



Note

Preparation of an unusual fluoroalkyl phosphinoyl chelate complex, $\{k^3\text{-P,C,P},k^1\text{-O-(CF}_3)_2\text{PCH}_2\text{C}_6\text{H}_3\text{CH}_2\text{P(CF}_3\text{)O}\}_2\text{Pt}_2$

Jeramie J. Adams, Navamoney Arulsamy, Dean M. Roddick*

Department of Chemistry, Box 3838, University of Wyoming, Laramie, WY 82071, United States

ARTICLE INFO

Article history:

Received 23 May 2008

Received in revised form 15 July 2008

Accepted 22 August 2008

Available online 29 August 2008

Keywords:

X-ray crystal structures

Platinum complexes

Pincer complexes

Phosphine ligand hydrolysis

Perfluoroalkyl phosphines

ABSTRACT

Electron poor cationic complexes $[(\text{CF}_3\text{PCP})\text{Pt(L)}]^+$ (where L = CO, NC_5F_5 , or acetone) react with H_2O in polar solvents via selective hydrolysis of a single P– CF_3 substituent to afford the spectroscopically-characterized phosphinoyl-bridged complex $\{k^3\text{-P,C,P},k^1\text{-O-(CF}_3)_2\text{PCH}_2\text{C}_6\text{H}_3\text{CH}_2\text{P(CF}_3\text{)O}\}_2\text{Pt}_2$ (**1**) in good yield. X-ray diffraction confirms the presence of a six-member Pt–P–O–Pt–P–O ring in a chair conformation. The presumed intermediate aqua complex, $(\text{CF}_3\text{PCP})\text{Pt}(\text{H}_2\text{O})^+$, is stable in dichloromethane, but when dissolved in more polar solvents readily converts to **1**.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The synthesis of new types of phosphine ligands remains an important component of metal coordination chemistry and homogeneous catalysis. We have recently reported the synthesis and initial coordination studies of the novel perfluoroalkyl-substituted “pincer-type” PCP chelating ligand, 1,3- $(\text{CH}_2\text{P}(\text{CF}_3)_2)_2\text{C}_6\text{H}_4$ (abbreviated as CF_3PCPH) [1]. Metallation of $(\text{cod})\text{Pt}(\text{Me})\text{Cl}$ by CF_3PCPH cleanly afforded $(\text{CF}_3\text{PCP})\text{PtCl}$, which readily undergoes halide abstraction by Ag^+ in the presence of CO to form the carbonyl cation $(\text{CF}_3\text{PCP})\text{Pt}(\text{CO})^+$. During the course of this work, we observed that exposure of acetone solutions of $(\text{CF}_3\text{PCP})\text{Pt}(\text{CO})^+$ to air resulted in the precipitation of a crystalline material which X-ray analysis has shown to be an unusual platinum dimer with bridging phosphinoyl acid groups derived from the apparent selective hydrolysis of a single P– CF_3 bond on the PCP ligand. In this note we report the synthesis and characterization of this unexpected product, and present some observations pertaining to the mechanism of its formation.

2. Results and discussion

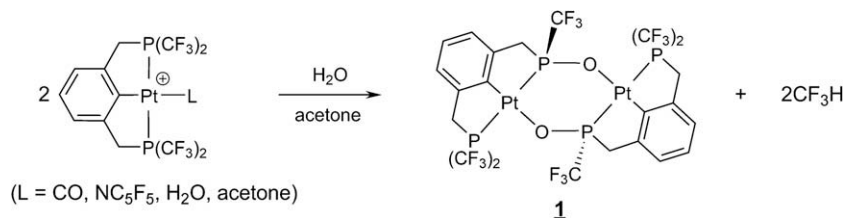
Exposure of the electron poor cationic complexes $[(\text{CF}_3\text{PCP})\text{Pt(L)}]^+\text{X}^-$ (where L is CO or pentafluoropyridine; and X is SbF_6^- or $\text{B}(\text{C}_6\text{F}_5)_4^-$, respectively) to ambient air or anaerobic conditions in the presence of H_2O , while dissolved in polar solvents such

as acetone, methanol, or ethanol, results in selective hydrolysis of a single P– CF_3 substituent and dimerization to give the complex $\{k^3\text{-P,C,P},k^1\text{-O-(CF}_3)_2\text{PCH}_2\text{C}_6\text{H}_3\text{CH}_2\text{P(CF}_3\text{)O}\}_2\text{Pt}_2$ (**1**) in good yield (Scheme 1). For the complex $(\text{CF}_3\text{PCP})\text{Pt}(\text{CO})^+\text{SbF}_6^-$, complete conversion and precipitation of **1** from reagent grade acetone under ambient air conditions required two weeks. Similar results were obtained in methanol and ethanol.

The NMR spectroscopy of **1** is consistent with its dimeric formulation. In ^1H spectra, in addition to overlapping aromatic resonances at δ 6.8 in $\text{DMSO-}d_6$, complex non-first-order resonances are seen between 3.35 and 4.02 ppm for the four inequivalent diastereotopic benzylic protons. ^{31}P NMR spectra exhibit mutually-coupled resonances at 77.1 and 87.2 ppm with $^2J_{\text{PP}} = 400$ Hz. The downfield resonance appears as a pentet due to coupling to one CF_3 group and the upfield resonance appears as a heptet due to coupling to two CF_3 groups, allowing us to assign these resonances to the hydrolyzed $\text{P}(\text{CF}_3)\text{O-}$ and unhydrolyzed $\text{P}(\text{CF}_3)_2$ units, respectively. ^{19}F NMR spectra show three doublets of equal intensity due to the three inequivalent CF_3 groups.

NMR control experiments were carried out with the labile pentafluoropyridine (pfpy) complex, $(\text{CF}_3\text{PCP})\text{Pt}(\text{pfpy})^+\text{B}(\text{C}_6\text{F}_5)_4^-$ [2]. Dissolution of the pfpy complex in freshly dried and vacuum distilled acetone- d_6 resulted only in displacement of pfpy to form the acetone complex, $(\text{CF}_3\text{PCP})\text{Pt}(\text{acetone})^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**2**). Addition of 1 atm of O_2 to **2** resulted in no spectral changes after 3 days. However, addition of approximately 18 equiv of H_2O to an acetone solution of **2** resulted in complete conversion to the dimeric hydrolysis product after 5 h at ambient temperature. The generation of CF_3H as a hydrolysis product was confirmed by ^{19}F NMR.

* Corresponding author. Tel.: +1 307 766 2535; fax: +1 766 2807.
E-mail address: dmr@uwyo.edu (D.M. Roddick).



Scheme 1.

Interestingly, while the reaction between $(\text{CF}_3\text{PCP})\text{PtCl}$ and AgSbF_6 in acetone under ambient air also produced **1**, this same reaction in dichloromethane instead gave the aqua complex, $(\text{CF}_3\text{PCP})\text{Pt}(\text{H}_2\text{O})^+\text{SbF}_6^-$ (**3**) [2].¹ Complex **3** is indefinitely stable in dichloromethane at room temperature; however, addition of excess water to $(\text{CF}_3\text{PCP})\text{Pt}(\text{H}_2\text{O})^+\text{SbF}_6^-$ when dissolved in 1,2-difluorobenzene resulted in conversion to **1** after 1 h at 20 °C. The stability of the aqua complex in a low dielectric constant solvent such as dichloromethane for several weeks suggests that higher polarity solvents help to facilitate P–CF₃ bond hydrolysis.

2.1. Crystal structure of $\{k^3\text{-P,C,P,k}^1\text{-O}-(\text{CF}_3)_2\text{PCH}_2\text{C}_6\text{H}_3\text{CH}_2\text{P}(\text{CF}_3)\text{O}\}_2\text{Pt}_2$ (**1**)

Crystals suitable for X-ray diffraction were grown from an acetone solution of $(\text{CF}_3\text{PCP})\text{Pt}(\text{CO})^+\text{SbF}_6^-$ exposed to ambient air. The dimer resides on an inversion center and consists of a core six-member Pt–P–O–Pt–P–O ring in a chair conformation, with the plane defined by the Pt(1), P(2), O(1) unit tilted by 30.0° with respect to the plane defined by P2, P2A, O1, and O1A (Fig. 1). The pincer units have a P(1)–Pt(1)–P(2) angle of 165.2°, which is indicative of relatively little sterically-induced distortion [2]. The Pt(1)–P(1) bond distance of 2.2571(6) Å is virtually identical to the Pt(1)–P(2) bond distance (2.2549(6) Å) and indicates that replacement of a CF₃ phosphorus substituent with oxygen does not induce any major change in the platinum coordination environment. Several R₂PO-bridged platinum dimers have been reported [3,4]. The closest reported analog to $\{k^3\text{-P,C,P,k}^1\text{-O}-(\text{CF}_3)_2\text{PCH}_2\text{C}_6\text{H}_3\text{CH}_2\text{P}(\text{CF}_3)\text{O}\}_2\text{Pt}_2$ is $\{[k^2\text{-C,N-C}_6\text{H}_4\text{CH}_2\text{NMe}_2]\text{Pt}(\mu\text{-PPh}_2\text{O})\}_2$, which contains a metalated *N,N*-dimethylbenzylamine ligand and bridging Ph₂PO groups [3]. In this structure, the 6-atom core is a hinged conformation with a 48° angle between planes defined by each O–Pt–P–O unit. The P(2)–O(1A) (1.528(2) Å) and Pt(1)–O(1) (2.119(2) Å) bond lengths found in **1** are very similar to corresponding values (P–O: 1.53(1), 1.56(1) Å; Pt–O: 2.116(1), 2.098(11) Å) for this structure. The observed P–O bond lengths for **1** are slightly longer than bond lengths of 1.509(6)–1.517(4) Å reported for a (RO)₂PO-bridged (R = H or Me) ruthenium dimer, where the bridging group is viewed as a phosphine oxide donor, but shorter than P–O single bonds which range between 1.58 and 1.61 Å [5].

The mechanism underlying the formation of **1** is not obvious. Perfluoroalkyl-substituted phosphorus(III) compounds do not readily hydrolyze, though (CF₃)₃PO does readily react with water to form (CF₃)₂P(O)OH [6] and Ph₃C–P bonds are cleaved by strong Brønsted acids [7]. Of more relevance may be the P–C bond hydrolysis in (Binap)Ru(OAc)₂ by HOTf to selectively form a Ru(II)–PPh₂(OH) complex [5]. Control experiments indicate that $(\text{CF}_3\text{PCP})\text{Pt}(\text{L})^+$ (L = C₅F₅N or CO) cleanly generates **1** in the presence of water. Due to the highly electrophilic nature of the $(\text{CF}_3\text{PCP})\text{Pt}^+$

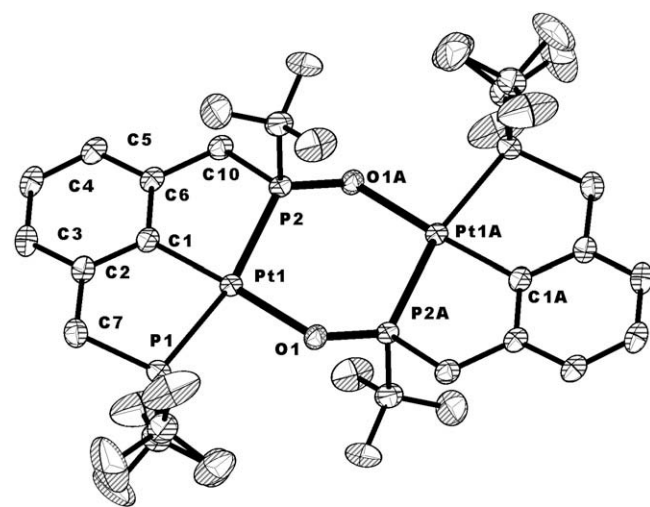


Fig. 1. Molecular structure of $\{k^3\text{-P,C,P,k}^1\text{-O}-(\text{CF}_3)_2\text{PCH}_2\text{C}_6\text{H}_3\text{CH}_2\text{P}(\text{CF}_3)\text{O}\}_2\text{Pt}_2$ (**1**) with atom labeling scheme (30% probability ellipsoids). 100.38(5); O(1A)–P(2)–Pt(1): 123.06(7); P(2A)–O(1)–Pt(1): 124.33(10).

moiety, the initially-formed water adduct $(\text{CF}_3\text{PCP})\text{Pt}(\text{H}_2\text{O})^+$ is expected to be highly acidic and may promote P–CF₃ bond cleavage [8]. The selective hydrolysis of only one P–CF₃ group to give **1** in good yield is likely due to precipitation of the dimer prior to subsequent hydrolysis. In a broader sense, the selective conversion of a symmetrical diphosphine R₂P(bridge)PR₂ to R₂P(bridge)PR(X) suggests that a metal templating approach may be developed where the X group offers a site for further ligand modification or polymer attachment [9].

3. Experimental

All manipulations were conducted under N₂ or vacuum using high-vacuum line and glovebox techniques unless otherwise noted. All ambient pressure chemistry was carried out under a pressure of approximately 590 torr (elevation ~2195 m). All solvents were dried using standard procedures and stored under vacuum. Aprotic deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. Elemental analyses were performed by Desert Analytics. NMR spectra were obtained with a Bruker DRX-400 instrument. ³¹P spectra were referenced to an 85% H₃PO₄ external standard. ¹⁹F spectra were referenced to CF₃CO₂CH₂CH₃ (δ –75.32). The synthesis of $(\text{CF}_3\text{PCP})\text{Pt}(\text{CO})^+\text{SbF}_6^-$ has been reported [1].

3.1. Preparation of $\{k^3\text{-P,C,P,k}^1\text{-O}-(\text{CF}_3)_2\text{PCH}_2\text{C}_6\text{H}_3\text{CH}_2\text{P}(\text{CF}_3)\text{O}\}_2\text{Pt}_2$ (**1**)

$(\text{CF}_3\text{PCP})\text{Pt}(\text{CO})^+\text{SbF}_6^-$ (0.210 g, 0.233 mmol) was dissolved in 3 mL of reagent grade acetone in the presence of ambient air. Slow solvent evaporation from a capped vial to ca. 1 mL occurred over 2

¹ Spectroscopic data for $(\text{CF}_3\text{PCP})\text{PCP})\text{Pt}(\text{H}_2\text{O})^+\text{SbF}_6^-$: ¹H NMR (CD₂Cl₂, 400.13 MHz, 20 °C): δ 7.32 (m, 3H; Ar), 4.08 (m, 4H; ArCH₂), 2.19 (br s, 2H; H₂O). ³¹P NMR (CD₂Cl₂, 161.97 MHz, 20 °C): δ 64.4 (m, ¹J_{PTP} = 3660 Hz). ¹⁹F NMR (acetone-*d*₆, 376.50 MHz, 20 °C): δ –53.5 (m, PCF₃). IR (Nujol, cm^{–1}): ν(H₂O) = 3453 cm^{–1}.

Download English Version:

<https://daneshyari.com/en/article/1311422>

Download Persian Version:

<https://daneshyari.com/article/1311422>

[Daneshyari.com](https://daneshyari.com)