

Carbon Dioxide as a Solubility “Switch” for the Reversible Dissolution of Highly Fluorinated Complexes and Reagents in Organic Solvents: Application to Crystallization

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Highly fluorinated organic or organometallic solid compounds can be made to dissolve in liquid hydrocarbons by the application of 20–70 bar of CO₂ gas. Subsequently releasing the gas causes the compounds to precipitate or crystallize, giving quantitative recovery of the solid. The resulting crystals can be of sufficient quality for single-crystal X-ray crystallography; the structures of Rh₂(O₂CCF₂CF₂CF₃)₄(DMF)₂, Rh₂(O₂C(CF₂)₉F)₄(MeOH)₂, Cr(hfacac)₃, and P{C₆H₃(3,5-CF₃)₂}₃ have been determined from crystals grown in this manner.

Introduction

Complexes containing highly fluorinated¹ ligands have applications in the fields of chemical vapor deposition,^{2,3} fluorous biphasic catalysis,^{4–9} and catalysis in supercritical CO₂ (scCO₂).^{10–12} However, their high fluorine content renders them insoluble in many organic solvents, makes them more likely to be obtained as oils rather than crystalline solids, and makes them particularly difficult to analyze crystallographically. We have observed a phenomenon which, among its possible applications, avails the experi-

mental chemist of a new method of preparing crystals of these complexes. We have found that expansion of an organic solvent by the application of gaseous (subcritical) CO₂ pressure increases the fluorophilicity of the solvent to such an extent that the solvent is able to dissolve highly fluorinated complexes. This phenomenon makes it possible to recrystallize such complexes for the purposes of purification or X-ray crystallography.

Carbon dioxide, in either the liquid or supercritical states, has a strong ability to dissolve highly fluorinated compounds, as shown by the solubility in scCO₂ of fluorinated polymers,^{13,14} fluorinated surfactants,^{15–17} and transition metal complexes containing fluorinated groups.^{10,12,18} Organic solvents in general have much poorer fluorophilicity, meaning that they are less able to dissolve highly fluorinated compounds.¹⁹ As a result, fluorous liquids such as perfluoroalkanes are immiscible with most organic liquids. However, recent work in our laboratories has shown that dissolution

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of CO₂ gas into organic liquids increases the fluorophilicity of the organic liquid such that it may become miscible with common fluorinated liquids.^{20,21}

Application of CO₂ gas pressure over an organic liquid causes the latter to expand in volume up to severalfold, forming an organic/CO₂ liquid phase mixture which is referred to as a “gas-expanded” liquid.^{22,23} This phenomenon is observed with almost any organic liquid but is not as dramatic in ionic liquids²⁴ and is not observed at all in ethylene glycol or water. The fact that some organic solids are soluble in organic liquids but not in expanded organic liquids has been used as the basis of the gas antisolvent (GAS) process for precipitating or crystallizing organic compounds.^{22,25,26} In the GAS process, the dissolution of CO₂ into a solution forces the solute to precipitate^{26,27} or crystallize.²⁸ Expansion of liquids by CO₂ or other gases has also been used as a method of modifying the rates^{29,30} of chemical reactions. It has not heretofore been used as a method of causing the dissolution of highly fluorinated solids, in what can best be described as an inverse GAS process.

Experimental Section

General Methods. Hydrogen gas (99.99% purity, Praxair) was used directly. CO₂ gas (99.9999% purity, SFC/SFE grade, Air Products) was passed through an oxygen trap before use. Solvents, reagents, and complexes were used as received. Rh₂(O₂C(CF₂)₃F)₄³¹ and Pd(phd)₂ (phd = 9-*H*-perfluoro-8,10-heptadecanedionato)³² were prepared by the literature methods. Cu(pnd)₂ (pnd = 5-*H*-perfluoro-4,6-nonanedionato)^{33,34} was prepared by Bertrand and Kaplan's method for Cu(hfacac)₂.³⁵

The high-pressure apparatus is similar to that described earlier²⁹ but with 160 mL steel vessels. Visual observations of phase

behavior were made by using a Jurgeson-type gauge as a pressure vessel, with a burst disk attached.

Safety Warning. Operators of high-pressure equipment such as that required for these experiments should take proper precautions, including but not limited to the use of blast shields and pressure relief mechanisms, to minimize the risk of personal injury.

Rh₂(O₂C(CF₂)₃F)₄(MeOH)₂ (complex **2**) was prepared by heating 32 equiv of HO₂C(CF₂)₃F with 1 equiv of Rh₂(OAc)₄ to 150 °C in a closed vessel without added solvent for 16 h, in analogy to Schurig's method for Rh₂(O₂C(CF₂)₃F)₄.³¹ The green crude product (a mixture of green Rh₂(O₂C(CF₂)₃F)₄ and white HO₂C(CF₂)₃F) was purified by crystallization from methanol, giving blue Rh₂(O₂C(CF₂)₃F)₄(MeOH)₂. IR: 1650 (s), 1429 (m), 1363 (m), 1214 (s), 1154 (s) cm⁻¹. The identification of Rh₂(O₂C(CF₂)₃F)₄(MeOH)₂ was confirmed by single-crystal X-ray crystallography, as described below.

Method of Recrystallization. Method A. Rh₂(O₂C(CF₂)₃F)₄ (30 mg, 28 μmol), toluene (0.4 mL), DMF (10 μL), and a small stir bar were placed in a small vial inside a steel pressure vessel. The vessel was warmed to 35 °C, and CO₂ (68 bar) was added. Pressures as low as 40–50 bar suffice with most compounds, so that the pressure of a CO₂ cylinder is sufficient and no pumps are required. The vessel was stirred magnetically (coupling of the magnetic stir bar to the stir plate below was confirmed visually prior to starting the experiment) for 30 min, after which the stirring was stopped, the water bath heater and agitator were turned off to minimize vibration, and the vent valve to the vessel was opened slightly so that approximately 1 mL of CO₂ gas escaped/min. The valve was adjusted daily to maintain this rate of CO₂ loss. After 1 week, the pressure had entirely escaped. The vessel was opened. Purple diamond-shaped platelet crystals of Rh₂(O₂C(CF₂)₃F)₄(DMF)₂ (compound **1**) found in the vial were removed, and one was analyzed crystallographically.

Method B. An alternative and frequently superior method was to release the CO₂ pressure over 1–4 h, after which the vessel would be opened, the vial would be capped tightly, and the vial would be left undisturbed on a shelf for 1 week. Crystals of complexes **2**, **5**, and tris(3,5-bis(trifluoromethyl)phenyl)phosphine were obtained by this method.

Rapid screening of the best conditions for recrystallization could be performed by placing 13 small glass vials uncapped and upright in a 160 mL reaction vessel. Different proportions of the organic liquid (usually a heavy alkane, cycloalkane, or toluene) and the fluorinated solid were placed in each vial, along with a micro stir bar. The recrystallization then proceeded using either of the two methods described above. For particularly volatile solids or solvents, the use of a single vial/vessel is preferred to avoid cross-contamination.

X-ray Structure Determinations. Crystallization of these compounds from organic/CO₂ mixtures cannot yield crystals that are free from the problems of –CF₃ and –(CF₂)_{*x*}CF₃ disorder seen when other solvent systems are used. The relatively flat conformational potential energy surface for CF₃ commonly gives rise to rotationally disordered groups. Similarly, –(CF₂)_{*x*}CF₃ chains present little in the way of van der Waals interactions to anchor their positions in a crystal structure. In the present structures, disorder of all these types is evident and was particularly severe in compound **2**. The use of low temperature in the data collection was a key factor in the successful modeling of these structures.

Rh₂(O₂C(CF₂)₃F)₄(DMF)₂·0.5toluene. A purple plate of dimensions 0.28 × 0.22 × 0.04 mm was mounted in the 92 K nitrogen cold stream provided by a CRYO Industries low-temperature apparatus on the goniometer head of a Bruker SMART 1000

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Table 1. Summary of Crystal Structure Determinations for **1**·0.5toluene, **2**·2MeOH, **5**, and **6**

	1 ·0.5toluene	2 ·2MeOH	5	6
formula	C ₂₉ H ₂₂ F ₂₈ N ₂ O ₁₀ Rh ₂	C ₄₄ H ₁₆ F ₇₆ O ₁₂ Rh ₂	C ₁₅ H ₃ CrF ₁₈ O ₆	C ₂₄ H ₉ F ₁₈ P
fw	1296.31	2386.39	673.18	670.28
temp (K)	92(2)	91(2)	91(2)	91(2)
cryst system	Triclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	2	1	4	8
<i>a</i> (Å)	10.558(2)	9.665(3)	8.7318(12)	12.3803(15)
<i>b</i> (Å)	10.580(2)	13.903(4)	12.9417(17)	12.9054(17)
<i>c</i> (Å)	22.011(4)	14.195(4)	19.074(3)	32.807(4)
α (deg)	82.041(8)	90.917(4)	90	80.539(7)
β (deg)	82.216(7)	95.208(4)	92.067(3)	80.590(4)
γ (deg)	63.234(8)	107.581(4)	90	85.248(5)
<i>V</i> (Å ³)	2166.6(10)	1808.9(8)	2154.0(5)	5092.4(11)
<i>D</i> _{calc} (g·cm ⁻³)	1.985	2.184	2.076	1.749
μ (Mo K α) (mm ⁻¹)	0.935	0.708	0.720	0.254
R1 (obsd data) ^a	0.068	0.157	0.033	0.068
wR2 (all data) ^b	0.177	0.464	0.092	0.188
GOF ^c	1.12	1.10	1.03	0.97

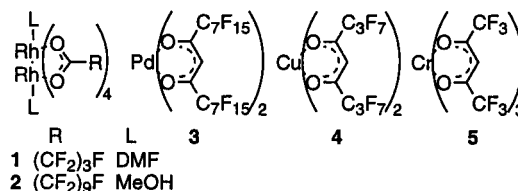
^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b wR2 = $[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. ^c GOF = $[\sum [w(F_o^2 - F_c^2)^2] / \sum (n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

diffractometer.³⁶ Diffraction data were collected with graphite-monochromated Mo K α radiation employing a 0.3° ω scan and approximately a full sphere of data to a resolution of 0.68 Å. An empirical correction for absorption was applied using the program SADABS 2.03.³⁷ A total of 29 485 reflections was collected, of which 13 233 were unique ($R(\text{int}) = 0.038$) and 9760 were observed ($I > 2\sigma(I)$). The structure was solved by direct methods (SHELXS-97³⁸) and refined by full-matrix least-squares on F^2 (SHELXL-97³⁸). Although large thermal motion was observed for several of the fluorine atoms, the best refinement and geometry did not employ split positions for these atoms.

Rh₂(O₂C(CF₂)₉F)₄(MeOH)₂·2MeOH. A violet needle of dimension 0.06 × 0.11 × 0.29 mm was used for structure determination which was carried out in the manner outlined above. Of the 13 954 reflections collected, 6585 were independent ($R(\text{int}) = 0.095$) and 3769 were observed. Disorder in the (CF₂)₈CF₃ tails was modeled by the use of two equal sets, A and B, except for C2, C12, C13, C14, C16, F20, F21, F22, F23, F27, and F28, which were common to both sets. A set of restraints was also employed, namely C–C distances of 1.54(2) Å for the backbone and 1.35(2) Å for C–F distances. Anisotropic refinement for these atoms yielded numerous nonpositive definite thermal parameters. Consequently, only Rh1 was refined with an anisotropic thermal parameter. The high resulting R values for this structure are a result of poor crystallinity (crystals are fragile, fibrous needles) and the extreme thermal motion of the fluorinated alkyl groups.

P{C₆H₃(3,5-CF₃)₂}₃. A colorless plate of dimensions 0.49 × 0.24 × 0.20 mm was selected for data collection. A total of 67 417 reflections was collected, of which 23017 were unique ($R(\text{int}) = 0.033$) and 17 854 were considered observed. There are four molecules in the asymmetric unit. Several of the CF₃ groups display large thermal motion, and four of these groups (out of 24 total) were refined with split positions. Additional details are in the CIF file.

Cr(hfacac)₃ (hfacac = 1,1,1,5,5,5-Hexafluoroacetylacetonate). The crystal used was a red-brown block of dimension 0.25 × 0.19 × 0.15 mm. A total of 29 586 reflections was collected, of

Chart 1

which 6235 were unique ($R(\text{int}) = 0.026$) and 5326 were considered observed. Refinement of this structure was routine.

Data from the crystal structure determinations are summarized in Table 1. Additional experimental information, including atomic positional parameters, is supplied in CIF format as Supporting Information.

Results and Discussion

Reversible Dissolution. Highly fluorinated complexes such as complexes **1–5** (Chart 1) were found to be insoluble or only partly soluble in liquid hydrocarbons but were highly soluble in the same liquids when 20–60 bar of CO₂ gas was present. For example, complex **2** (64 mg) was placed in a windowed vessel (Figure 1a) along with a stir bar and 5 mL of cyclohexane, all at 35 °C. The solid complex visually appeared to be completely insoluble. CO₂ pressure (59 bar) was added, resulting in a marked increase in the volume of the liquid phase and complete dissolution of the colored complex (Figure 1b). Note that CO₂ under these conditions is not supercritical and in the absence of the cyclohexane would be gaseous. The upper phase was gaseous and showed no discoloration, indicating that the complex is not dissolved therein. When the CO₂ pressure was released (slowly, so that the solvent was not lost by entrainment), then the liquid phase returned to its original volume and color and the complex precipitated (Figure 1c). The IR spectrum of the solid was identical to that of the original **2**. This experiment was repeated with only 43 bar, giving the same result. After the CO₂ pressure had been released, the amount of nonvolatile material remaining dissolved in the liquid phase was determined by transferring the liquid phase to a flask of

(36) Data collection, SMART v. 5.054; data reduction, SAINT v. 6.06; Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2000.

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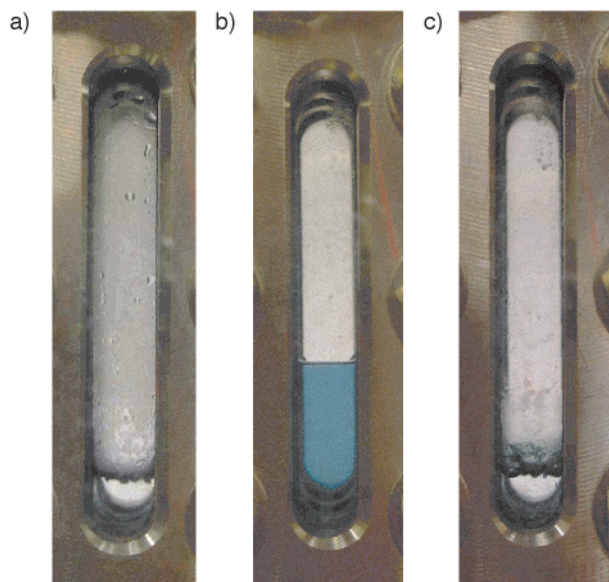


Figure 1. Effect of CO₂ pressure on the solubility of complex **2** in cyclohexane at 35 °C: (a) at 1 atm CO₂; (b) at 59 bar CO₂; (c) after the CO₂ has been released again.

known mass, removing the volatiles by vacuum distillation at room temperature, and weighing the flask again. The mass of solid residue, calculated by difference, was 0.1 mg, showing that greater than 99% of the solute had precipitated upon release of the CO₂.

Other complexes were found to exhibit similar behavior. Complexes tested include complexes containing 9-*H*-perfluoro-8,10-heptadecanedionato (phd) and 5-*H*-perfluoro-4,6-nonanedionato (pnd) chelating ligands such as Pd(phd)₂ (**3**, 68% F by mass) and Cu(pnd)₂ (**4**, 61% F by mass). Use of a “permanent” gas (i.e. one having a critical temperature far below room temperature) such as H₂ instead of CO₂ causes neither expansion of the liquid nor dissolution of highly fluorinated complexes. An alternative method of recrystallization, mixing a complex in a mixture of liquid propylene oxide and benzene and letting the liquids evaporate, has recently been reported to be effective for the crystallization of (C₁H₅)₂C₆F₄.³⁹

The fact that the complexes dissolve in the CO₂-expanded liquid is a demonstration of the fact that expansion by CO₂ renders organic liquids “fluorophilic”. Thus, expanded liquids represent inexpensive alternatives to perfluorinated solvents. One laboratory application of this phenomenon is the recrystallization of highly fluorinated complexes (see below). Other applications will be published separately.

Application of the Phenomenon to Recrystallization of Solids. The phenomenon described above was applied to the problem of obtaining crystals of several highly fluorinated complexes for the purposes of X-ray crystallography. Structures of such compounds are relatively rare in the literature⁴⁰ because the compounds are usually obtained as intractable oils and because of excessive thermal motion or disorder in

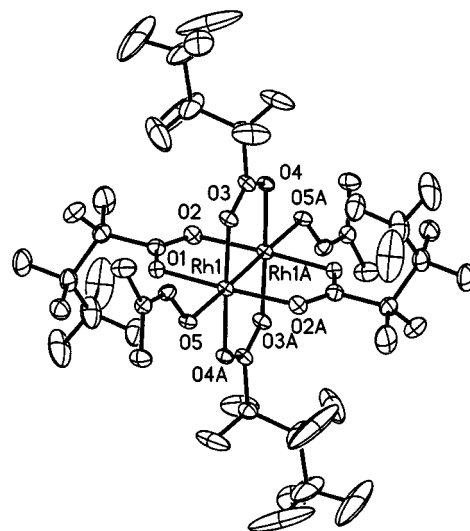


Figure 2. Drawing of Rh₂(O₂C(CF₂)₃F)₄(DMF)₂ (**1**) showing one of the two centrosymmetric molecules in the structure. Thermal ellipsoids are drawn at the 30% probability level. Selected distances (Å) are as follows (second molecule values are given in brackets): Rh1–Rh1A, 2.4165(8) [2.4167(8)]; Rh1–O1, 2.022(4) [2.026(4)]; Rh1–O2A, 2.045(4) [2.050(4)]; Rh1–O3, 2.036(4) [2.035(4)]; Rh1–O4A, 2.045(4) [2.042(4)].

the fluorinated alkyl chains. Although the latter problem is difficult to avoid, the former problem can be obviated by recrystallization of the complexes from CO₂-expanded solvents.

Recrystallization of fluorinated solids was achieved by first identifying an appropriate antisolvent: an organic liquid in which the solid is insoluble. The antisolvents used in our study were nonprotic nonpolar solvents such as alkanes, cycloalkanes, or toluene. Second, the solubility of the solid in the CO₂-expanded antisolvent was confirmed visually in a vessel with windows, as described above and shown in Figure 1. Then mixtures of the insoluble solid and the antisolvent, in various proportions, were exposed to 50–70 bar CO₂ and stirred to ensure dissolution of the solid in the expanded liquid. CO₂ was released, either (a) slowly over 1 week or (b) rapidly over 1–4 h, and the sample then left to complete crystallization at 1 bar.

Crystals of complex **1** (44% F by mass) were obtained by slow release of CO₂ from toluene. Crystals of complex **2** (62% F by mass) were obtained by rapid release of CO₂ from cyclohexane. The structures of **1** and **2** (Figures 2 and 3) show that the core of the complex is similar to those of other bis-adducts of Rh₂(O₂CR)₄. The Rh–Rh bond distances (2.416 and 2.404 Å for **1** and **2**, respectively) are shorter than that of Rh₂(O₂CCF₂CF₂CF₃)₄(TEMPO)₂ (2.431 Å, TEMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxy),⁴¹ comparable to that⁴² of Rh₂(O₂CCF₃)₄(MeCN)₂, and longer than that of Rh₂(OAc)₄(DMF)₂ (2.383 Å).⁴³ The Rh–O(carboxylate) distances (2.02–2.05 Å) are virtually identical in all five of these dirhodium carboxylate complexes. The motion

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(40) There are a few examples of X-ray structures of high fluorine content (>50% by mass) organometallic complexes.^{34,49–51}

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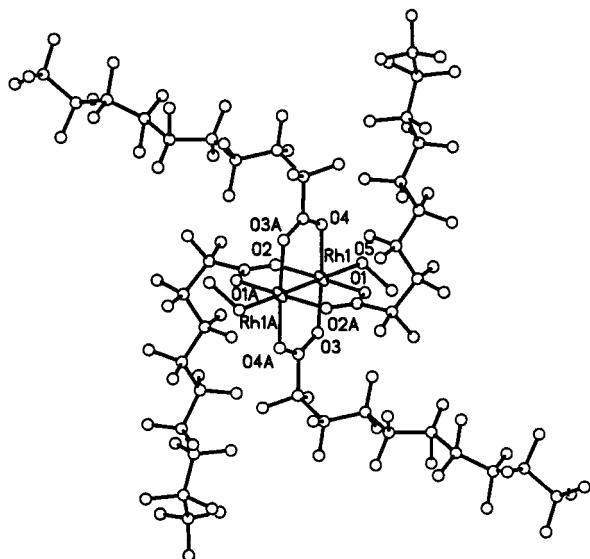


Figure 3. A drawing of **2**. Only one of the two orientations of the $(\text{CF}_2)_8\text{CF}_3$ groups is shown for clarity. The Rh's are drawn with anisotropic thermal ellipsoids at the 50% probability level; remaining atoms are drawn with circles of arbitrary size. Selected distances (\AA) are the following: Rh1–Rh1A, 2.404(3); Rh1–O1, 2.025(13); Rh1–O2, 2.066(14); Rh1–O3, 2.044(13); Rh1–O4, 2.035(14); Rh1–O5, 2.206(16).

of the fluorinated tails in **1** increases toward the end of the tails. Complex **2**, on the other hand, showed disorder over much of the length of its significantly longer fluorinated chains.

While phd and pnd complexes have negligible solubility in alkanes in the absence of CO_2 , complexes of other ligands with shorter perfluoroalkyl chains or lower fluorine content such as 1,1,1,5,5,5-hexafluoroacetylacetonate (hfacac) complexes (e.g. compound **5**, 51% F by mass) and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato (fod) complexes have some solubility in alkane solvents. Nevertheless, precipitation of hfacac and fod complexes from CO_2 -expanded decane was observed, and it was possible to crystallize such compounds from CO_2 -expanded decane. Crystals of compound **5** were obtained in this manner.

The molecular structure of solid $\text{Cr}(\text{hfacac})_3$ (**5**, Figure 4) was determined from these crystals; previously only the cell dimensions and space group of a hexagonal ($P6_3/mmc$) form of the solid were known.⁴⁴ Thomas et al.⁴⁵ reported that the *gas phase* structure of **5** was an exception to the stereochemical rules of Kepert,⁴⁶ which are equations for the prediction of the most stable twist angle, ϕ , for a given value of the normalized bite, b . The normalized bite is the O–O nonbonded distance divided by the M–O bond length. The twist angle refers to the angle of rotation of the upper triangular face of a $\text{M}(\text{bidentate})_3$ structure relative to the lower face; true trigonal prismatic structure gives a value of 0° while octahedral is 30° . The related parameter called pitch angle, θ , if one views the $\text{M}(\text{bidentate})_3$ structure as a three-bladed propeller, is the “angle of rotation of the blades (about their C_2 axes) relative to a D_{3h} reference configuration.”⁴⁵

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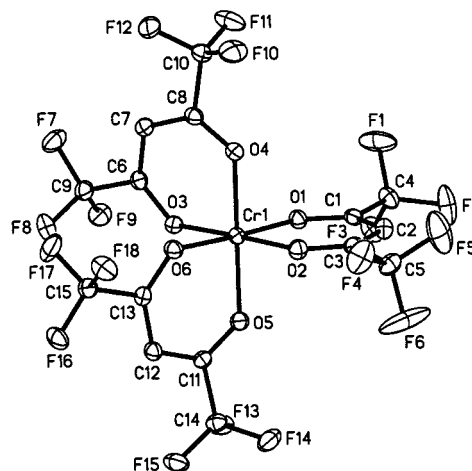


Figure 4. Drawing of $\text{Cr}(\text{hfacac})_3$ (**5**) with 50% probability thermal ellipsoids. Selected bond distances (\AA) are the following: Cr1–O1, 1.9594(11); Cr1–O2, 1.9556(12); Cr1–O3, 1.9513(11); Cr1–O4, 1.9638(12); Cr1–O5, 1.9601(11); Cr1–O6, 1.9500(11).

Table 2. Comparison of Selected Bond Lengths and Structural Parameters of $\text{Cr}(\text{diketonate})_3$ Structures

complex	Cr–O (\AA)	O–O (\AA)	b	ϕ (deg)	θ (deg)	ref
$\text{Cr}(\text{acac})_3$	1.961	2.79	1.42	35.4	30.4	47
$\text{Cr}(\text{hfacac})_3$ (gas)	1.957	2.69	1.38	37.6	30.1	45
$\text{Cr}(\text{hfacac})_3$ (solid) octahedron	1.957	2.78	1.42	36.5	31.0	this work
			1.414	35.3	30	45

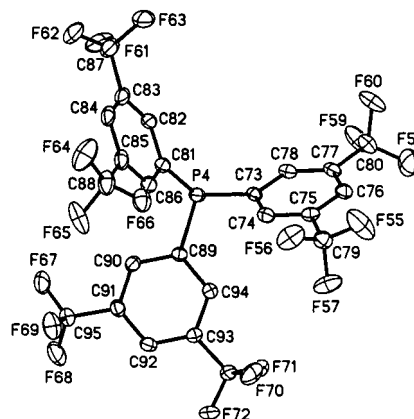


Figure 5. One of the four independent molecules of tris(3,5-bis(trifluoromethyl)phenyl)phosphine (**6**) is depicted with 50% probability thermal ellipsoids. The 12 P–C distances average 1.8364 \AA with an average deviation of 0.0016 \AA .

We have found that the *solid*-state structure of **5** is *not* an exception to Kepert's rules. The Cr–O bond lengths in the gas and solid structures are identical, but a significant difference lies in the O–O distances (Table 2) and therefore in the normalized bites. The low value of b observed for the gas-phase structure of **5** leads to a low predicted θ of 28° (30.1° observed). In contrast, the b of 1.42 in solid **5** is essentially the same as that in $\text{Cr}(\text{acac})_3$ and in an idealized octahedron and leads to a prediction of a twist angle of 30.3° , which is within 0.7° of the observed angle for solid **5**.

Organic solids containing highly fluorinated groups can also be crystallized by the new method. Tris(3,5-bis(trifluoromethyl)phenyl)phosphine (compound **6**, 51% F by mass) was crystallized by release of CO_2 from CO_2 -expanded

cyclohexane (16 mg in 100 μL cyclohexane), yielding colorless plates. In the structure (Figure 5), the P–C–P angles average 101.7° , slightly smaller than in more electron rich triarylphosphines such as $\text{P}(\text{C}_6\text{H}_4\text{-}i\text{-Cl})_3$ (101.9°) and PPh_3 (102.8°). The average P–C bond length is virtually identical to those in the other triarylphosphines. A tetracarbonyliron complex containing **6** as a ligand has been crystallographically characterized.⁴⁸

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Conclusions. The application of gaseous CO_2 to nonpolar aprotic solvents renders them temporarily and reversibly fluorophilic, enabling them to dissolve highly fluorinated solids. The release of the CO_2 pressure causes the quantitative precipitation or crystallization of the fluorinated solute. The application of this technique to the laboratory preparation of crystals for X-ray crystallography has been demonstrated.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $\text{Rh}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{-CF}_3)_4(\text{DMF})_2$, $\text{Rh}_2(\text{O}_2\text{C}(\text{CF}_2)_9\text{F})_4(\text{MeOH})_2$, $\text{Cr}(\text{hfacac})_3$, and $\text{P}\{\text{C}_6\text{H}_3\text{-}(3,5\text{-CF}_3)_2\}_3$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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