

Preliminary communication

**Synthesis and characterization of an organometallic phosphonic acid:
X-ray crystal structure of $[\eta^6\text{-}p\text{-C}_6\text{H}_4(\text{CH}_2\text{PO}_3\text{H}_2)_2]\text{Cr}(\text{CO})_3$** Robert W. Deemie^a, James C. Fettingner^b, D. Andrew Knight^{a,*}^a Department of Chemistry, The George Washington University, 725 21st Street, N.W. Washington, DC 20052, USA^b Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

Received 19 September 1996; revised 5 November 1996

Abstract

The transesterification and hydrolysis of $[\eta^6\text{-}p\text{-C}_6\text{H}_4(\text{CH}_2\text{PO}_3\text{Et}_2)_2]\text{Cr}(\text{CO})_3$ afforded the organometallic bisphosphonic acid $[\eta^6\text{-}p\text{-C}_6\text{H}_4(\text{CH}_2\text{PO}_3\text{H}_2)_2]\text{Cr}(\text{CO})_3$ (**3**) in 81% isolated yield. The bisphosphonic acid complex has been characterized by NMR and IR spectroscopies and its molecular structure determined by X-ray crystallographic analysis which represents the first structural analysis of an organotransition metal derived phosphonic acid. Compound **3** reacts with $\text{Zn}(\text{NO}_3)_2$ in aqueous methanol to give a hybrid inorganic–organometallic material in which the arene chromium tricarbonyl fragment remains intact.

Keywords: Chromium; Phosphonic acid

Layered phosphonates have received a great deal of attention recently owing to the wide variety of actual and potentially unique properties that such materials possess. The practical applications of metal phosphonates include energy storage, catalysis, ion exchange and enantioselective intercalation reactions [1–6]. Hong and Mallouk have successfully used bisphosphonic acids for the self-assembly of thin films possessing electroactive properties including a phosphonic acid derivative of ferrocene [7]. To date, the preparation of hybrid inorganic–organic phosphonate materials has been restricted to the use of fairly simple organic phosphonic acids, although Bujoli and coworkers have recently reported the use of a phosphonic acid functionalized manganese porphyrin for the preparation of a catalytically active metal phosphonate [8].

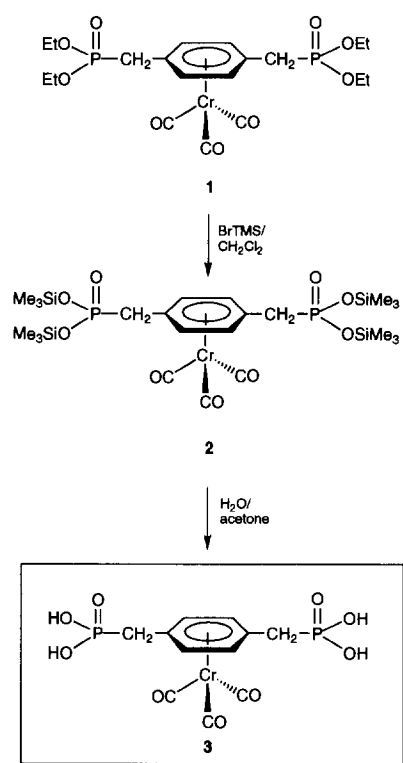
The intercalation of organometallic molecules into layered inorganic matrices has also been of theoretical and practical interest largely owing to their potential application as semiconductors, superconductors and catalysts [9]. Lee and Thompson prepared a layered zirconium hydrogen phosphate–manganese tricarbonyl compound by incorporating the organometallic molecule into the acidic layered host $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. Subse-

quent photolysis of the intercalated manganese carbonyl led to the dissociation of a carbonyl ligand and formation of a surface-supported organometallic complex containing manganese phosphinol bonds [10]. The intercalation of organometallic guest molecules into hosts such as tantalum sulfide, iron oxide chloride, zeolitic materials and urea has also recently been studied [11–14].

Our interest in this area is largely focused on the micro-environmental control of catalytically active molecules and the synthesis of stable pre-formed organometallic phosphonic acids. These acids can be used as building blocks for the preparation of covalently bonded three-dimensional inorganic–organometallic hybrid networks which may subsequently act as bifunctional or heterogenized catalysts. This communication describes the synthesis and first X-ray crystal structure analysis of an organotransition metal phosphonic acid and its subsequent incorporation into a hybrid inorganic–organometallic network.

The arene chromium tricarbonyl molecule was chosen as an ideal model for the formation of a hybrid organometallic phosphonate owing to the ease of synthesis, expected stability, and good spectroscopic handles. The synthetic strategy that we employed relied on the well known transesterification of a phosphonic acid diethylester using bromotrimethylsilane (TMSBr), followed by ester cleavage via aqueous hydrolysis to give the desired phosphonic acid. Thus, treatment of $[\eta^6\text{-}p\text{-}$

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$C_6H_4(CH_2PO_3Et_2)_2Cr(CO)_3$, **1** [15] with TMSBr in dichloromethane resulted in the formation of $[\eta^6-p-C_6H_4(CH_2PO_3(SiMe_3)_2)_2Cr(CO)_3]$, **2**. This reaction can be monitored conveniently using ^{31}P NMR spectroscopy, and a characteristic upfield shift from 24.2 ppm in the diethylester complex to 6.7 ppm for the trimethylsilyl ester is observed. The hydrolysis of **2** proceeded smoothly in acetone and the resulting organometallic bisphosphonic acid $[\eta^6-p-C_6H_4(CH_2PO_3H)_2]Cr(CO)_3$, **3** was isolated as a pale yellow powder in 81% yield following work-up (Scheme 1).¹ Compound **3** is both light- and air-sensitive in solution and in the solid state. The infra-red spectrum of compound **3** contains two intense absorptions in the carbonyl region

¹ Experimental procedure for **3**: a Schlenk flask was charged with $[\eta^6-p-C_6H_4(CH_2PO_3Et_2)_2]Cr(CO)_3$ [15] (0.165 g, 0.321 mmol) and CH_2Cl_2 (15 ml). Then bromotrimethylsilane (0.68 ml, 5.2 mmol) was added. The solution was stirred for 24 h and the solvent removed under oil-pump vacuum. The residue was taken up in acetone (15 ml) and water (0.074 ml, 4.1 mmol) was added via syringe. The solvent was removed under oil-pump vacuum and the residue triturated with dichloromethane (3×15 ml). The resulting pale yellow powder was collected by filtration, washed with ether, and dried under oil-pump vacuum to give **3** (0.105 g, 0.261 mmol, 81%). A small portion was crystallized from acetone- d_6 to give **3**·(CD_3) $_2$ CO as cubes suitable for X-ray analysis. Spectral data for **3**: IR (cm^{-1} , KBr): $\nu(O-H)$ 3400–2600, $\nu(CO)$ 1957, 1883, $\nu(P-O)$ 1280–900. 1H NMR (acetone- d_6): δ 4.60 (C_6H_4 , m, br), 2.81 ($2CH_2$, s, br). $^{31}P\{^1H\}$ NMR (acetone- d_6): δ 16.4 (s).

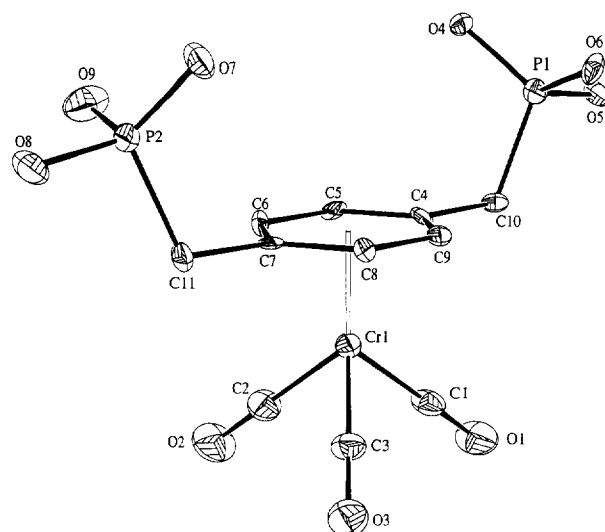
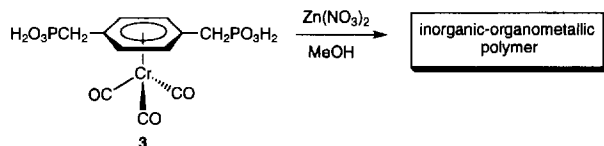


Fig. 1. ortep diagram of the structure of **3**. Hydrogen atoms and acetone solvate molecule have been omitted for clarity.

of the spectrum at 1957 and 1883 cm^{-1} which are a characteristic of the local C_{3v} symmetry of a chromium arene tricarbonyl molecule and broad absorptions at 3400–2600 and 1280–900 cm^{-1} , typical of organic phosphonic acids (ν_{P-OH} and $\nu_{P=O}$).

A single crystal of **3** was obtained by crystallization from acetone- d_6 and the X-ray crystal structure was solved (Fig. 1).² To the best of our knowledge this represents the first structurally characterized organotransition metal phosphonic acid. The geometry of **3** is a piano stool and bond distances and angles are typical of symmetrical 1,4-disubstituted chromium arene tricarbonyls. The phosphonic acid groups are *syn* to one another and directed away from the chromium tricarbonyl fragment presumably to avoid steric interaction with the chromium-coordinated carbonyl ligands. Surprisingly, the substituted arene ring is *syn*-eclipsed (*EE*) with respect to the carbonyl ligands and one might expect a staggered conformation (*S*) based on both electronic and steric considerations, especially in view of the fact that the alkylphosphonic acid substituents are electron donating as evidenced by the IR and 1H

² Crystal data for **3** ($C_{14}H_{18}CrO_{10}P_2$): $M_r = 460.22$, monoclinic, $P2_1/c$, $a = 10.9960(8) \text{ \AA}$, $b = 12.2501(8) \text{ \AA}$, $c = 14.1874(9) \text{ \AA}$, $\beta = 92.236(6)^\circ$, $V = 1909.6(2) \text{ \AA}^3$, $D_{\text{calcd}} = 1.601 \text{ g cm}^{-3}$ for $Z = 4$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 0.816 \text{ mm}^{-1}$, $T = 153(2) \text{ K}$. A yellow-green crystal with dimensions $0.125 \times 0.100 \times 0.100 \text{ mm}^3$ was placed and optically centered on an Enraf–Nonius CAD-4 diffractometer. The crystal's final cell parameters and crystal orientation matrix were determined from 25 reflections in the range $24.1 < 2\theta < 36.2^\circ$. Data were collected with the indices hkl , resulting in the measurement of 5276 unique reflections. The structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with $R(F) = 13.70\%$, $wR(F^2) = 12.18\%$ and $GOF = 1.011$ for all 2490 unique reflections [$R(F) = 5.37\%$, $wR(F^2) = 9.75\%$ for those 1343 data with $F_o > 4(F_\sigma)$].



Scheme 2.

NMR data (vide supra). Gilbert et al. [16] suggested that the conformation in symmetrical and asymmetrical 1,4-disubstituted chromium arene tricarbonyls can be independent of electronic and steric effects and the potential surface that dictates the carbonyl orientation can often be flat. It has also been suggested that subtle crystal packing forces can often play a significant role and this cannot be ruled out in **3**. A detailed analysis of the crystal structure and conformation in **3** will be published at a later date.

Preliminary investigations indicate that the organometallic phosphonic acid forms a hybrid inorganic–organometallic material. A methanolic solution of compound **3** reacted instantaneously with hydrated zinc nitrate in methanol and gave a pale yellow flocculent precipitate. After filtration, washing of the precipitate with water, methanol and ether, and vacuum drying, a yellow-green solid **4** was obtained (Scheme 2).³ The new hybrid material is remarkably robust for a chromium arene tricarbonyl derivative. It is air-stable, insoluble in water, polar and non-polar solvents and even concentrated mineral acids, although it can eventually be dissolved in aqueous 30% hydrogen peroxide.

The IR spectrum of **4** contains the expected bands in the carbonyl region at 1960 and 1876 cm⁻¹ indicating that very little distortion of the carbonyl ligands occurs when **3** is encapsulated into the matrix and suggesting that the arene chromium tricarbonyl moiety remains intact. An intense broad band in the region 1200–1000 cm⁻¹ is also observed arising from the –PO₃ absorptions. Analysis by X-ray powder diffraction showed no diffraction patterns suggesting that an amorphous structure was present. The complete lack of solubility in organic and polar solvents suggests a hybrid polymeric structure. Our current efforts are directed

towards growing single crystals of **4** to analyze further the molecular structure and the preparation of alternative organometallic phosphonic acids with rigid arene substituents which may allow the formation of a more ordered structural network.

The results described herein suggest that a preformed organometallic phosphonic acid can be readily encapsulated into a stable inorganic phosphonate matrix and we believe that the possibility for controlling the micro-environment of the organometallic moiety exists with judicious choice of phosphonic acid.

Acknowledgements

We are grateful for support from The George Washington University in the form of University Facilitating Funds and a Junior Scholar Incentive Award (to D.A.K.).

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³ Elemental analysis indicates a Zn/Cr ratio of 2.3:1.