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Phosphonate derivatives of pyridine grafted onto oxide nanoparticles

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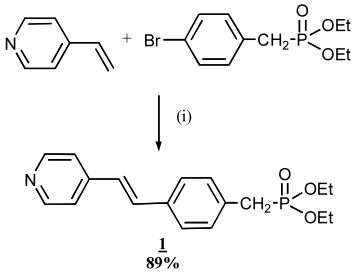
Abstract—The synthesis of phosphonate derived stilbazole **1** by using a Heck reaction is described. The reactivity of the pyridine moiety is studied. After hydrolysis of the ethyl phosphonate groups, the grafting of phosphonic acid derived stilbazole **5** on metal oxides TiO_2 or SnO_2 is reported. The accessibility and reactivity of the pyridine moiety at the surface is demonstrated. © 2002 Published by Elsevier Science Ltd.

Stilbazoles derivatives and π-conjugated compounds with a pyridine unit have been extensively studied for a wide range of applications, as ligands for transition metal complexes,[1] self-assembled monolayers (SAMs)[2] or in the field of organic–inorganic hybrid materials for Non-linear Optics (NLO).[3] Generally SAMs are based on the interactions of chlorosilanes with OH functions at the surface of oxides[4] or thiolates compounds adsorbed at the surface of gold.[5] In the case of *n*-alkylsilanes monolayers, the reaction is sensitive to traces of water, homocondensation could occur, with in homogeneities on the modified surface. In the case of thiols the use of gold, which is very expensive, could be a limiting factor. The formation of monolayers with carboxylic acids,[6] hydroxamic acids[7] and phosphonic acids[8] could be an issue to these problems. So we present here, the synthesis of a phosphonate derivative with a π-conjugated pyridine unit and the studies of the grafting onto oxides nanoparticles.



1
89%

Scheme 1. *Reagents and conditions*: (i) $Pd(OAc)_2$ (4 mol%), tris-orthotoluylphosphine (15 mol%), 6 equiv. Et_3N, toluene, 115°C, 12 h.

Diethyl 4-(2-pyridin-4-yl-vinyl)-benzylphosphonate **1** was obtained as described in Scheme 1. Heck reaction, in standard conditions,[9] of 4-vinylpyridine with diethyl 4-bromobenzylphosphonate, synthesized as described in the literature,[10] gave compound **1** in good yield.† We verified the reactivity of the pyridine moiety of compound **1**, which is a potential ligand for transition metal complexes (Scheme 2).

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† *Preparative method for diethyl 4-(2-pyridin-4-yl-vinyl)-benzylphosphonate* ***1***: In a two necked round-bottomed flask were placed 5 g of diethyl 4-bromobenzylphosphonate (16.3 mmol), 1.72 g of 4-vinylpyridine (16.3 mmol), 73.2 mg of palladium diacetate (0.326 mmol), 347 mg of tris-orthotoluylphosphine (1.14 mmol), 6.8 mL of triethylamine and the mixture was diluted in 25 mL of toluene. The reaction mixture was heated at 115°C under magnetic stirring. After 12 h the solution was allowed to cool to rt and then was filtered on Celite and washed three times with toluene. The filtrate was then concentrated to give a yellow liquid which was purified by chromatography column on SiO_2, (eluent: ethyl acetate). We obtained compound **1** after recrystallization on cyclohexane as white needles: $m = 4.83$ g, yield 89%. Mp = 62.2–64.1°C. ^{1}H NMR (200 MHz, $CDCl_3$, 293 K): δ 1.29 (t, $^3J_{HH} = 7.0$, 6H, CH_3); 3.20 (d, $^2J_{HP} = 21.9$, 2H, CH_2-P); 4.03 (m, $^3J_{HH} = 7.0$, 4H, CH_2-O); 7.03 (d, $^3J_{trans} = 16.0$, 1H, vinyl); 7.30 (d, $^3J_{trans} = 16.0$, 1H, vinyl); 7.35–7.55 (m, 6H, aromatic); 8.60 (d, $^3J_{HH} = 6.1$, 2H, CH-N). ^{13}C NMR (200 MHz, $CDCl_3$, 293 K): δ 16.8 (d, $^3J_{PC} = 6$, CH_3); 34.1 (d, $^1J_{PC} = 138$, CH_2-P); 62.6 (d, $^2J_{PC} = 6.8$, CH_2-O); 121.2; 127.6; 130.6; 132.8; 135.2; 144.9 (aromatics); 126.3; 133.1 (C vinyl); 150.6 (C-N). ^{31}P NMR (200 MHz, $CDCl_3$, 293 K): δ 27.2. HRMS (FAB$^+$, GT): 332.1400 (calcd for MH^+); 332.1416 (obs.).

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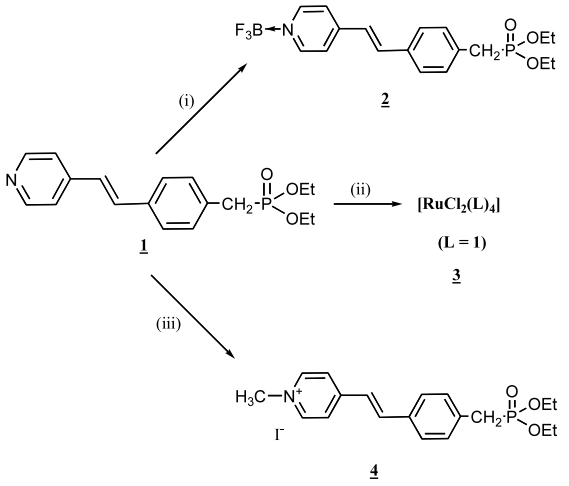
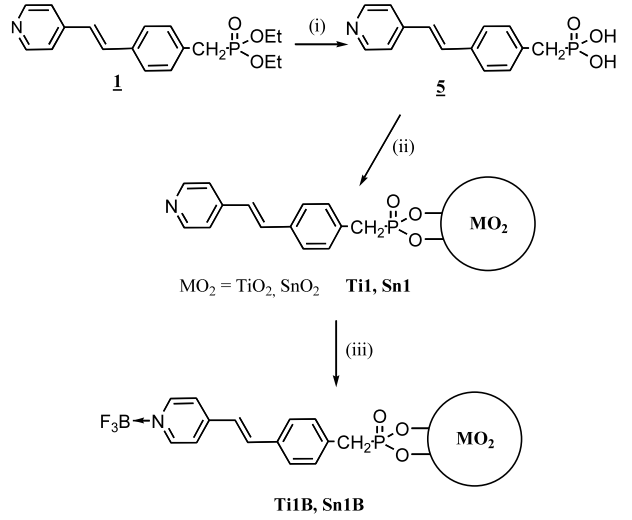


Scheme 2. *Reagents and conditions*: (i) 1 equiv. of $BF_3{\cdot}Et_2O$, THF, rt, 4 h; (ii) 0.25 equiv. of $RuCl_3{\cdot}xH_2O$, H_2O:EtOH (1:1), 100°C, 5 h; (iii) 1.5 equiv. of CH_3I, CH_3CN, rt, overnight.

Compound **1** treated in THF solution at room temperature with $BF_3{\cdot}Et_2O$ gave the corresponding Lewis acidic borane adduct **2**.[14] No complexation by the phosphonate function occurred. In the same way, based on the literature,[11] adding 4 equiv. of **1** to a solution of $RuCl_3{\cdot}xH_2O$ in a mixture of EtOH:H_2O (1:1) at reflux led to the corresponding ruthenium complex $[Ru(L)_4Cl_2]$ (with L = compound **1**). Finally, a solution of compound **1** treated with methyliodide in acetonitrile at room temperature gave the corresponding *N*-methylpyridinium salt **4**. These three reactions confirmed the good ability of the pyridine moiety to form adducts or metal transition complexes. ^{31}P NMR confirmed the stability of the phosphonate group, no modification of the chemical shift (27 ppm on average) was observed. The grafting of compound **5** on different oxide particles was next examined (Scheme 3).

Treatment of compound **1** with an excess of bromotrimethylsilane (3 equiv.) in dichloromethane at room temperature led to the corresponding phosphonic acid **5** after hydrolysis with excess of water (15 equiv.). We then performed the grafting reactions of acid **5** (Scheme 3) with two types of particle oxides, TiO_2 P25 Degussa (particle size of 21 nm) (**Ti1**), SnO_2 Merck (particle size 20 nm) (**Sn1**). The surface of TiO_2 and SnO_2 were modified by refluxing the particles for 3 days with phosphonic acid **5** dissolved in H_2O at 100°C, this solvent was chosen because of the low solubility of the acid **5**. A large excess of acid was used to ensure total coverage of the particle surfaces. The solids obtained were analyzed using elemental analysis and solid-state ^{31}P NMR spectroscopy. Solid-state ^{31}P hpdec mas NMR (Fig. 1) of acid **5** gave a symmetrical signal at $\delta = 21.1$ ppm, characteristic of a homogeneous compound. As benzylic phosphonic acids are usually shifted to 27–30 ppm,[13] compound **5** is in a zwitterionic form. The signals of **Ti1** and **Sn1** are shifted below 20 ppm, The unsymmetrical peaks width at half maximum have been enlarged to $\delta = 15$ ppm. These spectra indicate



Scheme 3. Grafting of precursor **5** and reactivity at the surfaces. *Reagents and conditions*: (i) a. 3 equiv. of Me_3SiBr, CH_2Cl_2, rt, 12 h, b. 15 equiv. H_2O, rt; (ii) H_2O, 100°C, 3 days; (iii) excess of $BF_3{\cdot}Et_2O$, THF, rt, 24 h.

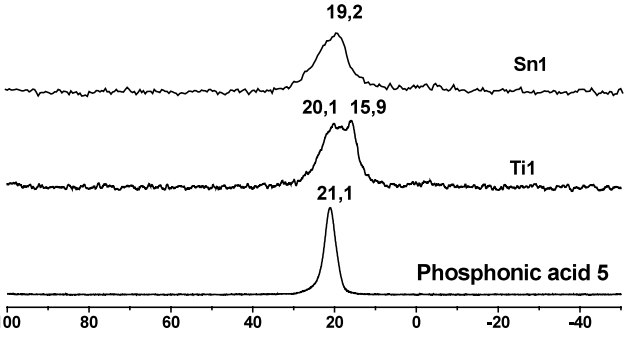


Figure 1. hpdec MAS ^{31}P NMR of solids **5**, **Ti1**, **Sn1**.

that the phosphonic group has reacted at the surface of the oxide with formation of P–O–metal bonds. The phosphorus atom has different environments on the surface of the oxide because of different coordination modes, one two or three P–O–metal bonds are likely to be involved in the anchoring at the surface (Scheme 3 corresponds to two P–O–M bonds). Elemental analysis showed a low ratio P/MO_2 between 1.5 and 2% characteristic of a monolayer coverage of **5** at the surface of the oxide particles.[12–14] In order to verify the reactivity of the pyridine functions at the surface, particles **Ti1** and **Sn1**, in suspension in THF, were treated with $BF_3{\cdot}Et_2O$ for 24 h. Solids **Ti1B** and **Sn1B** (Scheme 3) were characterized by solid-state ^{31}P and ^{11}B NMR spectroscopy. No modification of the ^{31}P NMR signals were observed, which confirmed that there was no modification of the phosphorus part anchored on the surface. Compounds **Ti1B** and **Sn1B** gave sharp solid-state ^{11}B NMR signals at $\delta = -1.8$ and -1.9 ppm, respectively, characteristic of borane adducts (Fig. 2).

Elemental analysis showed ratios B/N of 0.95 and 0.9 for **Ti1B** and **Sn1B**, respectively, which confirmed that

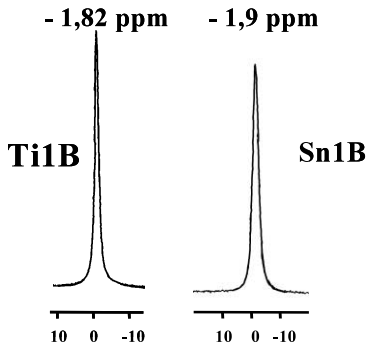


Figure 2. MAS ^{11}B NMR of **Ti1B** and **Sn1B**.

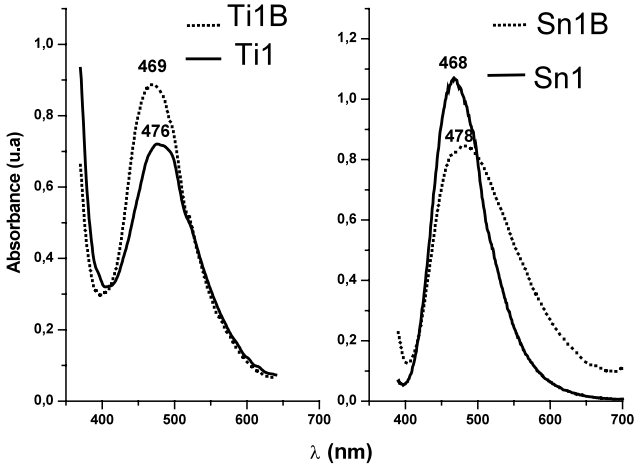


Figure 3. Fluorescence emission of solids **Ti1**, **Ti1B**, **Sn1**, **Sn1B**.

all the pyridine functions had reacted with boron. The pyridine moiety was thus accessible and was not protonated. The fluorescence spectra of **Sn1** and **Ti1** confirmed the presence of the chromophoric stilbazole, and reaction with BF_3 had no influence on the fluorescence emission of the stilbazole moiety (Fig. 3). Fluorescence spectroscopy confirmed that the organic part was not damaged after grafting on metal oxides then complexation by BF_3.

In conclusion we have shown that Heck reaction was efficient in the synthesis of difunctional compound **1** with π-conjugated pyridine and phosphonate groups. Reactions with the pyridine moiety were selective, as the phosphonate group was not damaged. Finally we have developed a way to form organic monolayers at the surface of metaloxide nanoparticles, and these monolayers are reactive. Further developments for applications of these compounds in supported catalysis, modified electrodes, chromatography are in progress.

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