

## A Highly Active and Stereoselective Montmorillonite Catalyst for Arylation of Conjugated Alkenes<sup>†</sup>

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Homogeneous Catalysis Discipline

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**Abstract :** A highly active and stereoselective heterogenised homogeneous catalyst montmorilloniteethylsilyldiphenylphosphinepalladium (II) chloride complex (Pd/P is 1:1) for arylation of conjugated alkenes is reported.

The arylation of alkenes was an important discovery in organopalladium chemistry made by Heck et al in late sixties that led to several useful synthetic reactions<sup>1,2</sup>. Although homogeneous catalysts have proven to be highly efficient but their conversion and stereoselectivity is moderate. The technique of immobilising complexes has been resorted to make homogeneous catalyst generally more attractive from industrial point of view. Teranishi and his co-workers have studied Heck arylation reactions using polystyrene supported palladium catalysts and obtained 75% stereoselectivity<sup>3</sup>. Later Anders Hallberg and his co-workers<sup>4</sup> have compared phosphinated polystyrene palladium complex with analogous homogeneous palladium complex, palladium salts, Pd/C in terms of catalyst activity and selectivity and found that polymer anchored catalyst with Pd/P - 1:1 is highly active, but noticeable deactivation of the catalyst on reuse was the main disadvantage.

Anchored catalysts supported on montmorillonite, a swellable smectite clay, have been used in recent past in very important selective organic transformations such as cis-hydrogenation<sup>5a,b</sup> and deuteration of alkynes<sup>5c</sup>, dienes to monoenes<sup>6</sup>, sequential hydrogenation of alkynes<sup>7</sup>, selective nitro reductions<sup>8</sup> and selective carbonyl reductions<sup>9</sup>. The clay anchored complexes have been reused without any noticeable deactivation<sup>10</sup>.

Recently in our preliminary communication we reported our discovery of molecular recognition in the arylation of acrylates using montmorilloniteethylsilyldiphenylphosphinepalladium(II) chloride catalyst<sup>11</sup>.


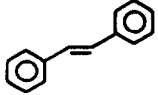
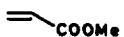
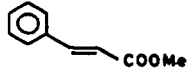
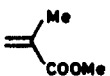
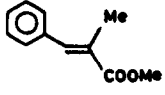

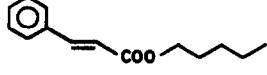

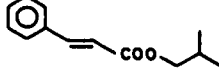

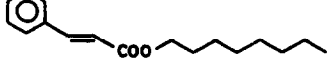
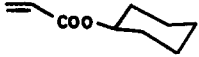
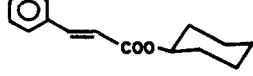
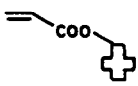
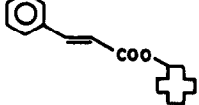

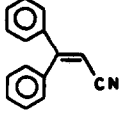

The aim of the present work is to study the arylation of the alkenes by arylhalide with clay anchored catalyst (I) and to compare the selectivity and activity with the widely used catalysts such as Pd(0) complex, Pd salts, Pd/C and polymer anchored palladiumphosphine complex (Pd/P = 1). In addition to this, synthesis of variety of unsymmetrical trans-stilbenes by cross-coupling of phenylvinylacetate with various iodobenzenes catalyzed by anchored catalyst (I) is also presented.

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<sup>†</sup> IICT Communication No. : 2820

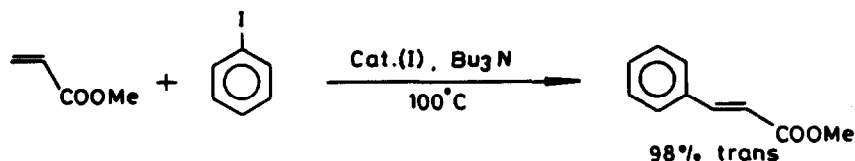
**Table -1**

**ARYLATION OF ALKENES BY MONTIMORILLONITE ETHYLSILYLDIPHENYL  
PHOSPHINE PALLADIUM (II) CHLORIDE CATALYST.**

ENTRY	SUBSTRATE	PRODUCT	TIME (hrs)	YIELDS <sup>a</sup>
1			2	98 (92) <sup>b</sup>
2			2	96
3			2	94
4			2	95
5			2	96
6			2	93
7			6	94
8			8	92
9			4	90
10		NO REACTION	—	—

a: By GC ; b: Isolated yield

The arylation of conjugated alkenes is catalyzed very rapidly with high turnover number and high trans selectivity using aryl iodide as arylating agent, tributylamine as base and catalyst (I) as catalyst. The trans selectivity is always near quantitative and no cis product is noticed (Scheme - 1).



Scheme - 1

As seen from the Table-1 the arylation reaction was carried out on various substituted acrylates ranging from alkyl to cyclic substituents with iodobenzene and obtained quantitative yields with 95% trans selectivity. When acrylonitrile (entry 9) was subjected for arylation, a double arylated product was obtained as an exceptional case. However, the cyclic acrylates required longer hours for completion of reaction due to the steric effects imposed by larger dimensions. Simple alkenes (entry 10) when subjected for arylation there was no reaction. The present catalytic system could arylate only the conjugated alkenes.

The arylation using bromobenzene are generally difficult if catalyst other than palladium (0) phosphine complexes are used<sup>12</sup>. The arylation was not possible on methylacrylate using bromobenzene as arylating agent in the present studies. The similar observation has been made by Teranishi et al<sup>13</sup> that in the reaction of bromobenzene with styrene using polymer bound tetrakis (triphenyl phosphine) palladium analogue as the catalyst, only traces of stilbene were found in that study.

A comparative account of homogeneous, polymer anchored and clay anchored catalyst showing their activity, % conversion, selectivity and recycling capacity is described in Table 2.

### Activity

The molar turn over number (TON) of the catalyst (I) in the arylation of both methylacrylate and styrene is 1175. On the other hand the polymer anchored palladium complex exhibited the TON 125 in the arylation of styrene and the homogeneous catalyst exhibited the TON 75 only<sup>13a,b</sup>. The eight fold activity than the polymer anchored catalyst and more than ten fold activity than the homogeneous catalyst exhibited by clay anchored catalyst can be correlated to change in the electronic environment. Further the lattice points in the highly acidic<sup>14</sup> intercalated clay material seems to activate the alkenic bond much more effectively than the other supports such as polymer and activated carbon.

The activity of clay anchored catalyst is very much consistent, as can be seen from Fig. 1 showing % conversion as a function of time in the arylation of methylacrylate with iodobenzene at 100°C where a comparative account has been brought out. It is evident from Fig. 1 the near straight line was obtained with regard to the clay catalyst (I) despite using ten times lower in concentration of catalyst compared with other systems. The result indicated that the conversion is independent to the reactant concentration. Thus it differs from the systems such as  $\text{Pd}(\text{PPh}_3)_4$ , Pd polymer anchored, Pd/C etc.

### *Trans selectivity*

The exclusive formation of trans product in the arylation reaction with clay catalyst is an interesting phenomenon. The trans selectivity is 98% and no cis product is observed. The selectivity obtained is comparable with our earlier results in hydrogenation of alkynes to alkenes with high cis selectivity<sup>5b</sup>. Conversely, the trans selectivity is 70% and 78% with

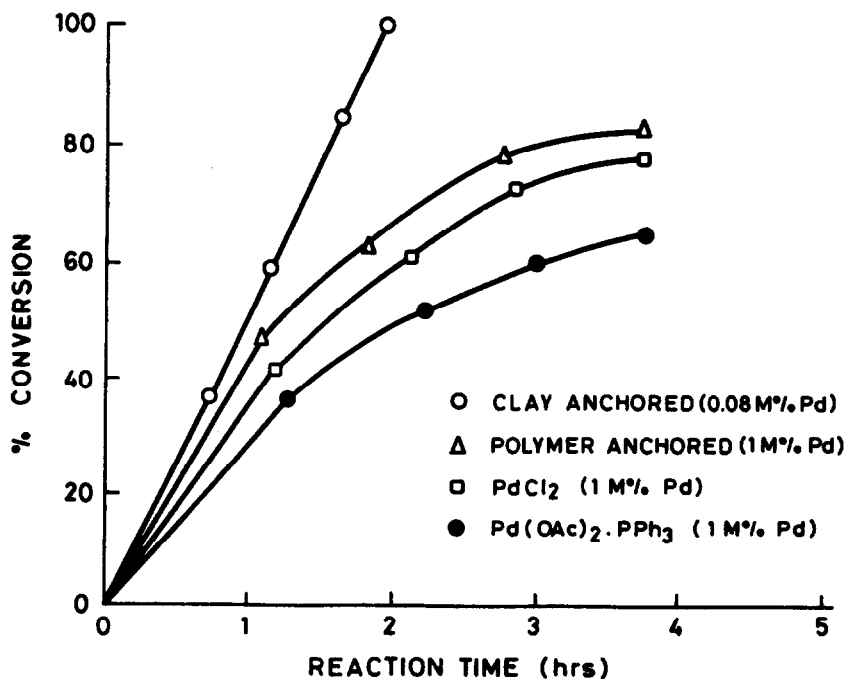


Fig. 1 Conversion as a function of time for the arylation of methylacrylate with iodobenzene at 100°C

homogeneous catalyst<sup>15</sup> and polymer anchored catalyst respectively<sup>3</sup> with remaining being cis and other byproducts. Thus the absolute trans inductivity obtained in the present catalytic system is due to the effect of montmorillonite support.

### Recycling

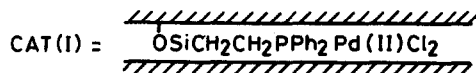
The recycling capacity shown in Table-2 for four recycles is almost constant in case of clay anchored catalyst without any deactivation. On the other hand, noticeable deactivation was displayed in case of polymer anchored catalyst<sup>3</sup>. It is thus demonstrated that montmorillonite is most superior support even for reuse.

**Table-2.** Comparative account of homogeneous, polymer anchored and clay anchored catalysts

	Homogeneous catalyst	Polymer anchored catalyst	Clay anchored catalyst
% Conversion	75	80	99
Activity (Turn over number)	75	125	1175
Selectivity (% trans product)	70	78	98
Recycling (%)	-		
1st cycle		78	98
2nd cycle		74	96
3rd cycle		66	94
4th cycle		61	92

In an attempt for arylation of vinylacetate with iodobenzene diarylated trans products i.e., trans stilbenes were reported<sup>16</sup> recently as a novel single pot reaction for substitution and cross coupling of vinylacetate to trans stilbene by catalyst (I). When the reaction mixture was subjected periodically for GC-MASS during the reaction trans phenylvinylacetate was formed first which was converted subsequently and simultaneously to trans stilbene, no styrene was observed in the reaction. These results indicate that nucleophilic substitution of vinylacetate afforded trans phenylvinylacetate and trans stilbene was formed subsequently by the coupling reaction likely in a concerted way.

Employing this strategy we synthesized various unsymmetrical trans stilbenes from phenylvinylacetate (Scheme - 2, Table-3) by cross coupling of various substituted iodobenzenes in quantitative yields catalyzed by heterogenised montmorilloniteethylsilyldiphenylphosphinepalladium (II) chloride (I) in a single step. The coupling reaction of phenylvinylacetate when conducted with iodobenzene under identical conditions in homogeneous phase catalysed by  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  gave negligible yield of coupling product.



R = o-OMe, p-OMe, o-Me, p-Me & Isopropyl

### SCHEME - 2

Hence, the successful cross-coupling of phenylvinylacetate with various iodobenzenes in presence of anchored catalyst is attributed to montmorillonite support and thus provide an evidence for the support directed coupling reaction. This simple and convenient synthesis can be easily adapted for synthesis of number of trans stilbene derivatives by changing the substituents on iodobenzene.

TABLE - 3 CROSS COUPLING REACTIONS OF PHENYL VINYL ACETATE BY CAT (I)

entry	substrate	products <sup>a</sup>	isolated yield %.
1			85
2			84
3			86
4			85
5			86
6			85

a: All the products were characterised by NMR & MASS.

Synthesis of unsymmetrical trans stilbenes assumes importance in view of their large molecular hyperpolarizable property suited for the construction of non-linear optics<sup>17</sup> and their use as organic intermediates<sup>18</sup>. Synthesis of trans stilbenes usually involves tedious multistep synthetic procedures often resulted in poor to moderate yields. An arylation reaction of alkenes attempted by Heck using catalytic amounts of palladium salts afforded moderate yields on longer reaction hours<sup>19</sup>.

In conclusion synthesis of trans stilbenes via cross coupling of phenylvinylacetate catalysed by montmorillonite supported catalyst offers a better route with high activity and excellent yield.

## EXPERIMENTAL

### Preparation of catalyst

Montmorilloniteethylsilyldiphenylphosphinepalladium (II) chloride complex<sup>5b</sup> :

The Na-montmorillonite which was prepared from commercial montmorillonite K 10 (Fluka), a class of smectite clay by the procedure of Posner and Quirk was treated with 0.1N HCl to afford H-montmorillonite (10g) with 2-diphenylphosphinoethyltriethoxysilane (1.130 g, 3 mmol) obtained from Alfa in dry toluene under reflux in inert atmosphere for 48 hours affords inter-lamellar montmorillonite 2-diphenylphosphinoethylsilane. This on complexation with dichlorobis(benzylcyano) palladium (II) in dry benzene under stirring at room temperature gave yellow palladium (II) complex.

### Arylation procedure

The arylation of alkenes with iodobenzene was conducted by taking styrene (2.08 g, 20 mmols), iodobenzene (22 mmols), tributylamine (25 mmols) and catalyst (I) 50 mg (0.017 mmols of Pd) in a round bottom flask under inert atmosphere at 100°C. The formation of the product was monitored in gas chromatography by SE-30 column. The reaction mixture was washed with 5N HCl and the ether extract washed with brine solution which on concentration gave the arylated product trans stilbene (3.2 g) 92%.

M.P., NMR, Mass and IR of all the products in Table-1 are very well compared with the authentic compounds and confirmed.

### Cross coupling of phenylvinylacetate

Phenylvinylacetate (22 mmols) was reacted with iodobenzene (20 mmols) in presence of tributylamine (25 mmols) and catalyst (I) 50 mg (0.017 mmols of Pd) at 100°C under nitrogen atmosphere for 6 hrs under vigorous stirring. The formation of the product trans stilbene was monitored in GC SE-30 column. The work up was carried out by neutralising excess base by washing with 5 N HCl and the solution was extracted with ether and the ether extract washed with brine solution which on concentration and recrystallization in ethanol gave trans stilbene (1.5 g) yielding 85% based on iodobenzene consumed.

Physical characteristics of products in Table-3.

trans-2-methoxystilbene (entry 2) m.p. 58°C (lit.<sup>20</sup> m.p. 59°C)

trans-4-methoxystilbene (entry 3) m.p. 137°C (lit.<sup>20</sup> m.p. 136°C)

trans-2-methylstilbene (entry 4) b.p. 126°C (0.15 mm) (lit.<sup>21</sup> b.p. 125°C, 0.15 mm)

trans-4-methylstilbene (entry 5) m.p. 118-120°C (lit.<sup>21</sup> m.p. 119.5°C).

#### **Acknowledgement**

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