Preparative-scale Organometallic Chemistry in Supercritical Fluids; Isolation of $[Cr(CO)_5(C_2H_4)]$ as a Stable Solid at Room Temperature

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A miniature flow reactor has been developed for photochemical reactions in supercritical fluids; $[Cr(CO)_5(C_2H_4)]$ is isolated, for the first time, by the UV photolysis of $[Cr(CO)_6]$ in supercritical C_2H_4 at room temp. with a yield of *ca.* 40 mg per hour at *ca.* 80% purity as estimated by IR spectroscopy.

Supercritical fluids are attractive as reaction media[1] not only for their potential to tune the outcome of reactions[2a] but also for the promise of 'cleaner' chemical processes.[2b] It is, therefore, surprising that there have been very few reported cases where supercritical reactions have led to the isolation of new compounds. Equally, there has been little indication of how such fluids could be used in the laboratory for small-scale preparative chemistry. This communication describes a miniature supercritical flow reactor for photochemical reactions and illustrates its use by the prepration and isolation, at room temperature, of $[Cr(CO)_5(C_2H_4)]$, a compound previously believed to be thermally labile.[3]

We have already reported some of the possibilities[4] for organometallic photochemistry in fluids with critical temperatures, T_c, close to ambient (*e.g.* C_2H_4, T_c 9 °C; Xe, T_c 16.8 °C; CO_2, T_c 31.8 °C). These experiments were all carried out on a spectroscopic scale, usually involving <1 mg of compound. Some of the products, such as $[(C_5H_5)Re(N_2)_3]$,[4a] had not been observed previously at room temperature and, clearly there is interest in scaling up such reactions. The solubility of organometallics in supercritical fluids is usually lower than in conventional solvents so large static reactors would be required. It is not easy to carry out photochemical reactions in a high pressure reactor[5] and there are safety implications of larger volume reactors at high pressure. Furthermore, releasing the pressure at the end of the reaction would cause precipitation of solid product as a fine powder throughout the apparatus. These problems can be overcome by use of a flow reactor.

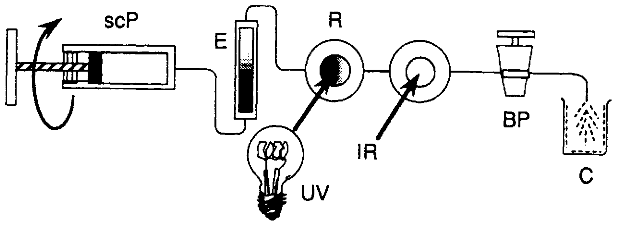


Fig. 1 Schematic view of the flow reactor. The components are labelled as follows: scP, the supercritical pump, either manually operated (High Pressure Equip. Co pressure generator Model 62-6-10) or pneumatically controlled (New Ways in Analytics Model PM-101) for pumping scC_2H_4; E, miniature supercritical extraction vessel, used as a reservoir for the solid organometallic reactant to be dissolved in the scC_2H_4; R, the water-cooled photolysis chamber|| (0.5 ml volume) for converting reactant to product; UV, photolysis lamp (Cermax 300 W high intensity illuminator with OP2 cold mirror and quartz focusing lens); IR, an optional IR cell to monitor the reaction, BP, a back-pressure regulator (Jasco Model 880-81) to release the pressure in a controlled manner and to precipitate the product; C, a container to collect the product.**

Laboratory-scale flow reactors share many of the advantages of their industrial counterparts,[6] *e.g.* low volumes for increased safety, scale-up of reactions merely by running longer, and the option of recovering, purifying and recycling the solvent. Fig. 1 shows a schematic view of our prototype flow reactor for photochemical reactions of organometallic compounds in supercritical C_2H_4, scC_2H_4, where the fluid is both solvent and one of the reactants. The apparatus is extremely straightforward to use; once the flow system has been assembled, the reactor loaded and the UV lamp switched on, the reactant is converted into the product merely by operating the pump. The product is precipitated by passing through the back pressure regulator and is deposited as a dry solid in the collection vessel.

$[Cr(CO)_5(C_2H_4)]$ was first observed as a thermally labile product during the photolysis of $[Cr(CO)_6]$ and C_2H_4 in liquid Xe solution.[7] Subsequently, [*trans*-$Cr(CO)_4(C_2H_4)_2$] was isolated as a stable crystalline solid from a similar low temperature reaction in hydrocarbon solution[3a] but, until now, $[Cr(CO)_5(C_2H_4)]$ has defied all attempts to isolate it. We have recently reported[4e] that photolysis of $[Cr(CO)_6]$ in scC_2H_4 leads to formation of $[Cr(CO)_5(C_2H_4)]$ which appears to be stable in scC_2H_4 solution for considerable periods of time. The spectra in Fig. 2 confirm that $[Cr(CO)_5(C_2H_4)]$ can be generated by photolysis of $[Cr(CO)_6]$ in scC_2H_4 in our flow reactor. At the same time, a yellow and rather air-sensitive solid product can be collected from the end of the reactor, at a

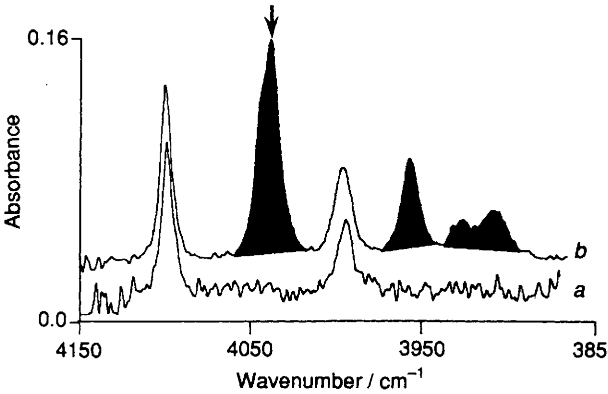


Fig. 2 IR spectra in the 2 × ν(C–O) region of the spectrum recorded in our flow reactor loaded with $[Cr(CO)_6]$ and scC_2H_4 (optical pathlength 5 mm), (*a*) spectrum recorded with the UV lamp switch off, showing the combination bands of $[Cr(CO)_6]$ and (*b*) spectrum recorded with the UV photolysis in progress; bands which appear on photolysis are coloured, the most intense band arrowed is due to the $a_1(\text{high}) + b_1$ or b_2 modes of $[Cr(CO)_5(C_2H_4)]$. Note that spectra in the fundamental ν(C–O) region (2000–1900 cm^{-1}) are largely obscured by absorptions of scC_2H_4 under these conditions.

|| The photochemical cell is a modified version of our high pressure IR cells. For details of the design and of the modular components used to build this flow reactor, see S. M. Howdle and M. Poliakoff, Proc. NATO ASI *Supercritical Fluids: Fundamentals for Application*, ed. E. Kiran, to be published. **SAFETY NOTE:** Experiments in supercritical fluids involve high pressures and should be approached with caution.

** Note that, when the reactor is operating normally, this container is not subject to high pressures but we have, nevertheless, used a stainless steel pressure vessel with a glass liner in case the back pressure regulator should jam open or the vent tube block.

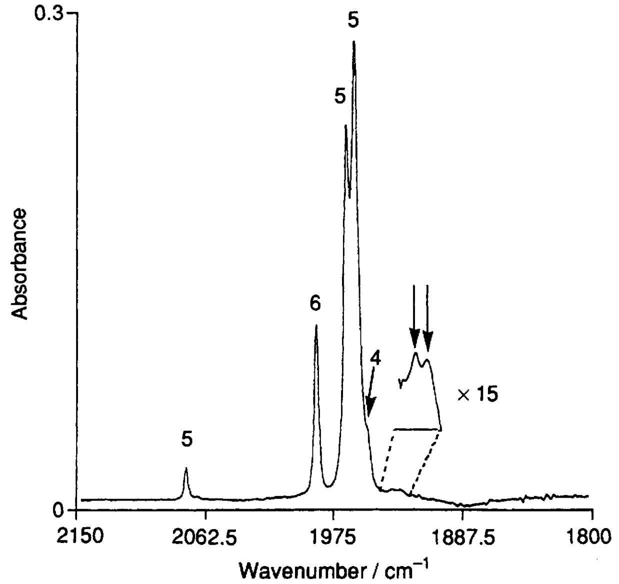
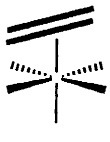


Fig. 3 IR spectrum in the ν(C–O) region obtained immediately after dissolving the crude reaction product in *n*-heptane saturated with C_2H_4 at room temperature. The bands are labelled as follows; 6, $[Cr(CO)_6]$; 5, $[Cr(CO)_5(C_2H_4)]$ (↓ indicates ^{13}CO satellites, shown with ×15 expansion in the absorbance); 4, [*trans*-$Cr(CO)_4(C_2H_4)_2$]. The relative absorbance of the bands suggest that the sample of $[Cr(CO)_5(C_2H_4)]$ is *ca.* 80% pure. Since $[Cr(CO)_5(C_2H_4)]$ decomposes slowly in solution under these conditions to generate $[Cr(CO)_6]$, the initial purity of the product was probably >80%.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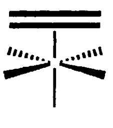
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rate of *ca.* 40 mg per hour.† This solid can be totally redissolved in *n*-heptane saturated with C_2H_4 and the IR spectrum, Fig. 3, shows the crude product to be largely $[Cr(CO)_5(C_2H_4)]$, with only minor contamination by $[Cr(CO)_6]$ and [*trans*-$Cr(CO)_4(C_2H_4)_2$]. The presence of η^2-C_2H_4 is confirmed by ^1H NMR spectroscopy‡ and ν(C–O) IR data§ agree exactly with published values.[3,7] The splitting of the strongest ν(C–O) absorption into *two* bands and the presence two natural abundance ^{13}CO satellites of *similar* intensity, arrowed in Fig. 3, indicate that $[Cr(CO)_5(C_2H_4)]$ adopts structure **1**, in which C_2H_4 eclipses one pair of CO groups, as suggested by earlier experiments.[7] The staggered structure **2**, with four equivalent CO groups, would give rise to an unsplit ν(C–O) band and two ^{13}CO satellites with substantially *different* intensities in this region.

In solution, the C_2H_4 ligand of $[Cr(CO)_5(C_2H_4)]$ appears to be labile. This, presumably, is the reason why $[Cr(CO)_5(C_2H_4)]$ has not been isolated before; any attempt to remove a conventional solvent by evaporation will also remove the C_2H_4 ligand. By contrast, precipitation from scC_2H_4 solution is very rapid and takes place under a pressure of C_2H_4. In addition, the expanding C_2H_4 gas probably cools the solid as it precipitates. Once in the solid state, $[Cr(CO)_5(C_2H_4)]$ is much more stable than in solution, an effect already reported for [$Cr(CO)_5$(*cis*-cyclooctene)].[8] Like the cyclooctene complex, $[Cr(CO)_5(C_2H_4)]$ promises to be a useful source of '$Cr(CO)_5$' but with the added advantage that C_2H_4 is, perhaps, easier to remove from solution than cyclooctene.

Our flow reactor has been used to generate a range of other ethene complexes, including $[W(CO)_5L]$, [*trans*-$W(CO)_4L_2$], $[(C_5H_5)Mn(CO)_2L]$ ($L = \eta^2$-C_2H_4). These reactions have the advantage that they are 'solvent-free' and the products are delivered as dry powdered solids as an integral part of the process. It has recently been shown that pumps of the type used in our reactor can easily be adapted for closed-cycle operation[9] so that the scC_2H_4 could easily be recycled. The reactor would work equally well with other supercritical solvents (*e.g.* $scCO_2$) and we are now developing apparatus for reactions involving H_2 and N_2 to exploit some of our other organometallic reactions[4] on a preparative scale.

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† Reaction conditions: scC_2H_4 (Air products) 1220 psi with a flow rate 32 ml min^{-1} (measured at atmospheric pressure; equivalent to *ca.* 2.5 g h^{-1}); UV photolysis cell temperature, 25–35 °C. There is little decomposition in the UV cell in a period >2 h and a reasonable mass balance ±5% has been obtained throughout the system.

‡ ^1H NMR; δ 2.67, C_6D_6 solution, room temp.

§ Wavenumbers (±0.1 cm^{-1}) of IR bands *n*-heptane, ν(C–O) region, 2077.6(a_1), 1966.1(b_1) and 1960.4 (overlapping a_1 and b_2); assignment based on structure **1**. Spectra recorded on Nicolet Model 205 FTIR interferometer, 2 cm^{-1} resolution.

¶ For a brief description of the NWA pump, see K. H. Pickel, *Proc. 2nd Int. Symp. Supercritical Fluids*, ed. M. A. McHugh, Johns Hopkins University, Baltimore, 1991, 457.