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Immobilization of the complexes $[Pd\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}\kappa P,P'\}X_2]$ (X = Cl, Br) onto STx–1 montmorillonite: An investigation of their performance as homogeneous or heterogenized Suzuki-Miyaura catalysts

Ioannis Stamatopoulos,[a] Maria Roulia,[a] Kalliopi A. Vallianatou,[b] Catherine P. Raptopoulou,[c] Vassilis Psycharis,[c] Marina Carravetta,[d] Christina Papachristodoulou,[e] Evamarie Hey-Hawkins,[f] Ioannis D. Kostas,[b]* Panayotis Kyritsis[a]*

Abstract: Two palladium complexes, $[Pd\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}\kappa P,P'\}X_2]$, X = Cl (**2**), Br (**3**), were synthesized and characterized by spectroscopic methods and X-ray crystallography. Complexes **2** and **3** contain a PdP_2X_2 square planar coordination sphere exhibiting small endocyclic P–Pd–P angles [71.49(4) and 71.53(5)°, respectively], the magnitude of which is controlled by the formation of the Pd–P–N–P four-membered chelating ring. Complexes **2** and **3** were found to be efficient catalysts in the Suzuki-Miyaura cross-coupling reaction of aryl bromides with phenylboronic acid at ambient or elevated temperature. At 100 °C, using 0.1 mol% of palladium loading, high conversions were observed even after 15 min. Both complexes were immobilized onto STx-1 montmorillonite clay via their $–Si(OMe)_3$ moiety, a process investigated by X-ray powder diffraction, X-ray fluorescence spectrometry, solid-state ^{31}P NMR spectroscopy and Scanning Electron Microscopy. The immobilized complexes, as heterogenized catalysts, displayed higher activity in the Suzuki-Miyaura coupling compared to the free complexes. However, loss of activity was observed upon catalyst recycling.

Introduction

Catalytic reactions leading to the formation of highly useful C−C bonds in synthetic chemistry, such as the Suzuki-Miyaura cross coupling, have been extensively investigated during the last five decades.[1] Metal complexes bearing bidentate phosphines are frequently employed as catalysts for this type of reactions.[2] In addition, *P*,*N*-containing ligands are amongst the most important and widely used heterodentate ligands for homogeneous catalysis.[3] Selected articles have been reported by some of us.[4]

The bis(phosphino)amine type of ligands, $(R_2P)_2N(R')$, in the following referred to as (P,P), constitute a well explored family of bidentate phosphines, affording a large number of transition metal complexes,[5] which are active catalysts in various types of reactions, as recently reviewed.[6] In addition to their catalytic properties, ligands of this type have been employed for the synthesis of dinuclear complexes as analogues of the Fe-only hydrogenase's active site.[7] A dinuclear complex of this type,[7c] along with a series of recently reported mononuclear complexes $[Fe(S_2C_6H_4)(P,P)(CO)]$,[8] are active electrocatalysts for the Hydrogen Evolution Reaction (HER).

The nature of the R and R′ groups confers different structural or electronic properties to the $(R_2P)_2N(R')$ ligands and their transition metal complexes. Such differences affect the catalytic reactivity of these systems, as it has been manifested in the case of chromium(0) complexes which are active catalysts for the oligomerization of ethylene.[9] In addition, Ni(II) complexes bearing (P,P) ligands have also shown catalytic activity. For instance, $[Ni(P,P)Br_2]$ complexes catalyze the oligomerization[10] or polymerization[11] of ethylene, whereas $[Ni(P,P)Cl_2]$ complexes are active catalysts in the polymerization of norbornene.[12] The catalytic reactivity in Kumada C−C coupling reactions of the complexes $[Ni(P,P)X_2]$, with X = Cl, Br, bearing (P,P) ligands in which R = Ph and R′ = (*S*)-CHMePh[13a] or $(CH_2)_3Si(OMe)_3$,[13b] has been explored by some of us. In parallel, these nickel(II) complexes have also been investigated as catalysts in Suzuki-Miyaura coupling reactions and showed only marginal reactivity. This observation prompted us to extend our studies, concerning the latter reactions, by investigating the analogous $[Pd(P,P)X_2]$ complexes.

A search in the Cambridge Structural Database (CSD)[14] revealed a large number of structurally characterized

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[a] Inorganic Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Zografou, 15771 Athens, Greece
E-mail: kyritsis@chem.uoa.gr
[b] National Hellenic Research Foundation, Institute of Biology, Medicinal Chemistry and Biotechnology, Vas. Constantinou 48, 11635 Athens, Greece
E-mail: ikostas@eie.gr
[c] NCSR "Demokritos", Institute of Nanoscience and Nanotechnology, 15310 Aghia Paraskevi, Athens, Greece
[d] School of Chemistry, University of Southampton, University Road, Southampton SO17 1BJ, United Kingdom
[e] Department of Physics, University of Ioannina, 45110 Ioannina, Greece
[f] Faculty of Chemistry and Mineralogy, Institute of Inorganic Chemistry, Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

[Pd(P,P)Cl$_2$] complexes.[15] However, no analogous [Pd(P,P)Br$_2$] complexes, and only one [Pd(P,P)I$_2$] complex, bearing the Ph$_2$PN(^{i}Pr)P(Ph)(Me) ligand,[16] have been reported in the CSD up to now. In addition, it should be stressed that no structurally characterized palladium(II) complexes containing the (Ph$_2$P)$_2$N(CH$_2$)$_3$Si(OR)$_3$ type of ligands have been reported as yet. The −Si(OR)$_3$ group of various ligands or complexes has been extensively employed as an anchor, enabling their immobilization onto solid supports, such as alumina and silica[17] or SBA-15 mesoporous sieves.[13b] On the other hand, to the best of our knowledge, immobilization of palladium(II) complexes onto the montmorillonite clay via –Si(OR)$_3$ moieties, has not yet been reported. For that reason, montmorillonite was chosen, in this work, to be employed as the immobilization framework of our palladium(II) complexes.

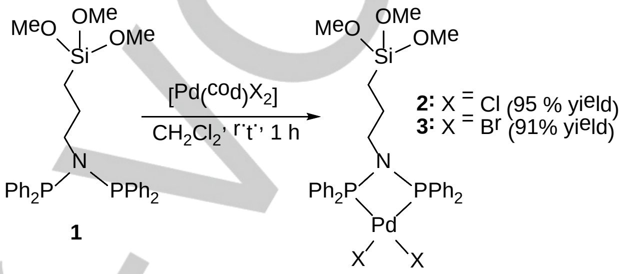
Montmorillonite is a swelling 2:1 layered phyllosilicate smectite clay mineral with small particle size (< 2 μm) and unusual intercalation properties.[18] This clay affords an appreciable surface area for the adsorption of both organic and inorganic species, thus producing layered clay-organic and clay-inorganic hybrid intercalation nanomaterials. Interactions between the parent clay and guest molecules play a vital role in the organization of elementary clay sheets and the self-association of guest compounds into the aluminosilicate two-dimensional interlayer.[19] The catalytic utility of K10-montmorillonite as a solid support for metal complexes or metal nanoparticles has been recently reviewed.[20] For instance, the immobilization of a series of bis-carbene-pincer complexes of palladium(II) affords active heterogenized catalysts towards the Heck reaction.[21] Also, intercalation of a platinum(II)-bis-phosphane complex catalyzes the conversion of dihydroxyacetone to ethyl lactate.[22] In addition, composites of montmorillonite-supported iridium[23] or palladium[24] nanoparticles catalyze hydrogenation reactions.

The work presented herein reports on the synthesis and characterization of the novel palladium(II) complexes [Pd{(Ph$_2$P)$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$-κ*P,P´*}X$_2$], X = Cl (**2**), Br (**3**). The structural properties of **2** and **3** are compared with those of previously reported [M(P,P)X$_2$], M = Pd, Ni; X = Cl, Br, I, complexes. Complexes **2** and **3** bear the –Si(OCH$_3$)$_3$ group, via which they were anchored onto STx-1 montmorillonite. The catalytic activity and selectivity of **2** and **3** in the Suzuki-Miyaura C−C coupling reaction was assessed. The catalytic performance, as well as the recyclability, of the montmorillonite-immobilized complexes **2/Mont** and **3/Mont** were also explored.

Results and Discussion

Synthesis and spectroscopic characterization of palladium complexes

The synthesis of palladium complexes **2** and **3** was achieved in high yields by treatment of [Pd(cod)Cl$_2$] or [Pd(cod)Br$_2$] (cod = 1,5-cyclooctadiene), respectively, with one equivalent of ligand **1** (Scheme 1). In the FT-IR spectra of the complexes, specific IR bands are assigned to IR spectral data of the ligand reported in the literature, for instance the bands at 2838 cm^{-1} {ν_{sym}(C-H) Si(OCH$_3$)} and 1185 cm^{-1} {vibration CH$_3$, Si(OCH$_3$)$_3$}.[17b] The ^{1}H-NMR spectra of complexes **2** and **3** are quite similar and assigned as shown in Figures S1 and S2, respectively. In the ^{31}P-NMR spectra of complexes **2** and **3**, only one singlet at 32.1 or 30.6 ppm is observed (Figures S3 and S4, respectively), suggesting equivalence of the two P atoms in each complex. These signals are significantly shifted upfield compared with those of ligand **1** at 62.2 ppm,[17b] due to shielding effects exerted by the metal-ligand coordination. Negative ESI-MS of the complexes (Figures S5-S6) showed peaks corresponding exactly to [M+X]$^-$ (X = Cl, Br).



Scheme 1. Synthesis of complexes **2** and **3**.

X-ray crystallography studies

The structures of complexes **2** and **3** contain discrete molecules (Figure 1) exhibiting a distorted square planar PdP$_2$X$_2$ core. Palladium(II) is coordinated by the (P,P) chelate, forming a four-membered Pd–P–N–P ring. In both cases, the PdP$_2$X$_2$ core is almost planar, showing a rather small (0.027 and 0.008 Å, respectively) mean deviation from the best plane defined by the Pd, P1, P2, X1 and X2 atoms, with the P1 atom exhibiting the largest deviation (0.038 Å) in complex **2** and the Pd atom (0.020 Å) in complex **3**. The four-membered Pd–P1–N–P2 ring is essentially planar, with the mean deviation from the best plane defined by these four atoms being 0.026 and 0.027 Å for **2** and **3**, respectively.

All bond lengths and angles of complexes **2** and **3** are listed in Tables S1 and S2, respectively. The Pd−P and Pd−Cl bond lengths of complex **2** (Table 1), are typical for [Pd(P,P)Cl$_2$] complexes reported in the literature.[15] As expected, the Pd−Br bond lengths of complex **3** [2.4609(5) Å] are slightly larger compared with the Pd−Cl ones of complex **2** [2.3536(11) and 2.3581(11) Å, Table 1]. In both complexes, the Pd−X bond lengths are larger and the P−N ones smaller, compared with those in the nickel(II) analogue [Ni{(Ph$_2$P)$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$-κ*P,P´*}Cl$_2$].[13b] In addition, the X1–Pd–X2 and P1–Pd–P2 bond angles are smaller compared with those in the above nickel(II) analogue.[13b] It is worth mentioning that the P−Pd−P endocyclic angles of complexes **2** and **3** [71.49(4)° and 71.53(5)°, respectively, Table 1] lie within the range (71.4° - 72.8°) reported in the literature for analogous [Pd(P,P)Cl$_2$] complexes.[15] The very small range in the magnitude of the endocyclic P−Pd−P angle is attributed to the formation of the Pd–P–N–P four-membered ring. Similar observations also hold for the analogous structurally characterized complexes [Ni(P,P)X$_2$], with X = Cl, Br, I, in which the endocyclic P–Ni–P angles range between 73.0° and 75.5°.[10-13, 25]

The complexes **2** and **3** are isostructural and are arranged in layers parallel to the (001) plane through C−H···π interactions (Figure 2). These layers are stacked along the c axis and interact through X···H (X = Cl, Br) hydrogen bonds (Figure 3). Bond distances and angles related to the intermolecular interactions in the structure of complexes **2** and **3** are listed in Table S3.

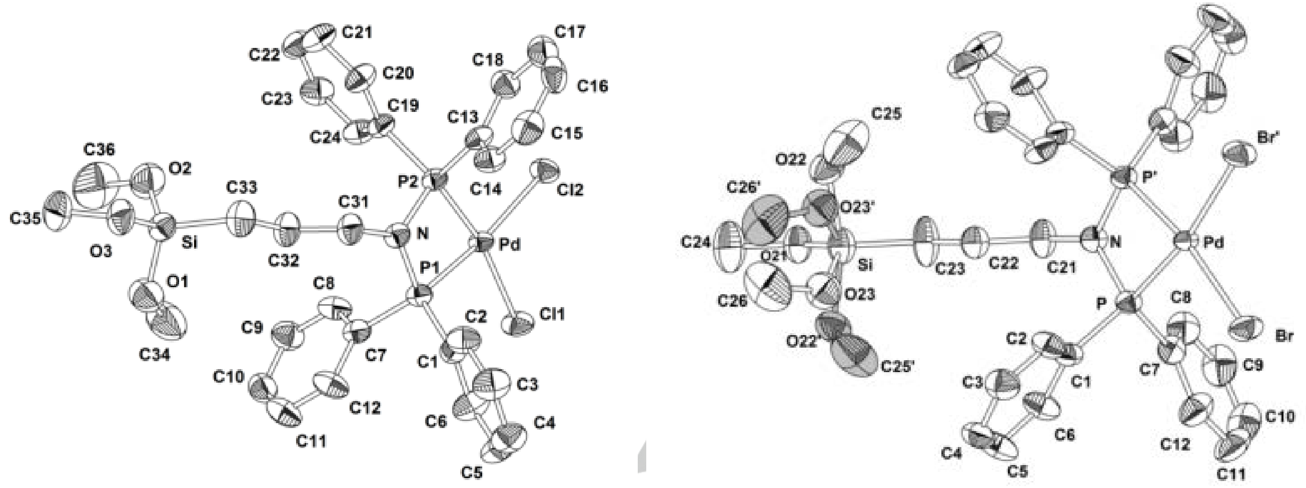
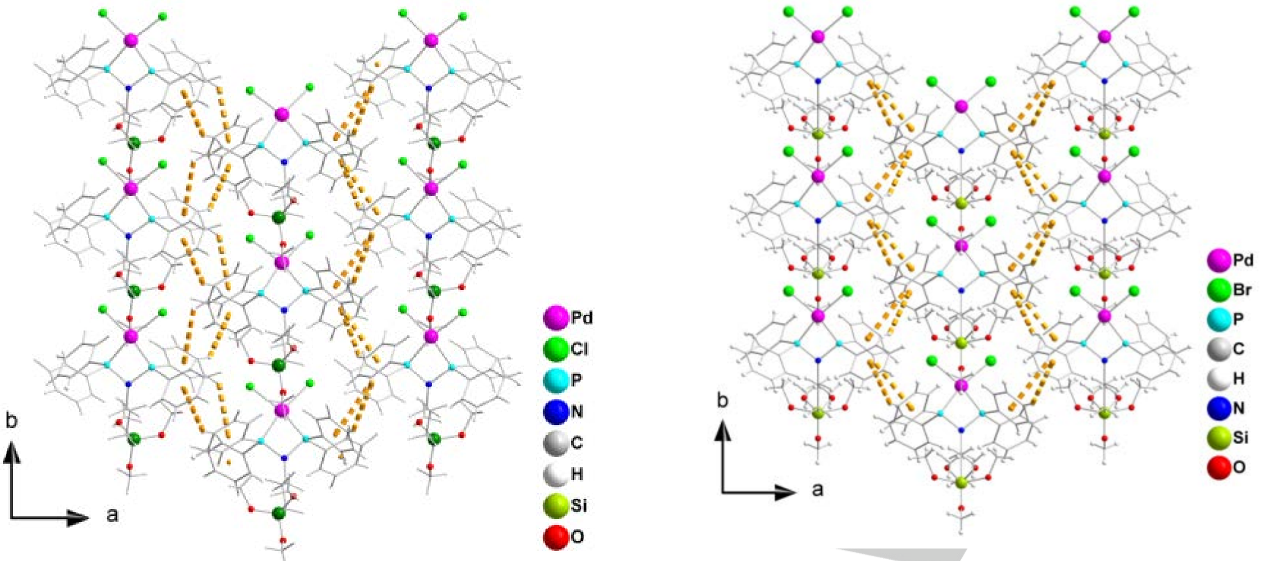


Figure 1. Partially labelled plot of complex **2** (left) and **3** (right) with ellipsoids drawn at 50% thermal probability level. Hydrogen atoms are omitted for clarity.Complex **3** resides on a mirror plane passing through the atoms Pd, N, C21, C22, C23, Si, O21, C24. The two methoxy groups of the trimethoxysilyl end of the ligand, defined by atoms O22, C25 and O23, C26, are disordered and arranged in two positions related by the mirror plane. The respective disorder sites are O22', C25' and O23', C26' and are indicated in gray color [('): 1.5-x, y,z].

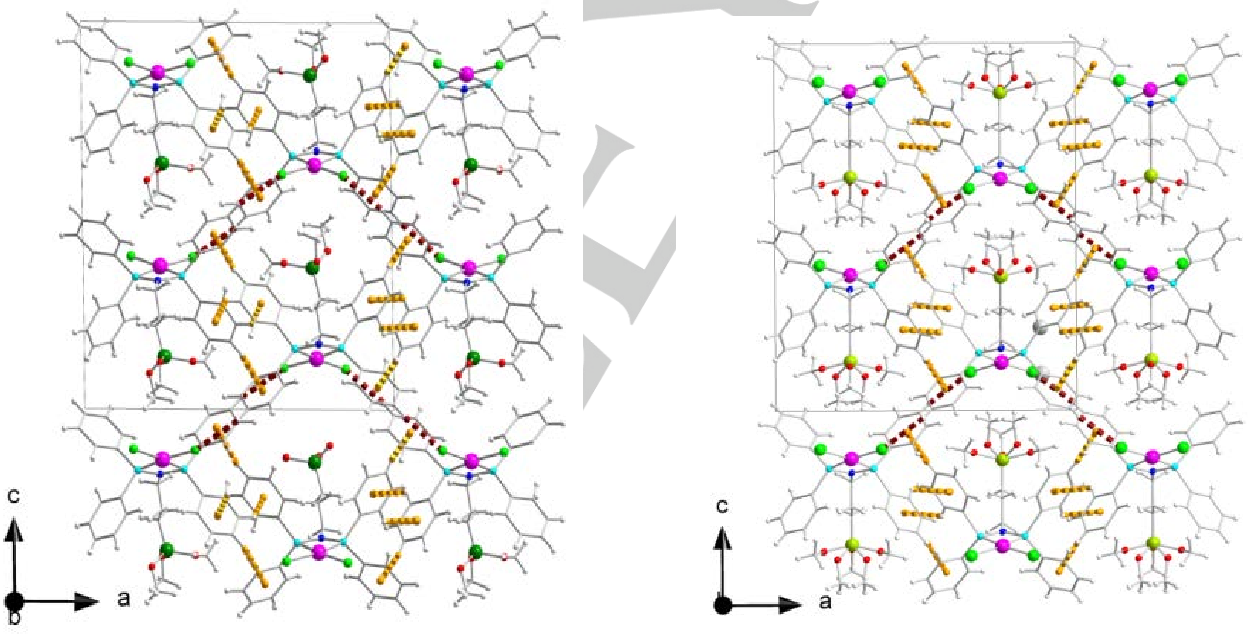
Table 1. Selected bond angles and lengths of complexes **2** and **3**.

Complex				Bond angles (°)			
	X1-Pd-X2	X1-Pd-P1	X2-Pd-P2	P1-Pd-P2	Pd-P1-N	Pd-P2-N	P1-N-P2
2	94.31(4)	96.08(4)	98.11(4)	71.49(4)	94.22(14)	93.93(13)	100.2(2)
3	95.24(2)	96.60(3)	96.60(3)	71.53(5)	93.88(12)	93.88(12)	100.5(2)
				Bond lengths, Å			
	Pd-X1	Pd-X2	Pd-P1	Pd-P2	P1-N	P2-N	
2	2.3581(11)	2.3536(11)	2.2138(12)	2.2210(11)	1.688(4)	1.690(4)	
3	2.4609(5)	2.4609(5)	2.2210(9)	2.2210(9)	1.688(3)	1.688(3)	



(a) (b)

Figure 2. Layers of complexes parallel to the (001) plane. The C−H···π intermolecular interactions, namely (a) C10-H10···Cg1, C11-H11···Cg2, C20-H20···Cg3 and C22-H22···Cg4 for complex **2** and (b) C6-H6···Cg1 and C4-H4···Cg2 for complex **3**, are indicated with thick dashed orange lines. The centroids Cg1, Cg2, Cg3 and Cg4 (for **2**) and Cg1, Cg2 (for **3**) are defined in Table S3.



(a) (b)

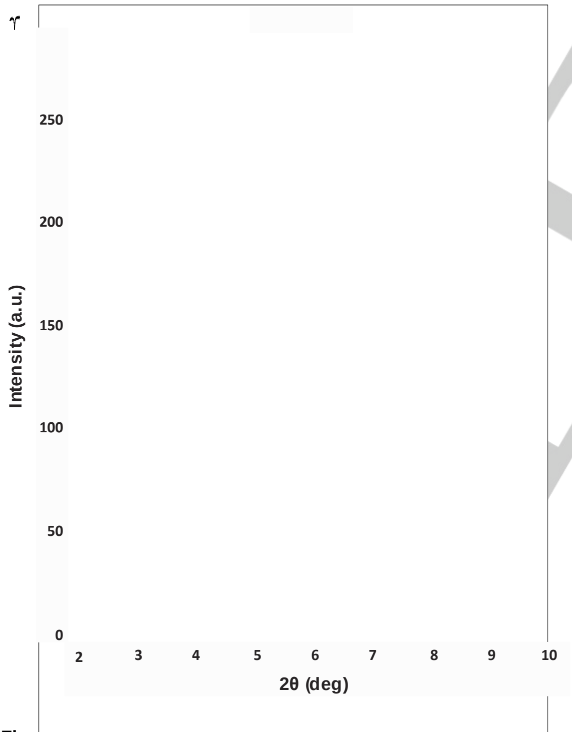
Figure 3. Stack of layers along the c axis through X···H (X = Cl, Br) hydrogen bonds (dark red lines) for (a) complex **2** and (b) for complex **3**. The color coding for C−H···π intermolecular interactions and atoms is the same as in Figure 2.

Immobilization of the complexes onto STx-1 montmorillonite

Complexes **2** and **3** were anchored onto STx–1 montmorillonite clay and the immobilized complexes **2/Mont** and **3/Mont** were studied by a selective combination of XRD, XRF, solid-state ^{31}P MAS NMR and SEM techniques, in order to probe the positioning of the anchored systems with respect to the clay lamellae.

XRD studies

The XRD diagrams of **2/Mont** (Figure 4) and **3/Mont** (Figure S7) are identical and demonstrate a sharp peak at 2θ = 5.8°, corresponding to well-oriented nanostructures with a basal spacing (d_{001}) at 1.52 nm and a 0.56-nm interlayer. In order to determine the orientation of the intercalated species, the size of complexes **2** and **3**, based on their crystal structure, was estimated: Their dimensions (height and depth) are between ca. 1.2 and 1.3 nm, and therefore they cannot fit into the interlamellar space of the clay. This is not unexpected, since the solvent, CH_2Cl_2, used for the immobilization experiment, does not favor the exfoliation of the clay. On the other hand, the parent Na^+ montmorillonite exhibits a basal spacing d_{001} of 1.29 nm (2θ = 6.9°).[19a] The above findings provide evidence that only a partial insertion of the complexes between the clay lamellae takes place, through their $–(CH_2)_3Si(OCH_3)_3$ tail, by which grafting to clay sheets is accomplished.



Figu

XRF studies

Determination of the Pd content in the immobilized complexes was crucial in determining the stoichiometric quantities with the required accuracy in the heterogeneous catalytic experiments. The Pd concentration in samples of the immobilized complexes was determined to be (0.74±0.05) % wt for **2/Mont** and (0.66± 0.06) % wt for **3/Mont**, corresponding to 7.1 and 6.5 mmol uptake/100 g clay, respectively, or 0.035 and 0.033 mmol complex uptake/0.5 g clay, respectively.

Solid-state ^{31}P MAS NMR studies

Figure 5 shows the ^{31}P MAS NMR spectra of the free and immobilized complexes. The solid-state ^{31}P MAS NMR peak of **2/Mont** (28.8 ppm) is much broader and slightly downfield shifted compared with that of the free complex **2** (25.6 ppm). This is also the case for **3/Mont** and **3**, exhibiting peaks at 27.7 and 24.1 ppm, respectively. The small upfield shift observed for **2/Mont** and **3/Mont** compared with the corresponding free complexes is tentatively attributed to small changes in the environment of the P atoms, imposed by the immobilization process. In any case, these data provide evidence that the first coordination sphere of both complexes **2** and **3** is essentially retained when they are immobilized onto the clay.

The peak of complex **3** is slightly upfield shifted compared with that of **2**, which is also the case for the solution spectra of the two complexes (Figures S4 and S3, respectively). These observations must be related to subtle differences in the first coordination sphere of the two complexes, as revealed by X-ray crystallography (*vide infra*).

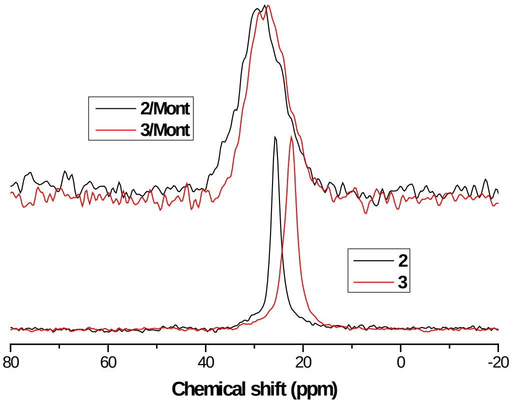


Figure 5. ^{31}P MAS NMR spectra of **2**, **3**, **2/Mont** and **3/Mont**.

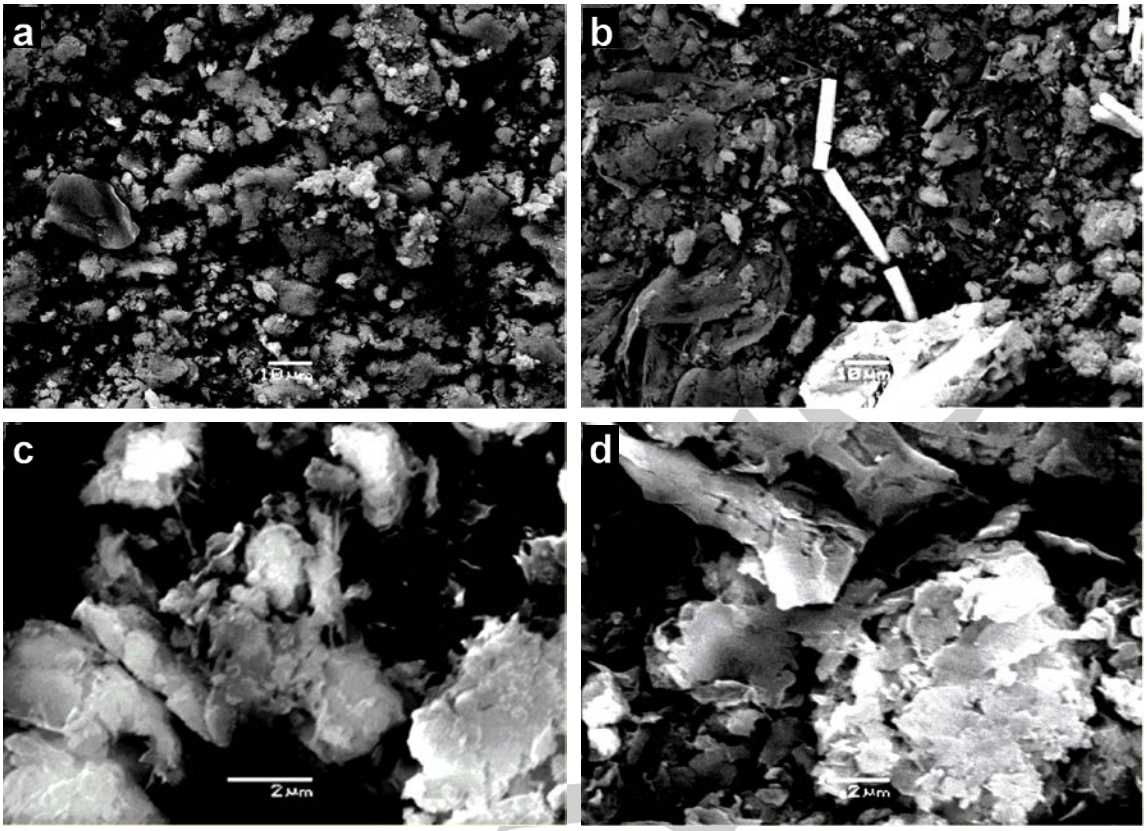


Figure 6. SEM micrographs of **2/Mont**, prior (a), (c) and after catalytic tests (b), (d). The white depositions are K_2CO_3. Highly magnified views of **2/Mont** particles (c) and sharp-edged K_2CO_3 aggregates (d).

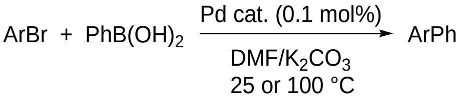
SEM studies

The immobilized **2/Mont** and **3/Mont** complexes were investigated by SEM. Figure 6a displays the surface of STx–1 montmorillonite after immobilization of complex **2**, showing that the typical lamellar structure of the intact clay[19a] turns into granular (1–20 µm particles). This surface appearance is also observed after the use of **2/Mont** as catalyst (Figure 6b). The lath-shaped rods in the middle of the micrograph and the large prismatic aggregates in the lower center of Figure 6b were identified as K_2CO_3 by EDS (Energy Dispersive Spectroscopy) microanalysis. Shown in a closer view, the micrographs of **2/Mont** prior (Figure 5c) and after (Figure 5d) catalytic tests, clearly show clay particles and K_2CO_3 aggregates, respectively. Identical results were obtained also for **3/Mont** (Figures S8a and b).

Catalytic activity in Suzuki Miyaura cross-coupling

Investigations on the catalytic activity of complexes **2** and **3**, as well as of the immobilized analogues **2/Mont** and **3/Mont**, in the Suzuki-Miyaura cross coupling (Scheme 2) of standard electron-rich and electron-poor aryl bromides with phenylboronic acid afforded the data presented in Table 2. Catalysis was performed under an argon atmosphere in DMF/K_2CO_3 at 25 or 100 °C for 24 h, using a relatively low palladium loading (0.1 mol%). With only some exceptions, conversion to unsubstituted biphenyl as homo-coupling by-product was negligible or relatively insignificant. Reactions at 25 °C catalyzed by complexes **2** or **3** showed that 4-bromoanisole is a less active substrate compared with 1-bromo-4-nitrobenzene and 4-bromobenzonitrile, as expected for substrates bearing electron donor moieties (compare entries 1 vs 11, 16 and 4 vs 14, 18). The activity of both complexes for the same substrate is very similar, and could be considered as satisfactory since conversions to coupling products are in the range 55–80 %. A reaction temperature at 100 °C afforded the expected biaryls in very high or quantitative yields for all cases (entries 20, 24, 26, 29, 31, 35, 37, 40). Although the reaction time was not optimized, the results obtained for complex **2** clearly demonstrate that the conversion to the coupling product is practically completed in relatively short time. Indeed, at 100 °C the conversion of 1-bromo-4-nitrobenzene is almost complete after 1 h (entry 32), while a reaction time of only 15 min was also efficient for a high conversion in the range 89–97 % for all substrates (entries 21, 27, 33, 38).

In some of the experiments reported in Table 2, the conditions employed (reaction temperature 25 °C, catalyst loading 0.1 mol% Pd) are milder compared with those in reported studies of analogous [Pd(P,P)Cl_2] catalysts (80 °C, 1.0 mol% Pd loading,[15k,q,r,t] or 90-110 °C, 0.1 mol% Pd loading).[15x] Although direct comparison with these catalysts is not possible due to different experimental conditions, our work shows that complexes **2** and **3** are active under relatively mild conditions.



$$\text{ArBr} + \text{PhB(OH)}_2 \xrightarrow[\text{DMF/K}_2\text{CO}_3\ \ 25 \text{ or } 100\ °\text{C}]{\text{Pd cat. (0.1 mol\%)}} \text{ArPh}$$

Scheme 2. Suzuki-Miyaura cross-coupling reaction.

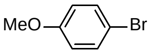
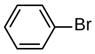
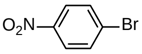
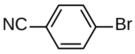
The immobilized complexes **2/Mont** and **3/Mont** exhibited a significant increase in the % conversion (up to 50%) compared to complexes **2** and **3** at ambient temperature for the deactivated 4-bromoanisole (compare entries 1 vs 2 and 4 vs 5), as well as for the non-activated bromobenzene (compare entries 6 vs 7 and 8 vs 9), indicating an improved catalytic activity of the immobilized complexes. The conversions of the activated substrates at room temperature by the immobilized complexes are similar to those observed by the corresponding free complexes. At higher temperature (100 °C), very high or quantitative conversion of the substrates was observed for both free and immobilized complexes. The feasibility of the recycling and reusing the immobilized catalysts was also examined in some representative experiments. The recovery of the immobilized catalysts from the reaction products was achieved via centrifugation. The catalytic activity of the recovered **2/Mont** and **3/Mont** was significantly lowered, even after the first recycling (compare entries 2 vs 3, 9 vs 10, 12 vs 13, 22 vs 23). This can be attributed to the deposition of solids, mostly K_2CO_3, onto the clay surface, and the subsequent blocking of the clay surface. The presence of K_2CO_3 was verified using SEM microanalysis.

Conclusions

The novel palladium complexes **2** and **3** were synthesized and characterized by X-ray crystallography and spectroscopic methods. To our best knowledge, complex **3** is the first structurally characterized [Pb(P,P)Br_2] complex reported to date. Complexes **2** and **3** contain a square planar PdP_2X_2 coordination sphere, exhibiting similar characteristics as analogous known palladium complexes. The intermolecular interactions (hydrogen bonds and C−H···π interactions) which are observed in the two structures were analyzed in detail.

The –Si(OCH_3)$_3$ moiety of the two complexes was employed to immobilize them onto STx-1 montmorillonite clay, affording the clay-immobilized **2/Mont** and **3/Mont** complexes. The latter were investigated by various physicochemical methods, like XRD, XRF, SEM and solid-state ^{31}P NMR spectroscopy. The free and the immobilized complexes were found to be efficient homogeneous and heterogenized catalysts, respectively, in the Suzuki-Miyaura coupling of aryl bromides. Under relatively low palladium loading, the free catalysts displayed high substrate conversion at 100 °C, even within minutes. Although the **2/Mont** and **3/Mont** complexes are more efficient catalysts compared with the free complexes **2** and **3**, their recyclability needs to be further optimized. In our ongoing research, efforts are made to carry out the immobilization of metal complexes onto other solid supports that could afford more efficient heterogenized catalysts.

Table 2. Suzuki-Miyaura coupling of aryl bromides with phenylboronic acid catalyzed by complexes **2** and **3** and immobilized complexes **2/Mont** and **3/Mont**.[a]

ArBr	25 °C				100 °C			
	Entry	Catalyst	Conversion(%)[b]		Entry	Catalyst	Conversion(%)[b]	
			ArPh[c]	PhPh[d]			ArPh[c]	PhPh[d]
	1	**2**	56	<2	20	**2**	93	3
					21[f]	**2**	89	traces
	2	**2/Mont**	75 (cycle 1)	traces	22	**2/Mont**	98 (cycle 1)	<2
	3	**2/Mont**	11 (cycle 2)		23	**2/Mont**	52 (cycle 2)	
	4	**3**	55	3	24	**3**	98	<2
	5	**3/Mont**	76	traces	25	**3/Mont**	100	traces
	6	**2**	70[e]		26	**2**	100[e]	
					27[f]	**2**	97[e]	
	7	**2/Mont**	88[e]		28	**2/Mont**	100[e]	
	8	**3**	68[e]		29	**3**	100[e]	
	9	**3/Mont**	87[e] (cycle 1)		30	**3/Mont**	100[e]	
	10	**3/Mont**	29[e] (cycle 2)					
					31	**2**	100	traces
	11	**2**	80	1	32[g]	**2**	99	1
					33[f]	**2**	95	traces
	12	**2/Mont**	82 (cycle 1)	8	34	**2/Mont**	100	traces
	13	**2/Mont**	44 (cycle 2)					
	14	**3**	75	6	35	**3**	100	traces
	15	**3/Mont**	70	<4	36	**3/Mont**	100	traces
	16	**2**	83	traces	37	**2**	>99	<1
					38[f]	**2**	94	2
	17	**2/Mont**	81	traces	39	**2/Mont**	100	traces
	18	**3**	83	1	40	**3**	100	traces
	19	**3/Mont**	79	traces	41	**3/Mont**	100	traces

[a] Reaction conditions: ArBr (1.0 mmol), $PhB(OH)_2$ (1.5 mmol), K_2CO_3 (2.0 mmol), DMF (1 mL), ArBr/Pd molar ratio = 1000:1, 24 h, argon.
[b] Determined by GC (*n*-decane as internal standard).
[c] Cross-coupling product.
[d] Homo-coupling by-product.
[e] Biphenyl was the only product formed.
[f] Reaction time: 15 min.
[g] Reaction time: 1 h.

Experimental Section

Materials and methods

All experiments were performed under inert atmosphere, using Schlenk techniques. The $(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$ (**1**) ligand[17b] and the complexes [Pd(cod)Cl_2] and [Pd(cod)Br_2][26] were prepared according to literature procedures. All other chemicals were commercially available. Ca^{2+}STx–1 montmorillonite, Texas (Clay Minerals Society Repository, University of Missouri – Columbia) was Na^+-saturated via ion exchange.

FT-IR spectra (average of 50 scans) were recorded at room temperature on a Shimadzu IR Affinity-1 spectrometer. Pellets of the specimens were prepared after mixing with dry KBr.

^1H and ^{31}P NMR solution spectra ($CDCl_3$) were acquired on a Varian 300 MHz spectrometer at 25 °C. Chemical shift values in ^1H NMR spectra were referenced internally to the residual solvent resonances, and the ^{31}P spectra were referenced to external 85% H_3PO_4 in H_2O.

Solid-state ^{31}P NMR spectra were acquired on a wide bore Varian 400 Infinity Plus spectrometer equipped with a 4 mm double resonance T3 probe. The samples were placed in a 4 mm zirconium oxide pencil rotor and spun about the magic-angle at 10 kHz. ^{31}P spectra were obtained using ramped cross-polarization with a contact time of 1.5 ms and SPINAL 64 ^1H decoupling during acquisition and referenced to 0 ppm using external 85% phosphoric acid. The experiments on complexes **2** and **3** were performed with 4 scans and 15 s repetition delay, while the experiments on **2/Mont** and **3/Mont** were recorded with 512 scans and with a repetition delay of 3 s.

Gas chromatography was undertaken using a Varian Star 3400 CX with a 30 m × 0.53 mm DB5 column. Electron impact gas chromatography – mass spectrometry was carried out using a Varian Saturn 2000 with a 30 m × 0.25 mm DB5-MS column.

HRMS was performed with a Thermo Scientific LTQ OrbitrapVelos (ESI) spectrometer.

X-ray powder diffraction patterns of the immobilized complexes were recorded on a Philips PW 1361/01 diffractometer by scanning at 1° (2θ) min^{-1} between 2 and 10° (2θ). Ni-filtered Cu Kα radiation (20 mA, 40 kV) was used. Oriented clay specimens were prepared by smearing the samples onto glass slides.

XRF measurements were carried out using a home-built spectrometry arrangement, equipped with an annular ^{109}Cd radioisotopic source and a CANBERRA SL80175 Si(Li) detector. The WinQxas software package of IAEA (International Atomic Energy Agency, Vienna, Austria) was used for spectrum analysis. Samples were measured in the form of 12-mm diameter pellets, prepared by mixing 10 mg of sample with 90 mg of cellulose microcrystalline powder. Quantification of Pd in the inorganic carrier was achieved with the use of a linear calibration curve, obtained from a set of in-house synthetic Pd standard pellets.

SEM micrographs of gold-coated samples of the immobilized complexes prior and after the catalytic experiments were acquired using a Jeol JSM-5600 scanning electron microscope.

Synthesis of palladium complexes

[Pd{$(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$-κP,P´}$Cl_2$] (2)

Ligand **1** (192 mg, 0.350 mmol) was dissolved in 10 mL CH_2Cl_2. Addition of [Pd(cod)Cl_2] (100 mg, 0.350 mmol) afforded a yellow mixture which was stirred for 1 h at room temperature. The solution was concentrated to a final volume of 3 mL. Subsequent addition of 15 mL n-hexane produced a yellow powder, which was collected by filtration and dried under vacuum (240 mg, 95%). IR (KBr, cm^{-1}): 511 (s), 569 (m), 696 (s), 720 (m), 751 (s), 824 (m), 866 (s), 998 (w), 1026 (w), 1079 (s), 1100 (s), 1108 (s), 1130 (s), 1185 (m), 1309 (m), 1436 (s), 2838 (m), 2943 (m), 3055 (w). ^1H NMR (300 MHz, $CDCl_3$): δ 0.2 (t, ^3J(H,H) = 7.7 Hz, 2H, Si-CH_2-), 1.2 (m, 2H, -CH_2-CH_2Si), 3.0 (m, 2H, N-CH_2-), 3.3 (s, 9H, Si-OCH_3), 7.5-7.9 (m, 20 H, H_{arom}). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 32.1 (s). HRMS (negative ESI-MS): calcd for $C_{30}H_{35}Cl_3NO_3P_2PdSi$ $[M+Cl]^-$ 757.9956, found 757.9971.

[Pd{$(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$-κP,P´}$Br_2$] (3)

Complex **3** was prepared from ligand **1** (146 mg, 0.267 mmol) and [Pd(cod)Br_2] (100 mg, 0.267mmol) by employing a similar procedure as described for **2**, in 91% yield (198 mg). IR (KBr, cm^{-1}): 511 (s), 569 (m), 696 (s), 720 (m), 751 (s), 824 (m), 866 (s), 998 (w), 1026 (w), 1079 (s), 1100 (s), 1108 (s), 1130 (s), 1185 (m), 1309 (w), 1436 (s), 2838 (w), 2943 (w), 3055 (w), 3078 (w). ^1H NMR (300 MHz,$CDCl_3$): δ 0.2 (t, ^3J(H,H) = 7.7 Hz, 2H, Si-CH_2), 1.3 (m, 2H, -CH_2-CH_2Si), 3.0 (m, 2H, N-CH_2), 3.3 (s, 9H, Si-OCH_3), 7.5-7.9 (m, 20 H, H_{arom}). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 30.6 (s). HRMS (negative ESI-MS): calcd for $C_{30}H_{35}Br_3NO_3P_2PdSi$ $[M+Br]^-$ 889.8426, found 889.8447.

Immobilization of complexes on STx–1 montmorillonite

Complexes **2** and **3** were anchored onto STx–1 montmorillonite clay by the following procedure: 50 mL CH_2Cl_2 and 500 mg of degassed Na^+-montmorillonite were stirred for 24 h. Subsequently, 0.35 mmol of complex **2** or **3** was added and the mixture was left under stirring for 2 d. The mixture was then centrifuged (3000 rpm, 20 min), and dried at room temperature, affording the immobilized catalysts **2/Mont** and **3/Mont**, respectively.

General experimental procedure for the Suzuki-Miyaura coupling

Aryl bromide (1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), K_2CO_3 (276 mg, 2.0 mmol), DMF (1 mL), complex **2** or **3** (1 μmol) or the appropriate amount of the immobilized complex **2/Mont** or **3/Mont** (1 μmol of Pd) were stirred at room temperature or at 100 °C for 24 h. The solvent was then removed under reduced pressure. The residual mixture was diluted by H_2O (10 mL) and extracted by CH_2Cl_2 (2×6 mL). The combined organic fractions were dried (Na_2SO_4), stripped of the solvent under vacuum, the residue was re-dissolved in 5 mL of CH_2Cl_2, passed through celite and analyzed by GC and GC-MS. Conversions were determined by GC analysis. All biaryls are known compounds. The immobilized complexes **2/Mont** and **3/Mont** for the recycling experiments were recovered by centrifugation, washed three times with 10 mL of CH_2Cl_2 and were dried prior to use. The recovered **2/Mont** and **3/Mont** for SEM analysis were washed three times by 10 mL H_2O in order to remove residual K_2CO_3 and salts formed during the reaction and then dried.

X-ray crystallography

Crystals of **2** and **3** suitable for X-ray crystallography studies were obtained by the layering method using CH_2Cl_2/n-hexane (1:3, v/v) as solvents. Single crystals of **2** ($0.11 \times 0.23 \times 0.50$ mm) and **3** ($0.05 \times 0.29 \times 0.58$ mm), were taken directly from the mother liquor and immediately cooled to –113 °C. Diffraction data were collected on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite-monochromated Cu Kα radiation. Data collection (ω-scans) and processing (cell refinement, data reduction and absorption correction) were performed using the CrystalClear program package.[27] Important crystallographic data are listed in Table S4. The structures were solved by direct methods using SHELXS-97[28] and refined by full-matrix least-squares techniques on F^2 with SHELXL2014/6.[29] Almost all hydrogen atoms for both complexes were located by difference maps. For complex **2**, some phenyl and methylene hydrogen atoms, as well as all the methyl hydrogen atoms, were introduced at calculated positions. Additional crystallographic data for complex **2**: $2\theta_{max}$ = 130.00°; 452 parameters refined; $(\Delta/\sigma)_{max}$ = 0.001; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.985/-0.675 e/Å^3. In the case of **3**, two of the three methyl groups of the trimethoxysilyl end, those defined by O22, C25 and O23, C26 atoms, are at two disordered positions related by a mirror plane (Figure 3) and thus they were refined using the Part -1 command. The hydrogen atoms for these groups, as well as some of the phenyl ones, were introduced at calculated positions and were refined as riding on their respective bonded atoms. The rest of hydrogen atoms were refined isotropically. All non-hydrogen atoms for both complexes were refined anisotropically. Additional crystallographic data for complex **3:** $2\theta_{max}$ = 130°; 263 parameters refined; $(\Delta/\sigma)_{max}$= 0.004; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.84/-0.89 e/Å^3.

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Keywords: Palladium complex • PNP Ligand • immobilized complex • STx–1 montmorillonite • Suzuki-Miyaura cross-coupling • Crystal structure

Supplementary Information

CCDC-1577206 (for **2**) and CCDC-1577207 (for **3**) contain the supplementary crystallographic data, which can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The Supporting Information related to this article is available free of charge and contains copies of NMR and HRMS spectra, as well as crystallographic data, of complexes **2** and **3**.

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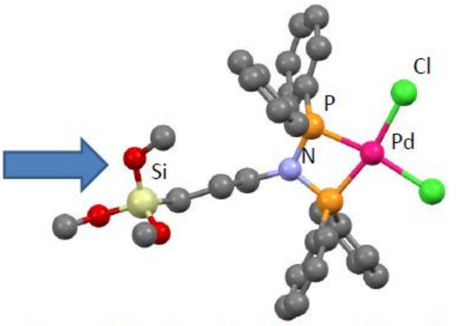
Entry for the Table of Contents

Layout 1:

FULL PAPER

The structurally and spectroscopically characterized complexes $[\mathrm{Pd}\{(\mathrm{Ph_2P})_2\mathrm{N}(\mathrm{CH_2})_3\mathrm{Si}(\mathrm{OCH_3})_3\text{-}\kappa P,P'\}\mathrm{X_2}]$ (X = Cl, Br) were immobilized onto STx–1 montmorillonite. Both free and anchored complexes catalyze Suzuki-Miyaura coupling reactions.



Immobilization of palladium(II) catalysts onto a clay via their $-\mathrm{Si(OMe)_3}$ moiety

Ioannis Stamatopoulos, Maria Roulia, Kalliopi A. Vallianatou, Catherine P. Raptopoulou, Vassilis Psycharis, Marina Carravetta, Christina Papachristodoulou, Evamarie Hey-Hawkins, Ioannis D. Kostas, Panayotis Kyritsis**

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Immobilization of the complexes $[\mathrm{Pd}\{(\mathrm{Ph_2P})_2\mathrm{N}(\mathrm{CH_2})_3\mathrm{Si}(\mathrm{OCH_3})_3\text{-}\kappa P,P'\}\mathrm{X_2}]$ (X = Cl, Br) onto STx–1 montmorillonite: An investigation of their performance as homogeneous or heterogenized Suzuki-Miyaura catalysts