DALTON
COMMUNICATION

Rhodium-mediated delamination of layered copper and zinc vinylphosphonates †

D. Andrew Knight,*[a] Vinny Kim,[b] Raymond J. Butcher,[c] Brandy A. Harper[a] and Terence L. Schull ‡[b]

[a] *Department of Chemistry, Loyola University, 6363 St. Charles Avenue, New Orleans, Louisiana 70118, USA*
[b] *Department of Chemistry, The George Washington University, 725, 21st Street, N. W. Washington, District of Columbia 20052, USA*
[c] *Department of Chemistry, Howard University, Washington, District of Columbia 20009, USA*

Received 12th November 2001, Accepted 16th January 2002
First published as an Advance Article on the web 31st January 2002

Zinc and copper vinylphosphonates were characterized by X-ray crystallography and IR, and have layered structures which undergo facile delamination on contact with aqueous solutions of rhodium trichloride.

Layered metal phosphonates as materials have potentially useful properties such as ion exchange, catalysis, and homogeneous catalyst supports.[1] One of our recent research objectives has been the preparation of covalently-bonded, catalytically active layered organometallic phosphonates which retain certain desirable features of both a homogeneous catalyst: high activity and selectivity in organic transformations, and a heterogeneous support: high thermal stability and greatly facilitated separation of solid catalyst from liquid reaction media. This objective may be achieved prior to the formation of the layered structure using well defined molecular organometallic phosphonates,[2] or post-layer formation *via* reaction of organic functional groups within the layered structure, with metal complexes.[3] Numerous intercalation studies performed on layered phosphonates have demonstrated that the interlayer region may be altered significantly by the inclusion of small molecules such as amines and alcohols.[4] Studies on the oxidative polymerization of aniline at high temperature within the layers of copper methylphosphonate led to the destruction of the layered structure *via* a possible redox process, resulting in the deposition of copper metal.[5] It is also known that layered metal organophosphonates undergo exfoliation under acidic conditions. As part of a study on the reactivity of metal vinylphosphonates with transition metal ions to give supported organometallic catalysts, we discovered a facile rhodium mediated delamination of layered copper and zinc vinylphosphonate.

Copper(II) and zinc(II) vinylphosphonates were prepared by the reaction of vinylphosphonic acid and either $CuSO_4 \cdot 5H_2O$ or $Zn(NO_3)_2 \cdot 6H_2O$ in water at 70 °C. The reactions were carried out in the presence of urea, which slowly hydrolyses at the temperature of the reaction, releasing ammonia and slowly raising the pH of the solution. After a period of 72 hours, blue crystalline $[Cu(C_2H_3PO_3)] \cdot H_2O$ (**1**), and white crystalline $[Zn(C_2H_3PO_3)] \cdot H_2O$ (**2**) were formed in 80 and 71% yields respectively. § The new compounds were characterized using IR spectroscopy, TGA, elemental analysis, X-ray powder diffraction, and for compound **1**, single crystal X-ray diffraction. The X-ray powder data indicated the presence of a single phase for both **1** and **2**.

Surprisingly, no crystal structures have been reported for metal vinylphosphonates although one metal vinylphosphonate, $[Zr(C_2H_3PO_3)_2]$, has been known for some time.[6] Although compound **1** crystallized as rather large irregular plates and chunks, a suitable crystal was found which allowed us to obtain a single crystal X-ray analysis.¶ The molecular structure is shown in Fig. 1. The structure is clearly typical of a layered metal organophosphonate in which the vinyl groups project into the interlayer spaces of the structure, which is held together by van der Waal's forces.

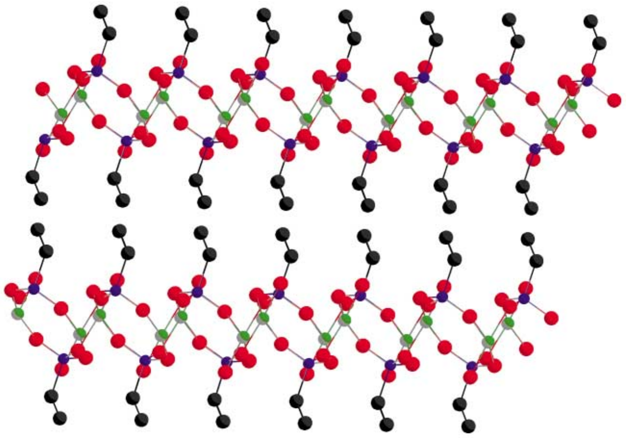

Fig. 1 Molecular drawing of compound **1** showing the layered structure. Hydrogen atoms are omitted for clarity. Color code: C, black; O, red; P, blue; Cu, green.

Fig. 2 shows the five-coordinate copper atom coordination sphere and the geometry is best described as a distorted tetragonal pyramid[7] not unlike that observed for the copper methyl and phenylphosphonates, $[Cu(CH_3PO_3)] \cdot H_2O$, and $[Cu(C_6H_5PO_3)] \cdot H_2O$,[8] in which three phosphonate oxygens, O(1), O(3)#2 and O(2)#1 and a coordinated water molecule (O1W) make up the base of the pyramid. The copper–oxygen bond distances are 1.961(3), 1.978(3), 1.932(3), and 2.001(3) Å respectively and are remarkably close to those reported for the methyl [1.928(4)–1.991(5) Å] and phenyl [1.921(4)–1.990 (4) Å] analogs reported by Zhang and Clearfield.[8] The fifth oxygen, O(3)#3, that occupies the apical site has a Cu–O bond length of 2.306(2) Å. The interlayer distance of 9.878(5) Å is equal to the length of the *a* axis, *cf.* 8.495(4) and 13.991 Å for the methyl and phenyl analogs respectively. This was independently confirmed from the X-ray powder diffraction pattern for **1** that indicated a *d*-spacing of 9.88 Å. Although a single crystal X-ray analysis of the zinc analog **2** was not undertaken, both IR and X-ray powder data were consistent with a molecular structure analogous to that found in $[Zn(C_2H_5PO_3)] \cdot H_2O$.[9] The interlayer spacing found in **2**, measured using X-ray powder diffraction, is 9.57 Å.

The presence of pendant vinyl groups in the layered metal phosphonates prompted us to investigate their reactivity with π-coordinating metal ions. To our surprise, when an aqueous

---

† Electronic supplementary information (ESI) available: ^{31}P NMR spectrum of the reaction of **2** with $RhCl_3$ in H_2O. See http://www.rsc.org/suppdata/dt/b1/b110356n/

‡ Present address: Center for Biomolecular Science and Engineering, Code 6950, Naval Research Laboratories, 4555 Overlook Avenue, SW, Washington, DC 20375, USA.

824 *J. Chem. Soc., Dalton Trans.*, 2002, 824–826 DOI: 10.1039/b110356n

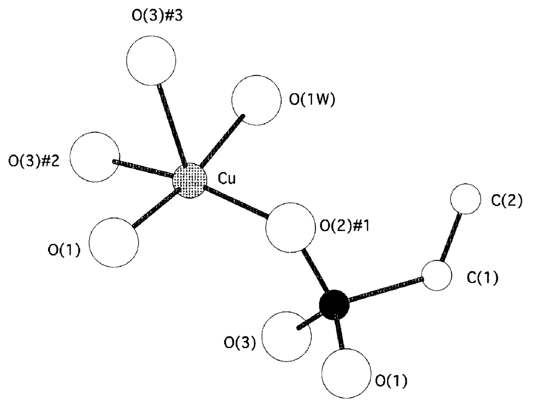

Fig. 2 A molecule of **1** showing coordination about the copper atom. Bond lengths (Å) for the non-hydrogen atoms: Cu–O(2)#1 1.932(3), Cu–O(1) 1.961(3), Cu–O(3)#2 1.978(3), Cu–O(1W) 2.001(3), Cu–O(3)#3 2.306(2), P–O(1) 1.527(3), P–O(2) 1.533(2), P–O(3) 1.540(2), P–C(1) 1.777(4), O(2)–Cu#1 1.932(3), O(3)–Cu#4 1.978(3), O(3)–Cu#5 2.306(2), C(1)–C(2) 1.309(7). Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z$. #2 $x, -y + 1/2, z + 1/2$. #3 $-x + 1, y + 1/2, -z - 1/2$. #4 $x, -y + 1/2, z - 1/2$. #5 $-x + 1, y - 1/2, -z - 1/2$.

solution of rhodium trichloride was added to a suspension of **1** (molar ratio Rh/Cu = 1.40–1.60/1.00) in water or methanol and stirred for 1 hour, the blue crystals completely dissolved to give clear, blood red solutions. The zinc vinylphosphonate **2** reacted in a similar manner to give homogeneous orange solutions. No evidence was found for the deposition of copper or zinc metal that might indicate a redox process taking place. The room temperature ^{31}P NMR spectrum of the reaction between zinc vinylphosphonate and Rh(III) contained two major resonances at 25.1 and 14.6 ppm with relative intensities 1.0 : 2.9 (although the line widths were extremely broad, see ESI†). The ratio of peak intensities did not change on varying the molar ratio Rh/Zn. The line broadness suggests either dynamic behavior of the resulting complex, or the presence of oligomeric/polymeric structures in solution. No significant changes were seen in the IR spectra of the solutions compared to the solid state materials, and it is worth noting the absence of a band that could be attributable to P–OH. In addition, removal of solvent from the reaction mixtures gave solids that were shown to be amorphous by X-ray powder diffraction. Redissolving the solids in water or methanol gave identical IR and NMR spectra to those recorded during the reaction. All subsequent attempts to crystallize a single compound from both of the reaction mixtures, using a variety of organic solvents (methanol, ethanol, diethyl ether, THF) failed. Clearly, the highly ordered, layered structure of copper and zinc vinyl phosphonate has been destroyed, and it is tempting to suggest that the interaction of the rhodium metal center with accessible vinyl groups results in slow delamination (Fig. 3). Delamination of layered organophosphonates has previously been reported, for example: the interaction of alkanethiols with cadmium methylphosphonate results in destruction of the layered structure, presumably *via* formation of stable Cd–S bonds.[10]

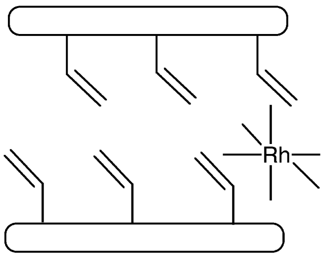

Fig. 3 Proposed interaction of rhodium complex with pendant vinyl groups of lamellar phosphonate.

To investigate the possible role that a π-olefin–Rh interaction may have in the reaction of **1** and **2** with rhodium trichloride, several control experiments were performed. The interaction of an aqueous suspension of zinc *phenyl*phosphonate with an aqueous solution of $RhCl_3$ was studied, and no reaction took place after several days of stirring at room temperature as evidenced by careful before and after weighing of the metal phenylphosphonate. Similarly, no reaction took place on raising the temperature to 80 °C for several days. This indicates that the presence of the *vinyl* group is important for reactivity. Changing the surface area of the metal vinylphosphonates to increase the interaction with rhodium chloride had little effect on the rate of dissolution and all attempts to further characterize the rhodium species in solution, *via* derivatization with phosphines or amines, met with little success. However, we were curious to know whether other transition metal ions would interact with copper and zinc vinylphosphonates, and the reaction of **1** or **2** with aqueous solutions of cobalt chloride was studied. After several weeks of stirring either **1** or **2** with $CoCl_2$ in water, no reaction was detected. While olefin complexes of Co(II) are known, the stability of these compounds is considerably less than the rhodium(III) analogs. This is due primarily to the increased overlap of the filled d-orbitals of the Group 9 transition metal with the π* antibonding orbital of the olefin ligand in the progression from cobalt to rhodium. Thus we suggest that the bonding interaction of cobalt ions with **1** and **2** is not sufficiently strong enough to result in the breakdown of the internal layered structure.

Aqueous solutions of $[RhCl_3(OH_2)_3]$ are known to be moderately acidic, which suggested to us that **1** and **2** were simply dissolving under acid conditions. Under our experimental conditions the pH of $[RhCl_3(OH_2)_3]$ was measured, and gave values in the range pH 2.3–4.5 depending on the batch of rhodium chloride used. A sample of **1** was suspended in a solution of hydrochloric acid with a known pH of 2.3 and rapidly stirred for 24 hours. No change in the appearance of the crystals was observed and the material was recovered without mass loss, confirming that **1** does not dissolve at this pH. Further work is in progress to understand the detailed nature of the rhodium-mediated delamination of metal vinylphosphonates.

The donors of the Petroleum Research Fund administered by the American Chemical Society are thanked for support of this work.

Notes and references

§ Preparation of $[Cu(C_2H_3PO_3)]\cdot H_2O$ (**1**). A 1 L round-bottomed flask was charged with copper sulfate (9.10 g, 57.0 mmol), vinylphosphonic acid (3.51 g, 57.0 mmol), and de-ionized water (350 mL). Urea (3.38 g, 56.3 mmol) was added to the solution, followed by an aqueous solution of NaOH (0.10 M), until the pH reached 2.8. The solution was heated in an oil-bath at 70 °C for 72 hours. The resulting crystals were collected by filtration and dried in air to give **1** as large blue plates (7.82 g, 80%). Anal. calc. for $C_2H_5PO_4Cu$: C, 12.81; H, 2.69. Found: C, 12.68; H, 2.77%.

Preparation of $[Zn(C_2H_3PO_3)]\cdot H_2O$ (**2**). A 1 L round-bottomed flask was charged with zinc nitrate (8.37 g, 44.2 mmol), vinylphosphonic acid (3.42 g, 31.7 mmol), and de-ionized water (350 mL). Urea (3.24 g, 53.9 mmol) was added to the solution, followed by an aqueous solution of NaOH (0.10 M), until the pH reached 2.8. The solution was heated in an oil-bath at 70 °C for 72 hours. The resulting crystals were collected by filtration and dried in air to give **2** as white needles (5.44 g, 71%). Anal. calc. for $C_2H_5PO_4Zn$: C, 12.68; H, 2.66. Found: C, 12.65; H, 2.63%.

¶ Crystal data for **1**: $C_2H_5PO_4Cu$, $M = 187.57$, monoclinic, space group $P2_1/c$, $a = 9.878(5)$, $b = 7.628(3)$, $c = 7.332(3)$ Å, $U = 549.5(4)$ Å^3, $Z = 4$, $D_c = 2.267$ Mg m^{-3}, μ(Mo-Kα) = 4.183 mm^{-1}, $F(000) = 372$, $T = 293(2)$ K, 1254 independent reflections ($R_{int} = 0.0293$) with $2\theta < 55°$. Refinement of 95 parameters converged at final $R1$ [for selected data with $I > 2\sigma(I)$] = 0.0487, $wR2$ (all data) = 0.1216.

X-Ray powder patterns were recorded on a Scintag XDS-2000 automated powder diffractometer, fitted with a graphite monochromater, using Cu Kα 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 an external silicon standard. Step scanning was performed with a step size of 0.03° 2θ and a count time of 27.5 min.

Single crystal X-ray measurements were made using a Siemens P4S diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares methods based on F^2 using the SHELXTL package.[11] Two peaks in the final difference map had a value greater than one electron per cubic Ångstrom, with distances of 0.99 Å to the copper atom and 0.79 Å to the phosphorus atom respectively. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to the water oxygen atom (O1W) were located in difference Fourier syntheses and refined isotropically. The three hydrogen atoms bonded to carbons were treated as riding atoms. CCDC reference number 168372. See http://www.rsc.org/suppdata/dt/b1/b110356n/ for crystallographic data in CIF or other electronic format.

1 See for example: A. Clearfield, *Metal Phosphonate Chemistry*, in *Progress in Inorganic Chemistry*, K. D. Karlin, ed., John Wiley & Sons, New York, 1998, vol. 47, p. 271; G. Alberti, in *Comprehensive Supramolecular Chemistry*, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle and J.-M. Lehn, eds., Pergamon, Oxford, 1996, vol. 7, p. 151.

2 D. Villemin, P.-A. Jaffrès, B. Nechab and F. Courivaud, *Tet. Lett.*, 1996, **38**, 3905; D. Deniaud, B. Schollorn, D. Mansuy, J. Rouxel, P. Battioni and B. Bujoli, *Chem. Mater.*, 1995, **7**, 995.

3 R. H. Lane, K. P. Callahan, R. Cooksey, P. M. DiGiacomo, M. B. Dines and P. C. Griffith, presented at the Symposium on Immobilized Homogeneous Catalysts, Kansas City, 1982.

4 See for example: G. Cao, H. Lee, V. M. Lynch and T. E. Mallouk, *Inorg. Chem.*, 1988, **27**, 2781; R.-C. Wang, Y. Zhang, H. Hu, R. R. Frausto and A. Clearfield, *Chem. Mater.*, 1992, **4**, 864.

5 G. B. Hix, V. C. Maddocks and K. D. M. Harris, *Polyhedron*, 2000, **19**, 765.

6 M. B. Dines and P. M. DiGiacomo, *Inorg. Chem.*, 1981, **20**, 92.

7 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijm and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

8 Y. Zhang and A. Clearfield, *Inorg. Chem.*, 1992, **31**, 2821.

9 S. Drumel, P. Janvier, P. Barboux, M. Bujoli-Doeuff and B. Bujoli, *Inorg. Chem.*, 1995, **34**, 148.

10 G. Cao, V. M. Lynch and L. N. Yacullo, *Chem. Mater.*, 1993, **5**, 1000.

11 G. M. Sheldrick, SHELXTL Crystallographic Suite for PC, Siemens Analytical Instrument Division, Madison, WI, USA, 1997.