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Complexes exhibiting non-conventional solubility: synthesis and characterization of *trans*-$Pt[(CF_3(CF_2)_5(CH_2)_2)_3P]_2Cl_2$☆

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Abstract

Synthetic approaches have been developed for preparing fluorocarbon solvent and liquid and supercritical CO_2 (sc CO_2) soluble organometallic complexes. To explore solubility in these media, the synthesis of a number of organometallic complexes containing the phosphine ligand $(CF_3(CF_2)_5(CH_2)_2)_3P$ **2**, is reported. The platinum(II) complex, *trans*-$Pt[(CF_3(CF_2)_5(CH_2)_2)_3P]_2Cl_2$ **1**, has been synthesized, isolated, and characterized by X-ray crystallography and ^{31}P-NMR spectroscopy. Complex **1**, $PtC_{48}H_{24}Cl_2F_{78}P_2$ crystallizes in the triclinic space group $P\bar{1}$, with $a = 11.632(2)$, $b = 16.970(2)$, $c = 20.838(3)$ Å; $\alpha = 71.67(1)$, $\beta = 80.22(2)$, $\gamma = 88.18(2)°$; $Z = 2$, and R_F $(R_{WF2}) = 0.0789$ (0.108) for 8095 reflections. The Pt coordination is *trans* square planar with the long fluoroalkyl chains of the $(CF_3(CF_2)_5(CH_2)_2)_3P$ ligands being nearly perpendicular to the coordination plane. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Platinum; Phosphine; Crystal structure; Solubility

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1. Introduction

There has been considerable recent interest in supercritical CO_2 (sc CO_2) as an environmentally safe reaction medium, for example, in the production of new and environmentally friendly polymers [1]. Catalysts soluble in sc CO_2 are crucially important for certain types of reactions, such as the catalytic production of dimethylformamide from CO_2 [2]. A general method has been devised to determine the solubility characteristics of small molecules in supercritical fluids at various temperatures and pressures [3]. This method predicts the effect of the solvent on a substrate based on the absorbance spectrum of certain dyes. The spectrum of the dye changes as the solvent environment changes. The process by which this spectrum changes is termed solvatochromism [4]. An improved solvatochromic method of characterization was developed using a dye containing a perfluoroheptyl group to increase solubility [5]. Over much of the temperature and pressure regime of sc CO_2, the solubility is much the same as perfluorohexane. Complexes that are freely soluble in perfluoroalkyl solvents should also be freely soluble in liquid and sc CO_2.

Few transition metal complexes are soluble in perfluoroalkyl solvents. Complexes such as transition metal perfluorophthalocyanines, $MF_{16}Pc$, are completely insoluble in perfluoromethylcyclohexane at room temperature [6]. Perfluorophthalocyanines can be thought of as approximately planar molecules and as such have fluorine atoms in only two dimensions. Sufficient fluoroalkyl substituents appear to be a necessary requirement to impart CO_2 solubility.

The hydroformylation of olefins in a novel fluorous biphase system using $HRh(CO)(\mathbf{2})_3$ as the catalyst has

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☆ Dedicated to Harvey J. Schugar on the occasion of his 60th birthday.

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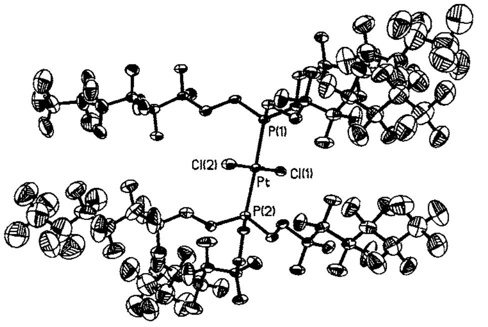

Fig. 1. Molecular structure of **1**. Thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms have been omitted for clarity.

already been demonstrated [7a,b]. Hydroformylation has also been performed in sc CO_2 [8]. Asymmetric catalytic hydrogenation in sc CO_2 has also been reported [9]. New synthetic methods that provide potential catalysts with non-conventional solubility is an important goal in order to take full advantage of the solvent. Reported here are the synthesis of a number of organometallic complexes containing the phosphine ligand $(CF_3(CF_2)_5(CH_2)_2)_3P$, **2**, which contains two methylene spacers designed to control the electron withdrawing effects of fluorine, while retaining fluorous and CO_2 solubility. The platinum(II) complex, *trans*-$Pt[(CF_3(CF_2)_5(CH_2)_2)_3P]_2Cl_2$ **1**, has been synthesized, isolated, and characterized by X-ray crystallography and ^{31}P-NMR spectroscopy.

2. Results and discussion

To date, very few crystal structures of metal complexes containing long fluoroalkyl chains have been reported [10]. A view of the *trans* square planar Pt complex **1** is given in Fig. 1. The fluorous alkyl chains are nearly perpendicular to the Pt coordination plane. When viewing down the P–Pt–P axis the alkyl chains uniquely stagger approximately C_6 from the Cl–Pt–Cl axis with two chains stacked doubly. The Pt coordination bond distances are very similar to those found for *trans*-$Pt((NCH_2CH_2)_3P)_2Cl_2$ in the solid state [11]. In that structure, the alkyl chains are also nearly perpendicular to the Pt coordination plane, while the two chlorides lie in two quadrants and the alkyl chains form two quadrants of three chains staggered approximately by C_{12}. Two other arrangements are known for R groups contained in *trans* square planar Pt bisphosphine dichlorides in the solid state. Those containing almost no staggering [12] and those containing approximately C_6 staggering [13].

The thermal motion of the fluorinated alkyl chains is as expected, higher at the ends of the chains. This behavior has been observed in other structures [14]. Another factor contributing to higher thermal motion in certain chains in the molecule over others is related to crystal packing forces. The molecular arrangement of the chains is such that the near neighbor interactions vary for each chain in the molecule. As the near neighbor interactions lessen, the corresponding thermal motion of the chain increases.

The presence of long fluorous alkyl chains connected to the phosphorus atom through an ethylene spacer imparts a number of potentially desirable qualities to the phosphine ligand. The electron-withdrawing effect of the fluorines should impart oxidative stability to the phosphorus atom over that of the more basic trioctyl alkyl phosphine [15]. The inertness of the aliphatic C–F bonds should also impart higher stability to the alkyl portion of the ligand over that of the corresponding trioctyl perhydroalkyl phosphine. The ethylene spacer also acts to insulate the phosphine from extreme electron-withdrawing effects, which can cause chemistry distinctly different from that of the common more basic donor phosphine analogues [16]. As $(CNCH_2CH_2)_3P$ is expected to have similar donating properties as triphenylphosphines [15] so should **2**. In *trans*-Pt bisphosphine dichloride complexes, comparable Pt–P bond distances are indicative of similar basicity due to the σ bonding and the amount of available π back bonding. In **1**, the average Pt–P bond distance is 2.315(4) Å which compares to *trans*-$Pt((CNCH_2CH_2)_3P)_2Cl_2$ with a bond length of 2.312(3) Å and a Pt–P distance of 2.316(1) Å for a *trans*-triphenynlphosphine complex [17]. Finally, the fluoroalkyl chains impart non-conventional solubility. That is, just two ligands on a metal center is enough to render the molecule freely soluble in fluorous media as well as in CO_2.

Even though **2** is expected to have a similar basicity to triphenylphosphine, ligand exchange was shown to be an effective synthetic route in the case of Pt(II), and Ru(II). Taking advantage of the solubility of the product in fluorous solvents, isolation in pure form can be affected in quantitative yield by simple separation without further purification. In order to ensure pure separation it is important to purify the perfluoromethylcyclohexane as described in Section 3 in order to remove any hydro contaminant in the solvent. This method was found to be ineffective in the case of Pd(II), the preparation of which required starting with compounds containing labile non-phosphorus ligands such as nitriles or COD. The explanation for this observation is not immediately obvious since the Pt(II) complex is expected to be more thermodynamically and kinetically stable than the Pd(II) analogue. The Ru(II)(**2**)$_4$Cl$_2$ complex was prepared by the biphasic synthetic method using $Ru((C_6H_5)_3P)_3Cl_2$ as the starting material. The product is isolated as a viscous orange oil. Complete elemental analysis is in very good agreement with Ru(II) having four **2** ligands associated with it. On the ^{31}P-NMR time scale, the complex exists in equilibrium as a number of species that were inseparable by chromatography.

Complex **3** was prepared for the purpose of comparison with compound to **1**. The ^{31}P-NMR of **3** is shifted upfield by 4.60 ppm to that of **1**. The *cis* complex of **3** has been reported as a very clean product [18] and the *trans* form was not reported presumably because of impurity. In an attempt to take advantage of the *trans*-effect, complex **3** was prepared from *cis*-Pt($CH_3CN)_2Cl_2$ but gives only 90% purity. Also present is the *cis* form (− 1.55 ppm) at ca. 4% and a likely dimeric form (50 ppm) at ca. 6%. Further purification of **3** was not attempted.

Complexes **1** and **4**, which contain only two phosphine ligands, were readily obtained as crystalline solids. On the other hand it is not surprising that **2**, which is a highly fluorinated tris *n*-octylphosphine, a complex with Ru(II) which contains four phosphine ligands, was only obtained as a viscous oil. The ^{31}P-NMR results for the four complexes are consistent with these observations. Complexes **1** and **4** give a very clean spectra of the *trans* conformation. From the crystal structure of **1** the visible steric constraints are evident that favor *trans* square planer form of the complex. This is consistent with obtaining pure *trans* forms of both **1** and **4**, when most synthetic procedures used to prepare bisphosphinedichlorides yield the *cis* isomer. Synthetic method III for the preparation of **1** was specifically used in an attempt to prepare the *cis* conformation. Barring solvent effects, the added bulk of the fluorine atoms overcomes the *trans*-effect for Pt, which is not observed in the perhydro version of the complex. The sterically crowded square-bipyramidal Ru(II) metal center forces different conformations to exist in equilibrium, which is evidenced by its ^{31}P-NMR spectra.

The solubility and stability of complexes **1** and **4** were examined by dissolving 90 mg of the complex in 6.0 ml of liquid CO_2 in a high pressure sapphire NMR tube. Over the entire range of temperature and pressure of the experiment for each of the complexes, a broadened ^{31}P-NMR spectra, which retained a constant peak width at half height, was observed. This was likely a dynamic effect due to the lack of spinning. A 6.12 mM concentration of **1** in CO_2 is on the order of a previously reported highly fluorinated phosphine complex [8]. At 25°C the complex is in the liquid CO_2 regime and upon heating passes near the critical point of CO_2 into the supercritical regime. There was an upfield shift of 1 ppm in the ^{31}P-NMR in CO_2 versus fluorous solvent. A modest interaction with CO_2 can not be ruled out at this time and will be further investigated.

This preliminary study effectively demonstrates the feasibility of synthesizing stable transition metal complexes which exhibit non-conventional solubility. These complexes should retain the reactivity characteristics of classical triphenylphosphine complexes while being soluble in fluorous or CO_2 media. Studies designed to explore the reactivity of these complexes in non-conventional media are in progress.

3. Experimental

All manipulations were conducted under argon using Schlenk and glovebox techniques. Methylenechloride, pentane, hexane, and toluene were distilled from CaH_2. Perfluoromethylcyclohexane, PFMCH, was purified by repeated extractions with methanol followed by three cycles of pump–freeze–thaw. Compound **2** was obtained as in Ref. [7a]. All other reagents were used as purchased from Strem or Aldrich. Melting points were determined with a hot-stage apparatus and are uncorrected. IR spectra were measured using a Mattson Galaxy Series FTIR 5000. Mass spectra were measured with a VG Analytical ZAB2-SEQ mass spectrometer and calibrated with a polystyrene standard. ^{1}H-, ^{19}F-, and ^{31}P-NMR were measured using a Varian Unityplus 500 spectrometer. For high pressure NMR studies, a custom made high pressure sapphire tube was used to determine solubility [19]. The spectra were obtained unlocked and without spinning and ^{31}P-NMR referenced to external H_3PO_4 standard. In a typical experiment, 90 mg of complex **1** was completely solubilized in 6.0 ml of liquid CO_2. The ^{31}P-NMR was monitored over a temperature range of 25–74°C during which the pressure varied from 900 to 1250 psi, respectively.

3.1. *trans*-$Pt[(CF_3(CF_2)_5(CH_2)_2)_3P]_2Cl_2$ (1)

3.1.1. Method I

To a suspension of 200 mg of *cis*-$Pt(C_6H_5CN)_2Cl_2$ (0.42 mmol) in 8 ml of CH_3CN, a solution of 908 mg of $(CF_3(CF_2)_5(CH_2)_2)_3P$, **2**, (0.85 mmol) dissolved in 8 ml PFMCH was added to give a biphasic mixture. The mixture was stirred overnight giving a colorless CH_3CN phase and a very pale-yellow PFMCH phase. The phases were separated and the PFCMH was removed by vacuum giving a pale-yellow solid. Suitable X-ray quality crystals were grown by dissolving **1** in 4 ml of perfluorobenzene followed by slow vapor diffusion of hexane. ^{31}P-NMR (PFMCH): δ 10.66 (t, ^{1}J Pt–P = 2528 Hz). IR (KBr pellet, cm^{-1}): 1240 (s), 1211 (s), 1188 (s), 1142 (s), 1123 (sh), 1072 (m), 747 (m), 730 (m), 709 (m), 650 (m), 567 (m), 531 (m). m.p. 82–83°C.

3.1.2. Method II

To a suspension of 100 mg of *cis*-$Pt((C_6H_5)_3P)_2Cl_2$ (0.13 mmol) in 8 ml of CH_3CN, a solution of 280 mg of **2** (0.26 mmol) dissolved in 8 ml PFMCH was added to give a biphasic mixture. The mixture was stirred overnight giving a colorless CH_3CN phase and a very pale-yellow PFMCH phase. The phases were separated and the PFMCH was removed by vacuum giving a pale-yellow solid. ^{31}P-NMR (PFMCH): δ 10.66 (t, ^{1}J Pt–P = 2528 Hz); m.p. 82–83°C; FD MS Calc. for $^{194}PtC_{48}H_{24}Cl_2F_{78}P_2$: 2409.4. Found: 2409.3.

3.1.3. *Method III*

To a solution of 70 mg of Pt(COD)Cl_2 (0.19 mmol) dissolved in 8 ml of CH_2Cl_2, 400 mg of **2** (0.37 mmol) was added and the mixture was stirred overnight giving a very pale-pink solution. The solvent was removed under vacuum giving a very pale-pink solid. ^{31}P-NMR (CCl_2FCClF_2): δ 9.92 (t, ^{1}J Pt–P = 2543 Hz); ^{19}F-NMR (CCl_2FCClF_2,$CFCl_3$ ref.): δ −82.0, −115.9 (t, $J = 15.0$ Hz), −122.6, −122.7, −124.0, −127.1; ^{1}H-NMR (CCl_2FCClF_2): δ 2.79 (br, 2H) 2.53 (br, 2H); m.p. 82–83°C; FD MS Calc. for $^{194}PtC_{48}H_{24}Cl_2F_{78}P_2$: 2409.4. Found: 2409.1.

3.2. *trans-Pt[(CH$_3$(CH$_2$)$_7$)$_3$P]$_2$Cl$_2$ (**3**)*

To a solution of 40 mg of *cis*-Pt$(CH_3CN)_2Cl_2$ (0.12 mmol) dissolved in 20 ml of CH_2Cl_2, 85 mg (0.23 mmol) of $(CH_3(CH_2)_7)_3P$ was added. The solution was stirred overnight. The solvent was removed under vacuum to give a yellow wax. ^{31}P-NMR (CCl_2FCClF_2): δ 5.32 (t, ^{1}J Pt–P = 2534 Hz); FD MS Calc. for $^{194}PtC_{48}H_{102}Cl_2P_2$: 1006.1. Found: 1006.1.

3.3. *trans-Pd[(CF$_3$(CF$_2$)$_5$(CH$_2$)$_2$)$_3$P]$_2$Cl$_2$ (**4**)*

To a solution of 100 mg of Pd$(CH_3CN)_2Cl_2$ (0.39 mmol) dissolved in 8 ml of acetonitrile, 831 mg of **2** (0.78 mmol) dissolved in 8 ml of PFMCH was added to give a biphasic mixture. The mixture was stirred overnight. The fluorous phase became dark yellow leaving a colorless acetonitrile phase. Yellow crystalline **4** can be obtained by slow evaporation of perfluorobenzene. ^{31}P-NMR (PFMCH): δ 14.2; ^{1}H-NMR (CCl_2FCClF_2): δ 2.77 (br, 2H) 2.60 (br, 2H). IR (KBr pellet, cm^{-1}): 1240 (s), 1211 (s), 1188 (s), 1142 (s), 1123 (sh), 1072 (m), 747 (m), 730 (m), 709 (m), 650 (m), 567 (m), 530 (m). m.p. 79–80°C; FD MS Calc. for $^{106}PdC_{48}H_{24}Cl_2F_{78}P_2$ 2321.3 Found: 2321.0.

3.4. *X-ray structure determination*

A very pale-yellow crystal of **1,** 0.10 × 0.20 × 0.50 mm lath, was mounted on the diffractometer. Diffraction measurements were made with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation. The Enraf–Nonius Structure Determination Package [20] was used for data collection. Crystal data and additional details regarding data collection and refinement are presented in Table 1. Intensity data were collected and corrected for decay, absorption (empirical), and Lp effects. The structure was solved by direct methods [21] and refined on F with full matrix least-squares techniques [22]. Following anisotropic refinement, all H atoms were placed at calculated positions; they were not refined. Selected bond distances and angles are given in Table 2.

Table 1
Crystal and refinement data for **1**

Empirical formula	$PtC_{48}H_{24}Cl_2F_{78}P_2$
Formula weight (g mol^{-1})	2410.60
Unit cell dimensions	
a (Å)	11.632(2)
b (Å)	16.970(2)
c (Å)	20.838(3)
α (°)	71.67(1)
β (°)	80.22(2)
γ (°)	88.18(2)
V (Å^3)	3846.8(10)
Z	2
$D_{calc.}$ (g cm^{-3})	2.081
Temperature (K)	258(5)
Space group	Triclinic, $P\bar{1}$
Crystal size (mm)	0.50 × 0.20 × 0.10
Index ranges	$0 \leq h \leq 12$, $-18 \leq k \leq 18$, $-22 \leq l \leq 22$
Reflections collected	11 256
Independent reflections	10 634
Max./min. transmission	0.821, 0.619
μ, (mm^{-1})	2.161
S^{a}	1.085
$I > 2\sigma(I)$	8095
R_F, R_{wF}^{a}	0.0789, 0.108
Radiation (λ, Å) graphite-monochromated	Mo–K$_\alpha$ (0.71073)
Residual electron density (e A^{-3})	1.4 and −1.0

[a] Definitions: $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$; GOF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{par})\}^{0.5}$, with weights $w = 1/[\sigma^2(F_o^2) + 0.18{*}P^2]$, where $P = [0.33333{*}\mathrm{MAX}(0,F_o^2) + 0.66667{*}F_c^2]$. Additional crystallographic details are given in Section 4.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 103278 for compound **1.** Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Structure factor tables can be obtained from R.T.S.

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Table 2
Significant bond lengths (Å) and bond angles (°) for **1**

Bond lengths (Å)			
Pt–Cl(2)	2.293(3)	Pt–Cl(1)	2.300(3)
Pt–P(1)	2.312(3)	Pt–P(2)	2.318(3)
P(1)–C(1)	1.823(10)	P(1)–C(17)	1.830(10)
P(1)–C(9)	1.842(10)	P(2)–C(33)	1.823(11)
P(2)–C(41)	1.827(10)	P(2)–C(25)	1.846(11)
Bond angles (°)			
Cl(2)–Pt–Cl(1)	179.68(13)	Cl(2)–Pt–P(1)	87.81(12)
Cl(1)–Pt–P(1)	91.97(11)	Cl(2)–Pt–P(2)	88.97(12)
Cl(1)–Pt–P(2)	91.25(11)	P(1)–Pt–P(2)	176.77(11)
C(1)–P(1)–C(17)	104.6(6)	C(1)–P(1)–C(9)	104.6(6)
C(17)–P(1)–C(9)	103.3(6)	C(1)–P(1)–Pt	114.4(4)
C(17)–P(1)–Pt	111.9(4)	C(9)–P(1)–Pt	116.7(4)
C(33)–P(2)–C(41)	105.5(5)	C(33)–P(2)–C(25)	105.1(7)
C(41)–P(2)–C(25)	102.5(6)	C(33)–P(2)–Pt	116.7(4)
C(41)–P(2)–Pt	111.7(4)	C(25)–P(2)–Pt	114.2(4)

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