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New Directions in Inorganic and Metal-Organic Coordination Chemistry in Supercritical Fluids

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Contents

I. Introduction

> *"There is no point in doing something in a supercritical fluid just because it's neat. Using the fluids must have some real advantage"*

These were the words of supercritical fluid guru, Val Krukonis, 11 years ago at the First International Symposium on Supercritical Fluids in 1988. His words are equally true today. Working with supercritical fluids involves high pressures and sometimes high temperatures. Nearly always, it will always be easier to carry out an experiment under conventional conditions than supercritically. Nevertheless, in this review, we show how using these fluids can give real advantages in coordination, organometallic, inorganic, and materials chemistry. We highlight the increasingly important role that supercritical fluids are playing in these areas of chemistry.[3−5]

Strictly, a supercritical fluid (SCF) is "any substance, the temperature and pressure of which are higher than their critical values" (Table 1). However, this definition is not of great value because few chemists would regard H_2 gas ($T_c = 33$ K, $P_c = 1.23$ MPa) as being "supercritical" at room temperature and 1.23 MPa pressure because its density under these conditions is far below its critical value ($\rho_c = 0.03$ g/mL). Thus, far below its critical density, a fluid ceases to display the nonideal properties typically associated with SCFs. These properties, sometimes termed a "hybrid of those of a liquid and a gas", include the ability to dissolve solids, miscibility with permanent gases, high diffusivity, low viscosity, etc. It is the exploitation of these properties, either individually or in combination, which enable chemists to use these fluids to access new areas of chemistry. A more useful definition of a SCF, therefore, is "any substance, the temperature and pressure of which are higher than their critical values, *and which has a density close to or higher than its critical density*". Throughout this review, we use the prefix "sc" to signify this supercritical state (e.g., $scCO_2$, scH_2O, etc.).

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Jawwad Arshad Darr was born in Bradford, West Yorkshire (U.K.), in 1970 and received his B.Sc. from the University of Manchester in 1991. His Ph.D. (Group 2, Eu and Yb triorganosiloxy- and tetraphenyldisiloxydiolate-complexes) and a year of postdoctoral research (Lanthanide oxide CVD precursors) at Imperial College (London) were completed under the supervision of Professor Michael Mingos after an initial period with Dr. Simon Drake. Thereafter, in March 1996, he joined the University of Nottingham where he is currently an EPSRC-funded postdoctoral research assistant in the Clean Technology research laboratories of Professor Martyn Poliakoff. His current research interests include the solubilization and transport of compounds in $scCO_2$ and the production of fine ceramic powders and catalyst materials using SCFs. Other research interests include, MOCVD and the synthesis and reactions of metal alkoxides, β-diketonates, acetates, siloxides, and polysiloxanes.

Martyn Poliakoff was born in 1947 in London (U.K.), studied Chemistry at Cambridge University (B.A., 1969), and studied for his Ph.D. (1973) on the matrix isolation of large molecules under the supervision of J. J. Turner, with whom he subsequently had a long and productive scientific collaboration. In 1972, he moved to the University of Newcastle upon Tyne and, in 1979, to the University of Nottingham, where he is currently Professor of Chemistry and holder of an EPSRC/Royal Academy of Engineering Fellowship in Clean Technology. In recent years, his research has focused increasingly on the chemical and analytical applications of SCFs. He has been awarded the Meldola Medal (1976) and Tilden Medal (1990) of the Royal Society of Chemistry and has held a Nuffield Foundation University Fellowship (1988/9) and a Royal Society Leverhulme Trust Senior Fellowship (1993/4). He has strong academic and industrial collaborations both within United Kingdom and internationally, particularly with Russia.

Table 1. Critical Data for Selected Substances

substance	T_c, K	P_c, atm	ρ_c, g/mL
Ar	150.8	48.0	0.53
CH_4	190.6	45.8	0.16
Kr	209.4	54.3	0.92
C_2H_4	283.1	50.5	0.22
Xe	289.8	58.0	1.15
C_2F_6	293.0	30.2	0.62
CHF_3	299.3	47.9	0.62
$CClF_3$	302.0	38.1	0.58
CO_2	304.2	72.9	0.47
C_2H_6	305.5	48.2	0.20
N_2O[a]	309.7	71.7	0.45
SF_6	318.7	36.7	0.73
propane	370.3	41.9	0.22
H_2S[b]	373.5	88.9	0.35
NH_3	405.6	112.5	0.24
pentane	470.2	33.3	0.23
^iPrOH	508.5	47.0	0.27
MeOH	513.7	78.9	0.27
EtOH	516.6	63.0	0.28
^iBuOH	548.2	42.4	0.27
benzene	562.1	48.3	0.30
$C_2H_4(NH_2)_2$ (en)	593.0	61.9	0.29
pyridine	620.2	55.6	0.31
H_2O	647.3	218.3	0.32

[a] *Safety Warning*! N_2O has similar critical parameters and rather better solvent properties than $scCO_2$ but there have been reports of explosions when scN_2O has been used with modest amounts of organic compounds (<1 g). Therefore, scN_2O should only be used with extreme caution! [b] H_2S is highly toxic.

Many nonspecialists are slightly bemused by the rather cavalier use of the phrase “near-critical” by those working in the field. A fluid is taken to be near-critical, when it is still a liquid but it has already begun to show some of the properties, particularly diminished density, normally associated with SCFs. The transition from a dense liquid to a less dense SCF does not occur instantaneously but over a distinct temperature range. Therefore, for each substance, there will be a temperature below T_c at which the liquid is already considerably expanded relative to the normal liquid but still denser than ρ_c. In practice, the term “near-critical” is used by different authors to describe a fluid the density of which has changed sufficiently for the particular property or effect under discussion to have become similar to that in a SCF. The imprecision arises because the necessary changes in density are different for different effects. Thus, for example, rapid expansion of supercritical solutions (so-called RESS, see Section II) can also be used to isolate labile organometallic complexes from *liquid* propene at room temperature as much as 70 °C below T_c,[6] but, by contrast, the speed of sound in CO_2 changes by 50% with a temperature change of *only 1.75* °C immediately below T_c.[3,7]

The properties of SCFs and their applications have been summarized quite effectively by Garrabos et al.,[8] who also describe a series of interesting applications (including supercritical drying, formation of composite materials, etc.) as well as outlining the sometimes overlooked effects of gravity on fluids near their critical point. Other reviews provide a good introduction to the industrial uses of SCFs.[4,5,9−13] In this review, we concentrate particularly on $scCO_2$ which has T_c close to ambient, because it is the fluid which has been the most widely exploited. However, we include substances as diverse as scKr, $scCH_4$, scH_2O, $scNH_3$, and $scH_2NCH_2CH_2NH_2$ (sc-en), which have had interesting chemical applications even though their critical temperatures are far from ambient.

SCFs occupy a point where pure and applied science meet head on. This is a feature which has attracted many workers to the field. It is also the reason this review covers such a broad range of topics from sophisticated spectroscopy and the isolation of labile organometallic compounds to the deposition of metal films, preparation of composite materials and the reprocessing of nuclear fuel. Broadly, we have reviewed those papers, published in the 10 years up to and including 1997, which concern some aspect of the synthesis or chemical exploitation of metal complexes, whether they be classical coordination complexes, organometallic compounds or simpler inorganic phases or compounds. Of course, we have included a number of key papers published earlier than this and some papers which have appeared in the first six months of 1998. We have deliberately excluded the areas of aerogels and supercritical drying[8,14−17] and the very large area hydrothermal mineral syntheses[18] which would warrant reviews of their own. This review complements those by Savage[19] on scH_2O and by Noyori[20] and Baiker[21] on homogeneous and heterogeneous catalysis, respectively. Therefore, we have not covered these areas in depth. Our review also has relevance to several other areas highlighted in this series of *Chemical Reviews*. The field is unusual in that much of the recent SCF work has been published in conference proceedings, which frequently run into several volumes for a single conference. Copies of most of the proceedings, cited in this review, can be obtained from the International Society for the Advancement of SCFs (address: I.S.A.S.F., ENSIC, 1 Rue Grandville − B. P. 451, F-54001 NANCY, France).

Our research group entered the field of SCFs through the use of these fluids, particularly scXe,[22−24] as solvents for IR spectroscopy.[25] As will become clear, scXe is one of the very few solvents available to IR spectroscopists at room temperature, which is totally transparent across the entire mid- and far-IR regions. This spectroscopic interest has remained with us and so this review contains a number of spectroscopic studies where the compounds of interest were never isolated for one reason or another, because such studies probably lie outside the areas of other reviews in this issue. However, the field of vibrational spectroscopy in SCFs was reviewed quite recently by our group[25] and that material will not be repeated in detail here. It is, nevertheless, worth pointing out that the efficiency of modern X-ray crystallography means that experiments in conventional synthetic chemistry are sometimes carried out *on a smaller scale* than some of the “spectroscopic” experiments described below!

Section II of this review, “Solubilities and Separation in SCFs”, provides the necessary technical background. It includes a brief discussion of the vapor−liquid-phase behavior most relevant to the review, describes the more important factors which affect the solubility of metal complexes in supercritical solution, outlines some of the methods for measuring solubility in SCFs and, finally, discusses the different strategies for precipitating solutes from supercritical solution. The main part of the review concerns chemical applications, which have been divided into two somewhat overlapping categories, “Transport Applications of SCFs” (Section III) and “Synthesis and Reactions” (Section IV). Section III is divided into two main sections of Metal Solubilization and Extraction (Part 1) and Materials Chemistry (Part 2). The former covers the different types of SFE experiments, matrices/media and complexant ligands which are commonly studied, as well as a number of important reports of SFE applications for the cleanup of “real world” or simulated metal wastes (e.g., highly toxic or radioactive samples). Section III (Part 2A) covers SCF thin film deposition (SFT CVD) of materials using soluble molecular precursors, while Parts 2B and 2C of the same section cover composite materials synthesis and spray coatings, respectively.

Section IV covers “Synthesis and Reactions” (in SCFs). Part 1, describes a range of thermal reactions in which SCFs (e.g., scH_2O, sc-alcohols, and scNH_3) are used to prepare materials such as fine ceramic powders and novel inorganic phases (via hydrolysis, reduction, etc.) from molecular or ceramic precursors. This section also discusses organometallic reactions in SCFs (Part 2), e.g., C−H activation, dinitrogen, and dihydrogen and alkene complexes, the use of photochemistry, both for spectroscopy and for synthetic applications and related thermal reactions of organometallic compounds. The review concludes with some comments on homo- and heterogeneous catalysis by supported metals or complexes in supercritical solution (Section IV; Part 3), followed by brief “Conclusions and Outlook” (Section V).

Chemical reactions in SCFs have been reviewed extensively. Naturally, there are differences in both the depth of the coverage of these reviews and their relevance to inorganic chemistry. There has been a considerable number of short nonspecialist articles which taken together provide a useful overview. Boock et al. take examples from scH_2O,[26] as do Clifford and colleagues in an excellent paper,[27] Bartle and Clifford[28−30] concentrate more on properties, and, reviews by Howdle and Poliakoff give a broader range of reactions.[9,31] The review by Savage and co-workers[32] is particularly strong on chemical applications of scH_2O while that of Eckert et al.[13] is specifically aimed at materials applications. The review by Noyori et al.,[33] provides a convenient introduction to homogeneous hydrogenation, our own chapter discusses organometallic chemistry in some detail,[34] and the review by Wai and co-workers[35] gives a good overview of the problems of metal extraction with scCO_2. There are also several more theoretical papers on the effects of SCFs on the rates of chemical reactions and other processes.[29,36−39] Finally, it should be noted that the book by McHugh and Krukonis[40] remains one of the best introductions to the whole field of SCFs, even though its coverage of chemical reactions is rather brief.

II. Solubilities and Separation in Supercritical Fluids

1. Phase Behavior

Although reaction chemists are frequently inclined to ignore the phase behavior of SCFs, the topic is of

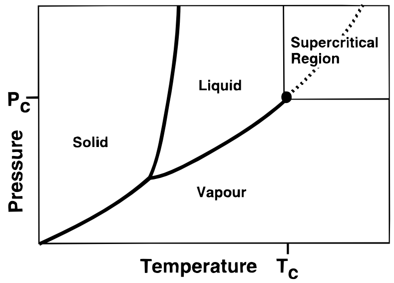


Figure 1. $P-T$ phase diagram for a pure substance, which is traditionally used to define the supercritical region. The dotted line indicates approximately the conditions needed to maintain the critical density at temperatures above T_c. Note that this diagram cannot be used to represent a real chemical reaction system which necessarily involves several components.

central importance to chemical reactions because the whole course of a reaction can be affected by whether a particular system is single or multiphase. Phase behavior warrants a separate review of its own.[41] Nevertheless, it is important to make a number of points here. First, the simplest chemical reaction will involve at least three components (starting material, product, and solvent) and most reactions of chemical interest will involve more. Somewhat ironically, it is often forgotten that the almost ubiquitous "supercritical phase diagram", Figure 1, refers only to a *pure* substance. A binary mixture requires a *three-dimensional* phase diagram, Figure 2, and the phase behavior of ternary or higher component mixtures cannot be represented fully in a 3-D diagram; at best, only part can be shown, for example by restricting the diagram to a particular pressure.

Phase behavior is well understood by specialists but can appear counterintuitive to reaction chemists. Thus, in the system CO_2/H_2, there is a narrow temperature range for a particular composition where an increase in pressure may cause a single phase mixture to *separate* into two phases and then back into a single phase as the pressure increases further.[42] This behavior is probably the cause of the anomalous effects[43] observed in the Raman spectrum of H_2 in CO_2. In general, an increase in pressure initially causes a steady increase in the line width of the $S_1(1)$ rotation band of H_2 dissolved in $scCO_2$. Much less broadening is observed in pure H_2. At certain combinations of temperature and composition, the line width reaches a plateau over a particular pressure range with no increase in line width as the pressure increases; then suddenly the increase in line width resumes. The effect was originally attributed[43] to clustering of $scCO_2$ but a very careful Fourier transform Raman study[44] suggests that it was the consequence of phase separation, which was undetectable in the narrow bore capillary cell used for the initial Raman spectroscopy. Nevertheless the line width of the Raman bands of H_2 remains a particularly good method for ensuring that H_2 and $scCO_2$ are properly mixed in flow reactors.[45] Very recently, the Raman spectrum of H_2 in $scCO_2$ has been recorded to pressure of more than 50 MPa (500 bar).[46]

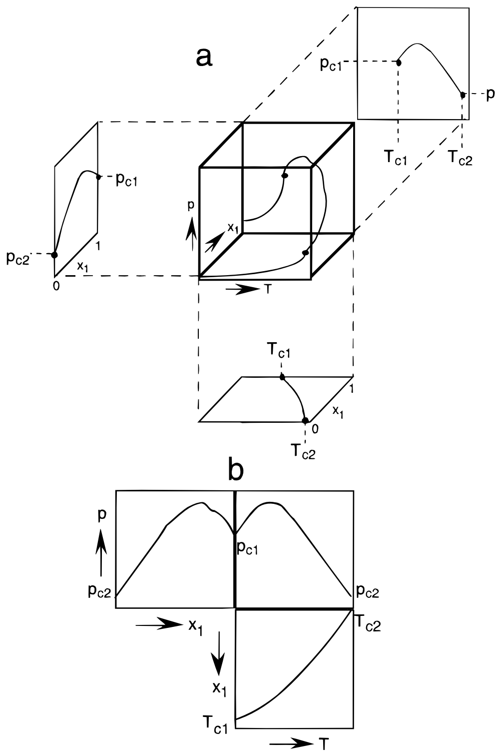


Figure 2. Different methods for plotting the type 1 phase behavior of a binary mixture. (a) The p,T,x_{i-} cube showing the vapor pressure curves of the pure components with their critical points (black circles) and the binary critical curve connecting them. The three possible projections of the binary critical line on either the $p-x$, $T-x$, or $p-T$ surface are also shown as an exploded view. Note that other types of binary phase behavior will have a more complicated diagram.[40] (b) Shows the three two-dimensional projections of the binary critical curve displayed as if the cube has been cut open along its axes and flattened.[7] (Reproduced with permission from A. Kordikowski et al., *J. Phys. Chem. B* **1997**, *101*, 5853. Copyright 1997 American Chemical Society.)

The simplest way to detect phase separation is to use a view cell, provided that the window gives a view of the whole interior of the cell; such cells are illustrated in McHugh and Krukonis's book.[40] There are alternative approaches; an ingenious chromatographic method for determining phase behavior has recently been described,[47] and we have reported an acoustic method which is particularly suited to complex mixtures where phase boundaries may be indistinct and rather difficult to observe in a view cell.[7]

In conclusion, it is important to give the nonspecialist reader a strict warning about phase behavior. Beware! In an experiment with several components dissolved in a solvent, you cannot ensure that the whole reaction mixture is in a single homogeneous phase merely by looking up the value of T_c of the pure solvent and then heating the reaction vessel to that temperature; the actual critical parameters of the mixture may be substantially different from that of the pure solvent. Furthermore, the values of T_c and P_c of a reaction mixture can change substantially during the reaction,[48] as shown in Figure 3 for the catalytic hydroformylation of propene in $scCO_2$ [$C_3H_6 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO + (CH_3)_2CHCHO$].

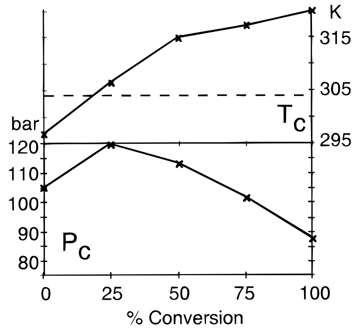


Figure 3. Plots showing the experimentally measured change in T_c and P_c during the course of a reaction, the hydroformylation of propene in $scCO_2$. This reaction, first reported[124] by Rathke et al., generates *n*- and isobutyraldehyde in the ratio 8:1. The critical points were measured acoustically[48] for a series of mixtures corresponding to different degrees of conversion of reactants into products. Initial conditions were C_3H_6:CO:H_2, 1:1:1 with an overall concentration 25 mol % in CO_2. The system contains six components, and in the context of this experiment, T_c and P_c refer to the conditions needed to bring the entire system into a single phase. Note that, as the reaction proceeds, T_c changes from a value well below that of pure CO_2 (indicated by a dashed line) to well above it. By contrast, all values of P_c are above that of CO_2 (73.8 bar) and P_c passes through a maximum during the reaction. This means that under certain pressure regimes, the reaction could become multiphase, even though it began and finished as a single-phase system.

2. Solubility in Supercritical Fluids

The fact that solids can dissolve in compressed gases has fascinated chemists since the time of Hannay and Hogarth.[49−51] The reasons why they dissolve are really beyond the scope of this review. Nevertheless, a few general points are needed as background. The majority of supercritical experiments are carried out in $scCO_2$ which is not a particularly good solvent. A useful rule-of-thumb is that $scCO_2$ has solvent properties similar to *n*-hexane. If something dissolves in *n*-hexane, it will probably also dissolve in $scCO_2$ and vice versa. The most numerous exceptions to this rule are fluorinated compounds which show a solubility in $scCO_2$ much higher than that in alkanes. Indeed, DeSimone has coined the term "CO_2-philic" for such fluorinated compounds.[52,53] The precise reason for this enhanced solubility has been the subject of considerable research, particularly by McHugh in connection with partially fluorinated polymers.[54,55] Smith and co-workers suggested that the enhanced solubility of fluorinated alcohols might be due to effects on H-bonding to CO_2 but this explanation cannot be true for all of the fluorinated compounds with enhanced solubility because many of these do not contain any H groups suitable for bonding.[56] Another theory, proposed by Beckman and co-workers, is that the solubility enhancement results from special interactions of electron rich fluorines in C−F bonds with relatively electron poor CO_2 molecules.[57] A very recent paper by DeSimone and co-workers,[58] describes an elegant investigation of solvent density on the NMR spectra of fluorinated and non-fluorinated hydrocarbons dissolved in $scCO_2$. Most interestingly, the effect of solvent density on ^{19}F chemical shifts provides a strong indication of specific F−CO_2 interaction. A detailed IR spectroscopic study of CO_2 interactions with polymers by Kazarian and colleagues,[59] suggested inter alia, that there was a weak electrostatic interaction of CO_2 with the C−F dipole of poly(vinyl fluoride). This interaction was manifest by a ca. 4 cm^{-1} splitting of the υ_2 mode of CO_2.

Whatever the precise reason for the solubilizing effect of fluorination, we cite several examples where fluorinated ligands improve the solubility of metal complexes. It is therefore not surprising that considerable research effort has gone, and continues to go, into the design of new CO_2-philic ligands.[57,60−64]

In general, the solubility of a compound in a SCF is related to its vapor pressure; the higher the vapor pressure, the higher the solubility[65] (in the limit, a gas is totally miscible with the fluid). At the same time, solubility at a given temperature increases with increasing pressure (i.e., with increasing fluid density). The vapor pressure and density effects can lead to somewhat counterintuitive behavior. Thus, heating a supercritical solution from T_c *under constant pressure*, initially leads to a *fall* in solubility because the density of the fluid decreases; further heating results in increased solubility because the vapor pressure of the solute rises proportionately faster than the density of the fluid falls. This so-called retrograde crystallization has been used to separate binary mixtures of solutes.[66] By contrast, heating a solution *under constant volume* (i.e., in a closed cell) does not lead to a drop in solubility because the density remains constant.

Organic or inorganic compounds can be added to the SCF to increase its solvent power. These so-called "modifiers" can be extremely effective, with MeOH being one of the most common. One mode of action can be shown to involve solute-modifier H-bonding.[56,67−70] Obviously, it is crucial that the modifier/fluid combination should be in a homogeneous single phase under the conditions of a given supercritical experiment and the best modifiers are those which do not raise the value of T_c of the modified mixture significantly above that of the unmodified fluid. This is indeed true of MeOH/$scCO_2$ and recently we showed that refrigerant, R134a, CH_2FCF_3, can be added to CO_2 up to ca. 10% without increasing T_c significantly.[7] Alkyl phosphates and related compounds show particular promise as modifiers for metal complexes, especially in extraction and separation processes (Section III; Part 1).[71−73] An interesting variation described by Cooper et al.[74] uses a fluorinated dendrimer to extract a dye which is normally insoluble in $scCO_2$.

There are a variety of methods for measuring solubility in SCFs; most can be classified as spectroscopic, gravimetric, or chromatographic.[75−82] In the spectroscopic method, the difficulty lies in establishing a reliable value for the extinction coefficient of the solute. In general, extinction coefficients for UV−visible spectra of metal complexes[81,82] are less sensitive to the precise solvent conditions than are those for IR bands, the widths of which change even with modest changes in the pressure of the fluid. Changing solvents can produce a dramatic change in IR extinc-

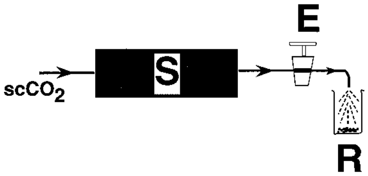


Figure 4. Simplified schematic representation of an apparatus for measuring solubility gravimetrically. $scCO_2$ is pumped through a bed of solute followed by expansion of the CO_2 (which lowers the solvent power of the fluid) and recovery of the precipitated solute. The figure is labeled as follows: S, solute; E, expansion valve; and R, recovery vessel.

tion. Thus, on changing from scXe to $scCO_2$, the maximum absorbance[83] of the ν(C−O) bands of $Cp^*Mn(CO)_3$ drop by ca. 50% and the line widths increase by 2×. A more quantitative approach has been made by Fayer and co-workers who used their elegant picosecond IR pump−probe experiments[84] to investigate the change in vibrational lifetime of the T_{1u} ν(C−O) state of $W(CO)_6$ as a function of solvent density in $scCO_2$, scC_2H_6, and $scCHF_3$.[85] In some cases, however, molar absorptivities can change as much in the UV[86] as in the IR,[69] but these are in chemical systems rather different from those considered in this review.

Gravimetric methods for measuring solubility can involve a whole range of different designs but, as shown schematically in Figure 4, many involve pumping a given volume of SCF through a bed of solid solute and weighing the amount of recovered product.[87,88] Gravimetric techniques can also be used for the solubilities of liquids in SCFs; for example, the method has very recently been used to establish the solubility of organophosphorus compounds[73] of relevance to supercritical nuclear reprocessing (Section III; Part 1D) and for calculating the solubilities of liquid metal chlorides (e.g., $TiCl_4$) in $scCO_2$.[88] Ashraf-Khorassani and colleagues have pointed out that conventional solubility measurements can be carried out in either static or dynamic modes, which are susceptible to slow diffusion of solute through the SCF and mass transfer limitations, respectively.[89] Gravimetric techniques can also often be unreliable as a result of solute loss/decomposition (due to heating of the restrictor) during collection, leading to inaccuracies in the solubility measurements. However, a novel technique for measuring metal chelate solubilities, which avoids the need for direct solute collection after depressurization, was recently reported at the 5th Conference on SCFs. It has been developed by Stiver and colleagues (based on an idea by Bertrand and Kaplan[90]) and relies on the relationship that the resonant frequency of a piezoelectric quartz crystal is proportional to the mass of solute on it. Thus, the amount of metal chelate which dissolves in a given amount of SCF (and hence is lost from the crystal surface) can be calculated from the shift in the measured resonant frequency of the piezoelectric crystal between the initial loading of the solute (prior to introduction of the SCF) and after depressurization.[91] A recent adaptation of this technique using a quartz crystal microbalance, has also been demonstrated to be an accurate and simple method for measuring the solubility of gases *in polymers* at high pressures.[92] Therefore, in principle, this technique could provide a real time method for monitoring polymer impregnation by a solute/gas, or for calculating the solubilities of solids in SCFs. Another relatively new method for measuring solubility involves measuring the dielectric constant of the supercritical solution; the advantage is that the method can be applied to very concentrated solutions.[93]

The chromatographic method involves the partitioning of the solute between the stationary and mobile phases. The method relies on the approximation that, in certain circumstances, the degree of retention of a particular solute is qualitatively inversely related to the solvating power of the mobile phase for the particular solute.[78] The solubility of ferrocene in SCFs has been studied in more detail than most and has been measured by the three major methods, spectroscopically,[77] gravimetrically, and chromatographically.[94] These determinations corrected an earlier claim[40] which inadvertently exaggerated the solubility of ferrocene; 20 wt % was claimed when the true value is closer to 3%. Recently, Kazarian and co-workers have exploited this solubility to impregnate ferrocene into poly(methyl methacrylate).[95] As described below, a considerable amount of solubility data for chelated metal complexes has recently been reviewed (see Section III).[89,96]

Finally, one should heed the advice of McHugh and co-workers on dissolving polymers in SCFs:[55] “A fruitful approach to choosing an appropriate SCF solvent is to determine which liquid solvents dissolve the polymer and then find an SCF solvent that mimics the properties of the liquid solvents rather than force fitting CO_2 for a particular situation.”

3. Experimental Strategies for Supercritical Chemistry

There are a wide variety of experimental approaches to SCFs. McHugh and Krukonis[40] describe a number of techniques and Morgenstern et al. have discussed equipment for catalytic reactions.[97] On a small-scale, reactions can be carried out in autoclaves similar to those used for conventional high-pressure experiments. Care is needed with some fluids, such as scN_2O[98] and scC_2H_4 ($>10^4$ psi, 660 MPa) as these fluids can decompose very rapidly with a huge and almost instantaneous pressure rise.[40]

Closed autoclaves have the disadvantage that one cannot monitor the progress of the reaction within. Whyman[99] pioneered techniques for fitting spectroscopic windows to high-pressure autoclaves and such equipment, although somewhat large, can be used for supercritical experiments. Buback[100] has reviewed spectroscopy in SCF solution and discussed the design of cells and the criteria for identifying the most appropriate spectral region for monitoring particular reactions. He has also provided some practical guidance for high-pressure spectroscopy.[101] A recent and quite interesting design of IR cell with two sets of windows (rather reminiscent a pair of binoculars) has been described by Kazarian.[102] These windows make the cell particularly suitable for investigating the impregnation of polymers.[103,104] One

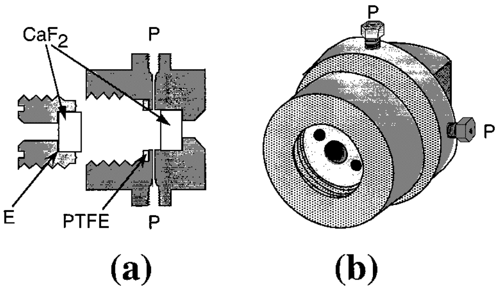


Figure 5. Two views of a miniature cell[105] for IR spectroscopy in SCFs close to room temperature: (a) cross section and (b) perspective view. The components in a are labeled as follows: CaF_2, calcium fluoride windows (1 cm thick); E, epoxy resin; P, threaded ports; PTFE, Teflon spacer. (Reproduced with permission from S. G. Kazarian et al., *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1275. Copyright 1995 VCH Publishers.)

pair of windows allows the spectrum of the fluid to be recorded while the other permits the fluid *plus* the polymer to be monitored.

Our group in Nottingham has developed a miniature cell for high-pressure spectroscopy, Figure 5, which can easily be modified for particular applications.[105] It has been used for near- and mid-IR,[106] FT-Raman,[44,107] and UV spectroscopy, for nanosecond time-resolved IR measurements,[108,109] for UV photolysis,[110] photoacoustic calorimetry,[107] and for a whole variety of organometallic reactions.[45,111-114] For spectroscopic experiments in SCFs with relatively high P_c and T_c values (e.g., scH_2O), Johnston and colleagues have employed titanium optical cells with sapphire windows.[115]

The use of sealed glass capillary tubes is a quite different and very simple approach to supercritical reactions in solvents with high values of T_c. Such tubes often cannot withstand high pressures but pressure problems can be avoided by placing the capillaries in an autoclave filled with the *same* liquid as is sealed into them (Figure 6a). In this way, the pressure outside the capillary always follows that inside, as the autoclave is heated. This technique has been used extensively by Kolis and co-workers and is based on the method of Rabenau.[116] The extension of this method is to use microbore capillaries, such as those used in supercritical chromatography. This approach was used to record Raman spectra of supercritical mixtures,[117] and with a long length of folded capillary, to record high-pressure NMR spectra in SCFs (Figure 6b).[118-121] This equipment was recently used for the in situ photochemical synthesis and NMR spectroscopy of $Cp'Mn(CO)_2(C_2H_4)$ in scC_2H_4.[122] and for the ^{19}F NMR of fluorocarbons in $scCO_2$.[58] High-pressure NMR can, of course, be carried out in modified autoclaves,[123,124] or in sapphire tubes[125] which are sufficiently strong to withstand the pressure. Indeed, the first SCF ^1H NMR spectrum of $CpMn(CO)_2(\eta^2\text{-}H_2)$ was obtained in such a sapphire tube.[121] Fused silica capillaries have also been employed for the acquisition of X-ray absorption fine structure (XAFS) spectra of sub- and SCF solutions of $CpMn(CO)_3$.[126]

We have applied a modular principle to the design of supercritical apparatus to enable laboratory workers to modify and optimize their equipment relatively rapidly. The concept is illustrated in Figure 7. Such a system provides very great flexibility. It allows experiments to be carried out on a very small scale, but it can also be used to build highly effective flow reactors (see Section IV; Part 2).

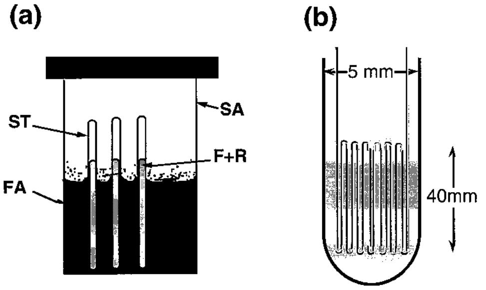


Figure 6. (a) Glass capillary approach to synthesis in SCFs with high values of T_c. The SCF is generated by heating a liquid in the capillary inside an autoclave, filled with the same liquid so as to minimize the pressure difference across the walls of the capillary. If a metal rather than glass capillary is used, it is possible to arrange for the capillary to be pinched-off under high pressure so that the composition of different phases can subsequently be analyzed at ambient conditions. The figure is labeled as follows: ST, sealed glass tube; SA, sealed autoclave; FA, fluid in the autoclave; F+R, fluid + reactants in glass tube. (b) The method used by Yonker and co-workers for recording NMR spectra of SCFs in a narrow bore capillary tube folded within a conventional NMR tube. (Redrawn from D. M. Pfund et al., *J. Phys. Chem.* **1994**, *98*, 11846.)

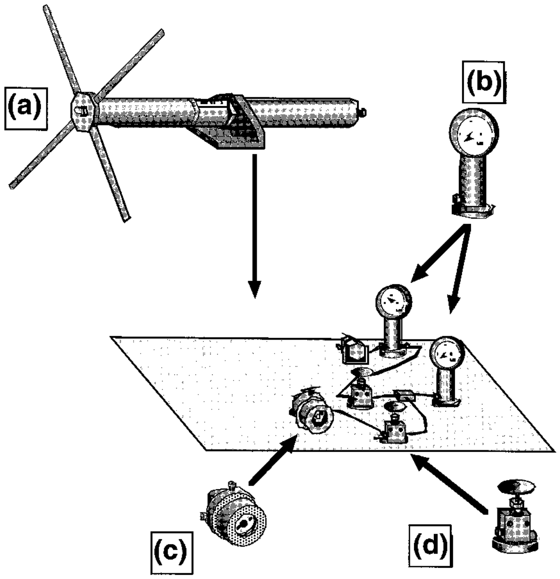


Figure 7. Modular approach, developed in Nottingham, for assembling small-scale apparatus for chemistry in SCFs. The components are labeled as follows: (a) hand-pump, (b) pressure gauge, (c) high-pressure miniature cell for IR spectroscopy, and (d) high-pressure tap. The small components are mounted on magnets and are set up on a steel table so that the overall arrangement can be quickly modified.

4. Precipitation of Solids from Supercritical Solution

The precipitation of solid products from SCF solutions is of considerable importance to this review, since much of the work is concerned with the synthesis of coordination compounds or the preparation of materials. The simplest method, which can be used with fluids with critical temperatures well above ambient, is to allow the fluid to cool and liquefy. The solid can then be recovered by conventional filtration, evaporation, etc. This is the method of choice when using sealed glass or quartz tubes,[116] as shown in Figure 6a. However, rapid cooling the fluid does not allow much control over the morphology or the particle size of the precipitated solid. By contrast, there are a range of techniques which do provide a higher degree of control over the precipitation; these techniques involve (i) rapid expansion, (ii) antisolvent precipitation, or (iii) atomization of a fluid or liquid-like phase.

A. Rapid Expansion of a Supercritical Solution (RESS)

The RESS technique plays a significant role in two very different areas of this review, formation of thin films and the isolation of labile organometallic compounds. The technique of RESS itself was developed by Smith and colleagues in the late 1980s,[127−130] but, it originates from the first papers by Hannay and Hogarth who reported that expansion of scEtOH led to the precipitation of dissolved $CoCl_2$ like snow.[49−51] The idea of precipitating fine particles was then foreshadowed semihumorously in 1968 by Jones under the pseudonym Daedalus:[131]

> *"Now if this gas (scH_2O containing dissolved sugar) were suddenly released, it would expand explosively back to normal pressures where it certainly cannot dissolve the sugar—which must therefore be precipitated from the gas as a dispersed molecular powder."*

In 1986/87, Smith and colleagues showed that a wide range of fine powdered materials can be prepared by expansion of SCFs. Their apparatus was relatively simple (see Figure 8) consisting of a reservoir of supercritical solution and an expansion nozzle.[127−130,132,133] They made a careful study of the effects of the various nozzle parameters on the size and morphology of the particles produced.

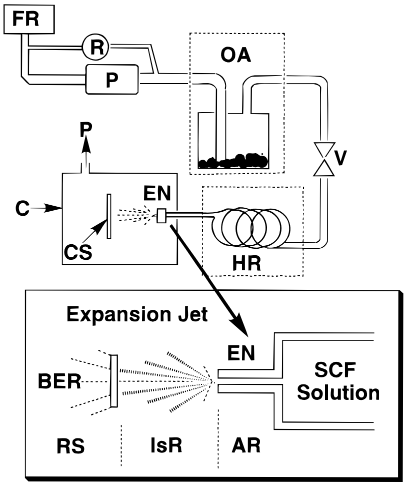


Figure 8. Schematic illustration of the RESS apparatus as used for supercritical water. Inset: the RESS expansion. The figure is labeled as follows: FR, fluid reservoir; R, pressure regulator; P, pump; OA, optional autoclave; V, valve; HR heated region; EN, expansion nozzle; CS, collection surface; C, collection chamber; AR, adiabatic region; IsR, isentropic region; RS, RESS spray; BER, background expansion region. (Adapted from D. W. Matson et al., *Ind. Eng. Chem. Res.* **1987**, *26*, 2298.)

The technique has been extensively investigated by Debenedetti et al.[134−137] who have also analyzed the precipitation process theoretically. They concluded that in most cases, the precise conditions of flow rates and nozzle design dictate the particle sizes and morphologies (e.g., microspheres, whiskers, etc.). Their observation that composite materials can be generated by coprecipitation of two different substances dissolved in the same SCF solution,[135,136] is very striking, although this approach has yet to be exploited widely by materials scientists. One recent report, however, suggests that this may be a route into the synthesis of sophisticated microcomposite pharmaceutic/polymer materials for controlled drug release applications (see later in Section III; Part 2B).[138]

The advantage of RESS is that it produces a relatively narrow distribution of particle sizes, which can be particularly important for drug delivery systems in which inhalation and retention of drugs in the body can be optimized.[139] Furthermore, it is very rapid, and does not require a vacuum, factors both of which are of considerable importance in the isolation of organometallic compounds with highly labile ligands.[45,111,140] Such compounds usually decompose when attempts are made to isolate them from conventional solvents (e.g., by evaporation under vacuum), because the ligands are removed at the same time as the solvent. RESS can also be used on stable organometallic complexes. Recently, Clifford and co-workers reported the use of RESS to generate fine particles of metal carbonyls.[133] The disadvantage of RESS is that it can only be applied to materials which are soluble in SCF and, since the solubility of most materials in SCFs is relatively low, a large amount of fluid is needed to prepare a small amount of particles. RESS is therefore a comparatively costly technique in terms of fluid usage and can only be used in laboratory experiments or processes involving high value added products, such as pharmaceuticals.

By contrast, the solubility of liquids in SCFs usually is much higher than that of solids, reflecting inter alia their higher vapor pressures. Therefore, liquids can usually be separated from supercritical solution merely be reducing the pressure, which causes phase separation. The process can be much cruder than with a solid because the morphology of the solute is not relevant. Such partial depressurization has been used, for example, in the recovery of product from continuous catalytic hydrogenation in SCFs.[141,142] Partial depressurization is also important for product recovery in polymer fractionation.[40,143]

B. Antisolvent Precipitation

The use of SCFs as antisolvents is a technique more recent than RESS but already it has become the focus of intense industrial research.[144−146] Although the technique has much promise for inorganic chemistry, so far its chemical applications have been fewer than those of RESS.[3] The use of supercritical antisolvents is similar to the well-established use of layering of poor solvents above a solution to induce

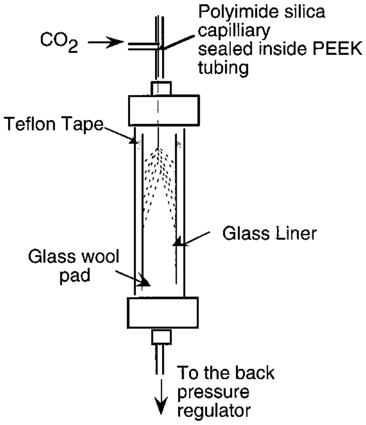


Figure 9. Schematic view of the antisolvent precipitation apparatus developed in Nottingham. The principal features are the use of a capillary rather than a nozzle, the flowing of the $scCO_2$ and the use of a loosely fitting glass liner, lightly plugged with glass wool to capture the precipitate. The liner can be removed without disturbing the precipitate and patterns of precipitation, variations in particle size, etc. can be easily observed. (Adapted from P. A. Hamley et al., in Proc. 5th Meeting on Supercritical Fluids, Nice, France, 1998; p 895.)

precipitation/crystallization in normal synthetic chemistry. Supercritical antisolvents were pioneered by Krukonis and Gallagher[147] but have since been developed by many others. There are several variants, each with its own acronym (see list in Part VI), but almost all use CO_2. GAS involves injecting $scCO_2$ into an organic solvent[147−149] in an exact analogy of conventional antisolvents. PCA,[9,138,144,150−153] SAS,[145,146] ASES,[154,155] and SEDS (Solution Enhanced Dispersion by SCFs)[156] all involve injecting the organic solution into a vessel either containing dense CO_2 or co-injecting the CO_2 and organic solution into a common vessel.

Much of the difference between the techniques lies in the detailed design of the nozzles and precipitation chambers rather than in the overall principles. Figure 9 shows the design developed in our laboratory, in particular the use of a glass liner within the PCA vessel to enable the precipitated material to be removed without disturbing it.[3] In Section IV (Part 2), we describe how such a precipitator can be used to recover products from organometallic reactions.[157]

Regardless of the precise design of the antisolvent precipitator, the attraction of the technique is that the temperature and density of the $scCO_2$, and the flow rates of the different fluids can all be manipulated to control the particle size and the morphology of the precipitated material. Control of these factors is particularly important for pharmaceutical products and electrical/catalytic materials and it is in these fields that much of the recent work has been focused.[144] For example, Reverchon and colleagues reported[146] a two-stage process for the synthesis of small metal oxide (homo- and heterometallic) particles from metal−organic precursors (dissolved in organic solvents) which are precipitated using a supercritical antisolvent (SAS) and then subsequently calcined at high temperatures. Reasonable solubility of the conventional organic solvent in $scCO_2$ is a key requirement in all antisolvent experiments. Although H_2O is more soluble in $scCO_2$ than in many organic solvents, the solubility is not high enough for CO_2 alone to be used as an antisolvent for aqueous solutions.

C. Atomization and Related Technologies

Unlike RESS or antisolvent techniques, atomization (nebulization) is used to disperse fluids which are essentially insoluble in $scCO_2$. Instead, the $scCO_2$ is either dissolved or emulsified in the fluid phase. On expansion of the mixture through a nozzle or similar depressurization device, the $scCO_2$ comes out of solution almost explosively and disperses the fluid into fine droplets.[158−160] Atomization has been quite widely applied to inorganic materials to generate particles, coatings, or pigments.

The simplest, and most recent, manifestation is the work of Sievers and co-workers for dispersing aqueous solutions.[158−163] Their apparatus, shown schematically in Figure 10, consists of a “T” piece with very low dead volume, in which near-critical or $scCO_2$ is mixed with an aqueous solution. The solution can then be atomized into a vertical tube-furnace to generate metal oxide particles. It can also be applied to the formation of coatings and to disperse a wide range of water-soluble pharmaceuticals.[144,160]

Analogous atomization processes can also use SCFs to replace volatile organic compounds (VOCs) for the spray coating of paints or pigmented polymers for automotive topcoats, furniture lacquers, and aerospace and corrosion coatings. Currently, such spraying releases significant, and undesirable quantities of VOCs into the atmosphere (see UNICARB process in Section III, Part 2C).[1] A slightly different form of nebulization/atomization, involves dissolving $scCO_2$ into a heated solid or polymer. The result is a highly plasticized polymer which can be expanded through a nozzle; the droplets cool and form relatively uniform powders. This approach has been used by Eggers and Wagner,[164] and Knez and colleagues,[165] and, extended in a more sophisticated form, in the supercritical “VAMP” process for manufacturing powder coatings, recently commercialized by the Ferro Corporation (Cleveland, OH).[2,166] This process is explained in more detail in Section III; Part 2C.

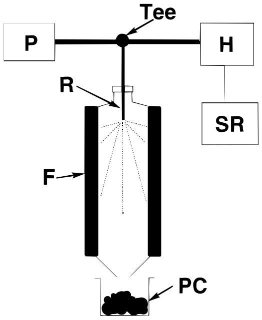


Figure 10. Schematic diagram for the experimental apparatus for the synthesis of fine powders by CO_2-assisted nebulization and pyrolysis. The apparatus is labeled as follows: P, CO_2 pump; Tee, low-dead-volume tee piece; H, HPLC pump; SR, solution reservoir; R, restrictor; PC, powder collector; F, furnace. (Adapted from C. Xu et al. Unpublished results, 1998.)

III. Transport Applications of Supercritical Fluids

1. Metal Solubilization and Extraction

A. Introduction

Supercritical fluid extraction and chromatographic separation of organic complexes from matrices such as soil samples, biomaterials, and natural products are well-proven and established techniques.[40,167−169] In comparison, the extraction of metal complexes using SCFs (primarily $scCO_2$) is relatively unexplored but it is gaining interest for a variety of applications such as replacement solvents for cleanup of hazardous solids or dissolved metal wastes.[170] By far the greatest amount of work in the area of SCF extraction (SFE) of metal complexes has been carried out by Wai and co-workers, who have written a number of excellent articles and comprehensive reviews on this subject.[35,71,171,172]

The nonpolar nature of $scCO_2$ means that most solid ionic metal salts do not dissolve directly (i.e., overcome lattice forces). Therefore, one must use modifiers or coordinating ligands (complexants) to increase solubilities of metal ions in the SCF phase. Modifiers such as MeOH can affect solubility in two ways or a combination of these. They can (i) coordinate to the metal center,[94] thereby reducing the overall polarity of the resulting coordination complex and, hence, improving solubility in $scCO_2$, or (ii) make the $scCO_2$ a more polar medium better able to dissolve the metal complex. A rather different strategy involves the use of fluorinated surfactants to dissolve ionic compounds in aqueous inverse micelles.[173] Although quite effective, the surfactants are usually too expensive to be employed on an industrial scale.

The solubilities and stabilities of both the metal complexes and the free ligands themselves in supercritical media under various conditions (P, T, pH, etc.) are vitally important because these will be the limiting factors for the extraction efficiencies of any metal/ligand system. The various methods for determining solubilities of metal complexes have been briefly discussed earlier in Section II. There have also been a number of theoretical studies for predicting solubilities.[96,174,175] Several reviews/articles have covered the solubilities of many compounds in SCFs,[65,80] including the review by Smith and co-workers, who obtained a qualitative indication of the solubilities of many surfactants and related molecules (some containing metal ions[176]) in $scCO_2$ by simple visual inspection using a high-pressure cell equipped with sapphire windows.[176,177] Recently, a new perfluoroether surfactant with manganese headgroups has been synthesized by Randolph and colleagues, which is capable of forming emulsions with large amounts of water in $scCO_2$.[178] Smart and co-workers also recently reviewed the solubility of 15 chelating agents and 49 metal-containing compounds in $scCO_2$, reporting that solubilites of apparently similar complexes can vary by many orders of magnitude, with solubilities of up to 56 g/L being possible.[35] Their review complements that of Ashraf-Khorassani and colleagues, who also compared the SFE of metal ions and chelates from different environments using dynamic and static techniques.[89]

B. Matrix Effects and Experiments

The extraction of metal ions necessarily requires them to be removed from some type of matrix, be it a solvent, a solid, or a more ill-defined material such as soil. The type of matrix/medium can have a great effect on the extraction efficiencies of any given ligand system. The majority of laboratory extraction experiments for the transport of metal ions using SCFs have involved three different types of matrix: (i) incorporated solid matrixes, (ii) aqueous media[170,179−181] (solution), or (iii) the solid itself[35,71] (metal salt/oxide etc.), see Figure 11. Extraction can be conducted in static or flowing (dynamic) modes or a combination of these. Of course solid matrices can be either wet or dry, while the pH of the metal containing solutions can vary.[71,182,183] Sometimes the extraction vessels contain a filter in the outlet (such as a glass wool plug) to prevent finely divided solid being blown out of the vessel by the SCF.

Typical matrices/media include contaminated soil sediments, natural water streams, solutions of industrial/manufacturing waste metals, and biomass (such as plants[184] or animal mater[185−187]) containing incorporated metal ions, all of which have possible environmental cleanup applications. In laboratory experiments, naturally impregnated matrices ("real world" samples) can be used or materials such as filter paper, cellulose, or sand can be artificially spiked with metal ions.[188−190] In practice, however, real soil or biomass samples sometimes contain strongly bound (chemically fixated) metals which cannot be efficiently removed by SFE methods.[191] Therefore, "spiked sample" experiments only provide a comparative indication of the extraction efficiencies for particular ligand systems. As will be shown later, the presence of water (often in trace amounts) within the matrix, dissolved in the SCF or as a solution containing metal ions,[179−190] can have a profound effect on ligand chelation, solubility, stability, extraction efficiency, and even ligand selectivity.[185,192] For example, dissolution of $scCO_2$ in a water solution can reduce the pH (to ca. pH 3) by formation of carbonic acid (see below).

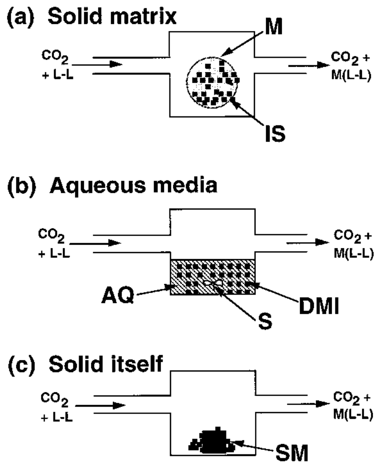
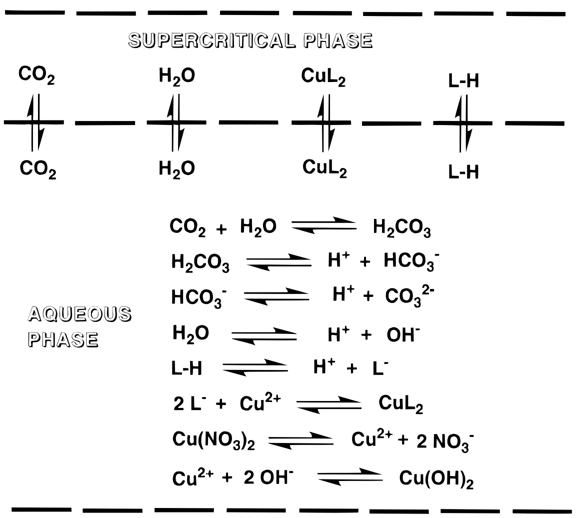


Figure 11. Three basic types of SFE experiments for the removal of metal ions directly from (a) a solid matrix, (b) an aqueous solution, and (c) the solid itself. The figure is labeled as follows: M, solid matrix; IS, incorporated or spiked metal ions; DMI, dissolved metal ions; S, stirrer; AQ, aqueous media; SM, solid metal ions/oxide, etc.; (L−L) = extractant; M(L−L) = metal complex.

Scheme 1



A number of groups have investigated the feasibility of removing metals from aqueous media using $scCO_2$/chelate (L−H) mixtures.[170,179−181] A simplified apparatus is shown in Figure 11 (type b). A great attraction of $scCO_2$ in extracting aqueous solutions is that it leaves virtually no residues in the water, while all organic solvents contaminate the aqueous phase to a greater or lesser extent, thereby posing additional problems of waste disposal. Chelation is a complicated process, as can be seen from Scheme 1, which shows the various equilibria involved in the transfer of Cu^{2+} (nitrate) from aqueous solutions to SCF.

In principle, however, the distribution of metal between the supercritical and aqueous phases is dependent on the various equilibrium constants and distribution coefficients, all of which are affected by temperature, pressure, concentration, etc. Furthermore, for such two phase extractions, rapid stirring can improve phase mixing to reduce extraction/equilibration times for the resulting metal chelate in the SCF phase (see Figure 11; type b). Thus, a dramatic reduction in extraction efficiency was observed when stirring was not used for the extraction of Cu^{2+} from an aqueous solution using Li(FDDC) and $scCO_2$ and, as a result, such experiments showed poor reproducibility.[190] In addition, a very substantial increase in extraction efficiency of Cu^{2+} from aqueous solution was observed with increasing density of the CO_2 (going from sub- to supercritical density) (see Figure 12).

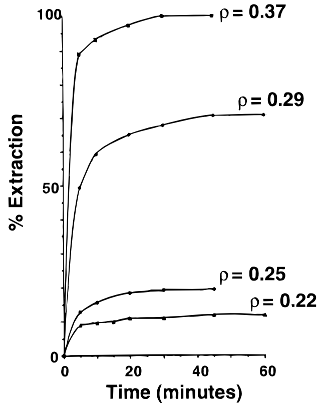
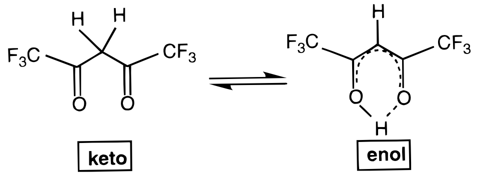


Figure 12. Rate of extraction of Cu^{2+} from aqueous solution with $scCO_2$ containing LiFDDC at 35 °C as a function of density. (Reproduced with permission from Laintz et al., *Anal. Chem.* **1992**, *64*, 2875. Copyright 1992 American Chemical Society.)

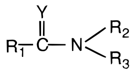
Scheme 2



C. Ligands and Complexes for Solubilization and Extraction

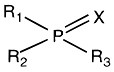
Taking into account the type of ligand (e.g., O, P, N donor, etc.) and/or any charge associated with that ligand, metal ions can be selectively or preferentially extracted from a mixture of metals. To obtain effective extraction of particular metal salts, "encapsulating" ligand(s) such as multidentate chelating ligands (e.g., crowns, macrocycles) and/or "bulky" Lewis bases tend to be used. Such ligands are able to overcome lattice/hydration forces via coordination/chelation in metal salts or aqueous solutions. Much interest in the use of fluorinated compounds for various applications in $scCO_2$ was generated after a report by Wai and co-workers which showed that fluorinated metal chelates possessed excellent solubilities in $scCO_2$ (relative to their non-fluorinated analogues). Indeed, one can minimize van der Waals intermolecular interactions in the coordination compounds formed, by using either ligands with fluorinated side groups (or pendant arms)[63,179,193−196] or sterically hindering ligands which tend to improve extraction efficiencies and solubilities in SCFs.

When choosing the most appropriate ligand for the selective extraction of a particular metal, variables such as the charge on the metal, ionic radii, and other coligands (e.g., oxo-, hydroxo-) have to be considered. The most common ligands used in SFE of metals include β-diketones, dithiocarbamates, macrocycles, organophosphorus reagents, hydroxamic acids, and other organic complexants (see Figure 13 for some examples). Key factors which have to be established for any extractant are the stability (both thermal/chemical) of the ligand and of the resulting metal complex at the working temperature, pressure,[191] density,[76,94] pH, etc. of the supercritical solution. For example, the presence of water in $scCO_2$ will influence the pH[197] which can dramatically affect the ability of ligands to form stable metal complexes (see earlier in Part B). β-Diketone ligands, which are often used in the neutral form, are believed to react with metal ions via the enol form of ligand.[72] The position of this equilibrium is dependent not only on the pH, but also on pressure, temperature, and even the electron-withdrawing nature of the substituent groups on the β-diketone ligand (R_1 or R_2 = CF_3, ${}^tBu$, Me, etc.).[96,183] It has been observed that under SCF conditions, fluorinated β-diketone ligands can be driven predominately into the enol form while, for non-fluorinated analogues such as acac-H, the equilibrium is closer to a 50:50 mixture (see Scheme 2 below for hfa-H).[96,198] Furthermore, it should also be noted that upon exposure to moisture, β-diketone ligands such as hfa-H have been known to undergo



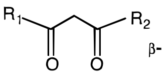
Dithiocarbamates, related amines and hydroxamic acids.

Name / Type	**Y**	**R_1**	**R_2**	**R_3**
FDDC	S	SH	CH_2CF_3	CH_2CF_3
DDC / DEDTC	S	SH	Et	Et
P3DC	S	SH	C_3H_7	C_3H_7
BDC / DBDTC	S	SH	^tBu	^tBu
DIBDTC	S	SH	^iBu	^iBu
P5DC	S	SH	C_5H_{11}	C_5H_{11}
DHC / HDC	S	SH	C_6H_{13}	C_6H_{13}
PDC / PDTC	S	SH	$-NC_4H_8-$	----
TDBDTC / BDC (salt)	S	$SN(C_4H_9)_4$	C_4H_9	C_4H_9
TDDC / DDC (salt)	S	$SN(C_4H_9)_4$	C_2H_5	C_2H_5
DDC (salt)	S	SNH_2Et_2	C_2H_5	C_2H_5
DDC (salt)	S	SNa	C_2H_5	C_2H_5
APDC / PDC (salt)	S	$S(NH_4)$	$-NC_4H_8-$	----
FDDC (salt)	S	SLi	CH_2CF_3	CH_2CF_3
EC	O	N(H)Et	H	Et
PFOHA	O	$(CF_2)_6CF_3$	OH	H
HFBHA	O	$(CF_2)_2CF_3$	OH	H
MPFOHA	O	$(CF_2)_6CF_3$	OH	Me
MHFBHA	O	$(CF_2)_2CF_3$	OH	Me



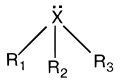
Organophosphorus ligands

Name	**X**	**R_1**	**R_2**	**R_3**
Cyanex 272	O	$CH_2CH(Me)CH_2CMe_3$	$CH_2CH(Me)CH_2CMe_3$	OH
Cyanex 302	S	$CH_2CH(Me)CH_2CMe_3$	$CH_2CH(Me)CH_2CMe_3$	OH
Cyanex 301	S	$CH_2CH(Me)CH_2CMe_3$	$CH_2CH(Me)CH_2CMe_3$	SH
D2EHTPA	S	$OCH_2CH(Me)CH_2CMe_3$	$OCH_2CH(Me)CH_2CMe_3$	OH
TBP	O	$O(n\text{-}C_4H_9)$	$O(n\text{-}C_4H_9)$	$O(n\text{-}C_4H_9)$
TBPO	O	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$
TPPO	O	$n\text{-}C_6H_5$	$n\text{-}C_6H_5$	$n\text{-}C_6H_5$
TOPO	O	$n\text{-}C_8H_{17}$	$n\text{-}C_8H_{17}$	$n\text{-}C_8H_{17}$



β-diketones

Name	R_1	R_2
acac-H	Me	Me
tta-H	Me	SCH=CH-CH=CH
tfa-H	CF_3	Me
hfa-H	CF_3	CF_3
tfbmz-H	CF_3	Ph
thd-H	^tBu	R_1
fod-H	^tBu	C_3F_7
tod-H	^tBu	$CH_2CH(CH_3)_2$
dmhd-H	^tBu	Me
dibm-H	$CH(CH_3)_2$	$CH(CH_3)_2$



Phosphine and monodentate amine ligands

Name / Type	X	R_1	R_2	R_3
Trimethylphosphine	P	Me	Me	Me
Fluorophosphine	P	$CH_2CH_2C_6F_{13}$	Ph	Ph
Fluorophosphine	P	$CH_2CH_2C_6F_{13}$	$CH_2CH_2C_6F_{13}$	Ph
Silylether methyl phosphine	P	$(CH_2)_2Si(OEt)_3$	Me	Me
Silylether phenylphosphine	P	$(CH_2)_2Si(OEt)_3$	Ph	Ph
TPA	N	Ph	Ph	Ph
THA	N	C_6H_{13}	C_6H_{13}	C_6H_{13}
TOA	N	C_8H_{17}	C_8H_{17}	C_8H_{17}
DnDA	N	$C_{12}H_{25}$	$C_{12}H_{25}$	H

Multidentate amines

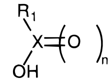
$(R_1)_2N[CH_2CH_2N(R_1)]_nR_2$

Name	n	R_1	R_2
en	1	H	H
trimen	1	Me	H
pmdien	2	Me	Me
hmten	3	Me	Me

Multidentate polyethers (glymes)

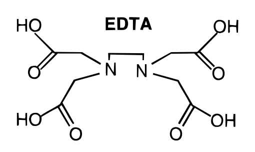
$CH_3O(CH_2CH_2O)_nCH_3$

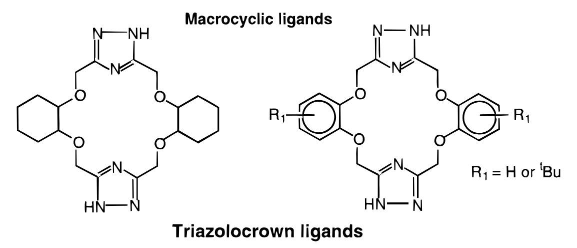
Name	n
dme	1
diglyme	2
triglyme	3
tetraglyme	4
heptaglyme	7

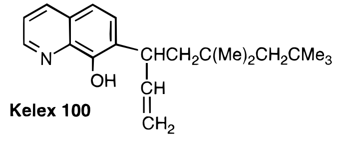


Selected acids

Name	X	n	R_1
Trifluoroacetic acid	C	1	CF_3
Oleic acid	C	1	$(CH_2)_7CH=CH(CH_2)_7CH_3$
Triflic acid	S	2	CF_3







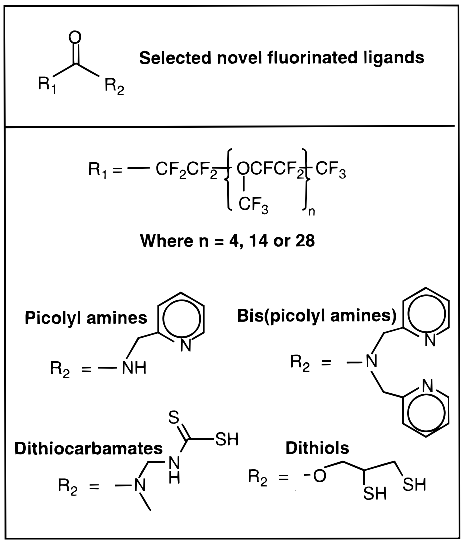


Figure 13. A selection of the more important ligands which have been used for metal solubilization and extraction in supercritical fluids.

irreversible hydrolysis reactions, which can also affect the extraction efficiencies of these ligands.[170,183,199]

In the absence of additional coordinating ligands, bis- and tris-β-diketonate metal complexes[75,180,200] of (+2) and (+3) metals usually show good solubility and stability in $scCO_2$. This is due to the highly hydrophobic exterior of the molecules which tends to shield the metal charges more efficiently than, for example, the single β-diketonate ligand of an alkali metal complex.[201] The solubility of any simple metal β-diketonate system can be improved, in principle, by additional coordination of neutral Lewis bases/chelates, which can increase shielding at the metal center(s) and/or reduce oligomerization.[183,202,203] For example, it has been observed that the volatilities or solubilities of lanthanide (and other metal) β-diketonate complexes in the gaseous phase or SCF solutions respectively can be enhanced further by additional complexation of neutral Lewis base ligands to the metal center(s).[183,203−206] Furthermore, it has been recently shown that organophosphine oxide adducts of lanthanide β-diketonates can be separated efficiently by SCF chromatography (SFC) using neat $scCO_2$ as the mobile phase.[202]

In general, metal complexes of fluorinated β-diketonates (such as hfa-H) show superior solubilities in SCFs compared to their non-fluorinated analogues (e.g., acac-H) (Table 2).[87] The high solubilites of complexes such as $Pd(tod)_2$, $[Cu(hfa)_2]\cdot H_2O$, [Ag(hfa)-(tetraglyme)],[207] $Al(hfa)_3$, and $Ln(\beta\text{-diketonate})_3$[200] in SCFs has led to them being used as precursors to their respective metal/metal oxides in a range of materials applications (Section III; Part 2).[208−210]

By contrast, the alkali metal/pseudo alkali metal (e.g., NH_4^+) salts of dithiocarbamate ligands rather than the free ligands themselves, are usually employed to extract or separate metals (via a salt metathesis reaction).[211−214] Other alkali metal−organic complexes such as sodium−dioctylsulfosuccinate have been used in the mobile phases in SFC as the counterion in “ion-pair SFC” to assist analytical separation of organic molecules.[215] A range of metal dithiocarbamate complexes have also been tested for solubility in SCFs and, as with other ligand systems, the solubilities of metal complexes in $scCO_2$ could be significantly improved by use of butylated or fluorinated substituents or by increasing the linear chain length(s) of the substituents (Table 2).[188−190,211,216] Even higher solubilities of metal dithiocarbamate compounds can often be achieved by the presence of modifiers such as MeOH (as ca. 5−10% mixtures).[186,189]

Uncharged coordinating ligands such as organophosphorus reagents can significantly improve the solubilites of certain metal−salt or metal−organic complexes in SCFs by coordination.[35,62,71,217] Some of these ligands are already used commercially for the conventional extraction and separation of U and Pu from nuclear waste (see later, Section III; Part 1D).[218,219] Therefore, the solubilties of the free organophosphorus ligands and their coordination compounds are of considerable interest to the nuclear industry.[35,71,172,220−222] Strong positive synergistic effects have been observed in $scCO_2$ when a mixture of fluorinated β-diketones (e.g., hfa-H, fod-H) and organophosphorus ligands (e.g., TBP) are used in tandem for the extraction of lanthanide/actinide samples from solid or liquid matrices.[72] This synergism was not observed for the same organophosphorus ligands with non-fluorinated β-diketones analogues such as acac-H.[192 35] Similarly, other organophosphorus Lewis bases have been used to render complexes soluble in SCFs, such as for the homogeneous hydrogenation catalysts, e.g., $[Ru(PMe_3)_4(H)_2]$, and $[Ru(PMe_3)_4(Cl)_2]$ (see Catalysis, Section IV; Part 3),[222] and the SFT CVD precursors to thin metal films (e.g., $[Cu(hfa)(PMe_3)]$ for Cu films).[208]

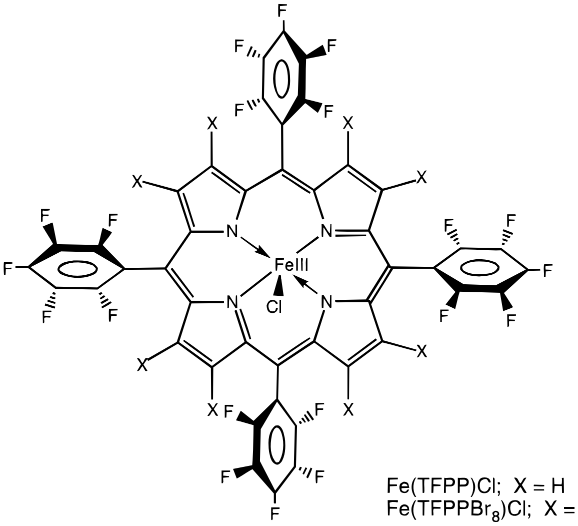


Figure 14. CO_2-soluble metalloporphyrins used to catalyze homogeneous oxidation in $scCO_2$.[228] UV−vis spectroscopy gave a qualitative indication for the lower limits of solubility 18 μM for Fe(TFPP)Cl (X = H) and 10 μM for $Fe(TFPPBr_8)Cl$ (X = Br). At 40 °C and 5000 psi, neither compound has significant solubility in liquid CO_2.

Macrocyclic (polydentate) ligands such as porphyrins, crown ethers, and calixarenes can discriminate between different size cations according to the size match between the “ligand cavity” and ionic metal radius.[196,223−225] These free ligands can be either neutral or charged (often via pendant arms or substituents) giving rise to neutral (soluble) metal coordination complexes (Figure 13).[223,225,226] Examples of macrocyclic ligand systems investigated for SCF extraction, catalysis (Figure 14), coordination chemistry or solubility, include a range of calixarene,[35,196,227] substituted triazolocrown systems,[225] fluorinated porphyrins,[96,228] and cyclam[94] ligands. The Ni−cyclam complex was reported by Cowey and coworkers, only to have significant solubility in $scCO_2$, in the presence of MeOH, which was presumed to coordinate to vacant trans sites on the Ni making the molecule less polar, and hence, more soluble.[94]

Other O-donor chelates such as neutral multidentate linear polyethers $[CH_3O(CH_2CH_2O)_nCH_3$, where $n = 1, 2, 3$, etc.] do not yet appear to have found widespread use as SCF solubilizing coligands for metal complexes,[207] although they have recently been shown to improve the solubilities (and volatilities) of a range of metal β-diketonate complexes in conventional hydrocarbon solvents.[203,204,206,229] This is clearly an area of SCFs which is ripe for exploitation.

Table 2. Solubility of Selected Metal Complexes in Supercritical Fluids

complex	solvent[a]	conditions	solubility	ref(s)
β-Diketonates				
Li(acac)	scCO$_2$	29.4 MPa (60 °C)	0.01 mg/L	201
Cu(acac)$_2$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(0.8-2.3) \times 10^{-5}$ mol/L	75
Cu(acac)$_2$	scCO$_2$	12−22 MPa (150−170 °C)	6.2×10^{-6} to 1.1×10^{-4} mole fracton	87
Y(acac)$_3$	scCO$_2$	12−22 MPa (150−170 °C)	4.7×10^{-6} to 1.1×10^{-5} mole fracton	87
Ga(acac)$_3$	scCO$_2$	29.4 MPa (60 °C)	3.01 mg/L	201
In(acac)$_3$	scCO$_2$	29.4 MPa (60 °C)	2.63 mg/L	201
Mn(acac)$_3$	scCO$_2$	29.4 MPa (60 °C)	1.26 mg/L	201
Zn(acac)$_2$	scCO$_2$	29.4 MPa (60 °C)	1.01 mg/L	201
Co(acac)$_3$	scCO$_2$	29.4 MPa (60 °C)	0.62 mg/L	201
Mn(acac)$_2$·2H$_2$O	scCO$_2$	29.4 MPa (60 °C)	0.40 mg/L	201
Co(acac)$_2$·2H$_2$O	scCO$_2$	29.4 MPa (60 °C)	0.25 mg/L	201
Cu(acac)$_2$	scCO$_2$	29.4 MPa (60 °C)	0.21 mg/L	201
Cr(acac)$_3$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(1.7-19.1) \times 10^{-5}$ mol/L	75
Cr(acac-Br)$_3$	scCO$_2$	10.3−24.1 MPa (40 °C)	$(0.5-1.5) \times 10^{-5}$ mol/L	75
Cr(thd)$_3$	scCO$_2$	10.3−31.0 MPa (40 °C)	$(400.0-604.9) \times 10^{-5}$ mol/L	75
Cu(thd)$_2$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(6.2-74.2) \times 10^{-5}$ mol/L	75
Cu(dmhd)$_2$	scCO$_2$	13.8−34.5 MPa (40 °C)	$(3.7-36.2) \times 10^{-5}$ mol/L	75
Cu(dibm)$_2$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(9.2-88.4) \times 10^{-5}$ mol/L	75
Cu(tod)$_2$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(26.0-269.7) \times 10^{-5}$ mol/L	75
Cu(bzac)$_2$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(0.2-1.0) \times 10^{-5}$ mol/L	75
Y(hfa)$_3$	scCO$_2$	12−22 MPa (150−170 °C)	9.3×10^{-4} to 3.1×10^{-4} mole fracton	87
Ba(hfa)$_2$	scCO$_2$	12−22 MPa (150−170 °C)	7.9×10^{-5} to 1.6×10^{-4} mole fracton	87
Cu(hfa)$_2$·H$_2$O	scCO$_2$	10.3−34.5 MPa (40 °C)	$(152.0-414.0) \times 10^{-5}$ mol/L	75
Cu(hfa)$_2$	scCO$_2$	10.3−31.0 MPa (40 °C)	$(225.1-569.9) \times 10^{-5}$ mol/L	75
Cu(tfbzm)$_2$	scCO$_2$	13.8−34.5 MPa(40 °C)	$(0.7-4.3) \times 10^{-5}$ mol/L	75
trans-Cr(tfa)$_3$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(147.9-272.1) \times 10^{-5}$ mol/L	75
cis-Cr(tfa)$_3$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(67.3-190.8) \times 10^{-5}$ mol/L	75
Cu(tfa)$_2$	scCO$_2$	10.3−34.5 MPa (40 °C)	$(29.6-59.4) \times 10^{-5}$ mol/L	75
La(fod)$_3$	scCO$_2$	15.2 MPa (60 °C)	5.5×10^{-2} mol/L	192
Eu(fod)$_3$	scCO$_2$	15.2 MPa (60 °C)	7.9×10^{-2} mol/L	192
Thiocarbamates				
Na(DDC)	scCO$_2$	10.1 MPa (50 °C)	1.5×10^{-4} mol/L	76, 171
Na(DDC)	scCO$_2$	20.3 MPa (60 °C)	1.5×10^{-3} mol/L	35
Cu(DDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(1.4-11) \times 10^{-6}$ mol/L	479
Cu(DDC)$_2$	scCO$_2$	10.1 MPa (50 °C)	1.1×10^{-6} mol/L	76, 171
Ni(DDC)$_2$	scCO$_2$	10.1 MPa (50 °C)	8.5×10^{-7} mol/L	171, 211
Co(DDC)$_3$	scCO$_2$	10.1 MPa (50 °C)	2.4×10^{-6} mol/L	171, 211
Bi(DDC)$_3$	scCO$_2$	10.1 MPa (50 °C)	1.3×10^{-6} mol/L	76, 171
Bi(DDC)$_3$	scCO$_2$	15.2 MPa (50 °C)	9.0×10^{-6} mol/L	76, 171
Hg(DDC)$_2$	scCO$_2$	15.2 MPa (50)°C	8.2×10^{-6} mol/L	76, 171
Hg(DDC)$_2$	scCO$_2$ (5*)	15.2 MPa (50 °C)	3.0×10^{-5} mol/L	76, 171
Hg(DDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(6.8-53) \times 10^{-6}$ mol/L	479
Hg(DDC)$_2$	scCO$_2$	20.3 MPa (40 °C)	2.4×10^{-3} mol/L	257
Hg(DDC)$_2$	scCO$_2$	10.1−40.5 MPa (60 °C)	$(2.4-2.5) \times 10^{-3}$ mol/L	257
Pb(DDC)$_2$	scCO$_2$	15.2 MPa (50 °C)	1.2×10^{-6} mol/L	189
Zn(DDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(1.1-24) \times 10^{-6}$ mol/L	479
Cu(P3DC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(6.3-120) \times 10^{-6}$ mol/L	479
Hg(P3DC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(1.2-23) \times 10^{-5}$ mol/L	479
Zn(P3DC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(7.9-150) \times 10^{-6}$ mol/L	479
Cu(BDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(1.3-72) \times 10^{-5}$ mol/L	479
Hg(BDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(5.6-56) \times 10^{-5}$ mol/L	479
Zn(BDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(8.2-69) \times 10^{-5}$ mol/L	479
Cu(P5DC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(9-180) \times 10^{-5}$ mol/L	479
Hg(P5DC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(1-20) \times 10^{-4}$ mol/L	479
Zn(P5DC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(1.6-32) \times 10^{-4}$ mol/L	479
Cu(HDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(2.1-28) \times 10^{-4}$ mol/L	479
Zn(HDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(3.2-58) \times 10^{-4}$ mol/L	479
Hg(HDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(1.6-38) \times 10^{-4}$ mol/L	479
Cu(PDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(0.4-4) \times 10^{-6}$ mol/L	479
Hg(PDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(0.4-3.4) \times 10^{-6}$ mol/L	479
Zn(PDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(0.3-9) \times 10^{-6}$ mol/L	479
Pb(PDC)$_2$	scCO$_2$	15.2 MPa (50 °C)	5.1×10^{-7} mol/L	189
Zn[SCSN(C$_4$H$_9$)$_2$]$_2$	scCO$_2$	24.1 MPa (55 °C)	248×10^{-6} g/mL	216
Zn[SCSN(C$_2$H$_5$)$_2$]$_2$	scCO$_2$	24.1 MPa (55 °C)	11.9×10^{-6} g/mL	216
Zn[SCSN(C$_4$H$_5$)]$_2$	scCO$_2$	24.1 MPa (55 °C)	1.8×10^{-6} g/mL	216
Na(FDDC)	scCO$_2$	10.1 MPa (50 °C)	4.7×10^{-4} mol/L	76, 171
Cu(FDDC)$_2$	scCO$_2$	10.1 MPa (50 °C)	9.1×10^{-3} mol/L	76, 171
Cu(FDDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(9.1-40) \times 10^{-4}$ mol/L	479
Co(FDDC)$_3$	scCO$_2$	10.1 MPa (50 °C)	8.0×10^{-4} mol/L	211
Ni(FDDC)$_2$	scCO$_2$	10.1 MPa (50 °C)	7.2×10^{-4} mol/L	76, 171
Bi(FDDC)$_3$	scCO$_2$	10.1 MPa (50 °C)	$< 1.0 \times 10^{-7}$ mol/L	76, 171
Bi(FDDC)$_3$	scCO$_2$	15.2 MPa (50 °C)	7.3×10^{-4} mol/L	76, 171
Hg(FDDC)$_2$	scCO$_2$	20.3 MPa (40 °C)	1.4×10^{-2} mol/L	257
Hg(FDDC)$_2$	scCO$_2$	10.1−40.5 MPa (60 °C)	$(4.7-14.1) \times 10^{-3}$ mol/L	257
Hg(FDDC)$_2$	scCO$_2$ (5*)	15.2 MPa (50 °C)	1.2×10^{-2} mol/L	76,171
Pb(FDDC)$_2$	scCO$_2$	15.2 MPa (50 °C)	2.3×10^{-4} mol/L	189
Hg(FDDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(3-14) \times 10^{-3}$ mol/L	479
Zn(FDDC)$_2$	scCO$_2$	10.1−23.3 MPa (60 °C)	$(9.5-90) \times 10^{-4}$ mol/L	479

Table 2 (Continued)

complex	solvent[a]	conditions	solubility	ref(s)
		Organometallics		
$Fe(Cp)_2$	$scCO_2$	13.4−33.6 MPa (40−70) °C)	ca. 3.2−27.0 g/L	78
$Fe(Cp)_2$	$scCO_2$	9.7−36.6 MPa (40−70 °C)	ca. 0.5−31.6 g/L	78
$Fe(Cp)_2$	$scCO_2$	$\rho = 5-17$ mol/L (40 °C)	0.005−0.15% mol	77
$Fe(Cp)_2$	$scCO_2$	13.41 MPa (40−70) °C)	$(4.8-1.4) \times 10^{-3}$ g/mL	94
$Fe(Cp)_2$	$scCO_2$	24.44 MPa (40−70 °C)	$(9.1-14.9) \times 10^{-3}$ g/mL	94
$Fe(Cp)_2$	$scCO_2$	33.55 MPa (40−70 °C)	$(12.1-20.7) \times 10^{-3}$ g/mL	94
$Fe(Cp)_2$	$scCO_2$	9.7−36.6 MPa (40−70 °C)	$(2.1-24.0) \times 10^{-3}$ g/mL	94
		Miscellaneous Compounds		
$Ni(C_{22}H_{22}N_4)$	$scCO_2$ (10*)	16.1−34.2 MPa (40−70 °C)	$(1.1-5.8) \times 10^{-5}$ g/mL	94
$Ni(C_{22}H_{22}N_4)$	$scCO_2$ (10*)	16.1−37.2 MPa (40−70 °C)	$(1.0-5.6) \times 10^{-5}$ g/mL	94
Fe(TFPP)Cl	$scCO_2$	ca. 34 MPa (40 °C)	18×10^{-6} mol/L (lower limit)	228
$Fe(TFPPBr_8)Cl$	$scCO_2$	ca. 34 MPa (40 °C)	10×10^{-6} mol/L (lower limit)	228
$UO_2(NO_3)_2{\cdot}2TBP$	$scCO_2$	10.1−30.4 MPa (40−60 °C)	0.003−0.498 mol/L	217
$UO_2(NO_3)_2{\cdot}2TBP$	$scCO_2$	25.3 MPa (60−120 °C)	ca. 2.0×10^{-3} mol/L	96
$UO_2(NO_3)_2{\cdot}xH_2O{\cdot}yTBP$	$scCO_2$	25.3 MPa (60−120 °C)	ca. $(1.3-2.0) \times 10^{-3}$ mol/L	222
Cu−Cyanex 272	$scCO_2$	20.3−30.4 MPa (60 °C)	0.083−0.51 g/L	35
Cu−Cyanex 301	$scCO_2$	10.1−30.4 MPa (60 °C)	0.022−12.06 g/L	35
Cu−Cyanex 302	$scCO_2$	20.3−30.4 MPa (60 °C)	0.9−7.83 g/L	35

[a] Key: (5*) = 5% MeOH modified, (10*) = 10% MeOH modified.

Furthermore, the polyether chain lengths can be varied, possibly providing opportunities for “size”-selective extraction of metals. Similarly, monodentate (NR_3) or multidentate amine ligands ($R_2N[CH_2CH_2N\{R\}]_nR_1$ where R = organic group, $n = 1, 2, 3$, etc.) have not yet found wide use as solubilizing ligands in SCFs (Figure 13).[230] However, solubility measurements for a range of amines in SCFs have shown that phenyl-substituted amines have particularly low solubilities in such media.[231] Furthermore, primary amines can react with CO_2 to form carbamates.[40]

Amines such as en and NH_3 itself, are of course known to dissolve metals/inorganic materials (Section IV; Part 1), but dissolution is often relatively slow. $scNH_3$ has also been investigated for the recovery of metals from spent catalysts which would otherwise have been consigned to landfill sites or been recovered by relatively expensive processes involving toxic solvents. Thus, McPartland and co-workers have shown that metals (e.g., cobalt) can be recovered from catalyst materials using both supercritical and subcritical ammoniacal mixtures.[232] They observed improved extraction of cobalt using supercritical aqueous NH_3 compared to subcritical conditions. This enhancement was attributed to the superior transport properties (mass transfer enhancement) of the supercritical solvent.

Many classical organometallic complexes are known to dissolve in SCFs such as $scCO_2$. These include ferrocene and its related derivatives,[94,233] some metal chlorides,[88,234,235] and a whole range of metal carbonyls such as $Co_2(CO)_8$, $Fe(CO)_5$, and $Mn_2(CO)_{10}$ (homogeneous catalysts),[124,236−238] cyclopentadienyl complexes such as $CpMn(CO)_3$[105,239] and Cp_2M (M = Co, Ni),[238] and alkyl complexes,[238] e.g., $MeReO_3$. Kreher et al. concluded that $scCO_2$ is not a very good solvent for some of these compounds.[238] These are often more soluble in liquid CO_2 (which is relatively dense) than in $scCO_2$ near its critical density and temperature.[238] A highly detailed study on the solubility of $Mo(CO)_6$ in $scCO_2$ has been carried out by Warzinski and co-workers.[240,241]

In many cases, metal−organic complexes are known to undergo interesting chemistry under supercritical conditions. For example, complexes such as $[(COD)PtMe_2]$ have been used[242] for the preparation of Pd nanoparticles via SCF infusion into polymers followed by thermal treatment (see Section III; Part 2B). Organotin and organolead species have also been studied for ease of extraction of these complexes from a variety of solid and liquid (aqueous) matrixes using SCFs.[186,243−246] Quite often, these complexes can be solubilized in the presence of modifiers/chelating agents for efficient extraction, and can then be analyzed immediately using “on line” methods.

Raynor and co-workers analyzed a range of organometallic complexes of tin, iron, and arsenic using the relatively new technique of SFC inductively coupled plasma mass spectrometry.[247] Other techniques such AED,[248] micellar electrokinetic capillary chromatography,[246] FAAS,[249] and atomic fluorescence spectrometry[250] have also been used in conjunction with SFE/SFT for the speciation and analysis of different organometallic compounds.

Beckman and colleagues, have used a different strategy to design and synthesize novel metal-chelating ligands which have particularly high solubility in $scCO_2$.[57,181] Their approach was based on highly “CO_2-phillic” groups such as those containing C−F bonds (fluorinated diketones,[75,230] fluoroalkyl, fluoroether, fluoroacrylate) and certain polysiloxanes[52] which should enhance the solubilities of ligands and, hence, possibly of any chelated complexes. They synthesized a number of high molecular weight perfluoropolyether ligands (based on Krytox functional oils from DuPont) with either picolylamine, dithiol, or dithiocarbamate functionalities and investigated the effect on solubility of changing the length of the CO_2-phillic “tail groups” (Figure 13).[57,60] The ligands containing fluoroether arms showed excellent efficiencies for the extraction of first row transition metals and platinum group metals from highly acidic solutions.[181] Fluorinated ligands which have recently been developed by other researchers for possible solubilization or extraction of metals in SCFs include metal triflates,[251,252] fluorinated hydroxamic acids,[194] tris(pyrazolyl)borates with perfluoroalkyl pigtails,[253] fluorinated phosphine oxides,[219] fluorinated porphyrins (Figure 14),[228,254] and fluorinated calix[4]arene hydroxamates (Figure 13).[195,196] In particular, the fluorinated calix[4]arene tetrahydroxamate ligands are capable of highly selective metal extractions from a range of matrixes.[196] Most recently, highly fluorinated phosphine ligands have been synthesized and used to prepare a series of fluorophosphine metal complexes which exhibit excellent solubilities in $scCO_2$ and other fluids.[61,63,193,255,256]

D. Rare Earth and Radioactive Metals

SCFs are becoming increasingly attractive as replacements for conventional organic solvents in many processes which require extraction or cleanup of hazardous metals (e.g., toxic or radioactive metals) from contaminated aqueous mixtures or solids/matrixes.[172] For example, the recovery of transuranic elements and long-lived fission products from acidic aqueous waste or from solid surfaces is of great importance in the management of nuclear wastes. Currently, the removal of uranium and plutonium from acidic aqueous media is achieved by extraction with a combination of hydrocarbon solvent (usually kerosene or dodecane) and the neutral complexing ligand TBP (the PUREX process).[172,222] Smart and coworkers have evaluated the extraction efficiencies of TBP and a number of similar coordinating ligands in $scCO_2$ (as the solvent) for the recovery of these metals from simulated nuclear waste.[71,217,222] $scCO_2$ is believed to have several advantages over conventional hydrocarbon solvents, including cheapness, ease of recycle, good stability to radiation, tunable solvent density (by variation in pressure), and the ability to precipitate the extracted compounds by depressurization (see Section II, Part 4A on RESS).

In a series of papers,[71,72,221] Wai and colleagues used $scCO_2$ solutions saturated with Lewis bases such as tri-*n*-butyl phosphate (TBP), tributylphosphine oxide (TBPO), tri-*n*-octylphosphine oxide (TOPO), or triphenylphosphine oxide (TPPO) to extract uranium and thorium ions from acidic solutions/solids. In one such study,[221] $scCO_2$ saturated with the Lewis base, was bubbled into a nitric acid mixture and held in a static mode for 15 min, followed by 15 min of flowing $scCO_2$ through the sample. As in the conventional extraction process (dodecane/TBP), the efficiency for extraction of the uranyl ions in $scCO_2$/TBP is strongly dependent on the concentration of the nitric acid. Furthermore, improvements in the efficiencies for the extraction of uranyl and thorium ions by $scCO_2$/phosphine oxide mixtures (TBPO, TOPO, or TPPO respectively) were observed. Interestingly, the fluorinated β-diketone, tta-H, shows a synergistic effect with these donor ligands leading to enhanced efficiency for thorium extraction.[221] Thus, using a mixture of tta-H and TPPO in $scCO_2$, an extraction efficiency of ca. 90% was obtained for thorium ions from 1 M HNO_3 at 60 °C/200 atm.[221] Complementary work on the extraction of solid uranyl nitrate $UO_2(NO_3)_2{\cdot}6H_2O$ using the same organophosphorus reagents was undertaken to estimate the solubility limitations and the stability of the adducted complexes in $scCO_2$.[222] For these experiments, the organophosphorus reagent was placed inside a reaction vessel, upstream of the uranyl nitrate with the two substances separated by a glass wool plug. A number of different extraction modes (static and dynamic) were compared for a range of organophosphorus ligands and the cell was even placed in different orientations to see whether there were any secondary phases containing $UO_2(NO_3)_2{\cdot}6H_2O$ being physically carried out of the reactor by the $scCO_2$ pressure (none were detected for the $scCO_2$/TBP system). The extraction efficiencies for removal of the nitrate salt by the ligands followed the order TBP > TBPO > TOPO > TPPO, which correlates well with the relative solubilities of these ligands in $scCO_2$.[221,222] Thus, one can assume that the more ligand which dissolves in $scCO_2$, the more ligand will be available to complex the metal and to transport the resulting compound.

Very recently, Shadrin and colleagues extended these ideas by using both fluorinated (as well as nonfluorinated) neutral phosphine oxide and fluorinated β-diketone ligands for the SFE of uranium, transuranics, and rare earth (lanthanide) salts from solid surfaces.[219] They observed that relatively high amounts of uranium, americium, and plutonium (>70%) could be removed from stainless steel, rubber, and asbestos surfaces, using $scCO_2$ containing TBP and hfa-H in the presence of water (Figure 11; type a). Experiments on "real world" contaminated stainless steel samples, also showed that >95% of the radioactivity could be removed.[219] They also investigated the SCF-assisted cleanup of stainless steel surfaces contaminated with uranium, americium, neptunium, and plutonium oxides using just hfa-H and water with the SCF.[218] These experiments were carried out with the metal oxide on steel samples, and the complexing agent and modifier placed in an extraction vessel with the $scCO_2$ added thereafter (static mode). After a set time, $scCO_2$ was flowed through the system (dynamic mode) for a fixed time period. The extraction efficiencies were highly dependent on the particular oxide phase of the element. Indeed, the oxides UO_2 (and ThO_2) could not be extracted in appreciable amounts under the conditions used. By contrast, UO_3 could be recovered in ≥75% yield above 100 atm. Also, PuO_2, Np_2O_3, and AmO_2 could be extracted from spiked stainless steel surfaces with a significant increase in the recovery of these elements being observed with $scCO_2$/hfa-H mixtures in the presence of water.[218] Multiple extractions of the actinide oxide samples from stainless steel under similar conditions, resulted in >97% of the material being extracted after three operations of SFE, with equally good results being observed for the cleanup of "real world" contaminated steel samples.

E. Highly Toxic Elements and Transition Metals

Accumulation of toxic metals in sediments and aquatic plants is of immense concern, especially with regard to the effective environmental monitoring and safe cleanup and disposal of these materials. Again, $scCO_2$ (containing extracting ligands) is a seductively attractive solvent for SFE of toxic metals due to its cheapness, chemical inertness, and relatively low critical temperature and pressure. In any research, it is prudent to begin with those metals which are extracted commercially in processes using conventional organic solvents. In this way, one can make direct comparisons of extraction efficiencies and selectivities between SCFs and conventional solvents. Most of the reported case studies have evaluated the extraction efficiency of different ligands in $scCO_2$ using spiked solid matrices such as sand or filter paper (see above) or occasionally of incorporated metals (such as in biomass). Smart and co-workers[191] used a series of commercially available reagents such as Kelex 100, Cyanex 272, 301, and 302, and D2EHTPA as ligands for the extraction of toxic heavy metals from a range of spiked or metal containing solid matrices. Initially, testing showed that these extractants had good stabilities in $scCO_2$, which is important if they are to be of commercial value where they must be recycled many times. Of these ligands, the S-containing organophosphorus reagents (D2EHTPA and Cyanex 301 and 302) were shown to extract heavy metals efficiently from their matrices under conditions of ca. 200 atm/60 °C. Kelex 100 showed a high selectivity for Cu^{2+}, which is unsurprising since Kelex 100 is used for extraction of Cu^{2+} with conventional solvents. The solubilities of the metal-containing complexes were calculated to be in the order of 0.15−12 g/L depending on the conditions and the extractant ligand. This suggests that the solubility of the compounds will not be the limiting factor for the cleanup of leachable metals from “naturally” contaminated samples or from matrices which have been spiked rather than those in which the metals are incorporated.

In another study,[225] ionizable crown ethers were used for the selective extraction of Hg^{2+} from a mixture of transition metal (T.M.) ions (including Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) through a sand/cellulose filter using MeOH modified $scCO_2$ (200 atm/60 °C) in the presence of small amounts of water. The high extraction selectivity for Hg^{2+} (and Au^{3+}) was attributed to the stability of the metal complex in the presence of water rendered acidic by dissolved $scCO_2$ (calculated to be ca. pH 3). Other divalent T.M. ions appear to be unable to form crown ether complexes in this pH range and, hence, are not extracted in appreciable amounts. This again underlines the importance of pH on the selectivity and the efficiency of extraction.

Samples of sand or filter paper spiked with Cd^{2+}, Pb^{2+}, and Hg^{2+} ions were used to evaluate the extraction efficiencies of a range of dithiocarbamates and fluorinated β-diketones in modified $scCO_2$ (5% MeOH).[189] One strategy was to place the extractant upstream of the spiked samples (separated by glass wool) using a 15 min static mode followed by 15 min of dynamic extraction (see Figure 11; type a) and conditions (T, P) were optimized. It was found that >95% recoveries of Cd^{2+}, Pb^{2+}, and Hg^{2+} ions could be obtained using LiFDDC, while 83−97% of the ions were recovered using either Et_2NH_2DDC or NaDDC. Recent complementary work by Ashraf-Khorassani and colleagues,[257] investigated the solubilities of mercury dithiocarbamates [$Hg(DDC)_2$ and $Hg(FDDC)_2$] in $scCO_2$, as well as the efficiency of extraction of the preformed chelates spiked onto a range of different matrixes. Similarly, the Wai group found that 68−96% of the ions were recovered from spiked sand samples when the fluorinated β-diketones, tfa-H, hfa-H, and tta-H, were used as the extracting agents, while APDC was ineffective for the removal of these ions from either spiked sand or filter paper under similar reaction conditions. One consistent fact is that higher recoveries of metal ions were achieved for modified $scCO_2$ (5% MeOH) rather than for pure $scCO_2$.[257] Furthermore, fluorination of the complexant ligand improves the solubility of the resulting T.M. chelate complex in $scCO_2$, leading to higher extraction efficiencies. Indeed, it has been suggested that the amount of extracted metal is largely dependent on the solubility of the T.M. chelate complex in the supercritical phase, assuming of course that sufficient chelating ligand is present within that phase.[35]

Another “cleanup” application of SFE is the removal of bioaccumulated toxic metals from animal or plant cells. SFE is particularly suited to biomaterials because of the superior transport properties and high diffusivities of SCFs, and the minimal risk of toxic solvent residues. Thus, a range of extractants (e.g., alkali/pseudo-alkali metal diethyldithiocarbamates) and neutral chelating ligands (Cyanex 302, hfa-H, thiourea, EDTA, and tris) have been tested for their effectiveness in the removal of Hg from biomaterials using MeOH (5%) modified $scCO_2$ (Figure 13).[184] The diethyldithiocarbamate compounds generally showed good efficiencies for the extraction of bioaccumulated mercury from aquatic plants. The fluorinated ligand FDDC which forms the most soluble complexes with mercury showed the highest extraction efficiency but NaDDC and APDC showed a moderate increase in extraction efficiency when the pressure of CO_2 was increased from 100 to 250 atm. Furthermore, the diethyldithiocarbamate complexes were generally shown to be more effective than Cyanex 302 (a commercial extractant for heavy metals) under similar extraction conditions in $scCO_2$, while the remaining neutral extracting ligands were relatively poor for the removal of Hg from the biomass.[184]

Arsenic (As) and antimony (Sb) are two elements found in natural water sources which show differing toxicological and physiological behavior depending on their oxidation states. For example, arsenite (As^{3+}) species show greater toxicity than arsenate (As^{5+}). Thus, environmental monitoring of levels of these and other toxic metals in natural waters or waste streams is important for pollution regulation. Since conventional chromatographic analysis (e.g., GC) can often be affected by thermal and chemical instability of the chelated metal complexes, Laintz and co-workers used SCF chromatography (SFC) for analysis because the lower temperatures of the SFC separations are better suited to thermally labile compounds.[212] They showed that trace quantities of As(III) and Sb(III) could be quantified by extraction from the aqueous media using LiFDDC, followed by SFC analysis. Indeed, the total concentration of As or Sb could also be established by conversion of all the species (both +3 and +5) in water to the trivalent state (using sodium thiosulfate and KI) followed by SFE/SFC of the trivalent FDDC complexes.[212] They also investigated the feasibility of removing Ni^{2+} and Zn^{2+} ions from spent aqueous electroplating solutions using β-diketones and concluded that for these types of waste metal solutions, fluorinated ligands appeared to be slightly better extractants.[170] Liquid CO_2 and $scCO_2$ performed equally well in most cases and, thus, it may be more economically viable to use an industrial extraction process to be based on subcritical rather than $scCO_2$ on grounds of lower capital costs and saftey.[170]

In contrast to the extraction of metals, there are many examples where SCFs have also been used for cleanup of metal and mineral surfaces,[258] sintered metallic pellets,[259] and clays[260]/soils. For example, high-grade scrap metal alloys produced from grinding waste can be recycled after degreasing with modified $scCO_2$.[258]

2. Materials Chemistry

The unique properties of SCFs can be exploited to synthesize interesting materials, currently not accessible using conventional solvents because of mass transport or diffusivity limitations. We now explain how metal–organic compounds, dissolved in SCFs or mixtures of SCFs and organic solvents, can be deposited onto the surfaces of substrates or be infused into bulk materials to make either conventional thin metal/metal oxide films or novel hybrid (composite) coatings and materials.

A. Supercritical Fluid Transport Chemical Vapor Deposition

The production of thin films of metals (and metal oxides) is an area of significant scientific and technological importance because the wealth of potential applications including the production of microelectronic devices,[261] luminous displays, or glasses with special optical properties.[262] One of the best known and simplest methods for thin film manufacture, MOCVD, involves the sublimation of a volatile metal complex (usually a metal–organic complex or metal halide), which is transported onto a substrate (often heated to induce decomposition).[204,261,263,264] The compound is then adsorbed onto the substrate where the supporting ligands are lost. The metal atoms formed on the substrate surface, then diffuse and agglomerate to form *"seeds"* for the growth of metallic/metal oxide films. The general requirements for CVD precursors include good shelf life, high volatility, thermal and air/moisture stability at room temperature and facile decomposition to the metal (or oxide) at relatively low temperatures.[265,266]

A number of alternatives to MOCVD have been suggested to overcome delivery problems of precursors which have poor volatility or low thermal stability. These include methods such as aerosol-assisted (AA) CVD,[267−269] spray pyrolysis,[270] spray MOCVD,[271] and SCF transport (SFT) CVD.[210,272−274] In SFT CVD, the metal compound (or mixture of metal complexes) is dissolved in a SCF and transported to a reaction chamber, where the solution is expanded through a restrictor into the chamber. This "RESS" expansion results in the formation of extremely small particles of the metal precursor. These particles then undergo decomposition to the metal/metal oxide (via pyrolysis, hydrolysis, oxidation, etc.) usually at the surface of a substrate (Figure 15).[210] Decomposition of the precursor can be induced in a number of ways, including resistive heating, laser-induced heating of the substrate surface or RF plasma induction heating (for scN_2O carrier fluid) of the expanding fluid. Pommier and co-workers have studied the decomposition of compounds such as "$Cu(hfa)_2$" to give metallic copper in $scCO_2$ and found that the decomposition temperatures are similar to those in the solid state. However, the addition of modifiers such as alcohols can reduce the thermal stabilities of complexes substantially.[87]

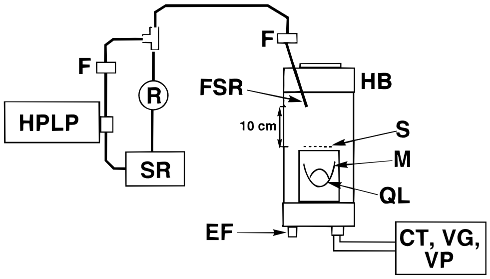


Figure 15. Schematic view of a typical apparatus for liquid solution-SCF transport chemical vapor deposition (SFT CVD) used for metal/metal oxide film deposition. The apparatus is labeled as follows: HPLP, high-pressure liquid pump; SR, solution reservoir; R, pressure regulator; F, filter; FSR, fused silica restrictor (for RESS deposition of the precursor); HB, heated block; S, substrate; M, reflector; QL, quartz lamp; CT, cold trap; VG, vacuum gauge; VP, vacuum pump; EF, electrical feedthrough. (Redrawn from B. M. Hybertson et al., *Mater. Res. Bull.* **1991**, *26*, 1127.)

The SFT CVD process[210] has certain advantages over MOCVD in that relatively nonvolatile precursors (which are often less toxic) can be used. Furthermore, the low critical temperatures for $scCO_2$ and other SCFs, allow thermally relatively unstable complexes to be used in the SFT CVD apparatus. This means that objects with complicated shapes can be coated after fabrication without losing their shape. Generally, precursors are required to exhibit good solubility and stability in the SCF, to ensure that good transfer (carryover) rates are achieved and to prevent the restrictor from clogging with undissolved particles.[272] Almost all of the existing MOCVD precursors can be used for SFT CVD but, in addition, a range of less volatile and less toxic complexes (which are unsuitable for MOCVD) make excellent SFT CVD reagents. Thus, although AgI and silver(I) triflate are too involatile to be used in conventional MOCVD processes, they can be used to make films of metallic silver using SFT CVD apparatus.[210,272]

For the more volatile compounds, decomposition reactions on the substrates follow the same pathways as those observed in MOCVD. Thus, Sievers and co-workers have observed that $Cu(thd)_2$, $Al(hfa)_3$, $Y(thd)_3$, and similar β-diketonates can be used as precursors for both MOCVD and SFT CVD to generate the respective metals/metal oxides (see Table 3).[272] The

Table 3. Table of Metal−Organic Complexes which Have Been Dissolved in SCFs for the Synthesis of Thin Films and Composite Materials

compound(s)	solvent	conditions	use/process	ref(s)
$[Ag(hfa)(n\text{-glyme})]_n$	$scCO_2$	ca. 13.6 MPa	composite material	319
$[Ag(hfa)(n\text{-amine})_x]_n$	$scCO_2$	ca. 13.6 MPa	composite material	319
[Ag(hfa)(COD)]	$scCO_2$	ca. 13.6 MPa	composite material	288
$[Ce(etfa)_4][NH_4]$	$scCO_2$	ca. 12.2 MPa	precursor/vicor glass composite	319
$[Ce(fod)_3]_2$(4 g)	$scCO_2$	ca. 12.2 MPa	precursor/vicor glass composite	319
$Al(hfa)_3$	sc-pentane	ca. 8.8 MPa/210 °C	SFT CVD of Al (680 °C)	272
$Al(hfa)_3$	$scCO_2$	14.3−19.0 MPa/40−70 °C	SFT CVD of alumina (100 °C)	272
$Cr(hfa)_2$	scN_2O	14.3−19.0 MPa/40−70 °C	SFT CVD of Cr_2O_3 (100 °C)	272
$Cr(acac)_2$	sc-acetone	ca. 8.8 MPa	SFT CVD of Cr (800 °C)	272
$In(acac)_2$	$scCO_2$	ca. 8.8 MPa/40−70 °C	SFT CVD of In (600 °C)	272
$Ni(thd)_2$	sc-pentane	ca. 8.8 MPa/210 °C	SFT CVD of Ni (600 °C)	272
$Cu(oleate)_2$	sc-pentane	ca. 8.8 MPa/210 °C	SFT CVD of Cu (740 °C)	272
$Cu(thd)_2$	sc-pentane	ca. 8.8 MPa/210 °C	SFT CVD of Cu (700 °C)	272
$Cu(thd)_2$	scN_2O	14.3−19.0 MPa/60 °C	SFT CVD of Cu (700 °C)	272
$Cu(thd)_2$	scN_2O	14.3 MPa/40 °C (RF plasma)	SFT CVD of CuO (RT)	272
$Cu(hfa)_2{\cdot}H_2O$	scXe, $scCO_2$		SFT deposition (ca. 400 °C)	273
$Cu(hfa)_2{\cdot}H_2O$	scC_2F_6, $scCF_3Cl$		SFT deposition (ca. 400 °C)	273
$Ni(hfa)_2{\cdot}H_2O$	scXe, $scCO_2$		SFT deposition (ca. 400 °C)	273
$Ni(hfa)_2{\cdot}H_2O$	scC_2F_6, $scCF_3Cl$		SFT deposition (ca. 400 °C)	273
$Pd(tod)_2$	sc-pentane	ca. 8.8 MPa/210 °C	SFT CVD of Pd (600 °C)	272
$Pd(tod)_2$	sc-pentane	ca. 8.20 MPa	SFT CVD of Pd (680−740 °C)	274
$Pd(tod)_2$	$scEt_2O$	ca. 8.2 MPa	SFT CVD of Pd (680−740 °C)	274
Ag(triflate)	$scEt_2O$	ca. 8.8 MPa	SFT CVD of Ag (600 °C)	272
AgI	sc-acetone	ca. 8.8 MPa	SFT CVD of Ag (600 °C)	272
$Y(thd)_3$	scN_2O	14.3−19.0 MPa/40−70 °C	SFT CVD of Y (687 °C)	272
$Y(thd)_3$ + "$Ba(thd)_2$" + $Cu(thd)_2$	sc-pentane	ca. 8.8 MPa/210 °C	SFT CVD of YBCO (800 °C)	272
$Zr(tfa)_4$	$scEt_2O$	ca. 8.8 MPa	SFT CVD of Zr (600 °C)	272
$Y(thd)_3$	scN_2O	14.3−19.0 MPa/40−70 °C	SFT CVD of Y (687 °C)	272
$Si(OEt)_4$	scN_2O	14.3−19.0 MPa/40−70 °C	SFT CVD of SiO_2 (100 °C)	272
$Si(OEt)_4$ + $P(OEt)_4$ + $B(OEt)_4$	scN_2O	14.3−19.0 MPa/40−70 °C	SFT CVD of BPSG (100 °C)	272
$CpMn(CO)_3$	$scCO_2$	8−20 Mpa/40 °C	polymer composite/IR probe	112, 455

same research group observed that polycrystalline Pd films could be deposited pyrolytically onto silica substrates (heated with a quartz lamp) using SFT CVD from solutions of $Pd(tod)_2$ in either supercritical *n*-pentane or sc-diethyl ether (see Figure 15).[274] Surprisingly, despite the use of an organic SCF, the deposited Pd films contained no detectable carbon contamination and were electrically conducting, albeit with a conductivity lower than that for bulk Pd.[274]

SFT CVD can also be used to produce mixed-metal alloy films because an intimate mixture of different metal−organic precursors can be dissolved in SCF solution and then deposited by RESS. Thus, alloy films containing Y, Cu, and Ba can be deposited from a supercritical *n*-pentane solution of $Ba_5(thd)_9(H_2O)_3$-OH, $Y(thd)_3$, and $Cu(thd)_2$. The stoichiometry of the metal−organic complexes can be controlled so that annealing of the resulting alloy in oxygen at 500 °C, yields a superconducting oxide film of composition $YBa_2Cu_3O_{7-x}$ (YBCO).[210,272] In principle, the final composition/ratio of metallic elements in a film deposited by SFT CVD can be controlled more precisely than that achieved using MOCVD apparatus.

SFT CVD can achieve much higher concentrations of the precursor in the gas phase than MOCVD. Therefore, it has been proposed[273] that the precursor could be decomposed in the supercritical solution itself (without depressurization), allowing rapid growth of metal/metal oxide films as a result of higher precursor concentrations. The apparatus is essentially the same as for SFT CVD but without the RESS stage.[275] Pommier and co-workers have used such a system to show that the alkoxide precursor $[Ti(O^iPr)_4]$ dissolved in a supercritical solvent (CO_2/2-propanol; T_c = ca. 180 °C, P_c = ca. 9.8 MPa) could be decomposed to TiO_2 by contact with a heated metal surface,[276] or alternatively, the $[Ti(O^iPr)_4]$ could be hydrolyzed in or on a wet porous support (in 10 min) to give homogeneous titania films of $<5\ \mu m$ thickness, which were built up from small particles (<400 nm).[277] Using this "high-pressure reservoir" technique, precursors such as $[Cu(hfa)_2]{\cdot}H_2O$ have been used to deposit metallic Cu films with higher O and C content than those produced by SFT CVD and MOCVD. This contamination is rationalized by the high concentration of the metal−organic resulting in pyrolysis of the organic ligands as the film is formed.[273]

B. Composite Materials Synthesis

Nanoparticles of metals or semiconducting materials often exhibit unique size-dependent optical, magnetic, and electrical properties.[278] However, it is often very difficult to prevent agglomeration of such small particles. The formation of small metal particles within solid polymers is especially attractive as the polymer matrix can prevent agglomeration. Indeed, there have been a number of recent reports on nanoparticles of ZnS, CdS, and other interesting inorganic materials, intimately dispersed within polymer matrices.[279] It is hoped that such composite polymer/inorganic hybrid materials may lead to useful electronic and optoelectronic devices or as novel biomaterials for prosthetic replacement.[279]

$scCO_2$ has aroused wide interest as an alternative medium for polymerization reactions[52,280−282] and extraction/fractionation of polymers.[143] Because of

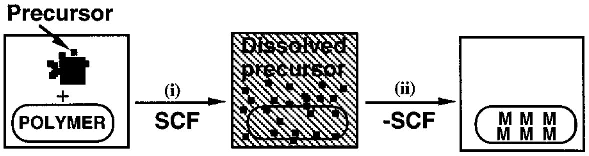


Figure 16. Schematic summary of the supercritical infusion method for the synthesis of metal/metal oxide composite polymers showing (i) the introduction of the SCF and the dissolution of the organometallic complex and (ii) the depressurization of the fluid prior to, or followed by the decomposition of the organometallic complex. The scheme is labeled as follows: shading = SCF; ■ = precursor; M M M = small metal/metal oxide particles incorporated in the polymer.

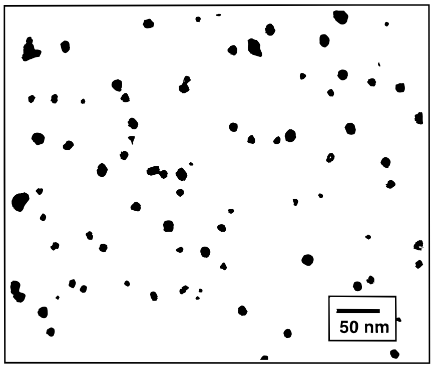


Figure 17. TEM image of Pt clusters in PMP formed by reduction of (COD)$PtMe_2$ after supercritical impregnation and subsequent removal of the SCF. (Modified and reproduced with permission from J. J. Watkins et al., *Chem. Mater.* **1995**, *7*, 1991.)

their high diffusivity and low viscosity, SCFs also provide suitable media for the impregnation of metal−organic or other complexes into polymers. $scCO_2$ has the ability to swell many polymers reversibly which further aids impregnation of a complex into the polymer.[92,283−285] Kazarian and co-workers have recently reported the use of FTIR or UV−vis spectroscopy to monitor the impregnation of polymers and related porous solids.[17,95,102,103,286,287]

Similar methods have been developed independently by a number of workers for the transport and impregnation of a metal-containing precursor (usually a metal−organic complex) into a polymer using a SCF (usually $scCO_2$). Then, decomposition of the impregnated metal precursor is induced either prior to, or after decompression of the SCF (Figure 16). If required, a subsequent flush of $scCO_2$ can be used to remove any $scCO_2$-soluble organic ligands still left in the polymer matrix. Removal of these residues is particularly important for the synthesis of biomaterials which have extremely stringent specifications for residual contaminant levels. One of the first examples was the $scCO_2$-assisted infusion of (COD)-$PtMe_2$ into the polymers PMP and PTFE respectively, which led to Pt nanoparticles (<50 nm diameter) in the polymer matrixes (Figure 17).[242,275] Smaller particles were obtained when the infused precursor, (COD)$PtMe_2$, was hydrogenated (to Pt + COD + $2CH_4$) following decompression of the $scCO_2$ (rather than prior to decompression).[275] Watkins et al. have recently extended this work with Pt and Pd to cover deposition of metal films on substrates and impregnation of catalyst supports. They have suggested the acronym CFD, Chemical Fluid Deposition, for this process.[275] Using a similar methodology, [Ag(hfa)-(COD)] (hfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, COD = cyclooctadiene) or [Ag(hfa)(L-L)] (L-L = multidentate ligands) were impregnated into polymers using $scCO_2$, and then either heated or exposed to light/air, resulting in metallized films on the polymer surfaces and/or metal clusters within the polymer.[207,230,288] Infusion techniques have also been adopted for the impregnation of pharmaceuticals into polymers using SCFs to make controlled-released drug materials[285] and for SCF-assisted dyeing of textiles with mordant dyes (in the presence of mordating metal ions).[289]

New techniques are currently being developed to combine the impregnation (and decomposition) of a metal chelate complex in a polymer as well as using the RESS method onto a heated substrate (as used in SFT CVD).[290] It is hoped that such systems will lead to single step polymer/metal codeposition. However, as yet the full potential of such systems does not appear to have been realized.

C. Spray Coatings

There is much interest in the use of SCF mixtures containing organic solvents and inorganic materials for spray coatings. Conventional high-quality coatings are formulated with a blend of “fast”, “medium”, and “slow” (or “tail”) solvents, each of which has a specific role. “Fast” solvents which reduce viscosity and allow good atomization of the spray, are rapidly lost (by evaporation) so that the coating does not run or sag once it has been applied to a surface. “Medium” solvents which can be removed by air-drying, allow some leveling of coatings while “slow” solvents which give smooth films/finishes, are usually removed by curing or baking procedures.

The UNICARB system, developed by Union Carbide, uses organic solvent formulations in which the “fast” and some of the “medium” solvents are replaced by $scCO_2$ (10−50 wt %)[1] with a claimed 30−70% reduction in VOCs. The coating mixture itself is liquid, not supercritical, but it contains CO_2 which is above its critical point. Because CO_2 is extremely volatile, film formation proceeds via a different pathway to that observed for conventional organic solvent blends. This process has been successfully adapted for applying a range of coatings, pigments (TiO_2, carbon black, aluminum flake, silica, clay, etc.), polymers, and commercial paints and lacquers. The process can easily be retrofitted into existing spray operations with little or no modification of the coating polymers (the only changes are in the solvent blends) but, like much new technology, it has not yet been widely adopted.

As discussed earlier (Section II), a heated solid or plastisized polymer can be dissolved in $scCO_2$ and can then be expanded through a nozzle to form fine powders. This approach has been followed, in a more sophisticated form, for the manufacture of composite materials for use as powder coatings. The supercritical “VAMP” process was recently commercialised by the Ferro Corporation (Cleveland, OH).[2,166] Powder coatings usually consist of an inorganic pigment (e.g., TiO_2) encapsulated in a polymer together with a cross-linking agent. Conventionally, the various components (pigment, polymer, cross-linker, etc.) are mixed in an extruder. The VAMP process is quite different. The pigment is mixed in $scCO_2$ with the *polymer*. Although the polymer is insoluble, $scCO_2$ causes it to swell; the higher the pressure, the greater is the swelling. Thus, raising the pressure *increases* the density of $scCO_2$ but *reduces* the density of the swollen polymer. In VAMP, the pressure and temperature are adjusted to match the densities of the two phases and to lower the glass transition temperature. The polymer forms what is, in effect, a “supercritical foam” with the pigment within the polymer phase rather than the $scCO_2$ phase. Finally, the mixture is expanded through a valve and the foam breaks up into a fine powder. The significance of the VAMP process is that *it uses relatively little $scCO_2$ to achieve the desired result.* Indeed, VAMP is at least 50% cheaper than conventional processing. Polymerization reactions in the presence of oligomer which has been “wetted” to the pigment have also been accomplished.

Such an approach obviously has applications in the manufacture of a wide variety of inorganic/organic composites, for example to produce synthetic bone material for medical use.[291] Using the Ferro Corporation’s process, a range of polymer/hydroxyapatite (HA) mixtures have been produced in which the HA does not appear to be damaged in any way by the incorporation process.[291] It is hoped that this new method will, in time, lead to the synthesis of novel biodegradable/HA blends in which the material forms a scaffold for the growth of new bone/tissue, to replace the naturally decaying implant. Bertucco and coworkers also used an analogous but rather crude process for drug encapsulation by simply stirring suspensions of model drugs such as potassium chloride in polymer solutions of a SCF, and then expanding the mixture. They observed that the polymer concentration had a marked effect on the particle incorporation process.[292]

IV. Synthesis and Reactions

1. Inorganic Materials from Thermal Reactions in Supercritical Fluids

A. Introduction

It will be clear from Section III that the synthesis of small or regular sized inorganic particles (metal oxide ceramics, chalcogens, etc.) and polycrystals are of particular interest due to their uses in coatings, electrical devices,[161,279,293−296] and catalytic materials.[297] Conventionally, materials such as homo- and heterometallic ceramics are prepared from the high-temperature firing of the respective metal oxides, which often leads to materials with low surface areas. Coprecipitation techniques[297,298] can also be employed to access such materials, but they require strict control of several variables (e.g., pH, temperature, and stirring rate) and there is no guarantee that homogeneous mixtures will be obtained. By comparison, sol−gel processes[299−303] and high energy mechanical ball-alloying methods[304] can produce relatively homogeneous mixtures. Nevertheless, sol−gel materials still require some postannealing to obtain crystalline products, while ball-milling involves prolonged mixing times. Finally, as reported earlier (Section II; Part 4) there are a number of precipitation/nebulization techniques by which SCFs/antisolvents can be used to prepare intimately mixed and/or small particle sized metal oxide materials.[144−146,160] We now turn our attention to the use of SCFs as crystallizing/transporting media for inorganic materials.

B. Supercritical Water

It has been known for some time that metal oxide particles can be synthesized in superheated media and that a large degree of control over the size and morphology of particles can be achieved by varying reaction times,[305,306] temperature, and concentration of the metal ions in solution, or by using modifiers.[297,307−309] More recently, SCFs, especially scH_2O, have been investigated as either crystallizing (often prior to annealing) and/or decomposing media (to the metal oxide from a salt). Subcritical and scH_2O are particularly suited to the synthesis of metal oxide powders from metal salt precursors because of their corrosive[310−312] and dehydrating properties.[27,32,313] Furthermore, there is opportunity to control particle sizes/shapes by relatively small changes in the temperature and pressure which affect density, diffusivity, etc.[314] Such reactions can be carried out in either batch reactors or flow systems and, in most cases, highly crystalline powders are obtained without the need for annealing. In flow reactors (See Figure 18),[315,316] the parameters of temperature and pressure and concentration (of metal ions) can be varied independently and these factors have been shown to control directly particle size, morphology, and size distribution.[314,317,318] In contrast, batch reactions tend to give less control and wider size distributions (as

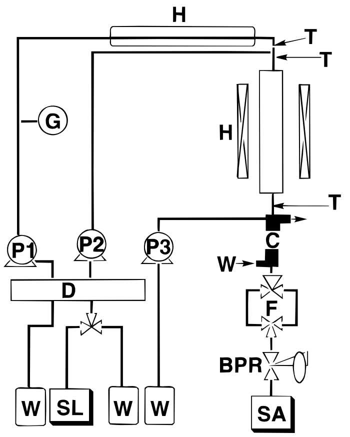


Figure 18. Hydrothermal flow reactor for the preparation and collection of fine particles in scH_2O. The apparatus is labeled as follows: W, water; SL, solution; SA, sample; D, degasser; P1, pump 1; P2, pump 2; P3, pump 3; G, pressure gauge; H, heater; T, thermocouple; C, cooler; F, filter; BPR, back pressure regulator. (Reproduced and modified with permission from Y. Hakuta et al., in Proc. 4th Int. Symp. on Supercritical Fluids; Sendai, Japan, 1997; p 255.)

Scheme 3

(i) Hydrolysis Step $M(NO_3)_x\,(aq) + xH_2O \longrightarrow M(OH)_x\,(s) + x\,HNO_3$

(ii) Dehydration Step $M(OH)_x\,(s) \longrightarrow M(O)_{x/2}\,(s) + x/2\ H_2O$

observed by XRD).[319] Control over particle size is particularly important for optical coatings such as titania (TiO_2) which can be used as a 'colorless' UV filter in suncreams (required particle diameters of ca. 20−50 nm), or as a "whitener" in coatings (maximum light scattering for particles between ca. 180−220 nm).[320] Conventional industrial methods for the manufacture of such ultrafine materials involve several separate processing stages which can significantly add to costs. Thus, cheaper and simpler processing methods for fine particle production are desirable.[320]

Subcritical and scH_2O have also attracted much interest as media for the recovery of metals (in the oxide form) from high level liquid waste streams.[317,321,322] The speed and simplicity of the technique are particularly appealing, soluble radioactive metals ions are merely precipitated from aqueous media. Thus, hydrothermal generation of metal oxides from the corresponding nitrates in scH_2O is believed to occur via a two stage decomposition mechanism in which the nitrate rapidly undergoes hydrolysis and dehydration (Scheme 3).[32,314,317,318,322]

This mechanism appears to hold for most nitrates [e.g., Fe(III), Co(II), Ni(II), Ti(IV), Ce(IV)],[32,318,321,322] apart from amphoteric metals such as Al, which form mixed oxide/hydroxides such as $[Al(O)(OH)]_n$.[314] By contrast, when the reaction is carried out in the presence of NH_3, there is formation of N_2 and N_2O.[323] It has been suggested that these products arise from the reaction between NH_3 and the HNO_3 produced by the first step in Scheme 3.

A number of workers in the area of hydrothermal crystallization of metal oxides have observed that the M:O ratios in the final products can vary according to the choice of starting material(s) in the reaction. For example, the degradation of iron(III) nitrate[314] (or sulfate) in scH_2O produces iron(III) oxide (α-Fe_2O_3), while, the iron(III) citrate complex $[Fe(NH_4)_2H(C_6H_5O_7)_2]$ decomposes to the magnetic oxide "magnetite" Fe_3O_4 [Fe(II) + 2Fe(III)].[314] It was tentatively suggested by Arai and co-workers that this may be the result of reduction of Fe^{3+} by CO gas produced by thermal decomposition of the citrate. It was further suggested that it might be possible to control the reducing or oxidizing atmospheres to some extent by the appropriate introduction of reductants/oxidants such as H_2, CO, or O_2.

To establish whether metallic elements themselves can be obtained from single precursors without additional reductant gases, Darr and Poliakoff have recently used metal−organic complexes rather than metal salts as reagents in scH_2O.[319] Their results suggest that certain metal−organic compounds are converted into partially reduced metal oxides or the metals themselves. This is in agreement with the report by Hirano and co-workers who pyrolyzed iron-containing divinylbenzene copolymers to yield a magnetite (Fe_3O_4 rather than Fe_2O_3)/carbon composite material under similar conditions.[324] Ni−Zn ferrite-dispersed carbon particles were also prepared using a similar route.[325] Other metal−organic precursors can give rise to the metallic elements themselves.[319] These preliminary results suggest that the main factors which determine the final oxidation state(s) of the products depend on the reduction potentials of the initially formed metal oxide (prior to reduction/oxidation) and the availability of reductant gases, or organic material which may be a source of such gases. Of course, it is relatively easier to reduce the coinage metal ions Cu(II), Ni(II), etc., and platinum group metals, while Fe(III) oxide (formed in situ) is reduced to a mixture of Fe^{II}/Fe^{III} oxide (magnetite), rather than metallic iron or iron(II) oxide. While the formation of metals or partially reduced metal oxides from metal−organic precursors in scH_2O is not surprising (it can be achieved without water), reactions in supercritical water allow some control over particle shapes and sizes (especially in a flow system).[319] Furthermore, the products are nearly always obtained in a highly crystalline form (at ca. 400 °C) which do not require postannealing.

The very high solubility of reductant gases in the supercritical media[27] appears to lead to decomposition (simultaneous hydrolysis and dehydration) together with the rapid reduction of the metal complex. The origin of the reductant gases is not clear, but there is some evidence to suggest the dissociation of water leads to H_2 and O_2; then H_2 reduces the metal oxide (to regenerate water), while the organic−ligands are oxidized and/or destroyed.[326] Furthermore, it is well-known that metals such as Mg or Zn can bring about hydrothermal dehydration with formation of hydroxides or oxides and H_2.[116] An alternative mechanism for the observed reduction might involve CO as the reductant gas.[314] The dissociation of water mechanism, however, is consistent with the observation[327] that H-bonding largely breaks down rendering the water *highly acidic* in nature at or near supercritical conditions.[115] Furthermore, a substantial decrease in density is observed for near-critical water which can affect equilibria in solution. This has been dramatically demonstrated by a very recent spectroscopic study of $K_2Cr_2O_7$ in aqueous solution.[115] For a fixed Cr(IV) and KOH concentration, the molal concentration of $HCrO_4^-$ species in solution increases with temperature (as monitored by UV−vis spectroscopy). However at temperatures near the critical point, the concentration of $HCrO_4^-$ falls dramatically (density also decreases substantially in this region). At such high temperatures, ion pair formation $\{(K^+)(CrO_4^{2-})\}$ becomes favorable, eventually leading to progressive ionic association and precipitation of $K_2Cr_2O_7$ at 420 °C (see Figure 19).[115,328]

If crystallization under supercritical conditions occurs rapidly, then scH_2O may be a suitable medium for the synthesis of heterometallic oxide materials, provided that the precursors themselves are heterometallic. Alternatively, the precursors could be co-dissolved metal salts, as long as the rates of conversion for the individual precursors are sufficiently rapid to precipitate homogeneous products. Thus,

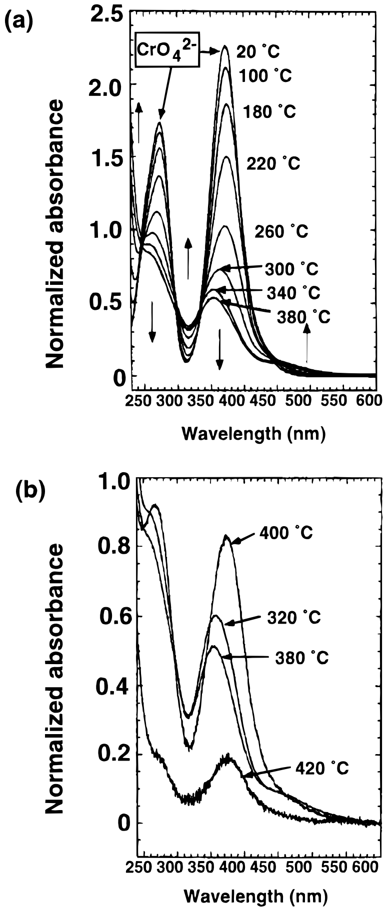


Figure 19. UV−vis spectra, showing the effect of temperature on the absorbance of a 2.50 × 10^{-4} mol/kg $K_2Cr_2O_7$ solution with 1.98 × 10^{-3} KOH at 27.6 MPa: (a) At lower temperatures, bands for CrO_4^{2-} are observed to decrease in intensity as the temperature rises, presumably as a result of an increase in $HCrO_4^-$ in solution. (b) At higher temperatures where the density also decreases substantially (near the critical point of water) the concentration of $HCrO_4^-$ decreases again. At such high temperatures, ion pair formation $\{(K^+)(CrO_4^{2-})\}$ becomes favorable, eventually leading to progressive ionic association and precipitation of $K_2Cr_2O_7$ at 420 °C.[115] All spectral absorbances have been corrected for changes in density. (Reproduced with permission from Chlistunoff et al., *J. Phys. Chem. B* **1998**, *102,* 3993. Copyright 1998 American Chemical Society.)

Arai and co-workers reported[317] a rapid and continuous method for the production of the magnetic mixed metal oxide, barium hexaferrite ($BaO{\cdot}6Fe_2O_3$), from the reaction of scH_2O and a metal hydroxide gel derived from an aqueous solution of $Fe(NO_3)_3$, $Ba(NO_3)_2$, and KOH.

RESS (see Section II; Part 4A) of scH_2O solution has been used to obtain small particles with well-defined shapes/size distributions or intimate mixtures of inorganic materials, usually amphoteric metal/nonmetal oxides.[127−130,132] Ziemniak[329] has discussed the properties and principles needed to predict the solubility of metal oxides in SCFs, while Brand[330] has examined a range of theoretical methods and problems associated with predicting metal oxide solubilities in scH_2O. Of particular note, however, is the fact that SiO_2 and GeO_2 are sufficiently soluble in scH_2O to be precipitated using RESS from scH_2O solutions.[130] This may explain why pure Ge powder has been observed to react with Pt plate in either subcritical or scH_2O with formation of fine crystals of the mixed Pt−Ge compounds Pt_3Ge, Pt_3Ge_2, Pt_2Ge (depending on conditions) on the surface of the Pt plate.[331] Presumably, some GeO_2 is formed, which then undergoes decomposition to the oxygen free mixed Pt−Ge crystals upon contact with the Pt plate[331]

C. Supercritical Alcohols

Subcritical alcohols have been shown to be excellent solventothermal media for the synthesis of a range of solid-state materials.[116,332,333] In comparison, there appear to be relatively few reports of such syntheses in sc-alcohols. A recent report by Hoffmann and colleagues,[334] suggests that the degree of H-bonding in sc-alcohols can be tuned as a function of density. Thus, the properties of sc-alcohol solvents can be tuned to suit a range of different applications. Pommier's group in France have developed both batch and semicontinuous reactors for the crystallization of metal oxide powders using sc-alcohols which usually have critical parameters lower than those of H_2O; e.g., for scMeOH, $T_c = 240$ °C (513.7 K)/$P_c = 81$ bar (78.9 atm). Therefore, quite often, sc-alcohols do not yield highly crystalline powders. Instead, sc-alcohols can be used as a preannealing treatment to improve the sinterability of ceramics.[335−338] For example, mixed CeO_2−ZrO_2 powders crystallized in MeOH at 250 °C, could be sintered to full density >1000 °C, while those prepared by calcination in air at a much higher temperature (1500 °C), sintered to only 95.2% of the full density.[338]

Conventional hydrolysis of metal alkoxide precursors are believed to lead to metal hydroxides or hydrated oxides via the formation of partially hydrolyzed intermediates such as oxo alkoxides, which can often be isolated in a crystalline form.[339] Hydrothermal treatment of metal alkoxides in sc-alcohols are of interest because the properties of SCFs allow rates of reactions to be controlled by changes in pressure, temperature, density, etc. SCFs usually encourage high nucleation rates with little subsequent growth of the nuclei themselves, thus leading to very small particles. Pommier and co-workers have used this approach to synthesize homo- and heterometallic submicron sized powders from alkoxide precursors. For example, they synthesized TiO_2 and $MgAl_2O_4$ powders from $Ti(O^iPr)_4$ or $Mg[Al(-OC_4H_9)_4]_2$ dissolved in scEtOH.[340−342] In experiments conducted in supercritical media at ca. 270 °C, they observed some incorporation of organic material into the partially crystallized powders. Above 350 °C, however, the products were highly crystalline anatase (TiO_2) and the spinel structure $MgAl_2O_4$ respectively.[343] Furthermore, high-temperature annealing of these products did not lead to detectable structural changes in the powders. More recently, they also reported the synthesis of $BaTiO_3$ powders from $BaTi(OC_4H_9)_6$ in a semicontinuous system, which combined hydrolysis with subsequent "on line" crystallization using a SCF.[344] This process has also been adapted for the production of thin films of TiO_2 from SCF solutions (see Section III; Part 2A).[276] Extensive kinetic and hydrothermal modeling studies have been performed for this reaction in order to understand the decomposition mechanisms and optimum conditions for the continuous production of TiO_2 powders.[345−348]

Recent developments involve both decomposition and sintering of Cr metal−organic complexes to Cr(III) oxide from sc-MeOH in a semicontinuous process.[349,350] The powders can be dried using a low-temperature N_2 flow, resulting in either crystalline or amorphous nanoparticles, depending upon the precise reaction and processing conditions. Other metal−organic complexes which have been decomposed to metal oxides in subcritical ethanol (at >200 °C) include magnesium β-diketonate (acac and hfa) complexes, which could be converted to crystalline MgO after heating to ca. 600 °C in air.[351] Amorphous powders were also obtained from scEtOH/$scCO_2$ mixtures, in which the T_c of the mixtures was lowered to ca. 110 °C. MgO powders have also been prepared from the corresponding methoxide derivatives using hydrolysis reactions (water) followed by treatment with scMeOH in a semicontinuous process.[352] A second French group, Sarrade and co-workers, recently reported a technique for the synthesis of silica, titania, and zirconia, from the alkoxide precursors, TEOS (tetraethoxysilane), $Ti(O^iPr)_4$, and $Zr(OBu)_4$.[353] The alkoxide was dissolved in $scCO_2$ (in an autoclave), and then allowed to react (via hydrolysis) with either an aqueous or ethanolic $scCO_2$ solution. A range of different particle morphologies could be obtained including spherical powders with or without spines, thin, or thick fibers, etc. These differences were the result of changes in hydrolysis rates, contact times, temperatures, pressures, and even the rates of the final pressure release.[353]

D. Supercritical Ammonia

It has long been known that certain metals can dissolve in NH_3 or mixed ammoniacal/organic solvents to give highly reactive species (at atmospheric pressure and low temperature). This has been widely used as a synthetic route to many metal−organic complexes because the metal is oxidized to M^{n+} and the ligands (L) are reduced to L^-. For example, this method has been employed to generate group 2 and lanthanide triphenylsiloxy complexes $[M(OSiPh_3)_x]_n$ (M = Ca to Ba or Eu, Yb) which are difficult to prepare using more conventional methods.[354,355] High-pressure ammoniacal reactions were first used ca. 30 years ago for the synthesis of amides, imides, and nitrides[356] The first review article[357] described the special apparatus required. Most of the early contributions in this rapidly expanding area of chemistry were reviewed in 1982.[358] A more recent review[332] by Sheldrick and Wachhold provides a good introduction to the general area of solventothermolysis of solid-state materials (chalcogenidometalates) which complements the highly regarded review by Rabenau which discusses the role of hydrothermal synthesis in preparative chemistry.[116]

NH_3 can coordinate to metal ions to form "$[M(NH_3)_6]X_2$" (M = metal; X = halide) complexes over a wide range of pressure and temperature. Thus, V and Cr iodides form $[V(NH_3)_6]I_2$ and $[Cr(NH_3)_6]I_2$ respectively in ammoniacal mixtures at atmospheric pressure. Similarly, $[Ni(NH_3)_6]Cl_2$ can be obtained from a mixture of $NiCl_2$ and NH_4Cl in aqueous NH_3 solution.[359] FeX_2 (X = Cl, Br) forms the corresponding $[Fe(NH_3)_6]X_2$ complexes in $scNH_3$ (400 °C). While $[Co(NH_3)_6]Br_2$ is obtained from $[Co_2(NH_2)_3(NH_3)_6]Br_3$ under similar reaction conditions.[359] Single-crystal X-ray diffraction studies of all these new $[M(NH_3)_6]X_2$ (X = halide) type compounds reveal them to be isostructural ($Fm3m$, $Z = 4$) with a $K_2[PtCl_6]$-type structure.

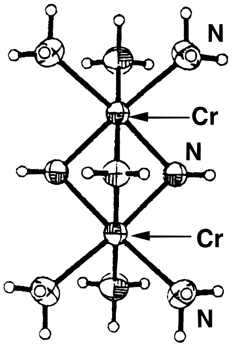


Figure 20. View of the $[Cr_2(NH_2)_3(NH_3)_6]^{3+}$ cation (50% probability ellipsoids), showing the three NH_2 groups bridging the two Cr ions. (Reproduced with permission from U. Zachwieja et al., *Z. Krystallogr.* **1993**, *206*, 247. Copyright 1993 Oldenbourg.)

Amide complexes have also been prepared in $scNH_3$, e.g., $[Cr_2(NH_2)_3(NH_3)_6]I_3$ was synthesized from the reaction of CrI_2 with $scNH_3$ (773 K/600 MPa).[360] A single-crystal X-ray structure of this compound reveals a $[Cr_2(NH_2)_3(NH_3)_6]^{3+}$ cation in which the NH_2 groups bridge between the two Cr ions (Cr−Cr = 2.65 Å) and the NH_3 ligands are terminally coordinated (see Figure 20). The gross structure contains an extensive H−I bonding network involving H atoms from both NH_2 and NH_3.[360]

The investigation of novel inorganic metal 2-D and 3-D polymers[361] has recently undergone a resurgence of interest with the use of superheated or supercritical amines or NH_3 as reaction media. Such fluids can act as both solvents and/or reagents in these reactions to produce inorganic phases at temperatures lower than typical solid-state synthetic routes. Indeed, it is possible to access metastable phases, unstable at higher temperatures, which are kinetic rather than thermodynamic products.[332] Thus, $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$ and $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$ were made in an experiment designed to yield novel bimetallic sulfide phases of general formula $Yb_xM_yS_z$ (M = Cu or Ag). In these experiments, "$[Yb(NH_3)_x(S)_y]$" (prepared in $scNH_3$ from Yb and S in a 1:8 molar ratio after 3 days of heating) was used as a reagent with Cu and Ag powders (and sulfur).[362] Single-crystal X-ray structural studies of the compounds reveal the Ln counterions to be coordinated by NH_3, while the Cu^+ and Ag^+ cations are coordinated to two S_4^{2-} groups which are either chelating or monodentate to the metal, giving $[M(S_4)_2]^{3-}$ units. Evidently, the structures represent metastable phases which are formed in these temperature (and pressure) regimes, but which are unstable at higher temperatures, yielding previously known ternary and binary phases.[362] The Lanthanum analogue of "[Yb-$(NH_3)_x(S)_y$]" was also reported using a similar synthetic route, i.e., metal (La) and S_8 in $scNH_3$. A single-crystal X-ray study, revealed this compound to exist as an ammonium salt $(NH_4)[La(NH_3)_9]S_5S$ which contains NH_4^+, disordered S_5^{2-} chains, lanthanum nonaamine cations, and discrete S^{2-} anions. Not surprisingly, the NH_3 in this complex was shown to be extremely labile, resulting in collapse of the crystal lattice.[363]

Unusual nitrides can also be formed at higher temperatures in $scNH_3$. For example, the copper(I) nitrate complex $[Cu(NH_3)_x]NO_3$ ($x = 2-3$) decomposes in $scNH_3$ (between 350 and 580 °C at 6 kbar pressure) to yield the diamagnetic nitride Cu_3N together with N_2 and H_2O. The X-ray structure of this metastable phase reveals a ReO_3-type structure in which the covalent N−Cu−N bond angle changes according to temperature (i.e., 173° at 21 °C and 176° at −143 °C).[364] When the reaction carried out in the presence of $[Pd(NH_3)_4](NO_3)_2$ at 500 °C/6 kbar, the silver-colored electrically conducting phases, $Cu_3Pd_{0.020}N$ and $Cu_3Pd_{0.0989}N$ were obtained.[365] These metastable phases decomposed at ca. 470 °C to give Cu_3Pd + dinitrogen (N_2). Single-crystal X-ray structural studies showed that the materials both have perovskite $CaTiO_3$-type structures of "Pd_xNCu_3" and are in the same space group ($Pm3m$) as observed for Cu_3N.[365] The novel compounds Mn_3N_2 and Fe_4N were synthesized using a similar method.[366,367] In these cases, good single crystals of the respective nitrides were obtained via addition of mineralizers (I_2 or alkali metals) which facilitated transport of the metals in $scNH_3$ {in the form of $[M(NH_3)_6]I_2$ (M = Fe or Mn) or $M'_2[Mn(NH_2)_4]$ (M′ = K, Rb)}, prior to conversion to the corresponding nitride material. Hexaamine cations, $[M(NH_3)_6]$ (M = Mn, Fe or Ni), were also observed in the unusual complexes $[M(NH_3)_6]Cu_8Sb_3S_{13}$ and $[Fe(NH_3)_6]AgES_4$ (E = As, Sb), prepared in $scNH_3$. The structure of $[Fe(NH_3)_6]Cu_8Sb_3S_{13}$ consists of bulky hexaamine cations residing in three mutually orthogonal channels created by the 3-D anionic network. In $[Fe(NH_3)_6]AgES_4$ (E = As, Sb), the anionic framework is a 1-D chain and there is some H-bonding between the hexaamine cations and the anionic lattice.[368]

Amide/NH_3 adducts have been used as reagents in most of the routes to homo- or heterometallic nitride compounds. However, Jacobs and co-workers have reported that the bimetallic nitride $Li_2Ta_3N_3$ can be synthesized from the reaction of the constituent metallic nitrides (Li_3N and Ta_3N_5) in $scNH_3$ (550 °C/0.6 GPa/5 days).[369] This reaction can also be carried out with either metallic Li or $LiNH_2$. Unfortunately, no single crystals suitable for a X-ray diffraction study could be obtained for this material. Nevertheless, XPD and neutron diffraction data of the pure powder showed that the structure is monoclinic ($C2/m$). The presence of Ta−Ta bonds were suggested by the diamagnetism of the compound and short Ta−Ta interatomic distances of 2.90 and 2.96 Å were reported.[369]

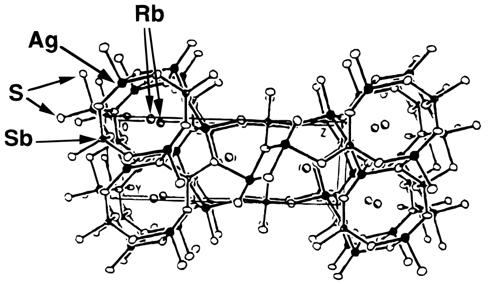


Figure 21. Unit cell of $RbAg_2SbS_4$ down the *a* axis. Atom types: antimony atoms are shown as 70% probability thermal ellipsoids, silver atoms are solid spheres, Rb atoms are highlighted, and sulfur atoms are 70% probability boundary ellipsoids. (Reproduced with permission from G. L Schimek et al., *J. Solid State Chem.* **1996**, *123*, 277. Copyright 1996 Academic Press.)

The chemistry becomes rather more diverse with the introduction of further elements to prepare quaternary "$A_wM_xB_yQ_z$" type phases (where A = group 1, M = transition metal, B = As, Sb, Q = S, Se). Four new quaternary antimony sulfides, MAg_2SbS_4, and M_2AgSbS_4 (M = K, Rb) were made by reaction of appropriate quantities of either K_2CO_3, K_2S_4, or Rb_2CO_3 with Ag, Sb_2S_3, and S_8 in $scNH_3$ at 160 °C/4 days. In some cases, the final stoichiometries of the major product(s) bore little or no resemblance to the ratios of the elements in the starting materials. For example, the reaction of K_2CO_3, Ag, Sb_2S_3, and S_8 was conducted in a 2:2:1:5 molar ratio producing crystals of $KAgSbS_4$, which could be separated manually from significant amounts of other phases, some of which were unidentified.[370] The structures of all except Rb_2AgSbS_4, contain 3-D anionic frameworks which are built up from either $[Ag_2SbS_4]^-$ or $[AgSbS_4]^{2-}$ groups consisting of Ag and Sb sulfide tetrahedra, which share either edges or vertices. The K^+ cations in the structures of KAg_2SbS_4 and K_2AgSbS_4 are located in two orthogonal, intersecting channels within the respective frameworks, while the Rb^+ cations in $RbAg_2SbS_4$ reside in three distinct 1-D channels (see $RbAg_2SbS_4$ in Figure 21). In contrast, the Rb cations in Rb_2AgSbS_4 are found in a double layer which separates the neighboring anionic framework layers. All of these new phases have been shown to be semiconducting and, unlike some of their structural analogues, e.g., $[BaAg_2GeS_4]$ and $[SrCu_2SnS_4]$, which were prepared at >500 °C,[371,372] these novel metal−silver−antimony−sulfides were prepared at much lower temperatures. This may explain why such a number of different but closely related kinetically stabilized structures were formed.

Using similar reagents but slightly higher temperatures, the related but novel compound KAg_2AsS_4 was synthesized from $scNH_3$.[373] The K^+ ions in $[KAg_2AsS_4]$, reside at the origin and body center of the anionic framework (see Figure 23) as observed in some of the previous alkali metal silver antimony sulfide structures.[373] Furthermore, the anionic framework is formed from condensation of nearly idealized Ag and Sb sulfide tetrahedra, sharing vertexes.[373]

If the relatively larger cations of Cs^+ are incorporated into these "$A_wM_xB_yQ_z$" type phases, a range of 1-D networks are formed depending upon the reagents and reaction stoichiometries employed.[374]

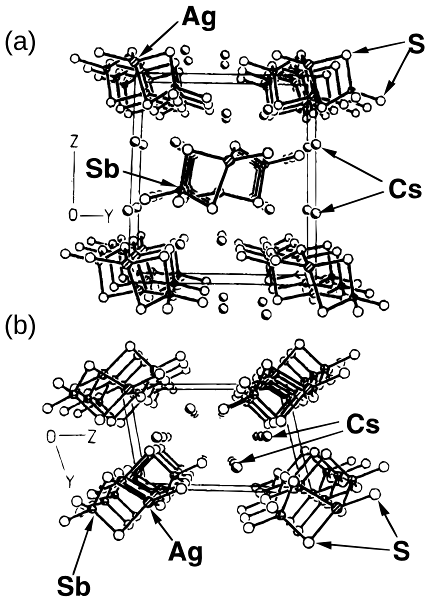


Figure 22. (a) Packing of the anionic columns, down the *a* axis, for α-Cs_2AgSbS_4 and (b) the packing of the anionic columns, down the *a* axis for β-Cs_2AgSbS_4. Cesium atoms are highlighted, antimony atoms are boundary ellipsoids, silver atoms are shaded (left to right), and S atoms are open spheres. (Reproduced from P. T. Wood et al., *Chem. Mater.* **1996**, *8*, 721. Copyright 1996 American Chemical Society.)

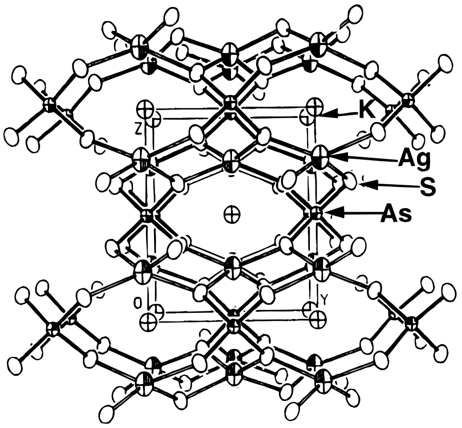


Figure 23. View of the unit cell of KAg_2AsS_4 parallel to the *x* axis. Bonds to the As atoms are shown as solid lines and bonds to the Ag atoms as open lines. S atoms are represented by boundary ellipsoids and the K^+ cation contacts and Ag1′ atoms have been omitted for clarity. Displacement ellipsoids are shown at 70% probability level. (Reproduced with permission from G. Schimek et al., *Acta Crystallogr., Sect. C* **1997**, *53*, 991. Copyright 1997 Munksgaard.)

Thus, four new phases ($Cs_3Ag_2Sb_3S_8$, α-Cs_2AgSbS_4, β-Cs_2AgSbS_4, and Cs_2AgAsS_4) were recently synthesized by heating Cs_2CO_3, Ag, M_2S_3 (M = As, Sb), and S_8 in $scNH_3$ for up to 6 days and <160 °C (Figure 22). The structure of $Cs_3Ag_2Sb_3S_8$ consists of condensed anionic $[Ag_2Sb_3S_8]^{3-}$ columns separated by Cs^+ cations. The remaining three structures are very similar; isolated MS_4^- (M = Sb, As) tetrahedra and their inversion generated partners are linked via silver cations to form infinite 1-D ionic columns. These isolated columns are separated by two crystallographically unique Cs atoms which interact with neighboring S atoms from the columns.[374]

Scheme 4

$$6\,NH_2^- + 3\,NO_3^- \longrightarrow 9\,OH^- + 4\,N_2 + NH_3$$

Unlike in scH_2O, the formation of oxo or hydroxo compounds in $scNH_3$ is quite rare. In one example, however, GeO_2 reacted with KNH_2 in $scNH_3$ (450 °C/6 kbar/5 days) to produce colorless crystals of $K_3GeO_3NH_2$ and of $K_3GeO_3NH_2{\cdot}KNH_2$ respectively, with tetrahedral $[GeO_3NH_2]^{3-}$ anions extensively H-bonded via either NH···O or NH···N(H) interactions.[375] Alkali metal amides have also been observed to react with T.M. nitrate complexes in $scNH_3$ by coproportionation pathways to give bimetallic hydroxides, N_2 and NH_3 (see Scheme 4). This route[376] led to ternary hydroxides of general formula $M^I_3[M^{III}(OH)_6]$ (M^I = K, Rb and M^{III} = Sc, Cr) from $scNH_3$ mixtures (523 K/3−6 kbar) within 1−3 months!

$Rb_3[Sc(OH)_6]$, $K_3[Cr(OH)_6]$, and $Rb_3[Cr(OH)_6]$ are isostructural (space group *R3c*, no. 167), while $K_3[Sc(OH)_6]$ has a unique structure (space group *R*-3*c*) compared to the others.[377] In each structure, the T.M. is essentially in six-coordinate pseudo-octahedral environments.[376,377]

In many of these examples, alkali metal carbonates have been used as precursors to alkali metal polychalcogenides complexes via disproportionation reactions. In one such reaction, stoichiometric quantities of Cs_2CO_3, SbS_3, and S_8 reacted in $scNH_3$ (160 °C/4 days) to give a new quaternary phase $Cs_5Sb_8S_{18}(HCO_3)$, in which some of the carbonate ions are retained as HCO_3^- (bicarbonate). The structure of this new material can be described as As−S ribbons linked by S_3^{2-} fragments to form layers with Cs cations and HCO_3^- anions located between. In contrast, the reaction of Cs_2CO_3 and SbS_3 in scMeOH (180 °C) led to isolation of the isotypic materials $Cs_3Sb_5X_9$ (X = S, Se).[333]

$scNH_3$ has also been employed in the synthesis of mixed organic/inorganic solid-state materials from metal−organic/organometallic precursors. Thus, $[PPh_4]_2[Sn(Se_4)_3]$ was reacted with SnSe in $scNH_3$ (135 °C/4 days), giving a mixture of $[PPh_4]_4[Sn_3Se_{11}]_2$ and $[PPh_4]_2[Sn(Se_4)(Se_6)_2]$ crystals, which could be separated manually.[378] $[PPh_4]_4[Sn_3Se_{11}]_2$ could also be obtained from a similar reaction conducted in $scCH_3CN$ without SnSe.[378] The structures of these materials consist of complicated 1-D tin selenide chains, containing mixtures of bridging mono-, di-, and tri-selenides. In all these cases, the formation of chainlike structures was attributed to the very large Ph_4P^+ cations, which stabilize one-dimensional chains. 2-D structures are also possible with the Ph_4P^+ cation, but they require sufficiently large inorganic ring systems/cavities which are not present here.

In a search for novel "Se−N" containing materials, Woollins and Kelly investigated a number of reactions involving Se_4N_4 in high pressure (but subcritical) NH_3. In one such reaction, a suspension of Se_4N_4 at ca. 50 atm reacted with *cis*-$PtCl_2(PMe_2Ph)_2$ to give the platinum complex $Pt(Se_2N_2)(PMe_2Ph)_2$.[379] It was concluded that liquid ammonia at high pressure is an excellent solvent for Se_4N_4, as NH_3 and Se_4N_4 do not appear to react with each other significantly.[379] Further, it is believed that this chemical route will

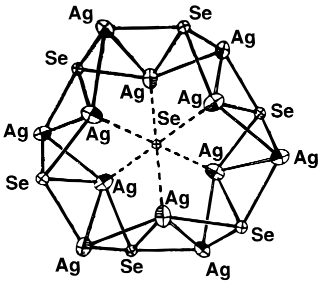


Figure 24. ORTEP view (50% probability) of the repeat ring unit in $K_2Ag_{12}Se_7$, showing labeling of the Ag and Se atoms. The rings stack in an infinite chain, forming tubes. (Reproduced from P. T. Wood et al., *J. Am. Chem. Soc.* **1992**, *114*, 9233. Copyright 1992 American Chemical Society.)

facilitate the synthesis of new inorganic phases containing Se−N chains or linkages.

E. Supercritical Amines

The results from superheated/supercritical NH_3, H_2O, and alcohols are complemented by the use of sc-amines such as ethylenediamine (en) by Kolis and co-workers for the synthesis of novel inorganic materials. Amines tend to have relatively low critical temperatures (150−400 °C), which, like $scNH_3$, permit the stabilization of kinetic phases rather than the thermodynamic phases, often formed in higher temperature regimes. In addition, the low viscosities of sc-amines make them highly suitable media for crystallizing materials. After, initial reactions aimed at the syntheses of Zintl phases,[361] Kolis and co-workers introduced transition metals into these systems resulting in the formation of unusual ternary solid-state compounds. Thus, $K_2Ag_{12}Se_7$ was prepared from the reaction of K_2Se_4, Se, and Ag powder (1:2:1 molar ratio) in sc-en at 300 °C for 6 days/2400 psi with up to ca. 80% yield.[380] The structure (single crystal X-ray diffraction) consists of stacked 18-membered anionic ring systems in which the rings interpenetrate to form a continuous column in the third dimension (see Figure 24). The sites along the axis of each column are partially occupied by Se atoms. The columns themselves are fused together, resulting in yet more channels in which the potassium cations can line up. In contrast to this stacked polymeric structure, unusual phases such as $[M_2Ag_6S_4]$ (M = Na, K), which contain closed shell bonding have also been synthesized in sc-en. These phases were prepared from mixtures of S, Ag, and M_2S (M = Na or K) in sc-en (also at 300 °C/2400 psi) for 6 days.[381] The crystal structures reveal that the Na and K compounds are isostructural, with frameworks consisting of Ag_6 octahedra (Figure 25), with four opposite faces capped by sulfur atoms. Adjacent octahedra are linked via long-range Ag···Ag interactions (Ag···Ag = 3.331 Å) on all uncapped faces. This generates a 3-D lattice with orthogonal channels linked by S atoms with large holes in the structure which accommodate the Na^+ or K^+ ions forming, in the case of K^+, six bonds to the face-capping S atoms.

Similarly, the reaction of Na_2CO_3, Cu, Sb_2S_3, and S (in a molar ratio of ca. 4:8:2:7) in sc-en for 6 days, produced orange crystals of the novel air stable 2-D polymer, Na_2CuSbS_3, in low yield. Unlike the rapid reactions in scH_2O, lengthy reaction times are often required to grow crystals at the optimal temperature for the formation of a particular phase(s). Notably, it was shown that when $Na_2S{\cdot}9H_2O$ was used as the source of Na instead of Na_2CO_3, only microcrystalline materials are obtained. Therefore, it appears that the choice of mineralizers (reagents) can have a dramatic effect on the final products. Also, changing the solvent from $scNH_3$ to sc-en can result in the formation of different phases. This can be plainly seen from syntheses of MAg_2SbS_4 and M_2AgSbS_4 (M = K, Rb) in $scNH_3$ where derivatives with a different formulation of $M_2Ag_3Sb_3S_7$ (M = K, Cs) can be obtained.[370] The As/Cu analogues of these Sb/Ag quaternary phases have also been reported.[382] For example, the ternary phase $KAsS_2$ was reacted with Cu powder in sc-en solvent to yield two new quaternary phases of $[KCu_2AsS_3]$ and of $[KCu_4AsS_4]$.[382] Since it was impossible to obtain 100% yield of any of these products, the amounts of reactants were adjusted to optimize yields of a particular product. The structure of $[KCu_2AsS_3]$ consists of a layered structure with Cu(I) ions linked by trigonal $AsS_3{}^{3-}$ anions in a complicated arrangement involving predominately Cu−S bonds and some As−Cu interactions with donation of the lone pair on the As atoms. Thus, all the As atoms are in T_d environments. Overall, this arrangement results in two parallel hexagonal mesh-like planes which are linked through the As−Cu and Cu−S−(Cu) bonds. These planes are separated by a layer of K^+ ions which are stabilized by lone pairs on S protruding from the periphery of the linked hexagonal planes. The structure of $[KCu_4AsS_4]$ is also extremely complicated[382] and consists of copper ions linked by $AsS_3{}^{3-}$ anions as well as $S_2{}^{2-}$ ions. Unlike the crystal structure of $[KCu_2AsS_3]$, the lone pairs on the As atoms are not involved in bonding to the copper ions. The overall structure gives rise to stacked (and linked) slabs containing oval holes, which are superimposed to give large channels running down the stacked layers. Two rows of K^+ cations are located in each of these oval channels and are stabilized by contacts to five neighboring S atoms. The structure also includes several short Cu−Cu interactions (ca. 2.6−3.0 Å).

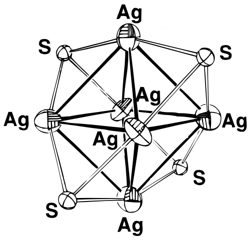


Figure 25. ORTEP view (50% probability) of the basic octahedral building block of $M_2Ag_6S_4$ (M = Na, K), showing labeling of the Ag and S atoms. (Reproduced with permission from P. T. Wood et al., *J. Chem. Soc., Chem. Commun.* **1993**, 235. Copyright 1993 Royal Society of Chemistry.)

Unlike the syntheses of heterometallic phases, the reaction of $W(CO)_6$ with K_2S_4 in sc-en for a few days (300 °C/3500 psi) leads to the thf-soluble compound $[W_4S_8(en)_4]S$ (or low yield after 10 h[116]).[383] X-ray diffraction reveals a tetrahedron of W atoms with

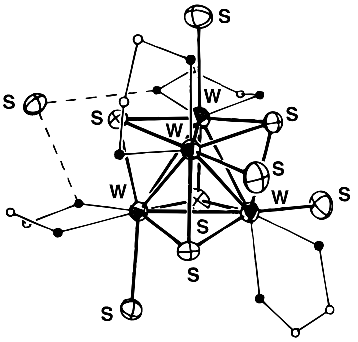


Figure 26. ORTEP plot (35% probability ellipsoids for W and S atoms) of $[W_4S_8(en)_4]S$, showing labeling of the W and S atoms and any H-bonding interactions between S atoms and en molecules. (Reproduced from P. T. Wood et al., *Inorg. Chem.* **1993**, *32*, 129. Copyright 1993 American Chemical Society.)

face-bridging S atoms and a terminal sulfide ion on each tungsten. The remaining coordination sites around the W atoms are filled by bidentate chelating en ligands (Figure 26). Terminal sulfide ions appear to be a rare structural feature but closer inspection shows that each of the lone sulfides are stabilized by three intermolecular H-bonding interactions.

Incorporation of the en ligand was also observed in the structure of $[Fe(en)_3]_2(Hg_2Te_9)$, a novel tellurometalate which contains $(Hg_2Te_9)^{4-}$ Zintl anions.[384] This black crystalline material was synthesized by the reaction of $HgCl_2$, $FeCl_2$ and Rb_2Te and Te in a 1:1:1:3 molar ratio in sc-en for 7 days at ca. 160 °C. The Zintl anions consist of five-membered Hg_2Te_3 rings in which a $(Te_3)^{2-}$ chain is terminally bonded via Te(4) and Te (7) respectively, to each Hg (1 and 3 positions) atom in the ring. Te(4) and Te(7) from the $(Te_3)^{2-}$ chains are also involved in weak interaction with their “opposite numbers” [i.e., Te(4) and Te(7)′] in symmetry-related neighboring anions to give a unique 1-D chain of $(Hg_2Te_9)^{4-}$ anions. These 1-D chains are separated by iron(II) tris(ethylenediamine) cations $[Fe(en)_3]^{2+}$.[384]

2. Organometallic Reactions in Supercritical Fluids

The study of organometallic chemistry and particularly organometallic photochemistry in SCFs has its origins in the work of Turner and co-workers in cryogenic matrixes[385−387] and in liquefied noble gas solution.[388] The impetus for Turner’s matrix isolation experiments was the desire to understand the geometries and properties of coordinatively unsaturated transition metal carbonyl fragments (e.g., $Cr(CO)_5$[385,386]), Scheme 5.

The results far exceeded the initial expectation and effectively laid the foundations for several whole fields of current research. The fragments were found to adopt structures much less symmetrical than anticipated and these geometries were elegantly rationalized by the late Jeremy Burdett[389]and by Elian and Hoffman.[390] One of the key concepts which first emerged in these matrix isolation studies was the fact that these metal centers are not “naked”. The metal forms surprisingly strong M−(noble gas) and M−(alkane) interactions, which were recently the subject of a *Chemical Review*.[391] As will be outlined below, SCFs have allowed such interactions to be studied in quite a new way.

Scheme 5

$$Cr(CO)_6 \xrightarrow{\text{UV, Ar matrix, 20 K}} Cr(CO)_5 + CO$$

Scheme 6

$$Cr(CO)_6 + N_2 \xrightarrow{\text{UV, } N_2 \text{ matrix, 20 K}} Cr(CO)_5N_2 + CO$$

Scheme 7

$$Ru(CO)_3(PPh_3)_2 + H_2 \xrightarrow{\text{UV, } H_2\text{, scXe, RT}} Ru(CO)_2(PPh_3)_2(H)_2 + CO$$

However, the characterization of metal carbonyl fragments was not the only outcome from Turner’s work. Rapidly, it became clear that reactive matrices such as N_2 could be used to generate coordinatively saturated, but potentially reactive complexes, e.g., $Cr(CO)_5(N_2)$, Scheme 6.[392]

These previously unknown complexes had an 18-electron configuration and, formally at least, might be expected to be thermally stable at temperatures greatly in excess of 20 K. Unfortunately, the design of matrix equipment at that time did not permit matrixes to be heated much in excess of 40 K without sublimation or collapse. Therefore, it was not possible to establish the thermal stability of such compounds in situ in the matrix. New techniques were required and Turner exploited the newly developed techniques for handling liquefied noble gases[393,394] to explore the behavior of dinitrogen and related compounds in fluid solution. Initial work[395] on $Cr(CO)_5(N_2)$ was quickly extended to a whole series of dinitrogen[396−398] and dihydrogen complexes.[399]

Xenon has a surprisingly short liquid range, only 4 °C between the melting and boiling points at atmospheric pressure. The low-temperature cells used to study these studies, based on Maier’s design,[393] increased the workable liquid range by operating under pressure, ≤ 20 atm, which permitted Xe to be used ≤ -30 °C. Surprisingly, many of the new complexes, e.g., $W(CO)_5(H_2)$, were thermally stable even at this relatively high temperature.[400] It was the need to study reactions at higher temperatures which prompted the first studies of organometallic reactions under supercritical conditions. Given the current interest in homogeneous catalysis in SCFs,[20,33,401] it is interesting to note that the first organometallic reaction[400] to be studied was the photochemical generation of the hydroformylation catalyst, $Ru(CO)_2(PPh_3)_2(H)_2$ (Scheme 7).

The area has developed considerably since these first experiments and a range of different properties of SCFs have been exploited for a whole variety of different chemical ends. However, organometallic reactions remain particularly important in the context of SCFs because it is one of the relatively few areas of supercritical chemistry where completely new compounds have been observed or isolated. The area was briefly reviewed three years ago[34] but, as we will show, there have been significant developments since then, particularly in the area of thermal reactions of labile organometallic complexes. For convenience, we divide the reported work into four areas (i) studies of interactions and kinetics, (ii) spectroscopic studies of dihydrogen and dinitrogen complexes, (iii) C−H activation, and (iv) photochemical and thermal reactions on a synthetic scale. Since several of the preceding sections have concerned solubility and solubilization, it is important to point out that a large number of organometallic compounds have relatively high solubility in $scCO_2$ and other SCFs with T_c near ambient temperature. Therefore, unlike most of the metal compounds discussed earlier, solubility is not always a limiting factor in the chemistry of organometallic compounds in SCFs, especially in experiments carried out on a spectroscopic scale. However, solubility can be a problem in homogeneous catalysis where the catalysts often have low solubility.[62,228]

A. Studies of Interactions and Kinetics

The work of Turner, briefly mentioned above, has left no doubt that, in solution, most[402] if not all[403] coordinatively unsaturated metal centers interact with the solvent. SCFs offer unique opportunities to study such interactions *because the density of the solvent can be varied without changing many of the other reaction parameters (T, concentration of the reactants, etc.).* In a broader context, this variable density also provides a new approach to studying the effect of solvent on reaction kinetics and intermolecular interactions (e.g., H-bonding[69]). This section describes how these processes have been monitored spectroscopically.

In general, organometallic compounds have rather broad UV−vis absorption bands which often have high extinction but which carry little structural information. By contrast, metal carbonyl compounds have very intense ν(C−O) IR bands which are narrow in solution and carry a substantial amount of information about the identity and geometry of the compound and the oxidation state of the metal center. Therefore, time-resolved IR spectroscopy, TRIR, a combination of UV−vis flash photolysis and fast (nano- or picosecond) IR spectroscopy, has proved to be a particularly powerful tool[404−406] for characterizing organometallic intermediates and excited states and for probing their reactions. Our group in Nottingham has played a significant role in developing TRIR in conventional solutions, and the presence of supercritical and TRIR techniques in the same laboratory has enabled us to apply these techniques to supercritical chemistry.

TRIR is a pump−probe experiment, involving a pulsed UV−vis laser to initiate the photochemical reaction and a second continuous IR laser to monitor the subsequent changes in IR absorption at a particular wavelength (Figure 27). Spectra are built up “point-by point” by repeating the IR monitoring at a series of different wavelengths.[404] A recent development has involved the use of “step-scan” FTIR which can monitor a wider spectroscopic range but it still requires repetitive photolysis to build up a spectrum.[407] As yet, step-scan techniques have only been applied to a very small number of supercritical systems.[408] An alternative approach involves array detectors to monitor many wavelengths simultaneously and, although it is currently extremely expensive, it promises to have many applications in supercritical systems in the future.

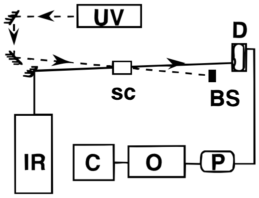


Figure 27. Schematic layout of the Nottingham TRIR spectrometer. The components are labeled as follows: BS, beam stop; C, computer; D, HgCdTe IR detector; IR, IR diode laser; O, digital storage oscilloscope; P, preamplifier; sc, supercritical cell; UV, Nd:YAG laser. (Reproduced with permission from M. W. George and M. Poliakoff, *J. Phys. Org. Chem.* **1998**, *11*, 589.)

The first papers on supercritical TRIR were largely concerned with overcoming the physical problems of carrying out experiments with high-pressure systems. One of our first experiments involved the recombination of the $Cp^*Fe(CO)_2^{\bullet}$ radical formed by photolysis of $[Cp^*Fe(CO)_2]_2$ in $scCO_2$.[409] As might have been expected, the reaction in $scCO_2$ appeared to be somewhat faster than in alkane solution.[410] $Cp^*Fe(CO)_2^{\bullet}$ is a 17-electron species, the reactions of which are relatively insensitive to the presence of residual quantities of impurities or H_2O in the $scCO_2$. By contrast, the behavior of 16-electron species, such as $Cr(CO)_5$, are very sensitive to such impurities and it is often forgotten that H_2O can be present in $scCO_2$ if the CO_2 is not dried rigorously before the experiment (conventional hydrocarbon solvents are relatively easier to dry). Most of the reported supercritical TRIR experiments have involved the use of samples in sealed cells rather than in flow systems such as are used in conventional TRIR.[405] Much effort therefore has been devoted to developing techniques to avoid the presence or build up of impurities in SCF-TRIR experiments.[108]

Interactions with Noble Gases (NG). The most comprehensive SCF-TRIR studies have involved interaction of metal centers with noble gases or CO_2. Such interactions were first studied in noble gas matrices,[386] and in liquefied noble gases by conventional FTIR spectroscopy.[411,412] Bergman and coworkers then applied TRIR to study such interactions in liquid noble gases[413] and Weitz and colleagues used TRIR in the gas phase.[414] There are several advantages of using SCF solvents for investigating these interactions:

(i) Unlike the gas phase,[406,415] UV photolysis in SCFs only causes loss of a single CO group at a time from the parent carbonyl molecule because the SCF is much denser than a gas and vibrational relaxation of the excited fragments is faster.

(ii) Unlike cryogenic liquids, there are no solubility problems with group 6 metal $M(CO)_6$ complexes; even scAr (T_c = 150.9 K) can be used successfully as a solvent for these experiments at room temperature.

(iii) scAr and scKr are very weakly coordinating solvents which permit the widest possible range of interactions to be studied because, obviously, one

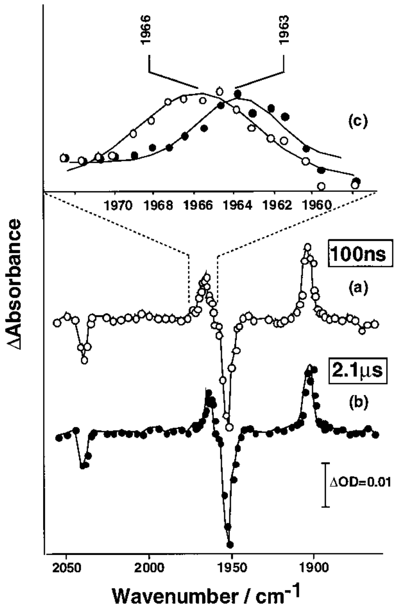


Figure 28. TRIR *difference* spectrum illustrating the use of scKr doped with Xe to reveal the presence of an M−Xe interaction. (a) spectrum ○, corresponding to 100 ns after 266 nm photolysis of $CpRe(CO)_3$ in scKr (3414 psi, 25 °C) in the presence of CO (30 psi) and Xe (50 psi) and (b) spectrum ●, 2 μs after photolysis. (c) an expanded plot of the region around 1965 cm^{-1}, showing the small but definite wavenumber shift between the spectra, corresponding to reaction $CpRe(CO)_2Kr + Xe \rightarrow CpRe(CO)_2Xe + Kr$. (Reproduced with permission from X. Z. Sun et al., *J. Am. Chem. Soc.* **1997**, *119*, 7521. Copyright 1997 American Chemical Society.)

Scheme 8

$$M(CO)_6 \xrightarrow{\text{UV, scNG, -CO}} M(CO)_5(NG) \xrightarrow{\Delta,\ +\ CO} M(CO)_6$$

cannot probe the coordination of ligands which coordinate to a metal center less strongly than do the solvent molecules themselves.

(iv) Unlike the gas phase, the ν(C−O) IR bands in SCF solution are narrow, with typical fwhm < 4 cm^{-1} in scXe. Thus, in SCF solution, one can repeat the classic experimental strategy of Perutz and Turner.[386]

This strategy was developed to distinguish between global solvent effects and stereospecific M−solvent interactions. It involves the use of a solvent, lightly doped with the interacting molecule. In such a doped solvent, specific interactions should produce small but detectable shifts in the wavenumber of ν(C−O) bands while generalized solvent effects should not. Figure 28 shows how George and co-workers used this approach in scKr doped with Xe to demonstrate the sequential interaction of Kr and Xe with a $CpRe(CO)_2$ fragment.[109]

The interaction of noble gases (NG) with the $M(CO)_5$ fragments has been systematically investigated by using TRIR to follow the reaction of $M(CO)_5(NG)$ with CO in different supercritical noble gases[108] (Scheme 8). The results are summarized in Figure 29. Assuming that the mechanism of the reaction is the same in all scNG, a longer lifetime indicates a stronger M−NG interaction. Thus, for a given metal, the strength of the interaction increases Ar < Kr < Xe, while for a given gas, the interaction follows the series Cr ≤ Mo ≤ W. Arrhenius studies on $W(CO)_5Xe$, gave the same value ca. 8.4 kcal/mol for the W−Xe bond energy as reported from liquid Xe and gas-phase experiments.[414]

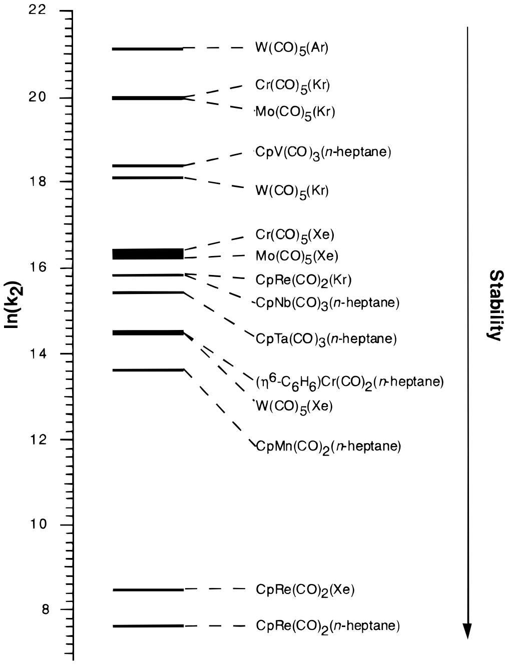


Figure 29. Schematic tabulation of the values of ln(k_2), the rate constant for the reaction with CO at 25 °C of the noble gas and *n*-heptane complexes discussed in the text. (Reproduced with permission from M. W. George et al., unpublished results, 1998.)

Figure 29 also contains data for the reactions of $CpM(CO)_2(NG)$ [M = Mn and Re] as well as for the corresponding alkane complexes. It is striking that the $CpRe(CO)_2$ moiety forms the strongest interactions and that $CpRe(CO)_2Xe$ has a remarkably long lifetime. Overall, the lifetimes in the figure, span 7 orders of magnitude. If, by chemical modification of the other ligands, the lifetimes of $CpRe(CO)_2Xe$ and $CpRe(CO)_2$(alkane) could be extended further by only 2 orders of magnitude, noble gas, and alkane compounds could probably be isolated.

Interactions with CO_2. A similar TRIR approach has been applied to the study of $M-CO_2$ interactions.[108] The most detailed study involves $W(CO)_5(CO_2)$ and the effect of the solvent density on the rate of its reaction with CO [to regenerate $W(CO)_6$].[108] There has been continuing controversy whether such reactions are primarily associative or dissociative. Figure 30 shows how increasing the density of the $scCO_2$ increases the lifetime of $W(CO)_5(CO_2)$ in a way quite consistent with a largely dissociative mechanism. Clearly, this approach could be extended to other SCFs and metal centers. Interestingly, Arrhenius measurements show that the strengths of the $W-CO_2$ and W−Xe bonds are almost identical.[108]

The photochemistry of $[CpMo(CO)_3]_2$ has been studied by TRIR both in *n*-heptane[416] and in $scCO_2$. A comparison of these two solvents reveals significant broadening of the lower wavenumber ν(C−O) band of $CpMo(CO)_3$ in $scCO_2$ compared to *n*-heptane. This band is assigned to the *e* mode of the $Mo(CO)_3$ moiety, which is almost split into two resolvable components

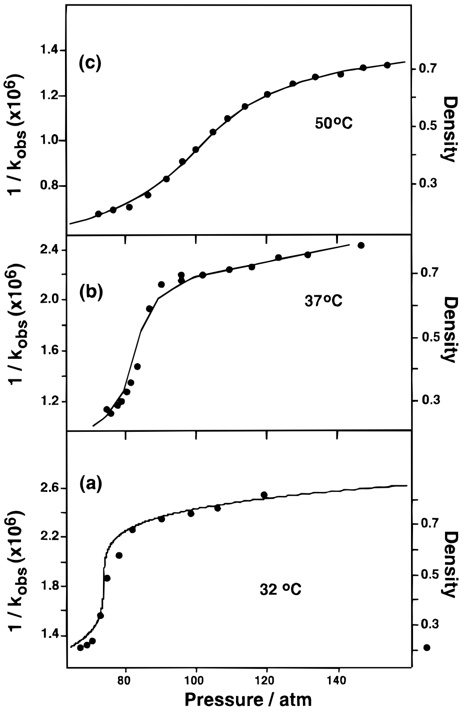


Figure 30. Plots showing the effect of pressure on the lifetime of $W(CO)_5(CO_2)$ in $scCO_2$ at three different temperatures. The data points indicate the lifetimes ($1/k_{obs}$ for the reaction $W(CO)_5(CO_2) + CO \rightarrow W(CO)_6 + CO_2$), measured experimentally by SCF-TRIR. The solid line shows the dependence of density on pressure for $scCO_2$ at the appropriate temperature. (Adapted with permission from X. Z. Sun et al., *J. Am. Chem. Soc.* **1997**, *119*, 7521.)

in $scCO_2$, consistent with an interaction with CO_2 lowering the local symmetry from C_{3v} to C_s.[417]

Interaction with CO_2 also produces very striking differences between the ν(C−O) bands of $CpMn(CO)_2(CO_2)$ and its Re analogue.[418] The IR spectrum of $CpMn(CO)_2(CO_2)$ is similar to that of other $CpMn(CO)_2L$ complexes [e.g., $CpMn(CO)_2(N_2)$[140]]. By contrast, the ν(C−O) bands of the Re compound are shifted *up in wavenumber* relative to the *e* mode of $CpRe(CO)_3$. Such an upward shift is indicative of oxidation of the metal center, possibly due to coordination of CO_2 via the C atom (for more details of coordinated CO_2, see the excellent reviews of Gibson[419] and Leitner[420]). Whatever its origin, the oxidation is reminiscent of that observed during the photochemical reaction of $CpRe(CO)_3$ with H_2 in scXe (see below).[239,435]

Kinetic Comparisons with Conventional Solvents. There is obvious and continuing interest in how reactions in SCFs differ from those in conventional solvents. TRIR clearly has the potential to quantify such differences, if any. The recombination rates of $CpMo(CO)_3$ radicals to form *trans*- and *gauche*-$[CpMo(CO)_3]_2$ have been measured by TRIR in *n*-heptane[416] and in $scCO_2$ at different solvent densities.[422,423] To calculate the second-order rate constant from the raw TRIR data requires a knowledge of the IR extinction coefficient, ϵ, of $CpMo(CO)_3$. Using a value derived from *n*-heptane and modified for the change in shape of the ν(C−O) band between *n*-heptane and $scCO_2$, the second-order rate constant apparently increased to a value *greater than diffusion control*, originally interpreted as evidence of "solvent clustering".[422] However, a more detailed investigation has shown that there is a pressure-dependent wavenumber shift in the ν(C−O) maximum of the $CpMo(CO)_3$ radical and that the second- order rate constant is diffusion controlled over the entire pressure range studied.[423]

By contrast, interpreting the relative rates of reactions of 16-electron intermediates between conventional and supercritical solvents is more complicated. Thus, TRIR has been used to compare the rates of reaction of $Cr(CO)_5$(solvent) with H_2 in $scCO_2$ and in *n*-heptane.[424] After adjustment of the raw data to allow for different pressures of H_2, it is found that the rate in $scCO_2$ is ca. ×16 that in *n*-heptane. This acceleration may be due in part to the miscibility of H_2 with $scCO_2$. However, without detailed evidence that the reaction has the same mechanism in the two solvents, it is difficult to estimate whether the difference in rate reflects any differences in the strength of the $M-CO_2$ and M−(*n*-heptane) interaction.

Eyring and co-workers have used UV−vis flash photolysis to compare the reaction of $W(CO)_6$ with L−L (L−L = 1,10-phenanthroline[425] and 2,2′-bipyridine[426]) in supercritical and liquid solution. The reaction initially generates $(CO)_5WL-L$ which then undergoes thermal loss of CO and ring closure to form $W(CO)_4(L-L)$. The ring closure is highly sensitive to solvent effects and therefore provides a good probe of the effect of the supercritical medium. For 1,10-phenanthroline,[425] the reaction is relatively fast and the volume of activation, $\Delta V^{\ddagger}$, changes from +36 cm^3/mol in liquid CO_2 to a staggering +7000 cm^3/mol in $scCO_2$ close to T_c. The change was attributed to the very high compressibility of CO_2 near T_c. Experiments with 2,2′-bipyridine were more difficult because of the low solubility of $(CO)_5W(L-L)$ in $scCO_2$. Indeed, we show later how the low solubility of $W(CO)_4(pyridine)_2$ in $scCO_2$ can be exploited for synthetic chemistry. Therefore, reactions involving 2,2′-bipyridine were carried out in $scCO_2$/benzene mixtures.[426] The ring closure is really quite slow under these conditions, taking nearly 200 s to reach completion. The changes in $\Delta V^{\ddagger}$ were less dramatic than with 1,10-phenathroline but there was a strong temperature dependence with a maximum close to T_c.

FTIR Spectroscopic Studies of H-Bonded Interactions. Interactions with the solvent are not the only type of interactions which can be affected by the density of the supercritical solvent and there has been a limited amount of SCF work on intermolecular H-bonding to uncharged metal centers.[427] Such H-bonding only occurs with strong acceptor centers such as $Cp^*Ir(CO)_2$ and good donors, e.g., perfluorinated alcohols, which have high acidity. In general, H-bonding is favored by decreasing solvent density[69] and the same has been found for bonding to metal centers.[427] Thus, when $Cp^*Ir(CO)_2$ and $(CF_3)_2CHOH$ were dissolved in scC_2H_6, a pressure change from 680 psi ($\rho = 0.12$ g/mL) to 3050 psi ($\rho = 0.41$ g/mL) shifted the equilibrium from favoring the H-bonded adduct

$Cp(CO)_2Ir\cdots HOR_F$ to favoring free $CpIr(CO)_2$ and R_FOH.[427]

This effect has implications for chemical reactions carried out in $scCHF_3$ where there is a possibility of H-bonding by CHF_3 to susceptible metal centers. Changes in solvent density could affect the degree of H-bonding and hence affect the chemistry. Kazarian and co-workers also described an unusual experiment[427] where a mixture of $Cp^*Ir(CO)_2$ and $(CF_3)_2CHOH$ were placed in a cell which was pressurized with scXe. The IR spectra showed the immediate formation of $[Cp^*Ir(CO)_2H]^+$ followed by much slower deprotonation to form the H-bonded adduct $Cp^*(CO)_2Ir\cdots HOR_F$. ($[Cp^*Ir(CO)_2H]^+$ could also be generated by the reaction of $Cp^*Ir(CO)_2$ with HCl in scXe, one of the rare cases where simple ionic compounds have been dissolved in a nonpolar SCF)[428] This deprotonation was rationalized as being an artifact due to the density of $(CF_3)_2CHOH$ being *less* than that of scXe; immediately after pressurization, the cell would have contained an emulsion of $(CF_3)_2CHOH$ in scXe with the protonated metal compound within the droplets of $(CF_3)_2CHOH$, which would have then dissolved slowly in scXe to give a homogeneous and much less acidic solution. This rather esoteric experiment serves as a warning. In many supercritical mixtures, there is a possibility that the density of the supercritical phase can become *higher* than that of the other phases in the system.[40]

It is beginning to become clear that H-bonding can also have an influence on homogeneous catalysis in SCF solution. For example, Jessop[429] and co-workers[430] have shown that addition of a fluorinated alcohol to $scCO_2$ increased both conversion and enantioselectivity. Furthermore, Bach and Cole-Hamilton reported[431] that the addition of a fluoro alcohol increased the rates of catalytic hydroformylation in $scCO_2$.

B. Dihydrogen and Dinitrogen Compounds

Dihydrogen compounds have been a source of interest ever since their discovery by Kubas.[432] Poliakoff and co-workers[388,399,400,433] have shown how a wide range of labile dihydrogen complexes can be generated photochemically in liquid Xe (LXe) solution by the general route, Scheme 9.

Because liquid Xe is totally transparent to IR, this work provided a wealth of IR data about these compounds, particularly for the ν(H−H) IR bands of the η^2-H_2 ligand, which lie in a region ca. 3000 cm^{-1}, often obscured by the absorption bands of conventional solvents. Even in liquid Xe solution at −90 °C, these bands are quite broad,[388] ca. 40 cm^{-1}.

As shown in Scheme 7, the first organometallic reaction in a SCF involved $Ru(CO)_3(PPh_3)_2$ and H_2 in scXe.[400] The immediate rationale for carrying out the reaction in *supercritical* rather than *liquid* Xe was the poor solubility of $Ru(CO)_3(PPh_3)_2$ in the liquid at lower temperature. However, the experiment did demonstrate how the high concentration of H_2 in scXe enabled $Ru(CO)_2(PPh_3)_2(H_2)$ to be generated at much lower temperatures than in the thermal reaction. This high concentration originates in the complete miscibility of the SCF and H_2, which has now become a chemically widely exploited property of SCFs.[33,45,123,141,142,237,239,401,434] The high concentration of H_2 also allows the lifetimes of labile dihydrogen compounds to be extended in SCF solution. Thus, $W(CO)_5(H_2)$ was sufficiently stabilized in scXe for the ν(H−H) IR band of its η^2-H_2 ligand to be recorded at *room temperature*.[388,400] Surprisingly the line width is identical to that in liquid Xe despite the much higher temperature and much lower solvent density and viscosity in scXe. Why the line width is independent of temperature still remains to be explained.

Scheme 9

$$L_nM(CO)_x + H_2 \xrightarrow{\text{UV, LXe, 180 - 240 K}} L_nM(CO)_{x-1}(H_2) + CO$$

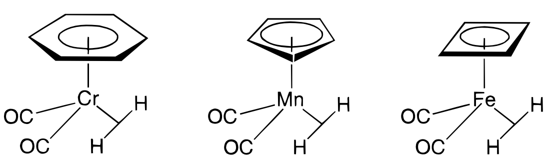


Figure 31. Illustration of some of the half-sandwich complexes, $(C_nH_n)M(CO)_2(\eta^2\text{-}H_2)$, generated photochemically by reaction of H_2 with the corresponding tricarbonyl compound in SCF solution. See Table 4 for a complete list of compounds generated in this way.

The supercritical experiments then developed into a systematic study[239,435] involving the generation of dihydrogen complexes of groups 6−8. Table 4 summarizes the range of compounds observed. The most interesting were the dihydrogen derivatives of the piano-stool $(C_nH_n)M(CO)_3$ complexes,[435] which showed greater thermal stability than the $M(CO)_5(H_2)$ complexes (Figure 31). This stability was not entirely unexpected because the $(C_nH_n)M(CO)_2$ moiety was already known to form extremely stable dinitrogen complexes.[436] Attempts have been made to quantify the strength of the M−H_2 bond dissociation energies in such compounds.[435,437] The first approach involved an Arrhenius analysis of the rate of reaction of $(toluene)Cr(CO)_2(H_2)$ with CO in scXe, exploiting the miscibility of H_2, CO, and scXe to keep the relative concentrations of gases constant as the temperature was varied.[435,438] The activation energy 73 ± 2 kJ mol^{-1} was close to the M−H_2 bond dissociation energies, later measured for $Cr(CO)_5(H_2)$[439] and $(C_6H_6)Cr(CO)_2(H_2)$[437] using high-pressure photoacoustic calorimetry (PAC) in *n*-heptane solution. PAC is an appealingly simple technique in which the energy released in a reaction is measured acoustically.[440,441] However, it is not easy to apply to high-pressure systems[107,437,439,442] and, so far at least, has proved extremely difficult to use on supercritical solutions.[443]

$CpMn(CO)_2(H_2)$, generated from $CpMn(CO)_3$, was the first reported dihydrogen complex of a group 7 metal[239] and, as explained below, it proved sufficiently stable to be isolated on a preparative scale. $(C_4H_4)Fe(CO)_2(H_2)$ was found to be thermally relatively stable even though it contains both dihydrogen and diene ligands.[435] The corresponding butadiene complex could not be generated even in liquid Xe at low temperature, presumably because of facile transfer of H_2 to the diene ligand. Unlike the experiments[400] on $M(CO)_5(H_2)$, there was no direct spectro-

Table 4. Organometallic Alkene (A), Dihydrogen/Hydride (H_2/H), Dinitrogen (N_2), and Related (R) Complexes which Have Been Synthesized in SCF Solution[a]

l	group 5	group 6	group 7	group 8	group 9
A	$CpNb(CO)_3(C_2H_4)$[449] $CpTa(CO)_3(C_2H_4)$[449]	**$Cr(CO)_5(C_2H_4)$**[45,110] ***trans*-$Cr(CO)_4(C_2H_4)_2$**[45,110] **$Cr(CO)_5$(propene)**[461]	**$CpMn(CO)_2(C_2H_4)$**[480] **$Cp'Mn(CO)_2(C_2H_4)$**[122,424] **$Cp^*Mn(CO)_2(C_2H_4)$**[140] **$CpMn(CO)_2$(propene)**[461] **$Cp^*Mn(CO)_2$(propene)**[461] $Cp^*Re(CO)_2(C_2H_4)$[444] $Cp^*Re(CO)(C_2H_4)_2$[444]		**$Cp^*Ir(CO)(\eta^2\text{-}C_2H_4)$**[111]
H_2/H		$(C_6H_6)Cr(CO)_2(\eta^2\text{-}H_2)$[435] $(C_6H_5Me)Cr(CO)_2(\eta^2\text{-}H_2)$[435] $W(CO)_5(\eta^2\text{-}H_2)$[388,400]	**$CpMn(CO)_2(\eta^2\text{-}H_2)$**[45,140,239,435] **$Cp'Mn(CO)_2(\eta^2\text{-}H_2)$**[45] **$Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$**[140,435] *cis*-$CpRe(CO)_2(H)_2$[239] *trans*-$CpRe(CO)_2(H)_2$[239,444] *trans*-$Cp^*Re(CO)_2(H)_2$[435]	$(C_4H_4)Fe(CO)_2(\eta^2\text{-}H_2)$[435] $Ru(CO)_2(PPh_3)_2(H)_2$[400]	$Cp^*Ir(CO)(H)(CH_3)$[111] **$Cp^*Ir(CO)(H)(C_2H_3)$**[111] **$Cp^*Ir(CO)(H)(C_2H_5)$**[111,114] $Cp^*Ir(CO)(H)_2$[111,114] $[Cp^*Ir(CO)_2H]^+[Cl]^-$[428] $[Cp^*Ir(CO)_2H]^+[(CF_3)_2CHO]^-$[427]
N_2		$(C_6H_6)Cr(CO)_2(N_2)$[435] $(C_6H_5Me)Cr(CO)_2(N_2)$[435] $(C_6H_3Me_3)Cr(CO)_2(N_2)$ $(C_6H_3Me_3)Cr(CO)(N_2)_2$ $(C_6H_3Me_3)Cr(N_2)_3$	$CpMn(CO)_2(N_2)$[140,435] **$Cp'Mn(CO)_2(N_2)$**[83] **$Cp^*Mn(CO)_2(N_2)$**[83,140,435] **$Cp^*Mn(CO)(N_2)_2$**[83,435] $Cp^*Mn(N_2)_3$[83,435] $Cp'Mn(CO)(PMe_{3-x}Ph_x)(N_2)$ $\{x = 0-2\}$[83] **$CpRe(CO)_2(N_2)$**[435,446] **$Cp^*Re(CO)_2(N_2)$**[435] $CpRe(CO)(N_2)_2$[435,446] $Cp^*Re(CO)(N_2)_2$[435] $CpRe(N_2)_3$[435,446] $Cp^*Re(N_2)_3$[435]	$(C_4H_4)Fe(CO)_2(N_2)$[435] $(C_4H_4)Fe(CO)(N_2)_2$[435] $(C_4H_4)Fe(N_2)_3$[435]	
R			$CpMn(CO)_2(N_2O)$[105] **$Cp^*_2Mn_2(\mu\text{-}CO)_3$**[140] **$Cp_2Re_2(\mu\text{-}CO)(CO)_4$**[447]		

[a] Those shown in bold have been recovered as solid materials, not necessarily pure). L = ligand/adduct.

scopic evidence for the presence of η^2-H_2 in any of these studies. Nevertheless, there was strong evidence that these compounds were indeed dihydrogen complexes and these conclusions were supported when some the compounds were isolated and NMR data became available.[45,122] The principal IR spectroscopic evidence was (i) the compound could not be generated in the absence of H_2, (ii) the ν(C−O) bands were similar in wavenumber and relative intensity to those of the corresponding dinitrogen complexes, (iii) the ν(C−O) bands showed small but reproducible shifts when prepared using D_2 rather than H_2, and (iv) the compound reacted thermally with excess N_2 (introduced into the cell after most of the H_2 had been vented) to give the corresponding dinitrogen complex. The formation of dihydrogen complexes has been likened to the arrested oxidative addition of R_3Si−H compounds to a metal center and we show below that η^2-H_2 and η^2-H−SiR_3 ligands are easily exchanged in thermal reactions under supercritical conditions (Figure 32).

Not all of the reactions with H_2 led to dihydrogen compounds. In particular, $CpRe(CO)_3$ reacted to give initially *cis*-$CpRe(CO)_2(H)_2$ and then the thermally more stable trans isomer.[239] More recently, the trans isomer has also been detected[444] by NMR in $scCO_2$. Neither of these compounds were new[445] but they had not previously been made by this route. Presumably the Re center forms a dihydride rather than a dihydrogen complex because of the lower ionization energy and greater electron density on the Re than Mn. Attempts to increase the electron density on the Mn center by changing substitutents on the Cp ring or replacing CO groups by σ donors[83] (e.g., PMe_3) failed to lead to any dihydride complexes of Mn. However, the electron rich compounds $CpIr(CO)_2$ and $Cp^*Ir(CO)_2$ both reacted with H_2 to give dihydrides.[111,114]

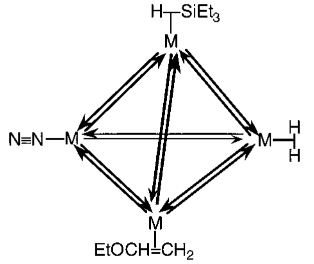


Figure 32. Schematic representation of the facile interchange of the ligands in $Cp^*Mn(CO)_2L$ complexes in $scCO_2$ solution. In this scheme “M” represents the $Cp^*Mn(CO)_2$ moiety. (Reproduced with permission from P. D. Lee et al., *Organometallics* **1998**, *20,* 524. Copyright 1998 American Chemical Society.)

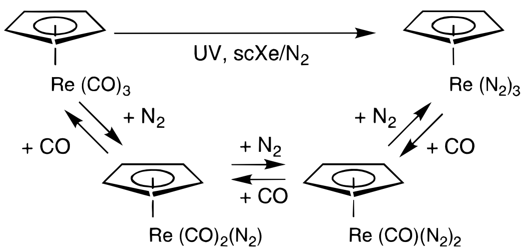
Scheme 10

$$L_nM(CO)_x + N_2 \xrightarrow{UV,\ SCF,\ RT} L_nM(CO)_{x-1}(N_2) + CO$$

Given their reaction with H_2, the photochemical reaction of carbonyl compounds with N_2 in SCFs is to be expected, Scheme 10. What is surprising is the fact that prolonged photolysis of some compounds leads to substitution of *two or even three* CO groups by dinitrogen. Such multiple substitution had previously been observed in low temperature matrices and occasionally in cryogenic noble gas solution.[433] However, the reaction of $CpRe(CO)_3$ with N_2, Scheme 11, was the first observation of multiple substitution at room temperature.[446]

Such reactions are unusual but now there is some understanding of the factors which determine which molecules undergo multiple substitution. Overall, increasing electron density appears to favor multiple

Scheme 11



substitution.[435] Thus, it occurs with $Cp^*Mn(CO)_3$ but not with $CpMn(CO)_3$, with $(C_6H_3Me_3)Cr(CO)_3$ but not with the C_6H_6 analogue. However both $CpRe(CO)_3$ and $(C_4H_4)Fe(CO)_3$ show multiple substitution even in the absence of Me substituents on the rings. Addition of a phosphine ligand does not promote multiple substitution in $CpMn(CO)_2(PR_3)$ complexes,[83] probably because, surprisingly, the presence of the PR_3 appears to destabilize thermally the monosubstituted compound, $CpMn(CO)(PR_3)(N_2)$, compared to $CpMn(CO)_2(N_2)$. The IR spectroscopy of these compounds is interesting because there appears to be a general effect by which the bands of a series of $CpM(CO)_{3-x}(N_2)_x$ compounds show near coincidences both in the ν(N−N) and ν(C−O) regions, overlaps which can be rationalized on a relatively simple force constant model.[83]

The reaction of $CpRe(CO)_3$ with N_2 has been studied in the most detail.[44,435,447] It never proceeds to completion; mixtures of the three $CpRe(CO)_{3-x}(N_2)_x$ species are always obtained. Initially, it was supposed that the reaction was limited by the build up of photoejected CO in the solution but the reaction is unaffected by addition of modest amounts of CO to the solution and almost identical results are obtained whether $Cp^*Re(CO)_2(N_2)$ or $Cp^*Re(CO)_3$ are used as starting compounds.[44] The reaction of $CpRe(CO)_3$ proceeds much better in scXe or scC_2H_6 than in $scCO_2$, which appears to suppress the substitution of the second and third CO groups by N_2. Possibly, this is connected with the transient oxidation of the Re center[418] which has been revealed by TRIR in $scCO_2$ (see above). Prolonged photolysis in scC_2H_6 leads to precipitation of dinuclear species and crystals of $Cp_2Re_2(\mu\text{-}CO)(CO)_4$ have been isolated from the reaction mixture.[447]

Photolysis of metal carbonyls in scC_2H_4 leads to substitution of CO by C_2H_4. Unlike N_2, C_2H_4 is sufficiently close to its critical point at room temperature to act as both solvent and reactant.[105,110,122] Howdle and Poliakoff showed[105] that photolysis of $Cr(CO)_6$ in scC_2H_4 led to sequential formation of $Cr(CO)_5(C_2H_4)$ and $Cr(CO)_4(C_2H_4)_2$. Linehan and colleagues[122] used this approach to generate and record the ^1H NMR spectrum of $Cp'Mn(CO)_2(C_2H_4)$ by in situ photolysis of $Cp'Mn(CO)_3$ in scC_2H_4, but it is still not clear why they obtained very poor conversions to $Cp'Mn(CO)_2(C_2H_4)$ compared to those obtained in other experiments.[140,424] Indeed, as described below, $Cp^*Mn(CO)_2(C_2H_4)$ can be prepared *quantitatively* by a thermal route.[424] Recently, the NMR experiments[444,448] were extended to the photolysis of $Cp^*Re(CO)_3$ in scC_2H_4. Interestingly, there was formation of not only the monoethene complex but also of $Cp^*Re(CO)(C_2H_4)_2$, in a manner reminiscent of the multiple substitution[446] of N_2 (see above). Very recently, Linehan et al. have extended their work to the photochemical synthesis of a new compound, $CpNb(CO)_3(C_2H_4)$ in scC_2H_4 and have studied the kinetics of its decay.[449] They suggested that loss of C_2H_4 is dissociative and that, therefore, the activation energy, 98 ± 2 kJ mol^{-1} is an indication of the $M-(C_2H_4)$ bond dissociation energy. The corresponding Ta compound is considerably more labile, presumably as a result of a weaker M−(alkene) bond. Below, we describe how reactions in scC_2H_4 can be carried out on a preparative scale to isolate new ethene complexes.[45,110,111,140]

Supercritical N_2O can also be used as a reactive solvent and spectroscopic data have been reported[105] for $CpMn(CO)_2(N_2O)$. The compound slowly decays in solution to form $CpMn(CO)_2(N_2)$, although it was never established whether this was due to the chemical reduction of the coordinated N_2O or to a reaction with N_2 which might have been present as an impurity in the scN_2O. It is important to reiterate the potential explosion dangers[98] associated with experiments in scN_2O.

C. C–H Activation in Supercritical Fluids

The selective activation of C−H bonds remains a major goal in contemporary organometallic chemistry. SCFs provide a range of unusual solvents in which to carry out such reactions. The solvents can either be chemically inert ($scCO_2$, scXe, etc.) or the reactions can be carried out “solvent-free” using the supercritical alkane ($scCH_4$, scC_2H_6, etc.) as both reactant and solvent. This is a valuable contribution because of the difficulty of finding suitably inert solvents for the activation of light alkanes. All of the published supercritical C−H activation experiments[111,113,114] have been carried out with $Cp^*Ir(CO)_2$, the reactions of which were first reported by Graham and co-workers.[450−452]

CH_4 has a critical temperature well below ambient (−83.9 °C). Therefore, comparatively high pressures (ca. 3500 psi) are required to obtain $scCH_4$ at room temperature with a density close to $\rho_c = 0.162$ gm/mL. Nevertheless, Figure 33 shows how $scCH_4$ can be used successfully as a solvent for C−H activation.[111] The solubility of $Cp^*Ir(CO)_2$ is relatively low even under these conditions but it is sufficient for the reaction to be followed spectroscopically. The same reaction can be carried[114] out in $scCO_2$ doped with CH_4 but the overall conversion appears to be higher in $scCH_4$.

Relatively low pressures are required to carry out reactions in scC_2H_6 but the photochemical C−H activation is extremely slow. Addition of H_2 to the reaction mixture causes a dramatic acceleration;[114] the reaction proceeds via the dihydride, $Cp^*Ir(CO)(H)_2$ (see Scheme 12).

Careful spectroscopic experiments[111] using mixtures of D_2 and scC_2H_6 showed that the hydride ligand in $Cp^*Ir(CO)(H)Et$ is derived from the C_2H_6 and not from the free H_2 (or D_2) in the solution. The precise photochemical role of H_2 has never been completely clarified. It is possible that the intermedi-

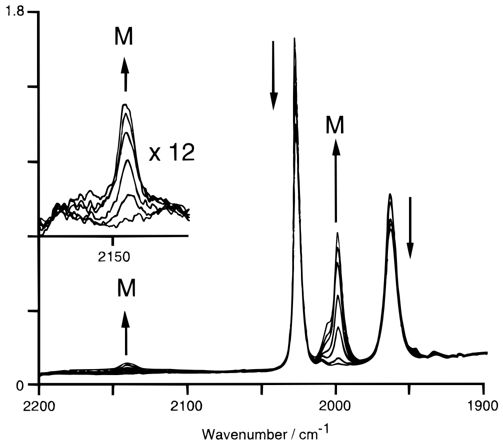
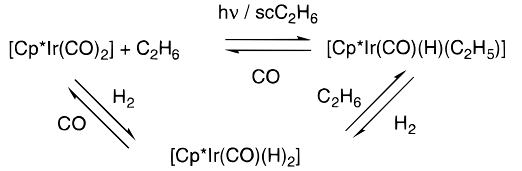
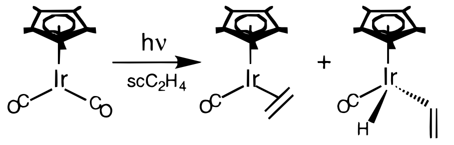


Figure 33. C−H activation of CH_4 in $scCH_4$ as shown by IR spectra, recorded at 5-min intervals, during the UV photolysis (>300 nm, 30 min total irradiation time) of $Cp^*Ir(CO)_2$ in $scCH_4$ at 270 atm pressure and 295 K. The bands of $Cp^*Ir(CO)_2$ are marked ↓, those of Cp*Ir(CO)(H)-Me are labeled M. The ν(Ir−H) region is shown as an inset with an expanded absorbance scale. Note that the growth of the band of Cp*Ir(CO)(H)Me is only partly matched by a decrease in intensity of the bands of $Cp^*Ir(CO)_2$ because this experiment was performed with a saturated solution of $Cp^*Ir(CO)_2$ containing excess solid and more material dissolved during the irradiation. (Reproduced with permission from J. A. Banister et al., *Organometallics* **1996**, *15*, 1804. Copyright 1996 American Chemical Society).

Scheme 12



Scheme 13



ate Cp*Ir(CO) is generated in different electronic states depending on whether it is formed from Cp*Ir-$(CO)_2$ or $Cp^*Ir(CO)(H_2)$. Alternatively, H_2 may have a more prosaic role in increasing the rate of photolysis because of some fortuitous improvement in overlap between the output of the UV lamps and the absorption spectrum of $Cp^*Ir(CO)(H_2)$. By contrast, C−H activation of C_2H_6 is largely suppressed in $scCHF_3$, even though reaction between $Cp^*Ir(CO)_2$ and H_2 occurs under these conditions. It is possible that C−H activation is suppressed by H-bonding of CHF_3 to the Ir center. Similar photolysis experiments[111] in scC_2H_4 led to both C−H activation of the C_2H_4 and to substitution of CO, Scheme 13. Both compounds were identified by IR and NMR.

The isolation of the products of C−H activation from conventional solvents often presents difficulties. By contrast, recovering them from supercritical solution (e.g., for NMR analysis) can be achieved relatively simply by RESS. In RESS, the compound is separated from the fluid without the use of vacuum, and the cooling effect of the expansion probably also helps to stabilize the compound while the solid is being formed. Indeed, one of the most important long-term results of these C−H activation experiments has probably been the development of effective methods for manipulating and recovering small quantities of organometallic compounds from supercritical solution. Below, we show how these techniques have been scaled-up for synthetic organometallic chemistry.

Attempts to activate the C−H bonds of polyethylene (PE) have led to a whole series of experiments involving the use of $scCO_2$ to impregnate organometallic compounds into polymers and other porous media. The immediate problem with the activation of PE was how to introduce $Cp^*Ir(CO)_2$ into PE without the use of solvents which could interfere with the subsequent photochemical reactions and it was solved by use of $scCO_2$. It was found that $scCO_2$ could impregnate organometallic compounds into the PE without leaving residues.[67,453] UV irradiation of Cp*Ir-$(CO)_2$ impregnated into PE in this way promoted significant activation of the C−H bonds[113] and formation of polymer-bound Cp*Ir(CO)(H)(polymer) which, unlike the unreacted $Cp^*Ir(CO)_2$, could not be extracted from the PE by $scCO_2$. Poliakoff and colleagues then developed this approach by investigating a number of other reactions involving organometallic compounds impregnated into PE. It was found that the photolysis of $CpMn(CO)_3$ in PE leads to formation of $CpMn(CO)_2(\eta^2\text{-C=C})_{polymer}$, the ν(C−O) frequencies of which were dependent on the nature of the residual unsaturation in the particular sample of PE (i.e., pendant, terminal, or in-chain C=C bonds).[112] This dependence of the frequencies was confirmed by a novel use of alkene model compounds,[112] allowing the photolysis of $CpMn(CO)_3$ to be used as an unusual but highly sensitive analytical probe of unsaturation in PE. UV photolysis of $W(CO)_6$ in PE can lead to isomerization of the C=C double bonds,[454,455] an interesting variation of catalytic olefin isomerization. The method can be used to prepare clean samples of isomerized PE because the $W(CO)_6$ can be completely extracted by $scCO_2$ after the isomerization has taken place. UV photolysis of $Fe(CO)_5$ in PE under a pressure of H_2 leads to hydrogenation of up to 80% of the C=C bonds,[454,455] while photolysis under an atmosphere of O_2 generates an oxide, most probably Fe_2O_3 within the PE matrix. All of these metal−carbonyl impregnation experiments had their origins in an unpublished experiment[456] where ferrocene was impregnated into silicone rubber.

In addition, the very careful IR study[59] by Kazarian et al. into the interaction of CO_2 with polymers provides some understanding of the factors influencing the impregnation and swelling of polymers by $scCO_2$. Recently, Kazarian and co-workers have independently impregnated ferrocene into poly(methyl methacrylate), a glassy polymer.[95] Impregnation of organometallics into PE has also been used as the basis of a new approach to matrix isolation, where PE matrixes are held in a high-pressure/low-temperature cell.[457,458] Using this technique, it was shown[286] that H-bonding by fluorinated alcohols suppressed the C−H activation of PE by Cp*Ir(CO)$_2$. This observation supports the possibility that H-bonding is the reason why C−H activation of C_2H_6 does not occur in scCHF_3, see above.

D. Synthetic Organometallic Chemistry in SCF Solution

In this section, we describe the development of flow reactors for laboratory-scale preparative reactions, particularly exploiting the use of RESS for recovery of otherwise highly labile products.[45,110,140,424] Since such compounds either decompose when dissolved in conventional solvents or cannot easily be recovered from them, the overall strategy must be to prepare the compounds in as pure a state as possible so that, ideally, no further workup or purification is necessary.

Apart from any safety considerations, the scale-up of supercritical reactions presents a number of unusual problems. Most substrates have critical temperatures far higher than that of CO_2 and so, to maintain supercritical conditions, reactions must either be run in very dilute solution or at high temperatures. However, dilute solutions prevent the processing of large quantities of material unless the reaction vessel is extremely large. These problems can be minimized, if not removed completely, by use of a continuous flow reactor. Equally, the gaslike nature of SCFs (low viscosity, good heat transfer, etc.) readily lends itself to flow reactors.

Reactions in scC_2H_4 and Propene. The prototype reactor [110] was designed for reactions in scC_2H_4, with the fluid acting both as solvent and as one of the reactants, Figure 34. A solid organometallic compound is dissolved in scC_2H_4, converted into product by UV irradiation, monitored by IR and finally precipitated by RESS as a fine powder, all as a single continuous process. Once the fluid pump is running, reactant is converted into product automatically, while the operator uses IR monitoring to optimize the reaction conditions.[45,110] The first major success was to isolate $Cr(CO)_5(C_2H_4)$ >80% purity directly from the reaction of $Cr(CO)_6$ and scC_2H_4 at a rate of ca. 40 mg h^{-1}. Although $Cr(CO)_5(C_2H_4)$ was already known in solution[459] previous attempts to isolate it had been thwarted by the lability of the C_2H_4; removal of the solvent also removed the ligand. RESS precipitation from scC_2H_4 is more rapid than conventional solvent evaporation, it does not involve heating of the solution and it maintains a high concentration of free ligand, C_2H_4, right up to the moment at which the solid is formed. Once precipitated, $Cr(CO)_5(C_2H_4)$ appeared to be moderately stable in the solid state. The relative intensities of the ν(C−O) IR bands of $Cr(CO)_5(C_2H_4)$ suggested that the C_2H_4 group is aligned with a trans pair of CO groups as found by Grevels and co-workers in the crystal structure of the related compound[459] $Cr(CO)_4(C_2H_4)_2$.

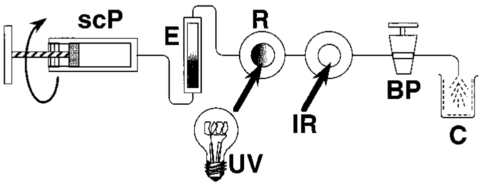


Figure 34. Schematic view of the flow reactor used for the isolation[110] of $Cr(CO)_5(C_2H_4)$. The components are labeled as follows: *scP*, the scC_2H_4 pump, either manually operated or pneumatically controlled; E, reservoir for the solid $Cr(CO)_6$; R, the photolysis chamber (0.5 mL volume) for converting reactant to product; UV, photolysis lamp; IR, IR cell for monitoring the reaction; BP, back-pressure regulator to release the pressure in a controlled manner and to precipitate the product; C, a container to collect the product. Similar apparatus has now been used to isolate $Cr(CO)_5$(propene).[461] (Reproduced with permission from J. A. Banister et al., *J. Chem. Soc., Chem. Commun.* **1993**, 1814. Copyright 1993 Royal Society of Chemistry.)

An unusual combination of techniques[460] has involved incorporating a high pressure/low-temperature cell[457] into the scC_2H_4 reactor. In this way, a PE film could be impregnated with $Cr(CO)_5(C_2H_4)$, freshly generated in the flow reactor. Once the PE had been impregnated, the cell could be mounted on a coldfinger and the photochemical reactions of $Cr(CO)_5(C_2H_4)$ with H_2, N_2, or C_2H_4 could be studied by low-temperature matrix techniques. Spectroscopic evidence was obtained for *cis*-$Cr(CO)_4(C_2H_4)(X_2)$ (X_2 = H_2 or N_2) and *mer*-$Cr(CO)_3(C_2H_4)_3$. An extension of this approach is to incorporate a vessel containing a porous inorganic solid, e.g., Al_2O_3, into the flow reactor. The solid is then impregnated with $Cr(CO)_5(C_2H_4)$, which can be transformed to the oxide merely by exposure of the impregnated solid to air. This provides a “low temperature” route to metal oxides which does not involve heating the sample above room temperature.[460]

Recently, the flow-reactor approach has been extended to the synthesis of propene complexes.[461] The critical temperature of propene is substantially above ambient, T_c = 91.6 °C, so that the reactions are carried out in *liquid* rather than supercritical propane but surprisingly the “RESS” precipitation is still effective. As with scC_2H_4, the compound is dissolved in propene, flowed through a UV irradiation cell, monitored by IR for optimization of conversion, and then precipitated through a back-pressure regulator (expansion valve). Thus, the previously unknown compounds $Cr(CO)_5$(propene) and CpMn(CO)$_2$(propene) were both isolated as solids contaminated with ca. 50% starting material, $Cr(CO)_6$ or CpMn(CO)$_3$. Although the product was being recovered by expansion of liquid, it was a relatively dry powder containing only modest amounts of free propene. Products were identified by low-temperature ^{13}C and ^{1}H NMR in toluene-d_8.

Although the photochemical reactors were successful, there were problems. Incomplete conversion of reactants to products is a feature of most photochemical reactions. In addition, deposits tended to build up on the window used for UV irradiation thereby terminating the reaction prematurely. Thus a thermal reactor was developed to a design similar to that of the photochemical reactor but with the photolysis cell replaced by a high-pressure coil immersed in an oil bath.[424] The initial target, CpMn(CO)$_2$(C_2H_4), could not be made directly from CpMn(CO)$_3$ which is thermally extremely stable and does not undergo

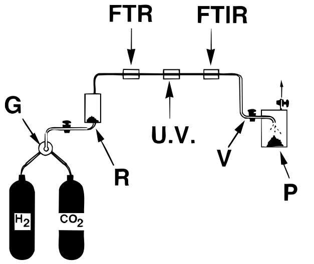
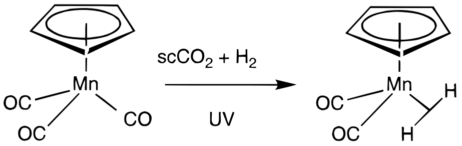


Figure 35. Schematic view of a photochemical reactor which uses H_2 mixed with $scCO_2$ for the synthesis of $CpMn(CO)_2(\eta^2\text{-}H_2)$. The reactor consists of a photochemical section, a gas-handling stage with two pumps and a mixing unit, and the method of adding $CpMn(CO)_3$ to the flowing fluid. The figure is labeled as follows: G, gas mixer; R, reactant; FTR, FT-Raman; V, expansion valve; P, recovered product. (Adapted from J. A. Banister et al., *Organometallics* **1995**, *14*, 3876. Copyright 1995 American Chemical Society.)

Scheme 14



thermal substitution reactions. Therefore conventional routes were used to prepare $CpMn(CO)_2NC^nPr$, which has the thermally very labile ligand, NC^nPr. Conversion to $CpMn(CO)_2(C_2H_4)$ was essentially quantitative with good yields of product.[424] The reactor was then modified to run with H_2/CO_2 mixtures but, sadly, yields of $CpMn(CO)_2(H_2)$ were negligible because $CpMn(CO)_2NC^nPr$ is thermally more stable than $CpMn(CO)_2(H_2)$. Nevertheless, this thermal flow reactor defined the conditions needed to generate labile compounds by a thermal route, conditions which resulted in the development of a semiflow reactor[140] (see next section).

Reactions involving H_2 and N_2. The isolation[45] of $CpMn(CO)_2(H_2)$ was technically a greater challenge than $Cr(CO)_5(C_2H_4)$ because it required a more complicated photochemical reactor using H_2 mixed with $scCO_2$ (Scheme 14). The isolation was important because $CpMn(CO)_2(H_2)$ was, and still is, one of the simplest thermally stable dihydrogen complexes. Figure 35 gives a schematic view of the reactor and Figure 36 shows the actual arrangement of components. The mixing of H_2 and CO_2 was confirmed by FT-Raman spectroscopy and the photochemistry was monitored by FTIR as before. $CpMn(CO)_2(H_2)$ transpired to be remarkably robust; it is a pale yellow solid melting to a brownish liquid at room temperature, displaying a thermal stability which contrasts with the relative lability of many other dihydrogen compounds. The same apparatus was used to isolate $(C_5H_4Me)Mn(CO)_2(H_2)$ which is a *liquid* but appeared quite as stable as the Cp analogue.[45] This shows that the stability of $CpMn(CO)_2(H_2)$ is not merely due to stabilization in the solid state.

The photochemical synthesis of $CpMn(CO)_2(H_2)$ eventually fails because of the build up of deposits on the photolysis window[45] and the formation of a solid Mn(II) carbonate, $MnCO_3$, by reaction with residual H_2O in the $scCO_2$. Therefore, thermal routes to $CpMn(CO)_2(H_2)$ were devised[140] with the development of a new semiflow reactor and *new* chemistry.

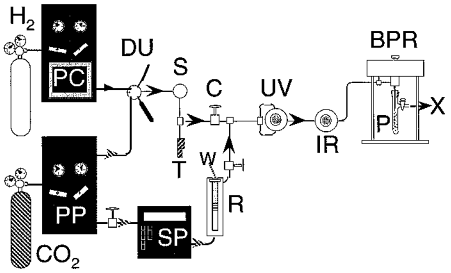


Figure 36. Actual layout of the reactor for the synthesis and isolation of $CpMn(CO)_2(\eta^2\text{-}H_2)$ from $CpMn(CO)_3$ and H_2 in $scCO_2$ (see Figure 35, for a schematic view). The components are labeled as follows (alphabetically): BPR, Back Pressure Regulator (Jasco Model 880-81); C, Control valve; CO_2, carbon dioxide cylinder; DU, gas dosage unit (NWA GmbH, Lörrach, Germany); H_2, hydrogen cylinder; IR, infrared cell (see Figure 5); P, solid product, $CpMn(CO)_2(\eta^2\text{-}H_2)$; PC, pneumatic compressor (NWA Model CU105); PP, pneumatic pump (NWA Model PM101); R, variable volume cell[40] containing a solution of $CpMn(CO)_3$ in an $H_2/scCO_2$ mixture; S, mixer with magnetic stirrer (Kontron M491); SP, syringe pump (Brownlee Lab Micro-gradient) containing $scCO_2$ to drive the piston of the variable volume cell; T, pressure transducer (RDP Electronics); UV, photolysis cell (a modified version of the IR cell); W, sapphire window of the variable volume cell; *X*, exhaust vent. The figure is not drawn to scale. (Reproduced with permission from J. A. Banister et al., *Organometallics* **1995**, *14*, 3876. Copyright 1995 American Chemical Society.)

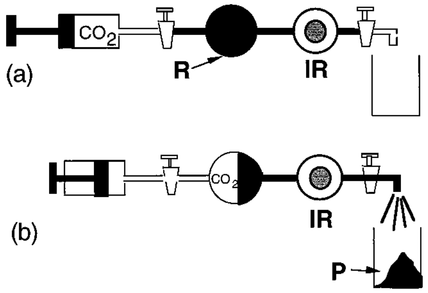


Figure 37. Schematic illustration of the principle of the thermal semi-flow reactor for the synthesis of $CpMn(CO)_2(\eta^2\text{-}H_2)$: (a) during reaction and (b) rapid precipitation of the product by RESS. The figures are labeled as follows: R, reaction mixture; P, product. See text for further details of how the reactor is used.

The semiflow reactor is shown in Figure 37. The principle is simple; the reaction takes place in a sealed vessel but the product is recovered by RESS precipitation as in the flow reactor. The key feature is the use of a piston in the reactor which allows small aliquots of reaction mixture to be driven into the FTIR cell at regular intervals so that the progress of the reaction can be monitored. Since $CpMn(CO)_2(H_2)$ is thermally rather labile, use of this semiflow reactor required the development of even more labile precursors. A whole series of ligands were evaluated before the selection of ethylvinyl ether, $H_2C{=}CHOEt$ (EVE). $CpMn(CO)_2(EVE)$ was itself a new compound, which could be smoothly converted into $CpMn(CO)_2(H_2)$, before precipitation by rapid expansion.[140] A particularly interesting observation was that, in $scCO_2$, the concentrations of EVE, N_2, and H_2 could be manipulated sufficiently for any one of the three

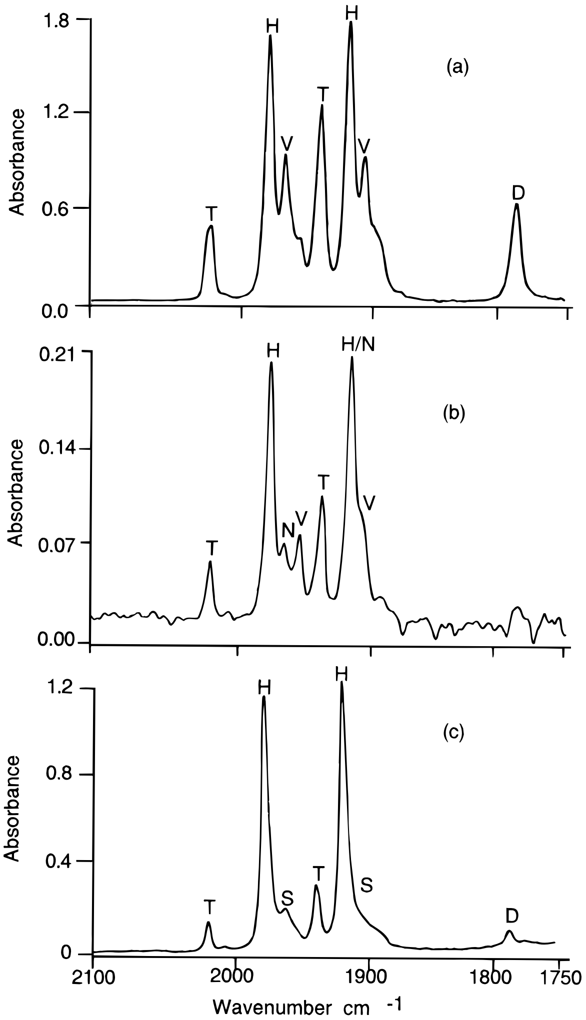


Figure 38. IR spectra (*n*-pentane solution) comparing the purity of the products isolated from different synthetic routes to $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$. In all spectra, bands are assigned as follows: V, $Cp^*Mn(CO)_2(EVE)$; H, $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$; T, $Cp^*Mn(CO)_3$; D, $Cp_2^*Mn_2(CO)_3$. (a) Products formed in the semi-flow reactor from $Cp^*Mn(CO)_2(EVE)$ in $scCO_2/H_2$. (b) IR spectrum of the products formed from the sequential reactions of $Cp^*Mn(CO)_2(EVE)$ with $scCO_2/N_2$ followed by reaction of $Cp^*Mn(CO)_2(N_2)$ with $scCO_2/H_2$ at room temperature for 4 h. Note that high pressures of H_2 depress T_c for CO_2/H_2 mixtures below room temperature. (c) IR spectrum of the products formed from the thermal reaction of $Cp^*Mn(CO)_2(\eta^2\text{-}H{-}SiEt_3)$, S, with $scCO_2/H_2$ over a period of 4 h. Comparison of the spectra shows that c is by far the most successful route for the synthesis and isolation of $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$. (Reproduced with permission from P. D. Lee et al., *Organometallics* **1998**, *20*, 524. Copyright 1998 American Chemical Society.)

$CpMn(CO)_2L$ complexes to be converted into either of the other two (Figure 32). This allowed a number of different routes to $CpMn(CO)_2(H_2)$ to be evaluated and the most effective was found to be the reaction of $CpMn(CO)_2(H{-}SiEt_3)$ with H_2 (Figure 38).

The implication of these observations is that the supercritical environment provides wider opportunities for ligand manipulation and exchange than are normally available in conventional solution. The concentrations can be altered so that labile ligands can be interchanged almost at will. Clearly there are excellent opportunities to exploit this freedom in other areas of chemistry.

Finally, it is worth noting a parallel between conventional and supercritical chemical synthesis. In many conventional synthetic laboratories, the strategy is to scope reactions by carrying them out in NMR tubes and then scaling up the successful chemistry in Schlenk tubes, where reactions are optimized by following the color changes in the tube. In a similar way, the supercritical reactions described above were scoped in IR cells, as in Figure 5. Successful chemistry was then scaled up in flow or semiflow reactors and optimized or monitored by changes in IR spectra.

E. Flow Reactions with Antisolvent Precipitation (The ROSA Technique)

Unfortunately, the flow techniques described above can only be applied to reactions where both reactant and product are *soluble* in the SCF. Although a range of fluids are supercritical close to room temperature (e.g., C_2H_4, CO_2, CHF_3, etc.), there is a huge variety of compounds which do not dissolve in any of them. The ROSA (Reaction in Organics with Supercritical Antisolvent) technique[157] was developed specifically for reactions where the products are *insoluble* in $scCO_2$.

The reaction is carried out in an organic solvent in a thermal flow reactor and the product is then precipitated by the $scCO_2$ antisolvent (see Section II; Part 4B), as shown in Figure 39. The high pressure of the $scCO_2$ (typically 10 MPa) means that the organic solvent also has to be pumped at a pressure which is higher than the critical pressure of most organic liquids (e.g., pyridine, $P_c = 5.63$ Mpa). The result is that the organic solvent can be heated right up through its critical temperature without boiling. Thus, it is possible to carry out reactions in highly superheated organic solvents in narrow pressure tubing without the use of large high-pressure autoclaves.

The operation of the ROSA reactor illustrated by the preparation of *cis*-$W(CO)_4(L)_2$ [L = pyridine or

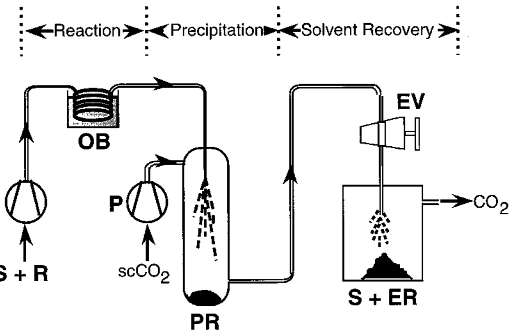


Figure 39. Diagram of the ROSA reactor with $scCO_2$ antisolvent precipitation. The apparatus is labeled as follows: S+R, solvent + reactants; P, pump; OB, oil bath; PR, product; EV, expansion valve; S+ER, solvent + excess reactant. The reactant and solvent are pumped at high pressure through a metal coil reactor immersed in an oil bath. The hot solution is cooled and is then flowed through a capillary into the precipitation vessel where it is mixed with flowing $scCO_2$. The product precipitates as a crystalline solid while the solvent and excess reactant dissolve in the $scCO_2$. The supercritical solution is then passed through a back pressure regulator which separates the CO_2 from the solvent and excess reactant.

3,5-lutidine]. Conventional refluxing of $W(CO)_6$ in pyridine at 115 °C leads to formation of the tris product, *fac*-$W(CO)_3(pyr)_3$. *cis*-$W(CO)_4(pyr)_2$ can only be separated from the mixture if the reaction is monitored continuously and is then stopped before completion.[462] Alternatively, *cis*-$W(CO)_4(pyr)_2$ can be obtained by superheating $W(CO)_6$ in pyridine to 210 °C in an autoclave.[463] The ROSA procedure is much simpler because it integrates reaction, separation, and purification into a single process.[157] Thus, pumping a 1% (w/v) solution of $W(CO)_6$ in pyridine through the reactor at 215 °C with a nominal residence time of 30 min leads to the precipitation of *cis*-$W(CO)_4(pyr)_2$ as yellow crystalline needles, 2–3 mm long. The size of the precipitated crystals could be varied by changing the flow rate of $scCO_2$; lower flow rates led to larger crystals. Similarly, the reaction of $W(CO)_6$ with 3,5-lutidine led to precipitation of crystals of the previously unknown *cis*-$W(CO)_4(3,5\text{-}lut)_2$, with excellent correlation between expected and obtained C, H, and N elemental analyses. When the ROSA reaction was repeated with $W(CO)_6$ dissolved in 1:1 mixture of pyridine and 3,5-lutidine, a mixture of products was obtained; approximately equal amounts of *cis*-$W(CO)_4(pyr)_2$, *cis*-$W(CO)_4(3,5\text{-}lut)_2$, and *cis*-$[W(CO)_4(pyr)(3,5\text{-}lut)]$.

Other reactions include the synthesis of $Cr(CO)_3$ derivatives of cyclophanes and of polystyrene by arene exchange with $(C_6H_5Me)Cr(CO)_3$.[464] The significance of the ROSA technique may well be much wider because *the same equipment can be used for almost any organic solvent without modification*. The apparatus is inherently scalable and reactions could be carried out on a much larger scale. Furthermore, the technique need not be restricted to organometallic chemistry and a similar approach could be applied to widely different areas of chemistry.

A very recent paper[421] by Dinjus and co-workers reported one of the first examples of organometallic chemistry in scH_2O. They studied the cyclotrimerization of $^tBuC{\equiv}CH$ and $PhC{\equiv}CH$ catalyzed by $CpCo(CO)_2$ and isolated a number of new organometallic compounds, including three isomers of CpCo(bis-substituted-cyclopentadienone), all of which were characterized by X-ray crystallography.

3. Homogeneous and Heterogeneous Catalysis

Homo- and heterogeneous catalysis in SCFs are important and rapidly expanding areas of chemistry. Since they are the subjects of comprehensive reviews by Noyori[20] and Baiker[21] in this special issue of *Chemical Reviews*, we merely highlight some recent developments of particular relevance to this review.

In recent years, there has been a increasing interest in CO_2 as a C_1-feedstock for the synthesis of organic chemicals[401,420] as well as replacement for organic solvents in industrially important catalytic reactions such as hydrogenation[141,142] and Friedel–Crafts chemistry.[465] $scCO_2$ is relatively cheap, widely available, nontoxic, and it has quite a low critical temperature and pressure. In addition, the miscibility of $scCO_2$ with H_2 (see Section IV; Part 2B) is particularly advantageous for hydrogenation reactions because the substrate and H_2 are in a single phase giving a high degree of control over the hydrogenation.[142] Relatively large changes in the density, viscosity, polarity, and solvent strength can be achieved by adjusting the temperature and pressure of the SCF which potentially enables greater yields and "tuning" of the product distribution.[466,142]

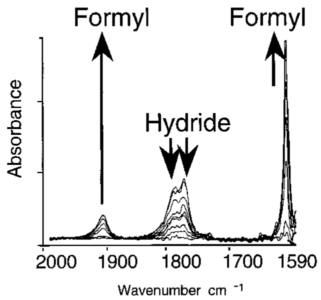


Figure 40. IR spectra showing the reduction of CO_2 in scC_2H_6. Normally, the reaction with CO_2 is very fast but here the concentration of CO_2 has deliberately been kept very low in scC_2H_6 so that the reaction can be followed spectroscopically by the decay of the two ν(M–H) bands of the hydride $Ru(dmpe)_2H_2$ and growth of the ν(M–H) and ν(C–O) bands of the formyl complex, $Ru(dmpe)_2(O_2CH)H$, being monitored in real time. (Reproduced with permission from J. L. King et al., unpublished results, 1998.)[478]

Scheme 15

$$CO_2\ (20\ atm) + H_2\ (85\ atm) \xrightarrow[50\ ^\circ C\ /\ ca\ 220\ atm]{catalyst\ /\ scCO_2\ /\ NEt_3} HC(O)OH$$

Reactions conducted in SCFs can also have advantages over gas-phase catalytic reactions which can suffer from low selectivities due to competing side reactions (due to higher temperatures) or conventional solution catalytic reactions which are often slower and involve substantial amounts of toxic solvents. As in conventional catalysis, reactions in SCFs can be either homo- or heterogeneous processes and can be conducted in either batch or flow systems.

Homogeneous catalysis in SCFs is developing particularly rapidly.[64,193,256,429,431] The metal-containing catalyst complex must of course be soluble in the SCF. Section II (Part 2) described how this can be achieved using particular solubilizing ligands on the metal center such as perfluoroalkyl-substituted arylphosphines. As in the case for SCF transport (for metal extraction), ligands with fluorinated side chains/pendant arms can improve the solubilities of complexes in $scCO_2$[61–63,193] or other fluids[255] even further. The most classic example of homogeneous catalysis is the hydrogenation of $scCO_2$ itself to formic acid, which can be catalyzed in $scCO_2$ by ruthenium hydride compounds $[Ru(PMe_3)_4(H)_2]$ or $[Ru(PMe_3)_4(Cl)_2]$, see Scheme 15.[33,401,434,467,468] Such reactions are particularly suitable for spectroscopic monitoring. Figure 40, shows how the primary step of CO_2 hydrogenation can be followed by FTIR.[461]

One of the attractions of SCFs for homogeneous catalysis is that rates[401] or selectivities[466] can be significantly higher than in conventional solvents. The acceleration in SCFs may originate, at least in part, in the higher concentration of "dissolved" H_2 in the SCF but several other factors must also be taken into account including higher diffusion rates, lower viscosities, and weaker interactions of CO_2 than

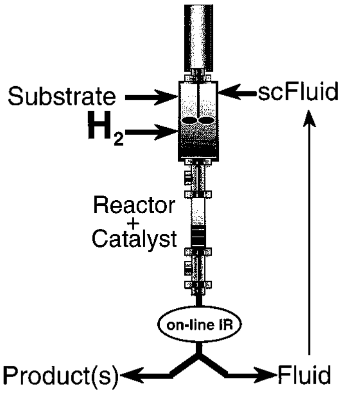
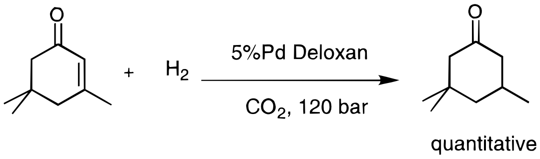


Figure 41. Block diagram of a flow reactor for continuous hydrogenation of organic compounds.[141,142] $scCO_2$, H_2 and the organic substrate are mixed and heated. The mixture is then passed through the reactor containing a fixed bed catalyst (usually a supported noble metal). There is the option of on-line FTIR monitoring before the product and CO_2 are separated by expansion (Reproduced with permission from M. W. George and M. Poliakoff, *J. Phys. Org. Chem.* **1998**, *11*, 589.)

Scheme 16



conventional solvents with coordinatively unsaturated reaction intermediates.

Total lack of flammability makes liquid and $scCO_2$ attractive as a medium for homogeneously catalyzed oxidation and epoxidation reactions. For example, Tumas and co-workers have recently reported[469] selective epoxidation by ^tBuOOH in CO_2 catalyzed by $VO(O^iPr)_3$ or $Ti(O^iPr)_4$. Interestingly the reactions showed little difference between near-critical and $scCO_2$ and the rates in CO_2 were slower than in CH_2Cl_2 but faster than in *n*-heptane.

In the past, the majority of “high pressure” homogeneous catalytic reactions have been conducted in batch systems which can present problems in scale up for SCFs because of the higher pressures needed for supercritical reactions. Therefore continuous processes are generally preferable for industrial-scale SCF reactions because they involve smaller, and hence safer, equipment. In addition, capital costs are likely to be lower than in batch systems.

A number of reports[141,142,470−473] of continuous hydrogenation using fixed-bed catalysts have been recently published. Here, we briefly describe one approach, Figure 41, which can be seen as an extension of the organometallic flow reactor illustrated in Figure 37. The organic substrate, H_2, and $scCO_2$ are pumped separately, mixed by rapid stirring to achieve a single phase, and then passed over a heterogeneous catalyst bed. Depressurization of the system downstream gives phase separation of the CO_2 and organic products, which can be tapped off or analyzed[141,142,417] (Scheme 16). Very good selectivities can be achieved by using precious metal catalysts on a functionalized metal support, such as the commercially available Deloxan, which has well-defined metal environments on the polyaminosiloxane backbone. This system uses a very small amount of catalyst; in the hydrogenation of isophorone, 1 g of catalyst can give >7.5 kg of product.[142] This flow system has also recently been adapted (with minor modifications) for continuous Friedel−Crafts alkylation reactions in $scCO_2$ using solid acid catalysts.[417,465]

A number of researchers are also looking at “green” alternatives to $scCO_2$ such as scH_2O for oxidation, reduction and other synthetic reactions.[326,474] For example, using stable metal−organic catalysts in scH_2O reactions is particularly interesting because the catalysts are soluble (thus homogeneous) under supercritical conditions and insoluble under subcritical conditions.[474] There is now considerable interest in developing novel metal catalysts for reactions in SCFs; these have recently included the use of highly stable (recyclable) Lewis acid ROMP catalysts,[252] the synthesis of hybrid materials[475,476] which have the advantages of both homo- and heterogeneous catalysts, and fluorous biphasic (homogeneous) catalysts which can be easily separated from the products. Phase-transfer catalysis in $scCO_2$/water mixtures is also gaining interest. The first example of such a system was demonstrated in 1996 by Morgensten and co-workers for the partial oxidation of cyclohexene to adipic acid using a Ru containing phase transfer catalyst.[97]

We believe that catalytic and analogous reactions conducted in supercritical media will become increasingly more attractive with the next generation of catalyst materials, specifically designed for SCF media,[61−63,193,256] particularly in view of environmental legislation requiring industry to reduce or eliminate toxic solvents from such processes.[477]

V. Conclusions and Outlook

In 1997, Michel Perrut, founder of the International Society for the Advancement of Supercritical Fluids, summed up recent progress in supercritical science:

> *“The 1980s were the decade of Extraction, the 1990s have been the decade of Materials, and the start of the next century will be the decade of Reactions.”*

Readers must judge for themselves whether the work summarized in this review bears out his view. Nevertheless, it should be clear that the different areas which have been covered in the review are at very different stages of development.

The use of SCFs for extraction is well established or, in the words[10] of Chien Wai, “over the hump”. In the extraction of metals, much of the current research can be seen to be focused on finding the optimal ligands for sequestering and solubilizing the target ions. This search is now beginning to lead to an understanding of the factors affecting solubility of such complexes.[96] When fully developed, this understanding will have a profound influence on the design of ligands for SCF reaction chemistry.

The role of SCFs for the production of materials is also reaching a degree of maturity. There appears to be very different behavior between the supercritical and subcritical regimes in the formation of crystalline metal particles. In many high temperature (ca. 400 °C) SCFs, catastrophic conversion of precursors leads to rapid formation of small, highly crystalline, particles. By contrast, agglomerated or amorphous material tend to be formed at subcritical temperatures, with either larger particles or partially crystalline materials. The choice of starting materials appears to be a very important factor, affecting the oxidation state(s) of the metals, type of phase(s) formed, particle size/shape as well as the degree of crystallinity. In addition, the high diffusivity of SCFs facilitate the synthesis of well-condensed/dense materials which are either highly crystalline or have better sinterability (above ca. 1000 °C) than ceramics prepared using more conventional methods. Thus, the synthesis of crystalline ceramics/chalcogens etc. can be conducted at much lower temperatures in SCFs than conventional high-temperature firing techniques. This has already opened routes to novel metastable (kinetic) products. The use of SCFs to create metal/polymer composites is just beginning and clearly this area will develop rapidly.

Although much has been done, the field of SCF reaction chemistry is far less developed than extraction or materials. Part of the reason is undoubtedly the understandable caution of reaction chemists to embark on experiments which involve high pressures, high temperatures, or even both. Nevertheless, this review has shown that new chemistry is beginning to emerge and that SCFs do provide access to new compounds. Most importantly, it is clear that SCFs offer chemists increased opportunities to control reactions. In supercritical media, chemists can manipulate the phase behavior of a mixture, can control the concentrations of dissolved gases, can alter the morphology of products, and can carry out their reaction in a cleaner, greener way.

The chemical future of SCFs seems bright but we must always remember that supercritical science is inherently interdisciplinary. We have previously criticized[31] the creeping compartmentalization of SCF research into analytical, process, materials, reactions, etc. This fragmentation must be resisted at all costs. Supercritical science must remain “single phase”. Only then will it be possible to exploit the unique and truly fascinating properties of SCFs to drive chemistry into the 21st century.

VI. Abbreviations

1-D (2-D, 3-D)	one- (two-, three-) dimensional
AA CVD	aerosol-assisted chemical vapor deposition
acac	pentane-2,4-dionate
acac-Br	3-bromopentane-2,4-dionate
AED	atomic emission detector
AES	atomic emission spectrometry
APDC	ammonium pyrrolidinedithiocarbamate
ASES	aerosol solvent extraction system
atm	atmospheres
aq.	aqueous
BDC/DBDTC	dibutyldithiocarbamate
BPSG	boron and phosphorus doped silicon glass
^{t}Bu	*tert*-butyl
bzac	1-phenylpentane-1,3-dionate
COD	cyclooctadiene
Cp	cyclopentadienyl
Cp′	methylcyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cyanex 301	bis(2,4,4-trimethylpentyl)dithiophosphinic acid
Cyanex 302	bis(2,4,4-trimethylpentyl)monophosphinic acid
Cyanex 272	bis(2,4,4-trimethylpentyl)phosphinic acid
CVD	chemical vapor deposition
D2EHTPA	bis(2-ethylhexyl)monothiophosphorous acid
DDC	diethyldithiocarbamate
dibm	2,6-dimethylheptane-3,5-dionate
dmhd	1,1-dimethylhexane-3,5-dionate
dmpe	$Me_2PCH_2CH_2PMe_2$
EC	ethyl centralite
EDTA	ethylenediamine tetraacetic acid
en	ethylenediamine
EVE	ethylvinyl ether, $H_2C{=}CHOEt$
FAAS	flame atomic absorption spectrometry
FDDC	bis(trifluoroethyl)dithiocarbamate
fod	2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionate
fwhm	full-width half-maximum (of spectral bands)
GAS	gas antisolvents
HDC	dihexyldithiocarbamate
hfa	1,1,1,5,5,5-hexafluoropentane-2,4-dionate
hmten	$Me_2N\{CH_2CH_2N(Me)\}_3Me$
Kelex 100	7-(1-)vinyl-3,3,3,5,5-tetramethylhexyl)-8-hydroxyquinoline
Ln	lanthanide
lut.	3,5-dimethylpyridine
LXe	liquid Xenon
MOCVD	metal organic chemical vapor deposition
NG	noble gas
P3DC	dipropyldithiocarbamate
P5DC	dipentyldithiocarbamate
PAC	photoacoustic calorimetry
P_c	critical pressure
PCA	precipitation using a compressed antisolvent
PDC	pyrrolidinedithiocarbamate
PE	polyethylene
pmdien	$Me_2N\{CH_2CH_2N(Me)\}_2Me$
PMPE/PMP	polymethylpropylene
^{i}Pr	isopropyl
^{n}Pr	*n*-propyl
psi	pounds per square inch
PTFE	poly(tetrafluoroethylene)
pyr/py	pyridine
R134a	CH_2FCF_3
RESS	rapid expansion of a supercritical solution
RF	radio frequency
ROSA	Reaction of Organics with Supercritical Antisolvent
RT	room temperature
ρ_c	critical density
SAS	supercritical antisolvent
sc	supercritical (e.g., $scCO_2$ = supercritical carbon dioxide)
SCF(s)	supercritical fluid(s)
SCF-TRIR	time-resolved IR spectroscopy in supercritical fluid solution.
SEM	scanning electron microscopy
SFC	supercritical fluid chromatography
SFE	supercritical fluid extraction
SFT	supercritical fluid transport
TBP	tri-*n*-butyl phosphate
TBPO	tribultylphosphine oxide
T_c	critical temperature
T_d	tetrahedral

TDBDTC	tetrabutylammoniumdibutyldithiocarbamate
TDDC	tetrabutylammoniumdiethyldithiocarbamate
TEM	transmission electron microscopy
TEOS	tetraethoxysilane
tfa	1,1,1-trifluoropentane-2,4-dionate
tfbzm	1,1,1-trifluoro-4-phenylbutane-2,4-dionate
thd	2,2,6,6-tetramethylheptane-3,5-dionate
thf	tetrahydrofuran
T.M.	transition metal
tod	2,2,7-trimethyloctane-3,5-dionate
TOPO	tri-*n*-octylphosphine oxide
TPPO	triphenylphosphine oxide
tris	tris(hydroxymethyl)aminomethane
tta	theonyltrifluoroacetonate
tta	1-thienyl-4,4,4-trifluoropentane-1,3-dionate
UNICARB	Union Carbide process for supercritical spraying of paints/coatings[1]
VAMP	Vedoc Advanced Materials Process (supercritical process for manufacture of powder coatings)[2]
VOCs	volatile organic compounds
XAFS	X-ray absorption fine structure
XPD/XRD	X-ray powder diffraction/X-ray diffraction.
YBCO	$YBa_2Cu_3O_{7-x}$

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