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An organometallic sol–gel route to layered zinc phenylphosphonate and encapsulation studies with η^6-$(C_6H_6)Cr(CO)_3$

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Abstract

Phenylphosphonic acid reacts with diethylzinc in toluene/THF to give a white gel. The gel was dried in air at room temperature for 8 h to give the layered compound $[ZnC_6H_5PO_3]\cdot H_2O$ (**1**). This process represents a convenient non-aqueous organometallic sol–gel route to a layered metal phosphonate material. Zinc phenylphosphonate synthesized using the sol–gel method is identical to that prepared using the conventional aqueous precipitation technique as determined by IR spectroscopy, thermal gravimetric analysis and powder X-ray diffraction. η^6-$(C_6H_6)Cr(CO)_3$ can be incorporated into the gel during the condensation reaction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Sol–gel; Layered phosphonate; Chromium; Carbonyl

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1. Introduction

The advantages of the sol–gel process as a technique are well documented and include the processing methods such as monolith formation, spin and spray coating, and fiber formation [1]. The process has recently been used to encapsulate homogeneous catalysts [2], form thin films of molecular sieves [3] and high-temperature superconductors [4], and to prepare ceramics [5] and ferromagnetic alloys [6] to name but a few. The sol–gel method for the synthesis of hybrid inorganic–organic materials, particularly using *non-aqueous* and *non-hydrolytic* methods, is currently receiving a great deal of interest, with the commonly explored routes involving the condensation of metal chlorides with oxygen donors such as ethers, alcohols or alkoxides [7].

The field of layered metal phosphonate chemistry has also been the subject of a great deal of interest in recent years. The research groups of Clearfield [8], Mallouk [9] and others [10] have made important progress towards understanding the nature of this important class of materials, and exciting new applications for layered metal phosphonates including catalysts [11], catalyst supports [12], chemical sensors [13], sorbents [14] and ferromagnets [15], continue to appear in the literature. The development of a low-temperature, non-aqueous sol–gel process for the fabrication of these materials would expand their future utility. Our involvement in metal phosphonate chemistry stems from an interest in the unique microenvironment that a lamellar mesophase can afford on a supported or 'heterogenized' organometallic catalyst, and we recently reported the synthesis of a zinc organometallic phosphonate containing a covalently bonded, bisphosphonic acid derived xylenyl chromium tricarbonyl via direct reaction of hydrated zinc nitrate and the arene chromium tricarbonyl in aqueous methanol (Eq. (1)) [16]. In unpublished work we have also shown that this catalyst is active for the selective oligomerization of phenylacetylene [17].

In contrast, molecular metal organophosphonates have been prepared via the condensation of a metal alkyl with an organophosphonic acid where a sterically demanding organic substituent is present. For example,

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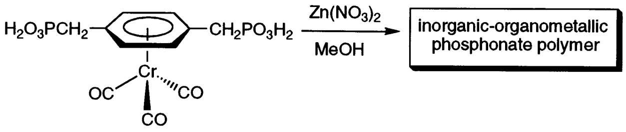
Barron described the synthesis of gallophosphonate $[{}^t\mathrm{Bu}_2\mathrm{Ga}\{\mu\text{-}\mathrm{O}_2\mathrm{P(Ph)OGa}{}^t\mathrm{Bu}_2\}]_2$ via the reaction of phenylphosphonic acid with 3 mol equivalents of t-$\mathrm{Bu}_3\mathrm{Ga}$ [18] and Mason reported the synthesis of a series of molecular gallophosphonates via the condensation of t-$\mathrm{Bu}_3\mathrm{Ga}$ and phosphonic or phosphoric acids [19]. Roesky and Kuchen independently reported the first molecular borophosphonate cages via the reaction of t-butylphosphonic acid with BEt_3 [20] and t-$\mathrm{Bu}_2\mathrm{P(O)(OSiMe}_3)_2$ with PhBCl_2 [21]. More recently, molecular titanophosphonates, have been synthesized via the reaction of $\mathrm{Cp^*TiMe}_3$ with organophosphonic acids [22]. During our search for non-aqueous, low-temperature routes to organometallic phosphonates we discovered that the reaction of diethylzinc and phenylphosphonic acid in THF/toluene led to the formation of a zinc phenylphosphonate sol–gel instead of the expected solid zinc phenylphosphonate. In addition, the catalytically active organometallic molecule η^6-$(\mathrm{C}_6\mathrm{H}_6)\mathrm{Cr(CO)}_3$ can be incorporated into $[\mathrm{ZnC}_6\mathrm{H}_5\mathrm{PO}_3]\cdot\mathrm{H}_2\mathrm{O}$ during the gelation process.



(1)

2. Experimental

2.1. General data

All reactions were conducted under dry N_2 using standard Schlenk-line and catheter-tubing techniques unless otherwise stated. IR spectra were recorded on a Mattson Galaxy 6020 (FT) spectrometer using KBr pellets. X-ray powder patterns were recorded on a Scintag XDS-2000 automated powder diffractometer, fitted with a graphite monochrometer, using Cu–K_α radiation. The diffractometer was operated in constant scan mode of 2.00° min^{-1} over the range $5° < 2\theta < 60°$ with zero point determined from a silicon internal standard. Step scanning was performed with a step size of 0.03° 2θ and a count time of 27.5 min. Powder samples were prepared by manual grinding using a mortar and pestle and were then bound to the sample holder with petroleum jelly. TGA was recorded on a Perkin–Elmer 7 Series Thermal Analysis System. Microanalysis was performed by Atlantic Microlab. Atomic absorption was performed by Galbraith Laboratories.Tetrahydrofuran was distilled from sodium/benzophenone. Diethylzinc (Aldrich), 1.0 M in toluene, and phenylphosphonic acid were used as received. η^6-$(\mathrm{C}_6\mathrm{H}_6)\mathrm{Cr(CO)}_3$ was prepared according to the literature procedure [23].

2.2. Preparation of $[\mathrm{ZnC}_6\mathrm{H}_5\mathrm{PO}_3]\cdot\mathrm{H}_2\mathrm{O}$ (1)

A Schlenk flask was charged with phenylphosphonic acid (1.739 g, 11.00 mmol), THF (50 ml), a stirrer bar, and cooled to −78°C (acetone/N_2). Then, diethylzinc (10.0 ml, 11.0 mmol, 1.1 M in toluene) was added dropwise with stirring. The cold bath was removed and the reaction mixture was allowed to warm to room temperature. On warming, the solution became viscous, stirring was stopped and eventually a homogeneous white gel formed. The gel was collected in air on a medium porosity frit, washed exhaustively with THF and dried overnight under water aspirator vacuum to give **1** as a white powder (2.447 g, 93%).

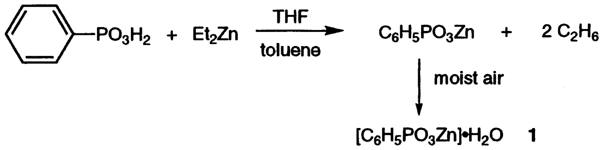
Encapsulation of η^6-$(\mathrm{C}_6\mathrm{H}_6)\mathrm{Cr(CO)}_3$ into **1**. A Schlenk flask was charged with phenylphosphonic acid (1.739 g, 11.00 mmol), η^6-$(\mathrm{C}_6\mathrm{H}_6)\mathrm{Cr(CO)}_3$ (0.173 g, 0.807 mmol) THF (50 ml), a stirrer bar, and cooled to −78°C (acetone/N_2). Then, diethylzinc (10.0 ml, 11.0 mmol, 1.1 M in toluene) was added dropwise with stirring. The cold bath was removed and the reaction mixture was allowed to warm to room temperature. On warming, the solution became viscous, stirring was stopped and eventually a homogeneous yellow gel formed. Analogous work-up to **1** gave **2** as a yellow powder (2.739 g,) which gradually turns pale green on prolonged exposure to air.

3. Results and discussion

3.1. Organometallic sol–gel route to $[\mathrm{ZnC}_6\mathrm{H}_5\mathrm{PO}_3]\cdot\mathrm{H}_2\mathrm{O}$

The preparation of layered zinc phenylphosphonate $[\mathrm{ZnC}_6\mathrm{H}_5\mathrm{PO}_3]\cdot\mathrm{H}_2\mathrm{O}$ (**1**) was first reported by Cunningham et al. [24] and involved the reaction of zinc chloride or zinc sulfate with phenylphosphonic acid in water at room temperature. Using this method, the metal phosphonate immediately precipitated out of solution, although crystalline samples of **1** could be prepared hydrothermally using more dilute aqueous solutions at higher temperatures. Clearfield and coworkers reported the single-crystal X-ray analysis of **1** [25] and made extensive studies on the intercalation of small molecules, such as primary amines, within the interlayer spacing [8b,d].

When a toluene solution of diethylzinc is added dropwise via syringe to a solution of phenylphosphonic acid in THF cooled to −78°C, and slowly warmed to room temperature, a noticeable increase in viscosity of the resulting clear solution is observed. The reaction presumably results in the elimination of ethane, and bubbles of an unidentified gas were observed immediately prior to gel formation. After a period of 5 min the solution eventually reached gelation point and the white gel was poured onto a frit in air and washed thoroughly with THF. The gel maintained its integrity for several hours on standing in air but after drying under aspirator vacuum overnight, a white powder formed which was subsequently identified as the known hydrated zinc phenylphosphonate $[ZnC_6H_5PO_3]\cdot H_2O$ (**1**) by several techniques (vide supra) (Eq. (2)).



(2)

In order to show that the sol–gel method ultimately gives an identical compound to that prepared using the aqueous precipitation route, a sample of $[ZnC_6H_5PO_3]\cdot H_2O$ was synthesized using the literature procedure [8d] and a direct comparison of the infrared spectra was made. Fig. 1 shows the IR spectra of compound **1** prepared by both the aqueous precipitation method (a), and via the organometallic sol–gel method (b). The spectra contain two bands centered at 3466 and 3430 cm^{-1} corresponding to the zinc-coordinated water O–H stretching modes and a band at 1626 cm^{-1} due to the bending mode. The three intense

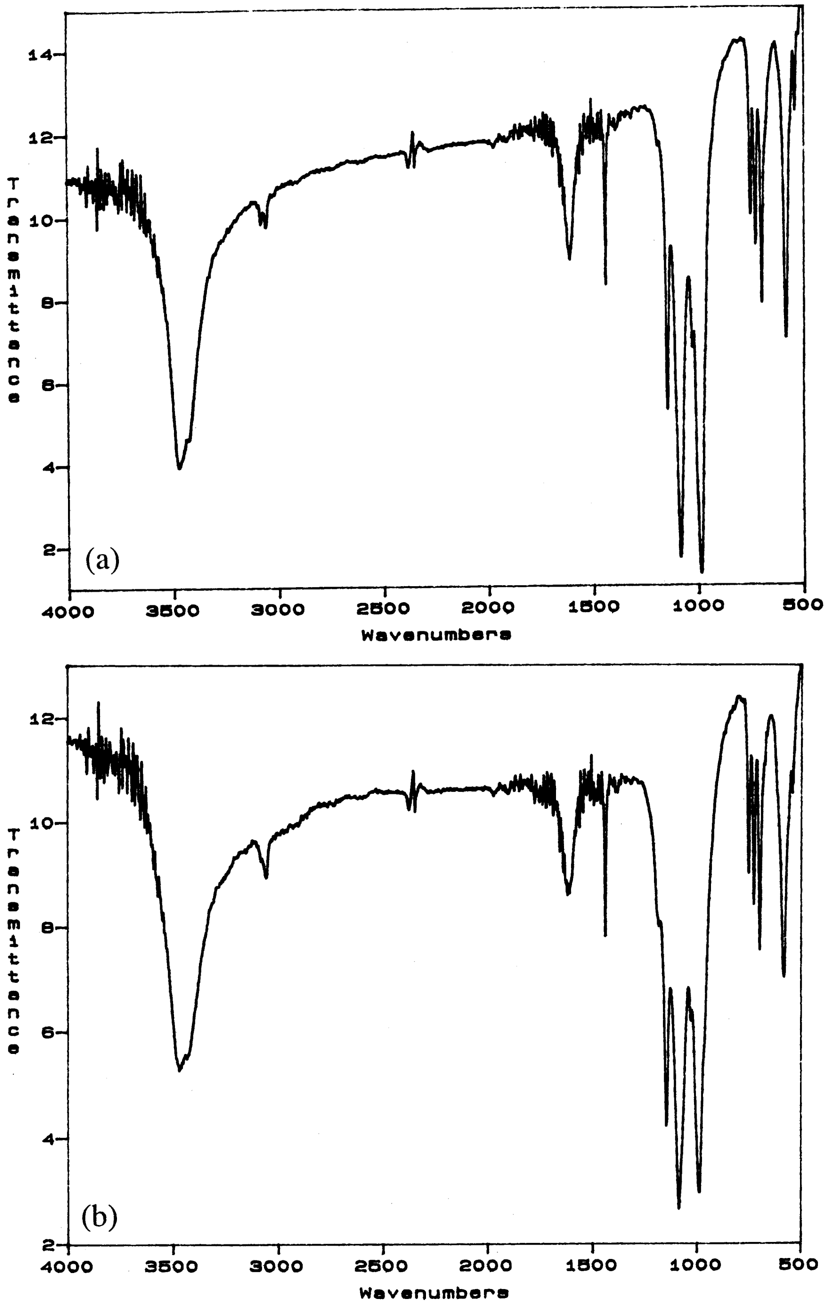


Fig. 1. Infrared spectra of **1** (KBr disk) prepared via (a) aqueous precipitation method (b) non-aqueous sol–gel method.

bands at 1144, 1084 and 986 cm^{-1} correspond to $-PO_3$ stretching modes and the four weaker bands at 748, 723, 694 and 579 cm^{-1} belong to the monosubstituted phenyl ring. The formation of the monohydrate form of zinc phenylphosphonate using the sol–gel method is not unexpected, as the sample was dried in air. Clearfield has reported that anhydrous zinc phenylphosphonate rapidly rehydrates on exposure to air [8d].

A direct comparison of the powder X-ray diffraction patterns of $[ZnC_6H_5PO_3]\cdot H_2O$ prepared by the aqueous and sol–gel methods further support the suggestion that the two samples are identical. Both patterns contain an intense reflection at 14.34 Å corresponding to the interlayer spacing, which is in agreement with the value reported previously [8d]. An overlay of the two patterns shows a direct peak match, although the peaks present in the sol–gel prepared sample are slightly broader than those in the aqueous sample. A thermal gravimetric analysis was also performed on the air-dried gel sample and indicated weight losses of 7.0% at 95°C and 24.7% and 525°C which correspond respectively to dehydration and loss of the organic portion of the phosphonate. These values match those reported in the literature for **1** [8b]. We are therefore reasonably confident that the sol–gel route gives an identical material to that prepared via the aqueous precipitation method.

3.2. Encapsulation of η^6-$(C_6H_6)Cr(CO)_3$ into **1**

When the condensation reaction described above was performed in the presence of the small organometallic molecule [η^6-$(C_6H_6)Cr(CO)_3$] a new yellow gel formed, indicating that the carbonyl had been incorporated into the zinc phenylphosphonate. After exhaustive washing of the sample with THF to remove excess [η^6-$(C_6H_6)Cr(CO)_3$], the sample was dried in air to give compound **2**. The infrared spectrum of **2** contains two medium intensity absorptions at 1962 and 1885 cm^{-1} in the carbonyl region of the spectrum corresponding to the A_1 and E bands and confirms the presence of intact [η^6-$(C_6H_6)Cr(CO)_3$] molecules with negligible perturbation of the chromium coordinated carbonyl ligands [26]. We previously reported the synthesis and characterization of the organometallic phosphonate [η^6-$(C_6H_5PO_3Et_2)Cr(CO)_3$] which has intense CO absorptions at 1981 and 1910 cm^{-1} [27] The lack of absorptions with these values may indicate the absence of chromium coordinated phenyphosphonate subunits which could possibly arise from arene exchange between [η^6-$(C_6H_6)Cr(CO)_3$] and $[ZnC_6H_5PO_3]\cdot H_2O$, although we suggest this with some caution due to the electronic differences between the phosphonic acid substituents (CH_3CH_2- vs. zinc ion). A chromium loading of 0.19–0.21% was determined using atomic absorption spectroscopy for several independently prepared samples. Evaluation of chromium leaching was attempted using Soxhlet extraction (THF) but extensive decomposition was observed.

The presence of zinc phenylphosphonate coordinated chromium tricarbonyl subunits would give rise to expansion of the interlayer distance due to the additional steric bulk. The X-ray powder pattern of compound **2** is identical to that present in **1** with an intense peak at 14.34 Å indicating that no layer expansion has occurred and that the arene chromium tricarbonyl has not been incorporated within the zinc phenylphosphonate layers. Thus the exact location of [η^6-$(C_6H_6)Cr(CO)_3$] within the zinc phenylphosphonate matrix is unknown and may simply involve the random attachment of surface bound molecules within the micro-structure of the metal phosphonate. The adsorption of arene chromium tricarbonyl compounds onto the surfaces of silica and alumina is well known and it has been suggested that metal carbonyl bonding to the surface of these supports is via carbonyl oxygen coordination to Lewis acid sites (e.g. Al^{3+}) or hydrogen bonding of surface hydroxy groups to the benzene rings [28]. Further studies on compound **2** are underway and the catalytic activity of **2** will be reported in due course.

In conclusion, we have studied a non-aqueous organometallic sol–gel route to layered hydrated zinc phenylphosphonate and an example of an encapsulated arene chromium tricarbonyl molecule, which are likely to broaden the application of metal phosphonates as materials. We are currently investigating the synthesis of other metal phosphonates using this method, including water-sensitive and thermally sensitive organometallic phosphonates which have catalytic activity, and these will be reported in future publications.

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