Photochemical Activation of C–H Bonds in Supercritical Fluids: The Dramatic Effect of Dihydrogen on the Activation of Ethane by [(η^5-C_5Me_5)Ir(CO)$_2$]

Margaret Jobling, Steven M. Howdle,* Michael A. Healy, and Martyn Poliakoff*
Department of Chemistry, University of Nottingham, Nottingham, England NG7 2RD

UV photolysis of [Cp*Ir(CO)$_2$] (Cp* = η^5-C_5Me_5) in supercritical CO_2 (scCO_2) doped with H_2 or C_2H_6 leads to the formation of [Cp*Ir(CO)(H)R] (R = H or C_2H_5) identified by IR spectroscopy; [Cp*Ir(CO)(H)(C_2H_5)] can also be generated by UV photolysis of [Cp*Ir(CO)$_2$] dissolved in supercritical ethane (scC_2H_6) and the efficiency of the reaction is increased greatly by the addition of H_2 at high pressures to the solution.

The photochemical activation of alkanes by [Cp*ML$_2$] complexes (Cp* = η^5-C_5Me_5; M = Ir and Rh) is an area of continuing interest.[1] A recurrent problem in such studies, however, has been in finding suitably inert aprotic solvents, particularly for those experiments involving the activation of low molecular weight alkanes (*e.g.* C_2H_6). Although a number of solvents including C_6F_6,[1d] perfluoroalkanes[1b] and liquid noble gases,[1f] have now been used successfully for C–H activation, each has its drawbacks; C_6F_6 transpired to be a 'reactive' solvent capable of forming stable η^2-C_6F_6 complexes[2] while many compounds are only sparingly soluble in perfluoroalkanes, liquid Xe or Kr.

In this communication, we show how supercritical carbon dioxide, scCO_2, combines the chemical inertness and solvent properties[3] needed for C–H activation studies at ambient temperatures. Furthermore, the complete miscibility of H_2 with scCO_2 and scC_2H_6 permits experiments which would be extremely difficult in more conventional solvents. This miscibility, which results in a much higher concentration of 'dissolved' gas than would be obtained with hydrocarbon

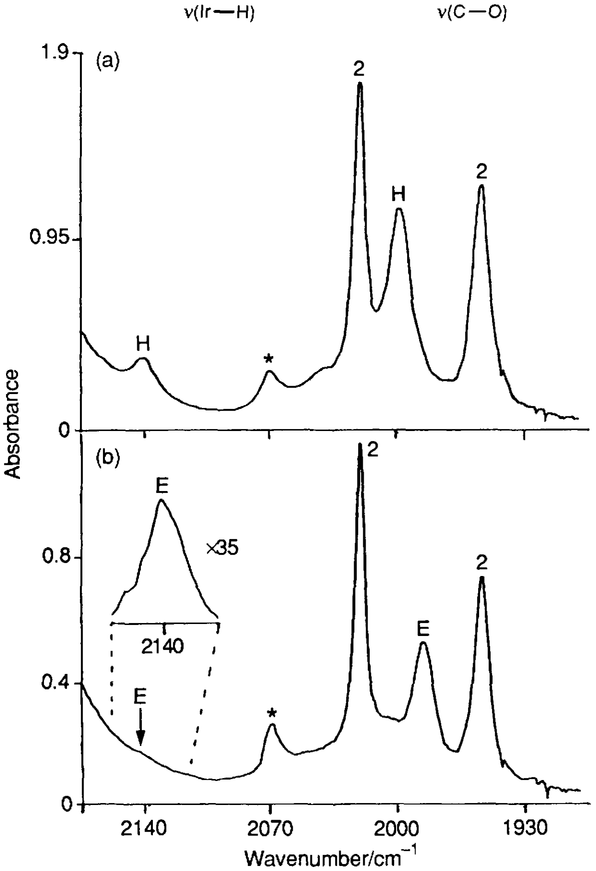

Figure 1. IR spectra showing the photochemical activation by $[Cp^*Ir(CO)_2]$ of (a) H_2 and (b) C_2H_6 in $scCO_2$ solutions. (a) spectrum was recorded after 60 min UV photolysis of $[Cp^*Ir(CO)_2]$ in $scCO_2$ (115 atm) with H_2 added to total pressure of 270 atm. Bands are labelled as follows: 2, unreacted $[Cp^*Ir(CO)_2]$; H, $[Cp^*Ir(CO)(H)_2]$ and *, a relatively weak absorption of the $scCO_2$ solvent itself. The slope in the baseline towards higher wavenumbers is also due to absorption by the $scCO_2$. (b) Spectrum was recorded after 10 min UV photolysis of $[Cp^*Ir(CO)_2]$ with C_2H_6 (47 atm) with CO_2 added to a total pressure of 225 atm. The bands marked E are assigned to $[Cp^*Ir(CO)(H)(C_2H_5)]$; other bands are labelled as in spectrum (a). Note that the ν(Ir–H) band of $[Cp^*Ir(CO)(H)(C_2H_5)]$ is much weaker relative to ν(C–O) than is that of $[Cp^*Ir(CO)(H)_2]$. Therefore, the ν(Ir–H) region in spectrum (b) is also shown digitally smoothed with a ×35 expanded absorbance scale and computer subtraction of the underlying absorption of the $scCO_2$.

solvents (*e.g.* heptane) under similar conditions, was the crucial factor in our earlier experiments[4] involving the photochemical generation of new transition metal dihydrogen and dinitrogen complexes in supercritical Xe at temperatures up to 80 °C.

Table 1. Wavenumbers,[a] cm^{-1}, of ν(C–O) and ν(Ir–H) IR bands in supercritical and conventional solvents.

Compound	$scCO_2$	scC_2H_6	Assignment
$[Cp^*Ir(CO)_2]$[b]	2020.5	2024.6	a′ ν(C–O)
	1953.9	1960.2	a″ ν(C–O)
	2001.3	2008.1	ν(^{13}C–O)
	1919.9	1929.4	ν(^{13}C–O)
$[Cp^*Ir(CO)(H)_2]$	2140	2140	ν(Ir–H)[c]
	1997.9	2004.0	ν(C–O)
$[Cp^*Ir(CO)(H)(C_2H_5)]$[d]	2142	2142	ν(Ir–H)
	1985.7	1992.2	ν(C–O)
$[Cp^*Ir(CO)(H)(CH_3)]$[e]	*ca.* 2138	2137[f]	ν(Ir–H)
	1990.4	1995.3[f]	ν(C–O)
$[(Cp^*)_2Ir_2(CO)_3]$	1930	1933[g]	ν(C–O)
	1759	1755[g]	ν(C–O)
$[(Cp^*)_2Ir_2(CO)_2]$	1690	1702[h]	ν(C–O)

[a] Spectra of supercritical solvents recorded on Nicolet 730 FTIR interferometer (16 K data points, 32 K transform points) error ± 0.2 cm^{-1} at a temperature of 31 ± 2 °C. [b] cf 2020 and 1953 cm^{-1} (hexane).[5b] [c] Unresolved bands due to symmetric and antisymmetric vibrations. [d] cf 2149 and 1982 cm^{-1} $[Cp^*Ir(CO)(H)(C_6H_{11})]$ in heptane[1b]. [e] cf 2149 and 1991.3 cm^{-1} CH_4 matrices at 10 K.[1c] [f] scXe solution with 700 psi CH_4 added. [g] C_6D_6 solution.[5a] [h] Hexane solution.[5b]

$[Cp^*Ir(CO)_2]$ is readily soluble in $scCO_2$ and UV photolysis† of such a solution in the absence of any added reactants does not lead to any reaction apart from the appearance of weak IR bands, after prolonged irradiation, assigned to trace amounts of the known dinuclear species $[(Cp^*)_2Ir_2(CO)_x]$ (x = 2 or 3), see Table.‡ When the photolysis is repeated in the presence of H_2, the formation of these dinuclear species is suppressed and $[Cp^*Ir(CO)(H)_2]$ is generated with ν(C–O) and ν(Ir–H) bands, marked 'H' in Figure 1(a), similar to those reported[1e] for $[CpIr(CO)(H)_2]$ (Cp = η^5-C_5H_5). This is a new route to $[Cp^*Ir(CO)(H)_2]$ but perhaps the most striking feature of the reaction is the complete inertness of the $scCO_2$ under these conditions.§ This inertness means that $scCO_2$ can be used as a solvent for C–H activation.

$$[Cp^*Ir(CO)_2] + H_2 \xrightarrow{h\nu} [Cp^*Ir(CO)(H)_2] + CO \qquad (1)$$

UV photolysis of $[Cp^*Ir(CO)_2]$ in $scCO_2$ doped with C_2H_6 gives rise to two new IR bands, marked 'E' in Figure 1(b), one in the ν(C–O) and the other in the ν(Ir–H) region. The bands can be assigned to $[Cp^*Ir(CO)(H)(C_2H_5)]$ by comparison with the spectra of known $[Cp^*Ir(CO)(H)R]$ species, Table 1. Although C_2H_6 is clearly being activated, the overall conversion is rather disappointing. Even with UV light filtered to minimise the effects of secondary photolysis,¶ the concentration of $[Cp^*Ir(CO)(H)(C_2H_5)]$ rapidly reaches a steady state.

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† *Safety note:* **Caution**: Experiments with supercritical fluids involve relatively high pressures of gases and should be approached with caution. Our miniature high pressure IR cell has been described previously.[4b,6] In the present experiments, it was used with a pathlength of 1.8 mm. C_2H_6 (Air Products) was condensed into the cold-finger of the cell using liquid nitrogen, CO_2 (Air Products 4.5 sfc Grade) was added using a Lee Scientific Model 501 computer-controlled syringe pump and H_2 (Air Products) was added directly from the cylinder using a high-pressure gas regulator. A Cermax 300 W Xe lamp filtered to give UV light, 200—400 nm, was used for photolysis with an additional >300 nm glass filter when required.

‡ The vapour pressure of $[Cp^*Ir(CO)_2]$ is too low at these temperatures for any IR bands to be observable in our cell in the absence of the supercritical solvent. The approximate concentration of $[Cp^*Ir(CO)_2]$ used in these experiments is 2 × 10^{-3} M, which is <1/10 of the saturated value.

§ There have been previous organometallic experiments involving CO_2 as a solvent but these have largely been aimed at the synthesis of new CO_2 complexes (*e.g.* M. G. Mason and J. A. Ibers, *J. Am. Chem. Soc.*, 1982, **104**, 5153). In these circumstances, lack of reactivity of CO_2 was a source of disappointment rather than a positive feature to be exploited.

¶ Rest and co-workers have shown[1c,1e] that filtered UV photolysis can improve the yield of C–H activated products in CH_4 matrices at 10 K. We found no improvement in final yield when our lamp was filtered >300 nm but the rate of reaction was considerably lower.

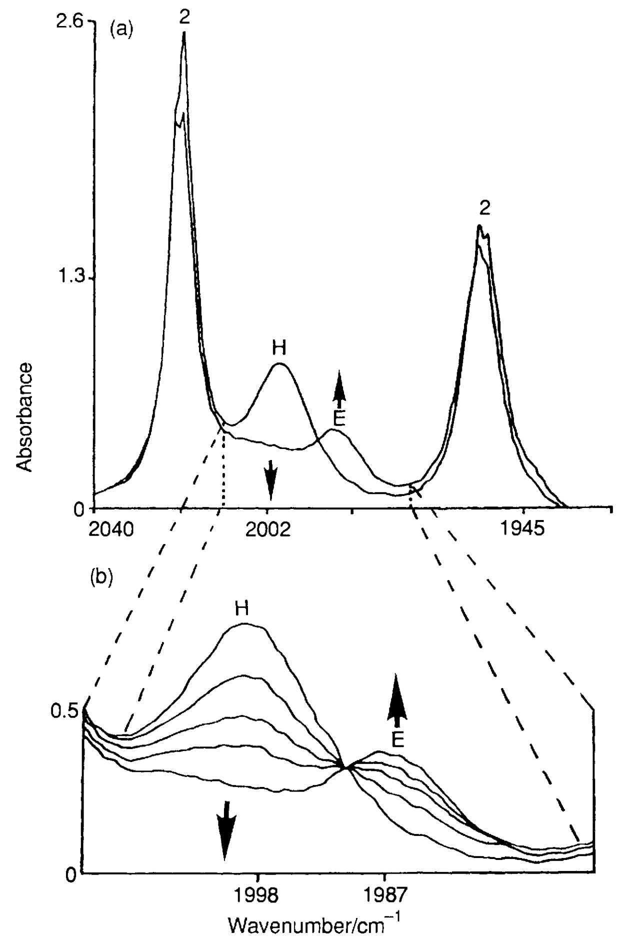

Figure 2. IR spectra in the ν(C–O) region showing the competitive C–H activation of C_2H_6 (45 atm) in $scCO_2$ (total pressure 180 atm) by $[Cp^*Ir(CO)(H)_2]$ and $[Cp^*Ir(CO)_2]$. (a) Spectra recorded before and after 90 min photolysis (>300 nm); note the reduction in intensity of band H due to $[Cp^*Ir(CO)(H)_2]$ and the corresponding increase in band E due to $[Cp^*Ir(CO)(H)(C_2H_5)]$ and the very small change in the bands of $[Cp^*Ir(CO)_2]$, labelled 2. (b) Enlarged portion of the spectrum showing the isosbestic point between the bands of $[Cp^*Ir(CO)(H)_2]$ and $[Cp^*Ir(CO)(H)(C_2H_5)]$; the spectra were recorded at *ca.* 20 min intervals.

$$[Cp^*Ir(CO)_2] + C_2H_6 \xrightarrow{h\nu} [Cp^*Ir(CO)(H)(C_2H_5)] + CO \quad (2)$$

It has been reported[1e] that $[CpIr(CO)(H)_2]$ is more efficient than $[CpIr(CO)_2]$ in the photochemical activation of C–H bonds both in conventional solvents and in cryogenic matrices. Elegant experiments with H/D labels showed that the detailed mechanism of C–H activation by $[CpIr(CO)(H)_2]$ is probably more complicated than mere formation of a $[CpIr(CO)]$ intermediate and may involve migration of H to the Cp ring.[1e] The relative efficiency of $[Cp^*Ir(CO)_2]$ and $[Cp^*Ir(CO)(H)_2]$ for C–H activation in $scCO_2$ can be compared directly by the following two-stage experiment:

(i) A mixture of $[Cp^*Ir(CO)(H)_2]$ and $[Cp^*Ir(CO)_2]$ is generated by UV photolysis of $[Cp^*Ir(CO)_2]$ in $scCO_2$ doped with H_2, as in Figure 1(a); (ii) the H_2 is vented (while freezing the CO_2 with liquid nitrogen in the cold finger of the cell), C_2H_6 is added, the cell is warmed and the carbonyl compounds redissolved.

When this solution, containing both $[Cp^*Ir(CO)_2]$ and $[Cp^*Ir(CO)(H)_2]$ is irradiated with UV light, there is smooth conversion of $[Cp^*Ir(CO)(H)_2]$ into $[Cp^*Ir(CO)(H)(C_2H_5)]$, while $[Cp^*Ir(CO)_2]$ is virtually unaffected, see Figure 2. Thus, like its Cp analogue, $[Cp^*Ir(CO)(H)_2]$ has the greater efficiency for C–H activation. The critical temperature of C_2H_6 is very close to that of CO_2‖ and C–H activation can be studied in scC_2H_6 in the absence of CO_2. The spectrum in Figure 3(a) shows the result of UV photolysis of $[Cp^*Ir(CO)_2]$ in scC_2H_6. Although $[Cp^*Ir(CO)(H)(C_2H_5)]$ is clearly formed, the overall conversion is no higher than in $scCO_2$ doped with C_2H_6 and even prolonged irradiation does not increase the conversion appreciably. There is, however, a striking difference when the same photolysis is carried out in scC_2H_6 with a high pressure of H_2 added. The yield of $[Cp^*Ir(CO)(H)(C_2H_5)]$ is increased greatly, significant quantities of $[Cp^*Ir(CO)(H)_2]$ are formed and the $[Cp^*Ir(CO)_2]$ starting material is almost totally destroyed, see Figure 3(b).

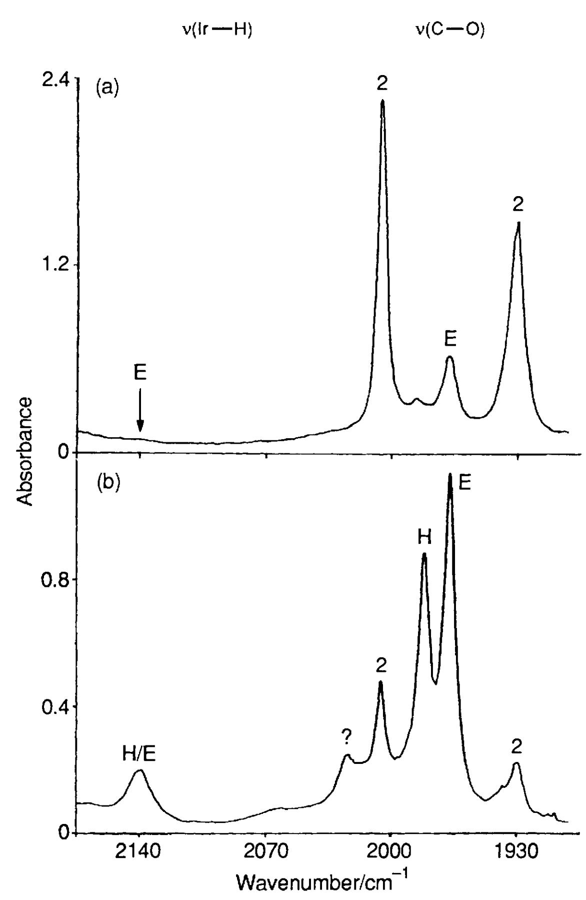

Figure 3. (a) IR spectrum obtained by UV photolysis 3 min of $[Cp^*Ir(CO)_2]$ in scC_2H_6 (68 atm.); bands marked E are due to $[Cp^*Ir(CO)(H)(C_2H_5)]$; (b) Spectra showing the strikingly different result of 10 min UV photolysis of $[Cp^*Ir(CO)_2]$ in scC_2H_6 (50 atm.) *with H_2 added* to a total pressure of 179 atm. The bands are labelled as follows: E, $[Cp^*Ir(CO)(H)(C_2H_5)]$; H, $[Cp^*Ir(CO)(H)_2]$; 2, residual $[Cp^*Ir(CO)_2]$ and '?', an unidentified, labile photoproduct.

$$[Cp^*Ir(CO)(H)_2] + C_2H_6 \xrightarrow{h\nu} [Cp^*Ir(CO)(H)(C_2H_5)] + H_2 \quad (3)$$

Even though we demonstrated the greater efficiency of $[Cp^*Ir(CO)(H)_2]$ for C–H activation in Figure 2, the effect of

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‖ The critical points of these substances are CO_2 (31 °C, 74 atm.) and C_2H_6 (32 °C, 48 atm.) compared to Xe (17 °C, 59 atm.) [*N.B.* 10.1 atm. = *ca.* 1 MPa.].

adding H_2 to scC_2H_6 is surprisingly large. Under the conditions of this experiment, the molar concentration of H_2 is nearly half that of C_2H_6.** Thus, generation of [Cp*Ir(CO)(H)(C_2H_5)] *via* [Cp*Ir(CO)$(H)_2$] [*i.e.* reaction (1) followed by reaction (3)] will be competitive with the direct formation from [Cp*Ir$(CO)_2$] as in reaction (2). The actual mechanism may be more complicated because a third IR band, marked '?' in Figure 3(b), is also observed in the reaction mixture. This band is due to a labile carbonyl species, which decays completely over a period of 12 h. Experiments are now in progress to probe the mechanism of this reaction in more detail.

The C–H activation in scCO_2 is not restricted to C_2H_6. Methane can be activated to form [Cp*Ir(CO)(H)(CH_3)] under similar conditions, although significant quantities of other metal carbonyl species are also generated. The chemical inertness of scCO_2 clearly has applications to other organometallic reactions and work is in progress to explore these possibilities.

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** At temperatures close to their critical temperature, fluids can show unusual behaviour, such as formation of solvent clusters around solute molecules.[3,7] Addition of high pressures of a gas, such as H_2 or He, to scC_2H_6 will lower the critical temperature significantly[3] and will alter the physical behaviour of the solvent. In this experiment, however, the role of H_2 appears to be chemical rather than physical because addition of He instead of H_2 to scC_2H_6 does not produce the same effect on C–H activation. One would expect that the effect of adding H_2 would be much smaller in a conventional solvent, given the lower solubilility of H_2.

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