pressure shows the "classic" shape normally associated with solids dissolving in supercritical fluids but, given the pressure limitations of our apparatus, we could not reach a high enough pressure to achieve saturation. Our conclusion was that the solubility was more than sufficient for a spectroscopic study but clearly the overall solubility of $Cp^*Ir(CO)_2$ in $scCH_4$ is much lower than in the other fluids used in this paper. The wavenumbers of species dissolved in $scCH_4$ are higher than in the other fluids (see Table 2), an observation consistent with weaker solvent-solute interactions in $scCH_4$. In contrast, $scCHF_3$ shows the largest shifts and, presumably, the strongest solvent-solute interactions.

Figure 11 summarizes the results of UV irradiation of $Cp^*Ir(CO)_2$ in $scCH_4$. The spectra clearly show that C−H activation occurs with formation of Cp*Ir(CO)(H)-Me. The most interesting feature of the reaction is the apparent ease of C−H activation. As explained above, the activation of scC_2H_6 by $Cp^*Ir(CO)_2$ is relatively inefficient. Even prolonged UV irradiation leads to a poor yield of Cp*Ir(CO)(H)Et unless H_2 is present. In contrast, photolysis of $Cp^*Ir(CO)_2$ in $scCH_4$ generates substantial amounts of Cp*Ir(CO)(H)Me. The barrier to activation by organometallic centers is predicted[38] to be low for CH_4, and the efficiency of the reaction in $scCH_4$ may reflect this. On the other hand, it may merely be a consequence of the particularly high concentration of CH_4 under these conditions. (For a given density of the fluid, the *molar* concentration of $scCH_4$ will be considerably higher than for scC_2H_6). Indeed, as explained below, the high molar concentrations of alkane and H_2 in supercritical solution may well account for the effect of added H_2.

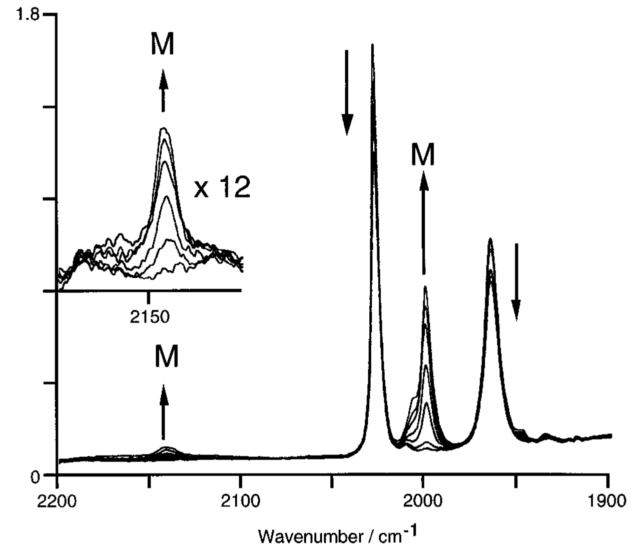
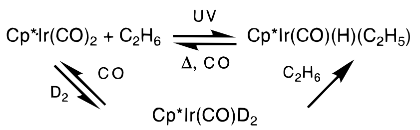


Figure 11. Series of IR spectra, recorded at 5 min intervals, showing the effects of UV photolysis (>300 nm, 30 min total irradiation time) of $Cp^*Ir(CO)_2$ in $scCH_4$ at 270 atm pressure and 295 K. The bands of $Cp^*Ir(CO)_2$ are marked ↓, those of Cp*Ir(CO)(H)Me are labeled M. As in previous spectra, the ν(Ir−H) region is shown as an inset with an expanded absorbance scale. The solution is more dilute than in the other fluids, but the absorbance values in these spectra are similar to those in the other figures, because the spectra were recorded with an optical path-length of 25 mm, ca. 10−25 times longer than those used with the other fluids. Note also that the growth of the band of Cp*Ir(CO)(H)Me is only partially matched by a decrease in intensity of the bands of $Cp^*Ir(CO)_2$ because, unlike the other experiments, this experiment was performed with a saturated solution of $Cp^*Ir(CO)_2$ and more material dissolved during the irradiation.

Scheme 3



Conclusions

Our experiments have used supercritical hydrocarbons as both reactant and solvent, thereby removing any complications due to added solvent in the system. We have found that, in D_2/scC_2H_6 mixtures, the first step is the photochemical activation of D_2 to form Cp*Ir(CO)-D_2 followed by the activation of C_2H_6 and the formation of the ^1H product Cp*Ir(CO)(H)Et (Scheme 3).

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[37] For a recent review on methane and its chemistry, see: Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987.

[38] Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177.

We have confirmed that photochemical C−H activation by Cp*Ir(CO)H_2 is more effective than by Cp*Ir$(CO)_2$. A similar effect has been found by Rest and co-workers[10] in CH_4 matrices, where CpIr(CO)H_2 is a more facile precursor of CpIr(CO) than is CpIr$(CO)_2$. Bloyce et al. showed that photolysis of CpIr(CO)D_2 in the presence of unlabeled neopentane led to the formation of CpIr(CO)(H)(*neo*-Pe) with D incorporated into the *neo*-Pe ligand.[39] However, our present experiments do not provide any information about possible incorporation of D into the ethyl group in the Cp*Ir$(CO)_2$/scC_2H_6/D_2 system.

The reason for the greater efficiency of C−H activation by Cp*Ir$(CO)_2$ and Cp*Ir(CO)H_2 is not immediately apparent, because both compounds should generate the same 16-electron intermediate, Cp*Ir(CO), which might be expected to react similarly irrespective of its origin. It should be noted, however, that only a small change in the relative rates of the processes would be sufficient to account for our observations. Thus, there are two plausible rationalizations of the effect, apart from invoking the possibility that photolyses of Cp*Ir$(CO)_2$ and Cp*Ir(CO)H_2 yield Cp*Ir(CO) in different electronic states.

Rationalization 1. In our experiments, the concentrations of both C_2H_6 and H_2 are many orders of magnitude higher than those used, for example, by Bergman and co-workers in time-resolved IR experiments on C−H activation,[40] experiments which led to the identification of a dissociative mechanism for C−H activation by Cp*Rh$(CO)_2$. Very high concentrations of entering ligand favor *associative* over dissociative processes. Our observations could then be rationalized by assuming that (i) there is an associative pathway for reaction of Cp*Ir$(CO)_2$ with H_2, which is accelerated relative to the dissociative reaction with C_2H_6 by the high concentration of H_2, and (ii) the combined effect of our UV lamp, the various UV extinction coefficients, and the quantum yields is to give a faster rate of formation of Cp*Ir(CO) from Cp*Ir(CO)H_2 than from Cp*Ir$(CO)_2$.

Rationalization 2. Picosecond transient spectroscopy has shown that reaction between coordinatively unsaturated organometallic intermediates and solvent is extremely fast, occurring within 1 ps.[41] More surprising has been the observation that, even in conventional solvents (e.g. *n*-hexane), relaxation of *vibrational* excitation in metal carbonyl compounds is much slower,[42] sometimes occurring on a timescale of 10^2 ps. One would not expect these relaxation rates to be much faster in supercritical fluid solution because the densities of the fluids are less than those of conventional solvents and their molar concentrations are only slightly higher. Thus, our experiments may well involve reactions of vibrationally excited intermediates, because the UV photon energy in our experiments is almost certainly higher than the bond dissociation energy of one Ir−CO bond or of two Ir−H bonds.[43] Therefore, photolysis of both Cp*Ir$(CO)_2$ and Cp*Ir(CO)H_2 should generate Cp*Ir(CO) with excess energy and, given a difference in strengths of 1 × Ir−CO and 2 × Ir−H bonds, the amounts of excess energy in Cp*Ir(CO) will be different for the two precursors. Our observations can then be rationalized by postulating a difference in reactivity between Cp*Ir(CO) intermediates with different levels of vibrational excitation. This rationalization could be tested, in principle at least, by picosecond TRIR experiments.

As in our previous work with supercritical solvents,[11c] rapid precipitation provides a convenient and effective means of recovering the products of the C−H activation reactions, products which are relatively difficult to isolate from conventional solvents. These experiments underline the fact the supercritical fluids allow very small samples of organometallics to be manipulated with high precision. Scale-up of these C−H activation reactions is limited by the poor quantum yield of the process and, although we have shown that it is possible to generate enough product for ^{1}H NMR analysis, FTIR has proved to be a surprisingly effective tool for characterizing the products of organometallic reactions under these conditions. Furthermore, the use of scCH_4 as a solvent opens up interesting new possibilities, particularly given its frequently unrecognized spectroscopic transparency.

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