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Palladium Complexes Supported on Hybrid Organic-inorganic Zirconium Phosphite: Selectivity in the Heck Reaction

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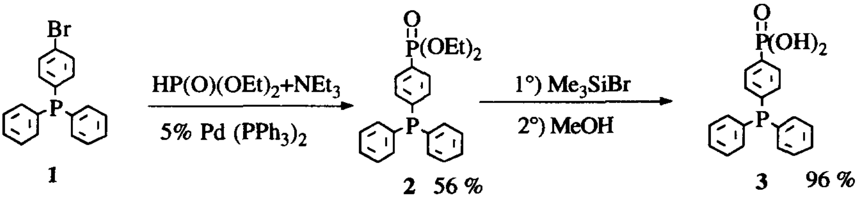
Abstract: Supported palladium complex on zirconium phosphite-phosphonate was made from triphenylphosphine phosphonic acid. The supported catalyst showed significant selectivity in the competitive Heck reaction between iodobenzene and different iodobenzoates. The reaction seems to take place between the lamellar of the catalyst © 1997 Elsevier Science Ltd.

Increasing interest has been devoted in the last few years to the using of supported catalysts for organic reactions.[1] Zirconium-phosphate has been until now scarcely used as support.[2] However, materials of the zirconium-phosphate family have a number of advantages, one of the noted characteristics of these compounds is their predictable structure skeletons.[3] Other important features are the simple reaction steps required to make then and the ability to affix the various organic groups on a solid support according to the Alberti's method which involves the reaction between zirconium chloride octahydrated and a phosphonic acid.[4]

In this communication, we describe the synthesis and the use of a new microporous organo-inorganic material, which possesses a palladium complex anchored to the inorganic sheet with covalent bonds.

The first step of this work was the synthesis of the phosphonic acid **3** according a way different from one described recently[5], while our own work was in progress (Scheme 1). We synthesised the phosphonate **2** from the phosphine[6] **1** by means of a palladium assisted phosphonation.[7] This phosphonate was transformed to the phosphonic acid **3** according to the Mc Kenna's method.[8]



Scheme 1 : synthesis of phosphonic acid **3**

The phosphonic acid was complexed with palladium chloride in DMF according the method described for triphenylphosphine.[9] The resulting complex **4** was a polymer which is soluble in aqueous hydrochloric acid.

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This solution of complex was used for the synthesis of the material described below. In the literature[10] H_3PO_3 was sometimes added to the mixture of phosphonic acid and zirconium chloride during the preparation of the material with the intention to use it as spacer which can increase the porosity of zirconium phosphonate. We used this methodology[11] for the preparation of palladium supported material **5**. The theoretical structure should be layered (Fig. 1). The palladium complex **4** which possesses two phosphonic functions, can be bonded to the same plane of zirconium sheet by the two phosphonic functions or, on the contrary, bonded by their functions to the same plane. Thus, the resulting material possesses a great complexity and X ray powder diffraction pattern appears diffused. Nevertheless, the NMR MAS ^{31}P (Fig. 2) gives 3 signals : -4.8 ($(ZrO)_3P\text{-}C$)[12], -15.9 $(ZrO)_3P\text{-}H$ and -18.1 ($Ar_3P\text{-}PdCl_2$) and microanalysis[13] indicates the following composition : $Zr(HPO_3)_{1,84}\,(C_{36}H_{18}Cl_2O_6P_4Pd)_{0,08}\,(H_2O)_{0,31}$.The FT-IR spectra show a characteristic band at 2400 cm^{-1} corresponding to P-H vibration.[14]

In a second step, we used the material **5** for the preparation of a supported catalyst **6** (Fig. 3) which was tested in a Heck type reaction which involves aryl iodides and methyl acrylate[15] (Scheme 2).

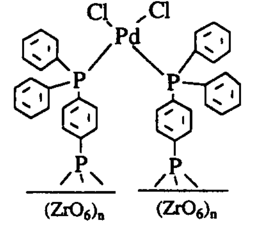


Fig. 1 : Proposed structure for **5**

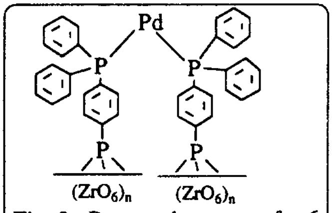


Fig. 3 : Proposed structure for **6**

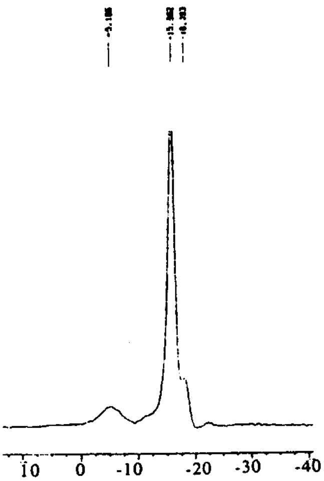
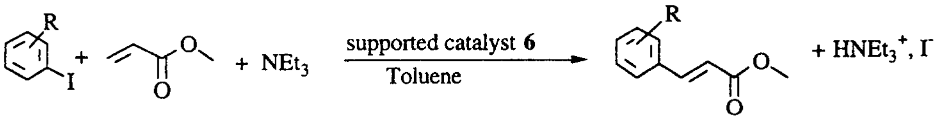


Fig. 2: ^{31}P MAS NMR of compound **5**

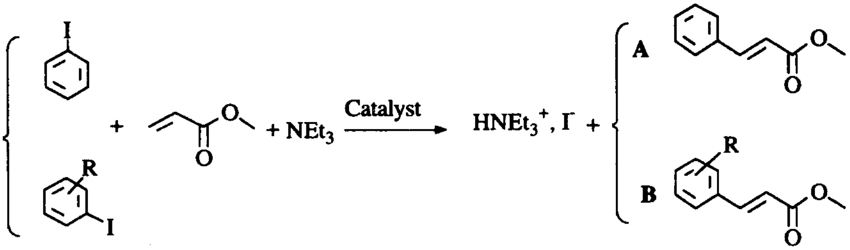
Supported catalyst **6** is obtained by reduction of palladium (II) complex to palladium (0) by triethylsilane and is active in Heck reaction. We shown that the catalyst can be recovered by decantation or centrifugation of the reactional mixture and can be reused without significant lost of activity if it is kept under inert atmosphere. In the presence of oxygen the activity of **6** was lost. Thus, the conversion rate was always about 87 % after 4 reuses.

No leaching of palladium in solution was observed, the small desactivation was attributed to the introduction of traces of oxygen during the manipulations. The reaction was monitored by GC and a total conversion of the iodobenzene was obtained after 24 h.



Scheme 2 : Heck reaction

In order to investigate the possible shape selectivity[16] due to a possible microporous structure of the supported catalyst **6**, competitive arylation reactions[17] were performed using two different aryl iodides : iodobenzene and methyl iodobenzoate or iodoanisoles (Scheme 3).



Scheme 3 : Competitive Heck reaction

We used the same experimental procedure as that described above with 1 equivalent of each substrate and 1.2 equivalent of methylacrylate. The ratio **A/B** of the products was determined by GC analysis after 24 h. The results obtained with **6** (Table 1) were compared with those obtained for a reaction performed in homogeneous conditions with bis(triphenylphosphine)palladium **8** as catalyst obtained by the reduction by Et_3SiH of the corresponding dichloride $[(PPh_3)_2PdCl_2]$ and with bis(triphenylphosphine)palladium supported on polystyrene (Fig. 4) prepared previously from **7** in our laboratory[18].

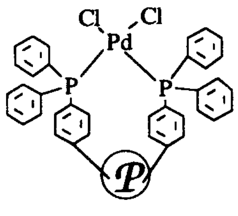
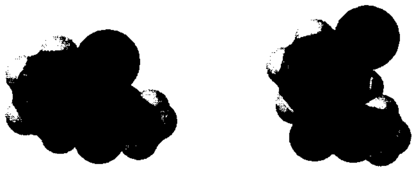


Fig. 4 : Proposed structure for **7**

The selectivity with the catalyst on the polymer and under homogeneous catalysis with **8** are similar, it is not the case with **6**.

This comparative study (Table 1) indicates that the catalyst **6** induces a selectivity in favour of the iodoaromatic with the smallest size, in particularly we notice that the effect is more important for the larger molecules 3-iodobenzoate or 3-iodoanisole than the sterically more hindered 2-iodobenzoate and 2-iodoanisole (see Fig. 5).

Fig. 5: CPK models from CAChe[19]
(C-I bond in the same position)



2-COOCH$_3$ 3-COOCH$_3$

Table 1: selectivity of Heck reaction

R	S_{homo}	S_{hetero}	S_{hetero}/S_{homo}
2-COOCH$_3$	2.0	8.4	4.2
3-COOCH$_3$	0.9	6.8	**7.5**
4-COOCH$_3$	1.1	4.3	3.9
2-OCH$_3$	1.3	4.1	3.7
3-OCH$_3$	0.8	3.3	**4.1**
4-OCH$_3$	0.8	3.0	3.1

S=selectivity=A/B
S_{homo}: selectivity under homogeneous conditions with **8**
S_{hetero}: selectivity under heterogeneous conditions with **6**

This observation means that this catalyst has active sites not only on the surface but also inside the lattice attainable owing to the porosity of this catalyst which should have a layered structure. According to the typical work-up we have also synthesised materials without spacer or with phosphate as spacer. In the first case, the resulting material was used for the competitive reactions [after reduction of palladium (II) to palladium

(0)], and no significant shape selectivity was observed. This result indicates that the phosphorous acid which acts as a spacer, has a dramatic importance in order to induce a shape selectivity. In the second case, the material does not catalyst the Heck reaction. That is probably due to the acidity of the hydroxyl groups coming from phosphates and hanging in the interlayer space.

This preliminary work has shown that palladium catalyst anchored by covalent bonds to zirconium-phosphite sheet is efficient for Heck reactions and is easily recoverable. We have also shown that a shape selectivity takes place at the time of competitive conditions if the catalyst sites are spaced by phosphorous groups.

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