Preparation of a new clay-immobilized highly stable palladium catalyst and its efficient recyclability in the Heck reaction

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The immobilization of a series of bis-carbene-pincer complexes of palladium(II) on montmorillonite K-10 affords the preparation of effective catalysts for the C–C coupling in a standard Heck reaction. The supported catalysts so obtained, show catalytic activity similar to their homogeneous counterparts. The determination of Pd content on the supported catalysts by XPS and elemental analysis, before and after each catalytic reaction, shows that leaching is negligible. Once the reaction conditions were optimized, we were able to recycle the catalyst at least ten times, without significant loss of activity.

Introduction

Over the last few years, there has been increasing interest in designing new synthetic methods that combine chemical efficiency with environmentally benign procedures. In this sense, one of the most challenging efforts is to find ways of catalyst recycling, since this would undoubtedly achieve both combined purposes.

Homogeneous catalysis affords a large number of routes to most transformations of organic substrates. However, the catalysts used are mainly unstable species with low lifetimes under the reaction conditions, this preventing the use of high temperatures (higher conversions, faster reactions) and catalyst recovering. The use of phosphine ligands in most catalysts seems to afford a route to catalyst deactivation since it is proposed that P–C bond cleavage may be implicated in the process.[1]

In the search of new phosphine-free robust catalysts, we previously described the synthesis of palladium complexes with tridentate pincer bis-carbene ligands, which have shown efficient catalytic activity towards C–C coupling.[2–4] The high stability of these catalysts is due to a combination of the chelate effect imposed by the tridentate ligand, and the thermal stability of late transition metal heterocyclic carbenes. These complexes, displayed high catalytic activity at higher temperatures (184 °C) than those normally used in Heck couplings, affording the highest turnover numbers yet reported for couplings with aryl chlorides.[3]

Heck reactions are a tough challenge for the design of recyclable systems. The reaction needs at least three reagents (halide, olefin, base) besides the catalyst itself. The salt generated by neutralization of HX and base in the last step of the catalytic cycle is accumulated in the reaction media, leading to an unexpected influence on the catalytic process such as degradation of the catalyst[5] or promotion of the reaction rate.[6,7] Due to the change of reaction mixture composition, the Heck process always works in a varying environment. Despite all these problems, some approaches to support[8] and heterogenizing Heck catalysts have given encouraging results. Common heterogenization procedures of Pd catalytic systems imply either immobilization of Pd catalysts on polymers,[9] or on modified mesoporous silica gel.[10] However, although some of these preformed heterogenized catalytic systems, such as the palladium bis-carbene complex immobilized in a functionalized polystyrene support prepared by Herrmann and coworkers,[9a] can be efficiently recycled in a Heck reaction, they suffer from the disadvantage of their preparation which requires multistep syntheses. Supported liquid phase catalysts, in which thin liquid film containing Pd-sulfonate phosphines complexes are supported on a porous silica, have provided good performance on C–C coupling, but leaching of the palladium species into the solvent questions whether the active species are attached to the solid support or whether they are dissolved palladium complexes.[6,11]

In the last years, we have focused on immobilizing catalytic systems in clay structures *via* adsorption or cationic exchange, as an easy and clean alternative for heterogenization. We have satisfactorily used montmorillonite K-10 in the preparation of heterogenized catalysts for asymmetric hydroboration,[12] reductive alkylation of primary amines,[13] and hydrogenation of imines.[14–16]

Based on our previous findings, we now report the catalytic activity of clay-heterogenized pincer-bis-carbene complexes of Pd in the coupling of phenyl halides with styrene.

Results and discussion

Preparation of the catalysts

According to our previous reported data, we found that pincer-heterocyclic-carbene ligands are good alternatives to phosphines in the design of new catalysts in C–C coupling reactions by the Heck method.[2–4] The compounds obtained, not only showed high efficiency in C–X activation (X = I, Br, Cl), but also showed an extremely high temperature stability which allowed the design of reactions at temperatures much higher than those often used in the Heck reaction. With this in mind, we thought that these catalysts could be excellent candidates for designing new recyclable C–C coupling catalysts, and

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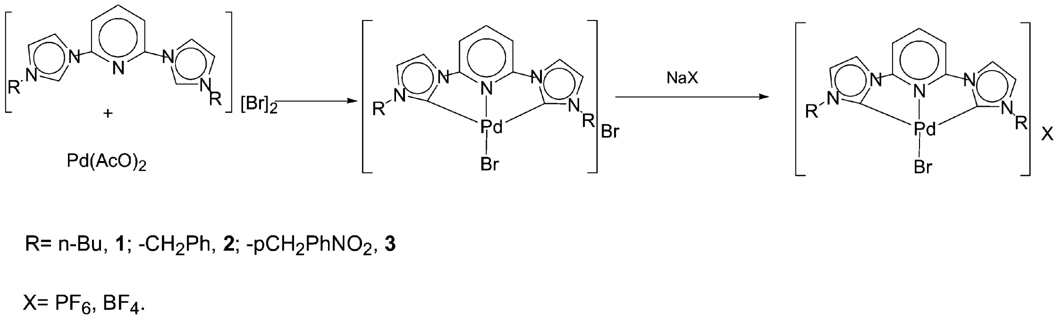


Scheme 1

we prepared a new series of complexes in order to achieve this purpose.

Scheme 1 shows the general procedure for the synthesis of the catalysts used. The preparation method is similar to the one reported in our previous papers for [PdBr(CNC-Bu$_2$)]Br, **1**-Br.[2–4] Compounds [PdBr(CNC-Bu$_2$)]PF$_6$, **1**-PF$_6$ [PdBr(CNC-Bz$_2$)]X, **2**-X, and [PdBr(CNC-PhNO$_2$)]X, **3**-X (X = Br and PF$_6$), are new, and their preparation and characterization are described in the Experimental section.

The immobilization process of the organometallic complexes **1**-Br, **2**-X and **3**-X onto the clays montmorillonite K-10 (MK-10) and bentonite (Na$^+$-M), was carried out by the solvent impregnation method previously described.[17] Thus, coloured solutions of the ionic complexes in anhydrous dichloromethane were stirred under N$_2$ with the solid support for 24 h. Both clays (MK-10 and Na$^+$-M), were previously dried at 100 °C, for 24 h to eliminate the small amount of adsorbed water that they may contain, in order to guarantee the maximum immobilization.[12] The amount of metal complex adsorbed by the clay was determined by XPS and atomic absorption spectroscopy (AAS). XPS was also used to characterize the chemical state of palladium present in the supported catalysts, before and after each catalytic reaction. The maximum palladium load achieved is 1.7% (weight) when determined by XPS analysis, and 0.8% for the elemental analysis of the bulk solid (AAS), for the grafting of **1**-Br onto MK-10 (B.E.T. surface area 221 m^2 g^{-1}). In order to confirm whether the structure of the catalyst remains unchanged upon immobilization, we performed the Raman spectra of both, free and supported catalyst (Fig. 1). The spectra of both systems conclusively revealed that, at least, the structure of the precatalyst remains the same upon immobilization. Whether the true catalytic species is the same in both, homogeneous and heterogenized systems, falls beyond the scope of this work, and may need a detailed mechanistic study. Remarkably difference was observed when preheated bentonite (Na$^+$–M), was used as support. Following the same impregnation procedure, the amount of metal complex adsorbed was only 0.05% of **1**-Br (bulk, by elemental analysis). These data are in agreement with the lower surface area of Na$^+$–M (53 m^2 g^{-1}) compared to MK-10. It is known that although both montmorillonite K-10 and bentonite are the same montmorillonite clay material, they show significant differences in crystallinity.[18] In fact, MK-10 is prepared from Na$^+$–M by acid treatment, which partially destroys the bentonite layer structure giving a disordered and increased surface area.

It has been reported that the mechanism of grafting the ionic complexes to MK-10, and Na$^+$–M, is different.[12,16] In the first case the interaction between counter cation and counter anion to MK-10 is likely hydrogen bonding, and in the second case the electrostatic attractions between the counter cation and the bentonite layers are the significant features of this immobilization (Scheme 2). The different entrapment of these catalysts on the clays could also imply differences in the activities when they are used as catalytic systems in the Heck reaction.

Catalytic results

To compare the activity and stability of the supported catalysts on MK-10 with their homogeneous counterparts, we performed the standard C–C coupling of PhI with styrene in both, homogeneous and heterogenized conditions (Table 1), using NaOAc as base. In the first stage of our research, we studied the catalytic activity of our catalysts at 180 °C for a reaction time of 2 h. In all cases, as we previously reported,[3] the high stability of the catalysts used allowed us to work under non-inert atmosphere and without any special precautions. A perfect correlation between the conversions in homogeneous and heterogenized conditions can be observed, therefore the activity of the catalyst does not decay upon immobilization. Even slightly higher rates are achieved with the heterogenized catalytic systems compared with their homogeneous counterparts. However, the conversions seem to depend on the catalyst used, being **1**-Br the most efficient one (entry 1 and 2, Table 1).

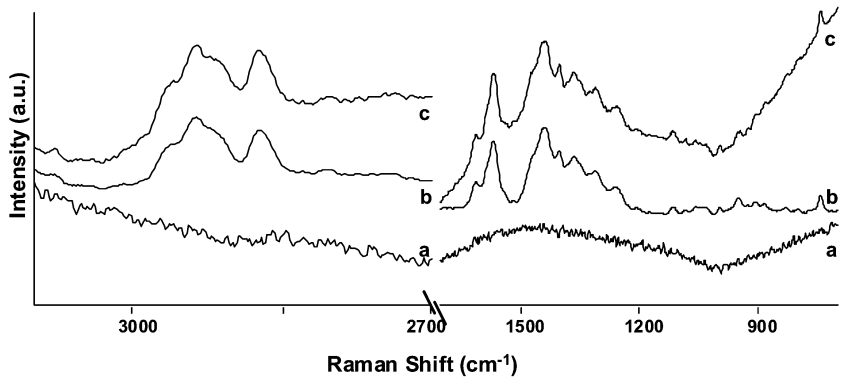
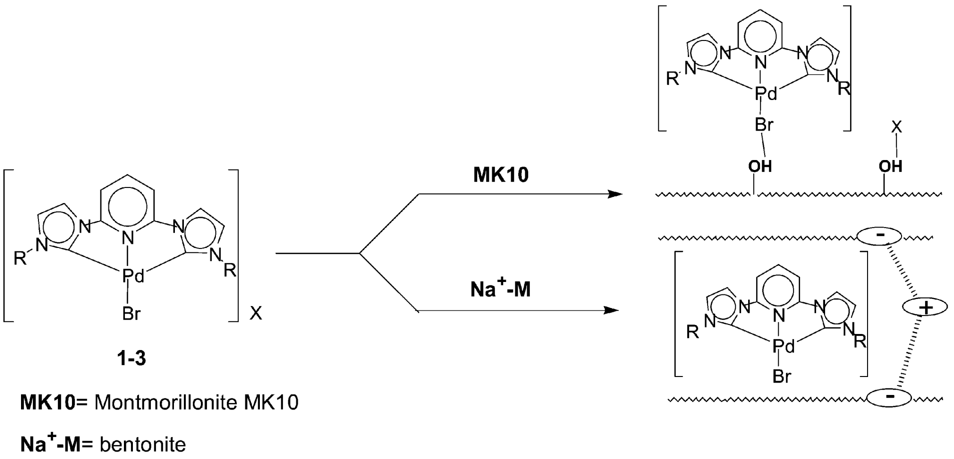


Fig. 1 Raman spectra of: (a) montmorillonite K10; (b) **1**-Br; (c) **1**-Br/MK-10.



Scheme 2

Removal of the supported catalyst by filtration and repeated C–C coupling reaction recycling is demonstrated, but a significant loss of activity is observed. The presence of active species in solution is not considered because no product was formed when styrene and phenyl iodide were added to a hot filtrate of the first run. Leaching of the palladium complex can be discarded because the amount of Pd(II), determined by elemental (AAS) and XPS analysis, in the solid before and after the catalytic consecutive reactions was mainly unchanged (Table 2). As far as the nature of the counter anion is concerned, the catalytic activity exhibited by the supported hydrogen bonded palladium complexes **1**-Br/MK-10 and **1**-PF_6/MK-10 is comparable to their homogeneous counterparts **1**-Br and **1**-PF_6. In addition, there is not any significant difference in the use of the ionic palladium complexes with the counterions studied, showing that the counter anion is not directly involved in the catalytic process. The drop of conversion on recycling is also independent on the nature of X, indicating that the lack of recyclability of these catalytic systems at that stage is not related to the stability of the ionic complexes adsorbed onto the clay.

Table 1 Influence of the catalytic system in the homogeneous and heterogenized C–C coupling of phenyl iodide and styrene[a]

Entry	Catalyst[b]	Number of Runs	Stilbene Yield[c] /%
1	**1**-Br	1	89
2	**1**-Br /MK-10	1	95.2
		2	52.9
		3	23.8
3	**1**-PF_6	1	79
4	**1**-PF_6/MK-10	1	83
		2	35
		3	14
5	**2**-Br	1	65
6	**2**-Br/MK-10	1	65
		2	35
		3	17
7	**2**-PF_6	1	64
8	**2**-PF_6/MK-10	1	75
		2	44
		3	11
9	**3**-PF_6	1	46
10	**3**-PF_6/MK-10	1	46.5
		2	35
		3	12

[a] Standard conditions: phenyl iodide (4 mmol), styrene (5.6 mmol) NaOAc (4.4 mmol), solvent (DEA, 5 mL), supported catalyst (0.004 mmol of metal complex, 0.1 mol%, in 0.5 g of MK-10). *T*: 180 °C. Time: 2 h; [b] MK-10: commercial montmorillonite K-10, (preheated at 100 °C for 24 h); [c] Conversion of the aryl iodide on *trans*-stilbene by C.G. using glycol-n-butyl ether as internal standard.

The drop of recyclability is not an effect of the temperature either. Thus in order to study the influence of the temperature on the conversions obtained, we carried out the above mentioned C–C coupling at several reaction temperatures (120°, 140° and 180 °C) and studied their time dependent-reaction profiles using the catalytic system that provided the highest activity, **1**-Br/MK-10. Fig. 2 indicates that both homogeneous and heterogenized systems show the same reaction profile at 120°, 140° and 180 °C. We reported that the homogeneous reaction is consistent with a mechanism in which the slow catalyst reduction step may not be involved,[3] so a similar mechanism may be operating in the heterogenized system, although further studies are being carried out in order to prove this theory. Maximum conversions, even though far from quantitative at 120° and 140 °C, were achieved after 3 hours.

Since montmorillonite K-10 readily adsorbs ionic species from solution, we suspected that NaOAc, used as the base on each consecutive C–C coupling run, could be simultaneously adsorbed onto the solid surface, hence saturating or blocking the catalytic active sites. Indeed, elemental and XPS analysis of the solids before and after its recycling, showed that the amount of Na and C adsorbed considerably increased upon the consecutive runs, (Table 2). XPS analysis also offers

Table 2 Elemental and XPS analysis

Catalyst	Number of runs	Base	Washing[a]	Pd/wt % bulk	XPS/ wt%
1-Br/MK-10	0	—	—	0.8	Pd (1.7) Si(29.3) C(10.3)
1-Br/MK-10	3	NaOAc	CH_2Cl_2	0.5	Pd(1.2) Si(20.6) C(14.1) Na(11.6)
			H_2O–CH_3OH[b]	0.43	Pd(1.9) Si(30.9) C(5.8) Na(2.3)
1-Br/MK-10	10	NEt_3	CH_2Cl_2	0.51	Pd(1.3) Si(27) C(18)

[a] All washings performed on the solid filtrate with 3 × 2 mL of solvent. [b] Same solid after washed with H_2O-CH_3OH.

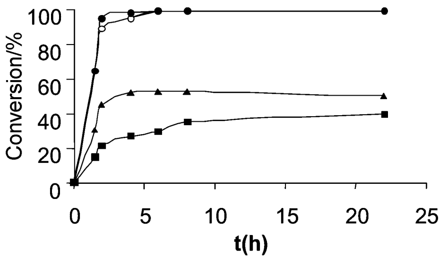


Fig. 2 Reaction profiles of the coupling reaction of PhI and styrene using **1**-Br/MK-10 (Het. 0.1% mol) at 120° (■), 140° (▲) and 180° C (●), and **1**-Br (Homo, 1% mol) as catalysts at 180 °C (○).

Table 3 Influence of the solvent in the washings of **1**-Br/MK-10 between the consecutive runs in the heterogenized C–C coupling of phenyl iodide and styrene[a]

Entry	Solvent[b]	Number of runs	Stilbene yield[c] /%
1	CH_2Cl_2	1	95.2
		2	52.9
		3	23.8
2	H_2O–MeOH	1	99
		2	88
		3	47
3	H_2O–CH_2Cl_2	1	97
		2	65
		3	35

[a] Standard conditions: phenyl iodide (4 mmol), styrene (5.6 mmol) NaOAc (4.4 mmol), solvent (DEA, 5 mL), supported catalyst (0.004 mmol of metal complex, 0.1 mol%, in 0.5 g of MK-10). *T*: 180 °C. Time: 2 h; [b] Washings performed on the solid filtrate (3 × 2 mL); [c] Conversion of the aryl iodide on *trans*-stilbene by C.G. using glycol-n-butyl ether as internal standard.

valuable information about the Pd(II) content on the surface of the solid. Fig. 3 shows the Pd3d spectrum obtained for **1**-Br/MK-10 before and after reaction. Before reaction, a maximum at *ca.* 337.8 eV (Pd3d$_{5/2}$) was observed, indicating the presence of Pd^{+2}, as the only Pd species. After reaction at 180 °C in the presence of NaOAc (Table 1, entry 2) the binding energy corresponding to palladium did not experience substantial changes and only the relative intensity of the peak was slightly reduced (Fig. 3). These results indicate that the oxidation state of palladium is not modified after each reaction. The decrease of the relative intensity of the Pd3d peak could be associated with the increase of carbon on the surface due to NaOAc adsorption. Moreover, bulk analysis of the solid before and after its use in the catalytic reaction, showed that the amount of C and Na considerably increases upon its use in the presence of NaOAc (Table 2). Thus, chemical analysis of palladium before and after reaction revealed that Pd bulk was practically unchanged. These data confirm our previous considerations that adsorption of NaOAc on montmorillonite K-10 may be the cause for the loss of activity. A similar effect is reported in literature where potassium acetate is used as base in Heck reaction with palladium-based supported liquid phase catalysts.[6] In that situation, the decrease of the reaction rate during the repeated runs, was explained by the adsorption of potassium acetate onto the catalyst surface.

In order to recover the catalytic activity after catalyst recycling, we studied two plausible solutions: i) keeping NaOAc as base, but washing the solid with H_2O–CH_2Cl_2 or H_2O–CH_3OH between the consecutive runs, in order to eliminate the amount of NaOAc adsorbed; ii) using NEt_3 as base, instead of NaOAc. The first purpose was suggested in basis to the fact that our catalyst shows great stability in a non-inert medium. The results obtained are shown in Table 3. As it can be seen, the catalytic activity can be more efficiently recycled between consecutive runs if washing of **1**-Br/MK-10 is carried out with H_2O–CH_3OH, (entry 2, Table 3). In fact the amount of Na and C adsorbed on the solid is significantly lower than those observed when washings were carried out only with CH_2Cl_2 or H_2O–CH_2Cl_2 (Table 3). These data confirm that a more efficient elimination of undesired ionic species is achieved upon more polar washings.

On the other hand, the use of the non-ionic base NEt_3 yields quantitative conversion of the substrate, even after the ten consecutive runs performed (Table 4), and using CH_2Cl_2 for washing of the solid. As expected, this base does not show any significant affinity towards surface adsorption, allowing the catalytic sites to remain active after being reused. The accumulated TON of this reaction is 13 000. As it can be seen from Table 4, there is a smooth decrease of catalytic activity after run 8. We attribute this decrease to the loss of recycled solid by the consecutive filtrations after each run, which diminishes the solid catalyst amount from 0.5 g (run 1) to 0.3 g (run 10). This suggestion is confirmed by the fact that the bulk and XPS

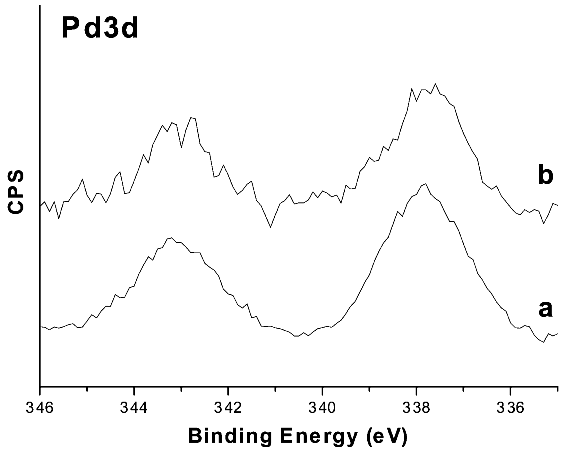


Fig. 3 Pd3d photoelectron spectra of **1**-Br/MK10, (a) fresh catalyst, (b) After 3 reaction runs, using NaOAc as base.

Table 4 Influence of the base NEt_3 on the recyclability of the catalytic system in the heterogenized C–C coupling of phenyl iodide and styrene[a]

Entry	Catalyst	Number of Runs	Stilbene Yield[b] /%
1	**1**-Br/MK-10	1	> 99
		2	95
		3	88
		4	89
		5	88
		6	90
		7	89
		8	85
		9	83
		10	79
2	**1**-Br/Na$^+$–M	1	> 99
		2	98
		3	74
		4	67

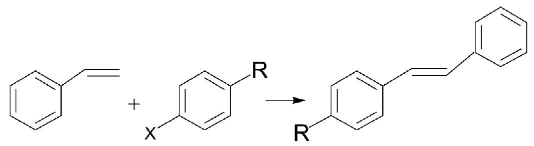
[a] Standard conditions: phenyl iodide (4 mmol), styrene (5.6 mmol) NEt_3 (4.4 mmol), solvent (DEA, 5 mL), supported catalyst (0.004 mmol of metal complex, 0.1 mol%, in 0.5 g of MK-10) *T*: 180 °C. Time: 2 h; [b] Conversion of the aryl iodide on *trans*-stilbene by C.G. using glycol-n-butyl ether as internal standard.

analysis of the solid after being used for ten times, shows very little decrease in the amount of the Pd(II) content (0.51, bulk; 1.3, XPS; Table 2). Under these optimized conditions for the reuse of the catalyst, we also explored the influence of the solid support **1**-Br/Na$^+$–M (bentonite) on the recycled C–C coupling reaction. As can be seen, the bentonite clay not only serves as a good support to immobilize the complex [PdBr(CNC-Bu$_2$)]Br, **1**-Br, but also the catalytic solid resulting, (**1**-Br/Na$^+$–M), provides a comparable catalytic activity to **1**-Br/MK-10. However, the recyclability is not as efficient from the same consecutive run (Table 4).

It is important to point out that no Pd(0) was found on the surface of the solids after being used in catalytic reactions.

Once we optimized our results on the Heck coupling of iodobenzene with styrene, we decided to extend the study to other substrates, in order to determine whether our catalysts could also be operative in C–C coupling of the less reactive C–Br and C–Cl bonds. The results that we obtained are shown in Table 5. When the reactions are carried out in the presence of NEt$_3$ as base, the yields on the desired product were very low both in homogeneous and in heterogenized conditions. We have previously reported the homogeneous reactions of this catalyst, and we saw that the use of NaOAc provided high yields on the desired products.[3] For the more unreactive aryl halides, the use of tetrabutylammonium bromide (TBABr) was necessary in order to achieve high conversions. With this in mind, we decided to carry out new reactions using NaOAc and TBABr in order to check whether we could reproduce our results in heterogenized conditions. As can be seen in Table 5, the conversions obtained when bromoaryl compounds are used (bromophenyl and 4-bromobenzaldehyde), are quasi-quantitative in the first run. Furthermore, for the more activated 4-bromobenzaldehyde, the reaction is complete in only one hour. Recycling of the catalyst, affords 4 consecutive runs without measurable conversion decay. After the fifth run, the conversion smoothly decreases, probably due to the reasons described above. For the unactivated bromide (phenyl bromide), the conversion decreases after the first run. The difference between these two systems may be due to higher adsorption of ionic species in the case of the reaction of phenyl bromide, since high conversions are only achieved for longer reaction times (10 h *vs.* 1 h). For the reaction with 4-chlorobenzaldehyde, the conversion was very low (15%), probably because the catalyst is deactivated by adsorption of undesired ionic species before the reaction is finished. In any case, we would like to point out that, at least, some C–Cl is activated under the conditions discussed. Further studies are being carried out in order to enhance the recyclability of the catalyst in the reactions of C–C coupling of chloro- and bromo- aryl species.

Table 5 Activation of C–Br and C–Cl in C–C coupling using **1**-Br as catalyst[a]



Catal.	Base	R	X	t/h	N of Runs	Yield/%[b]
1-Br	NEt$_3$	CHO	Br	2	1	89
1-Br/MK-10	NEt$_3$	CHO	Br	2	1	12
	NEt$_3$	CHO	Br	2	2	7
	NEt$_3$	CHO	Br	2	3	2
1-Br/MK-10	NEt$_3$	H	Br	10	1	25
	NEt$_3$	H	Br	10	2	12
1-Br/MK-10[c]	NaOAc	CHO	Br	1	1	>99
	NaOAc	CHO	Br	1	2	>99
	NaOAc	CHO	Br	1	3	97
	NaOAc	CHO	Br	1	4	>99
	NaOAc	CHO	Br	1	5	82
	NaOAc	CHO	Br	1	6	78
	NaOAc	CHO	Br	1	7	33
	NaOAc	CHO	Br	1	8	25
1-Br/MK-10[c]	NaOAc	H	Br	10	1	>99
	NaOAc	H	Br	10	2	82
	NaOAc	H	Br	10	3	40
1-Br/MK-10[c]	NaOAc	CHO	Cl	24	1	15

[a] Standard conditions: aryl halide (4 mmol), styrene (5.6 mmol) base (4.4 mmol), solvent (DEA, 5 mL), supported catalyst (0.004 mmol of metal complex, 0.1 mol%, in 0.5 g of MK-10) *T*: 180 °C. [b] Conversion of the aryl iodide on *trans*-stilbene by C.G. using glycol-n-butyl ether as internal standard. [c] Reactions performed with NaOAc with 20% of tetrabutyl bromide relative to the aryl halide.

Conclusion

Immobilization of a series of CNC biscarbene Pd(II) complexes on montmorillonite K-10 has afforded highly efficient supported catalyst for C–C coupling Heck reaction. Reaction profiles and chemical analysis of the solids obtained suggest that in all cases the reaction follows a mechanism similar to the homogeneous counterparts, where the supported catalyst remains unchanged after immobilization (Raman and XPS analysis). Analysis of the supported catalyst before and after being used has shown that leaching and chemical decomposition of the catalyst is negligible. The catalyst has been reused at least ten times, without important activity decay. The catalyst has been used in the activation of more unreactive C–Br and C–Cl bonds, providing high yields in the C–Br case.

Experimental section

General details

NMR spectra were recorded on a Varian Innova 300 MHz and 500 MHz, using CDCl$_3$ and DMSO-d6. The FT-Raman spectra were recorded on a Bio-Rad spectrometer, Model FT-Raman II. The 1.064 μm line of a Nd:YAG laser was used for excitation along with a germanium detector cooled to liquid nitrogen temperature. The Raman spectra were recorded at room temperature in the 180° scattering configuration using high-quality quartz tubes as cells. The laser power at the samples was 70 mW. The Raman spectra were corrected for instrumental response using a white light reference spectrum. The apparatus was working at ± 0.5 cm^{-1} resolution. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 II with a flame ionisation detector equipped with a column Ultra-2 (5% diphenylmethyl silicone and 95% dimethyl silicone) of 25 m. Chemical analysis of the catalysts were performed by atomic absorption spectrophotometry (AAS) in a SpectrAA-10Plus (Varian) spectrometer, after dissolving the solids in concentrated HCl at room temperature for 24 hours. Montmorillonite K-10 (MK-10) was purchased from Fluka and bentonite Na$^+$–M was purchased as Majorbenton B, from AEB Iberica S. A. Pre-dried clays were obtained as follows: 5 g of clay in a melting pot were kept in the oven at 100 °C for 24 h.

Pd oxidation state in the catalysts was determined by X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded on a VG-Escalab-210 electron spectrometer equipped with a multichannel detector. Spectra were excited by using the Mg Kα (1253.6 eV) radiation of a twin anode in the constant analyser energy mode with a pass energy of 40 eV. Vacuum during spectra acquisition was better than 3.10^{-9} mbar. For calculation of binding energies the peak of the C–(C,H) component coming from contamination of carbon 284.6 eV, was used as an internal standard. The surface composition was estimated from the corresponding XPS peak area ratios by using the relation:

$$\left[\frac{X}{Y}\right]_s = \frac{A_X}{A_Y}\frac{\sigma_Y}{\sigma_X}\frac{\lambda_Y}{\lambda_X}\sqrt{\frac{E_K(X)}{E_K(Y)}}$$

where A, σ, λ and E_K are the integral of each peak after S-shaped background subtraction, the effective ionization cross section, the escape depth and the photoelectron kinetic energy respectively. Cross section values were taken from Scofield[20] and the escape depth was calculated from the formulas given by Vulli and Starke.[21]

The compounds 2,6-bis(imidazol-1-yl)pyridine,[22] [CHNCH-(Bz)$_2$][Br]$_2$,[22] [CHNCH-(Bu)$_2$][Br]$_2$[2] and [PdBr(CNC-Bu$_2$)]-[Br][2] were obtained according to literature methods.

Synthesis of compounds

[CHNCH-(CH$_2$Ph-NO$_2$)$_2$][Br]$_2$. A mixture of 2,6-bis(imidazol-1-yl)pyridine (10 mmol) and 4-nitrobenzylbromide (30 mmol) in toluene were refluxed for 4 h. The white solid formed was filtrated and washed with Et$_2$O yielding pure [CHNCH-(CH$_2$Ph–NO$_2$)$_2$][Br]$_2$(95%). ^{1}HNMR (δ, DMSO-d_6): 5.67 (4H, CH$_2$), 7.45 (*d*, $J = 6.3$ Hz, 4H, Ph), 7.64 (*d*, $J = 6.3$ Hz, 4H, Ph), 8.2 (2H, CH, imid), 8.28 (*d*, $J = 7.8$ Hz, 2H, pyr) 8.62 (*t*, $J = 7.8$ Hz, 1H, pyr), 8.90 (2H, Ph), 11.22 (2H, imid). ^{13}CNMR (δ, DMSO-d_6): 52.3 (CH$_2$), 115.8 (C, imid), 120.8 (C, imid), 124–130 (*m*, CH, Ph), 137.3 (C, pyr), 142.1 (C, pyr), 145.9 (N*C*HN), 149.3 (C, pyr). Anal. calcd. for $C_{25}H_{21}N_7O_4Br_2$: C, 46.67; H, 3.27; N, 15.24; O, 9.96. Found: C, 46.55; H, 3.18; N, 15.37; O, 10.04%.

[PdBr(CNC-NO$_2$)]Br. This compound was obtained by a similar method to that described for [PdBr(CNC-Bu$_2$)][Br].[2] A solution of [CHNCH–(CH$_2$Ph–NO$_2$)$_2$][Br]$_2$ (642 mg, 1.0 mmol) and [Pd(OAc)$_2$] (224 mg, 1.0 mmol) was stirred in DMSO (10 mL) for 12 h at 70 °C. Subsequently, the reaction mixture was heated at 170 °C for 2 h and then cooled to room temperature. The solution was poured into CH$_2$Cl$_2$ (20 mL) and Et$_2$O was added (200 mL). The precipitate was washed with Et$_2$O, leaving pure [PdBr(CNC-NO$_2$)]Br as a yellowish solid (73%). ^{1}HNMR (δ, DMSO-d_6): 5.96 (4H, CH$_2$), 7.61 (*d*, $J = 6.0$ Hz, 4H, Ph), 7.73 (2H, CH, imid), 7.84 (*d*, $J = 6.0$ Hz, 4H, Ph), 8.61 (*d*, $J = 7.8$ Hz, 2H, pyr), 8.57 (2H, Ph), 8.62 (*t*, $J = 7.8$ Hz, 1H, pyr). ^{13}CNMR (δ, DMSO-d_6): 52.8 (CH$_2$), 109.9 (C, pyr), 120.1 (C, imid), 124.99 (C, Ph), 124.94 (C, imid), 131.1 (C, Ph), 144.2 (C, pyr), 150.8 (C, pyr), 167.1 (C-Pd). Anal. calcd. for $C_{25}H_{19}N_7O_4Br_2Pd$: C, 40.16; H, 2.56; N, 13.11; O, 8.55. Found: C, 40.19; H, 3.01; N, 13.28; O, 8.67%.

[PdBr(CNC-Bz$_2$)]Br. This compound was obtained by a similar method to that described above for [PdBr(CNC-NO$_2$)][Br]. A solution of [CHNCH-Bz$_2$][Br]$_2$ (553 mg, 1.0 mmol) and [Pd(OAc)$_2$] (224 mg, 1.0 mmol) was stirred in DMSO (10 mL) for 12 h at 70 °C. Subsequently, the reaction mixture was heated at 170 °C for 2 h and then cooled to room temperature. The solution was poured into CH$_2$Cl$_2$(20 mL) and Et$_2$O was added (200 mL). The precipitate was washed with Et$_2$O, leaving pure [PdBr(CNC-Bz$_2$)]Br as a yellowish solid (65%). ^{1}HNMR (δ, DMSO-d_6): 5.82 (4H, CH$_2$), 7.35 (*d*, $J = 6.2$ Hz, 4H, Ph), 7.48 (*d*, $J = 6.0$ Hz, 4H, Ph), 7.72 (2H, CH, imid), 8.12 (*d*, $J = 8.1$ Hz, 2H, pyr),8.57 (2H, Ph), 8.66 (*t*, $J = 8.1$ Hz, 1H, pyr). ^{13}CNMR (δ, DMSO-d_6): 53.2 (CH$_2$), 108.8 (C, pyr), 119.8 (C, imid), 124.81 (C, imid), 129.2 (*m*, 129.2), 136.5 (C, Ph), 147.2 (C, pyr), 150.2 (C, pyr), 166.3 (C-Pd). Anal Calcd. for $C_{25}H_{21}N_5Br_2Pd$: C, 45.66; H, 3.22; N, 10.65. Found: C, 45.15; H, 3.01; N, 11.23%.

For the preparation of the BF$_4$ and PF$_6$ derivatives, we applied the following general method: 200 mg of the Pd[Br] compound were dissolved in 5 ml of CH$_2$Cl$_2$ and added to a column chromatography packed with silica-gel (mesh 60 A) in hexane. The solution was eluted with gradient CH$_2$Cl$_2$–MeOH–KPF$_6$ (Pd[PF$_6$] compounds) or CH$_2$Cl$_2$–MeOH–NaBF$_4$ (Pd[BF$_4$] compounds), affording the corresponding pure compouds. [PdBr(CNC-Bz$_2$)][PF$_6$] (Yield 69%). Anal Calcd. for $C_{25}H_{21}N_5BrPdPF_6$: C, 41.54; H, 2.93; N, 9.69. Found: C, 41.25; H, 3.01; N, 10.23%. [PdBr(CNC-Bz$_2$)][BF$_4$] (Yield, 52%). Anal Calcd. for $C_{25}H_{21}N_5BrPdBF_4$: C, 45.18; H, 3.18; N, 10.54. Found: C, 45.19; H, 3.09; N, 11.12%. [PdBr(CNC-NO$_2$)][PF$_6$] (Yield 63%). Anal Calcd. for $C_{25}H_{21}N_7O_4BrPdPF_6$: C, 36.94; H, 2.36; N, 12.06; O, 7.88. Found: C, 37.05; H, 2.67; N, 13.02; O, 8.13%. [PdBr(CNC-NO$_2$)][BF$_4$] (Yield 59%). Anal. calcd. for $C_{25}H_{21}N_7O_4$-$BrPdBF_4$: C, 39.79; H, 2.54; N, 12.99. O, 8.48. Found: C, 39.85; H, 2.78; N, 13.15, O, 8.92%.

Preparation of the supported complexes

The ionic palladium complexes were immobilized in the following manner. Dichloromethane solutions (5 mL) of each complex (0.2 mmol) were prepared under nitrogen and added to a suspension of the solid support (MK-10 and Na$^+$–M) in deoxygenated dichloromethane (10 mL), and then stirred for 24 h under nitrogen at room temperature. The suspension was filtered off, the solid was washed with dichloromethane and dried under vacuum. The amount of metal complex immobilized on the clay was determined by AAS and XPS.

Homogeneous catalytic C–C coupling

NaOAc or NEt$_3$ (4.4 mmol) and the catalyst (0.1 mol%) were placed in a 3-necked flask fitted with a reflux condenser. Aryl halide (4 mmol), styrene (5.6 mmol) and solvent (5 mL) were added. The reaction vessel was placed into an oil bath preheated to the desired temperature. Products were characterized by gas chromatography.

Heterogenized catalytic C–C coupling

NaOAc or NEt$_3$ (4.4 mmol) and the solid catalyst (0.004 mmol in 0.5 g of clay; 0.1 mol%) were placed in a 3-necked flask fitted with a reflux condenser. Aryl halide (4 mmol), styrene (5.6 mmol) and diethylacetamide (5 mL) were added. The reaction vessel was placed into an oil bath preheated to the desired temperature. The solution was filtered off under vacuum in air and the filtrates were analysed by gas chromatography. The solid containing the complex was washed with polar solvents and dried under vacuum for 10 minutes and introduced to the 3-necked flask for another run.

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