DOI: 10.1002/ejic.200800743

On the Immobilisation of Catechol Phosphane Palladium Complexes on Titania

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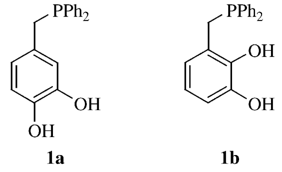
Keywords: Phosphanes / Palladium / Titanium / Immobilisation

Two isomeric bis(phosphane) palladium chloride complexes with functional catechol phosphane ligands were immobilised on different specimens of TiO_2. The solid materials were characterised by ^{31}P NMR spectroscopy both when dry and as suspensions in various solvents. The NMR spectroscopic studies demonstrated that the resistance towards leaching varies strongly with the nature of the carrier material and that the surface-bound complexes may become detached from the support in certain circumstances in the presence of solvents that are sufficiently polar or contain reactive components such as amines.

Introduction

The immobilisation of transition-metal complexes is currently receiving growing interest because of applications in areas such as catalysis, electrocatalysis, electrochromic displays, photodegradation of organic compounds and photovoltaics.[1–5] The particular appeal of immobilised complexes in catalytic applications is that they allow the combination of the advantages associated with homogeneous (e.g. high activity and selectivity) and heterogeneous catalysts (e.g. easy separation and potential to be recycled).[5] To date, many approaches to the preparation of immobilised complexes are known and these can be distinguished according to the choice of carrier materials which range from inorganic oxides to organic polymers or the method employed to anchor the molecular complexes to the support. Prominent types of binding interactions include covalent tethering, electrostatic attraction, adsorption and hydrophobic interactions.[6] An important strategy for the fixation of a molecular complex to the surface of a solid involves the use of functional ligands which contain, besides the metal-binding donor site, a second functionality which may be tailored to yield optimum interaction with the support.

We have recently started to explore the chemistry of bifunctional catechol phosphanes such as **1a**,**b**[7] which may bind to a transition metal by means of the phosphorus atom but remain capable of interacting with a second Lewis acid through the catechol unit (Scheme 1).



Scheme 1.

It was demonstrated that this functionality permits the assembly of molecular complexes such as **2** (Scheme 2) in which the phosphorus atoms and catechol units of two ligands bind specifically to a soft and a hard Lewis acidic site, respectively.[8,9] These compounds embody transition-metal bis(phosphane) complexes of a template-based chelate ligand and were shown to be active catalysts in C−C cross coupling reactions.[8] The individual binding sites of **1** can also be addressed specifically, thus enabling the construction of complexes such as **3**[9] and **4**[10] in which the ligands bind exclusively by means of the phosphorus atom or the catechol unit.

In view of recent reports[11,12] describing the synthesis of complexes of type **5** containing a catechol phosphane ligand **6** with a molecular structure similar to **1** and demonstrating the use of the catechol moieties to immobilise these complexes on TiO_2 nanoparticles, we anticipated that the catechol units in complexes such as **4** are not only capable of forming a molecular template but should likewise allow a similar interaction with a solid surface. In order to verify this hypothesis we studied the deposition of the complex **4** on TiO_2 and characterised the resultant materials by solid-state NMR spectroscopy. With respect to the possible use of the surface-bound complexes in catalysis,[8] we wanted to further typify the behaviour of the materials under conditions that mimic those of a catalytic process in which the

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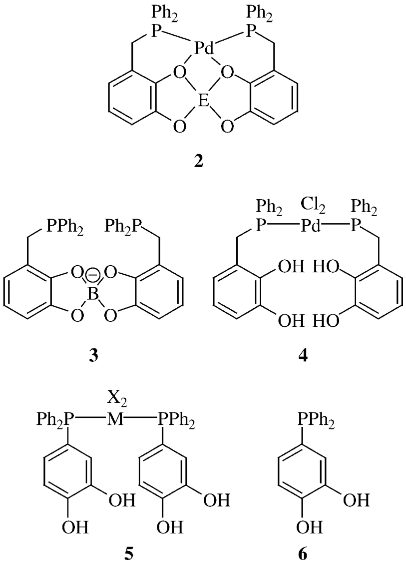


Scheme 2. **2**: E = $SnCl_2$, $SnMe_2$, B; **5**: MX_2 = $PdBr_2$, $PtBr_2$.

complexes are in contact with solvents and, especially in the case of C–C cross coupling reactions, a large excess of a strong base.[11] We have therefore also measured slow-spinning HRMAS NMR spectra of suspensions[13–18] of the immobilised complexes in different solvents. The results are reported here and indicate that the specific nature of the carrier material determines whether the complexes are robustly tethered to the surface or may leach back into solution and undergo base-induced reactions at the functional ligands.

Results and Discussion

Complexes $[PdCl_2(\mathbf{1b})_2]$ (**4**) and $[PdCl_2(\mathbf{1a})_2]$ (**7**) were prepared as described[10] from **1a**,**b** and $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene). Characterisation of the novel complex **7** by solution NMR spectroscopy reveals, as in the case of **4**,[10] the presence of a mixture of *cis* and *trans* isomers, which can be easily distinguished by their characteristic ^{31}P NMR spectroscopic data[10,11,19] [$\delta(^{31}P)$ = 33.3 ppm (*cis* isomer), 20.3 ppm (*trans* isomer), isomer ratio approx. 1:3 by integration]. Immobilisation of the complexes was accomplished in the same way as described for **5**[11] by stirring CH_2Cl_2 solutions of **4** and **7** with solid TiO_2 and filtering off the supernatant liquid. The immobilisation experiments were carried out with two different solid phases, viz. neutral titania (Merck, TiO_2 p.a., denoted as TiO_2; pH of 10% dispersion in water ≈ 7) and pyrogenic TiO_2 nanoparticles (Degussa TiO_2 P25, denoted as NP-TiO_2) with a slightly acidic surface (pH of 4% dispersion in water ≈ 3.5–4.5).

The successful deposition of both complexes on the solid carriers was readily monitored by solid-state ^{31}P NMR spectroscopy. The CP-MAS spectra of the surface modified materials are very similar to those of the pure, polycrystalline complexes (cf. Figure 1) and display a single intense sideband manifold with nearly unchanged positions of the isotropic line. The isotropic chemical shifts (Table 1) allow the assignment of these signals to the *trans* isomers which is also in accord with the known crystal structure of **4**.[10,20] As additional lines attributable to the *cis* isomers were undetectable, the solid-state NMR spectra can be seen as an indication that both the crystalline and surface-tethered complexes contain exclusively the *trans* isomers. The line widths of the signals for the surface-bound complexes on TiO_2 were somewhat larger (in case of **4**) or similar (in case of **7**) as those for the pure crystalline complexes whereas the NP-TiO_2-supported complexes displayed an increase in linewidths by nearly an order of magnitude (Figure 1). Similar effects have repeatedly been observed for surface-bound phosphane complexes[21,22] and also for the phosphane oxide derived from **6** but not for ligand **6** itself nor its complex **5**.[11] The major contribution to this broadening is presumably a substantial chemical shift dispersion which arises as a consequence of disordered surface environments.[22]

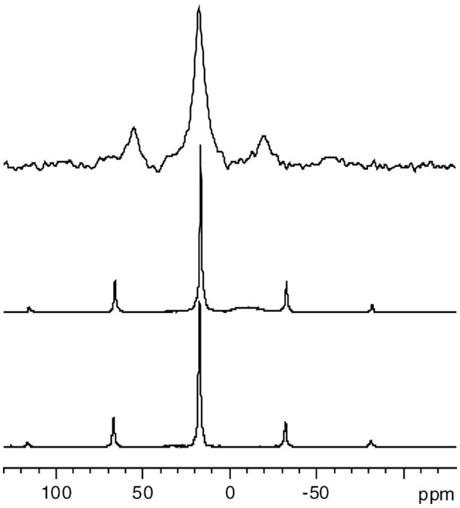


Figure 1. $^{31}P\{^1H\}$ CP-MAS NMR spectra of pure crystalline **7** (bottom trace) and of **7** immobilised on neutral titania (TiO_2, middle trace) and on TiO_2 nanoparticles (NP-TiO_2, top trace). Spectroscopic data are listed in Table 1. MAS frequencies were 8 kHz for the two lower and 6 kHz for the top trace.

The spectra of samples of **4**/TiO_2 and **7**/TiO_2 showed additional broad signals of low intensity centred around –9 ppm, signals which were absent in the spectra of the pure complexes (Figure 1) and indicate a small amount of a second surface-bound species to be present.[23] The isotropic shifts are close to the chemical shifts of the ligands **1a**,**b** (–13 to –15 ppm)[7] and, since the spectrum of a sample prepared by immobilisation of **1b** on TiO_2 contained an identical line as the only signal, we assigned these lines to the surface-bound phosphanes **1a**,**b**. Their formation can be explained by cleavage of the metal from **4** and **7**, and the observation of such decomplexation suggests that **4** and **7** are presumably less robust towards displacement of the phosphane ligands than **5** for which no similar behaviour has been observed.[11]

Table 1. Solid-state ^{31}P NMR isotropic chemical shifts (δ_{iso}), linewidths ($\Delta\nu_{1/2}$) and principal components of the CSA tensor (δ_{ii}) for complexes **4** and **7**.

Compound[a]	δ_{iso}	$\Delta\nu_{1/2}$ [Hz]	δ_{11} [ppm]	δ_{22} [ppm]	δ_{33} [ppm]	Ω[b]
4	22.4	120	97	22	–50	147
4/TiO_2	20.8	300	72	28	–38	110
4/TiO_2/CH_2Cl_2	20.4	86	77	28	–43	120
4/TiO_2/CH_3CN	22.5	130	73	32	–40	113
7	17.5	160	80	23	–50	130
7/TiO_2	17.7	100	82	19	–50	132
7/TiO_2/CH_2Cl_2	16.8	150	81	17	–50	131
7/NP-TiO_2	18.4	1100	–	–	–	–
7/NP-TiO_2/CH_2 Cl_2	19.1	600				
7/NP-TiO_2/CH_3CN	18.7	700				
7/NP-TiO_2/MeCN-amine[c]	17.2	900	–	–	–	–

[a] TiO_2 = neutral titania (Merck p.a.), NP-TiO_2 = titania nanoparticles (Degussa P25). [b] $\Omega = \delta_{11} - \delta_{33}$. [c] CH_3CN/NEt_3 (9:1).

Solid-state $^{31}P\{^1H\}$ CP NMR spectra of nonspinning samples of pure and surface-bound **4** and **7** on neutral TiO_2 displayed characteristic powder patterns which enabled deduction of the principal components δ_{ii} of the magnetic shielding tensors. Meaningful static spectra of samples on NP-TiO_2 could not be obtained since the discontinuities in the line shapes were blurred by the large chemical shift dispersion. The chemical shift parameters of pure **7** and **7**/TiO_2 (Table 1) do not differ appreciably whereas **4**/TiO_2 displays a markedly lower shielding anisotropy than pure crystalline **4** (cf. Figure 2).

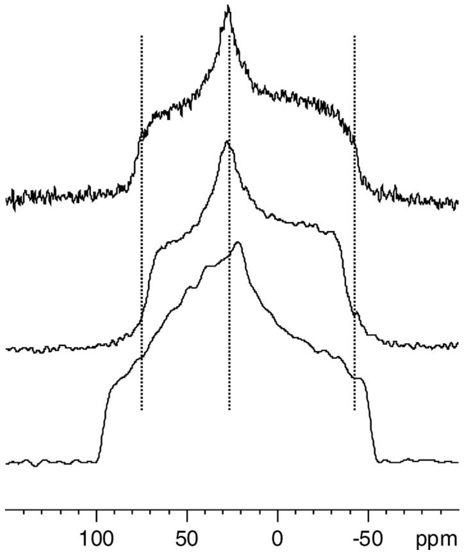


Figure 2. $^{31}P\{^1H\}$ CP NMR spectra of nonspinning samples of crystalline **4** (bottom), **4** on TiO_2 (middle) and a suspension of **4** on TiO_2/CH_2Cl_2 (top). The vertical lines were drawn for better comparison and illustrate the values of δ_{ii} of the top trace.

Slow-spinning CP-MAS NMR spectra of suspensions of **4**/TiO_2 and **7**/TiO_2 in CH_2Cl_2 display sideband manifolds with practically the same isotropic chemical shifts as the dry samples. Likewise, the anisotropic chemical shift parameters δ_{ii} of **7**/TiO_2 obtained from a CP-NMR spectrum of a nonspinning sample (Table 1) are the same as in the dry material and in pure **7**. In the case of **4**/TiO_2, however, the solvent induces a perceptible increase in the CSA and the span Ω of the CSA tensor in **4**/TiO_2/CH_2Cl_2 is midway between that in **4**/TiO_2 and crystalline **4** (cf. Figure 2). It is unlikely that these changes arise from a solvent-induced increase in the mobility of the surface-bound complex since this should lower the effective CSA. Instead, we suggest that the effect reflects variations in molecular conformations which accompany the interaction of the complex with the surface. A possible scenario, which has also been discussed for **5**,[12] is that tethering of the OH-moieties to the surface enforces changes in the orientation of the catechol units relative to crystalline **4**, thus explaining the difference between **4** and dry **4**/TiO_2. Addition of a solvent might then either induce further conformational changes or the observed deviations may be interpreted as directly reflecting the effects of solvation. For **7**, the different arrangement of the OH moieties can be considered to induce a larger spatial separation of the metal–phosphane unit from the surface and conformational changes are clearly less pronounced than in **4** and have no visible impact on the chemical shift.

In contrast to the suspension in CH_2Cl_2, the ^{31}P CP-MAS NMR spectra of suspensions of **4**/TiO_2 or **7**/TiO_2 in dmf displayed no signals at all (Figure 3, top trace). However, $^{31}P\{^1H\}$ MAS NMR spectra recorded with direct excitation of ^{31}P showed two sharp lines that were not accompanied by any rotational sidebands [**4**/TiO_2/dmf $\delta(^{31}P)$ = 34.3, 18.6 ppm, relative intensities 1:1.5; **7**/TiO_2/dmf $\delta(^{31}P)$ = 32.4, 18.8 ppm, relative intensities 1:0.7] and appeared at similar chemical shifts to the signals of the *cis* and *trans* isomers of complexes **4** and **7** in solution. The occurrence of accidental unwanted oxidation can be excluded as the P oxides of **4** and **7** exhibit different isotropic chemical shifts [$\delta(^{31}P)$ = 40–41 ppm both in solution[7] and as surface adsorbed species]. Acquisition of spectra of nonspinning samples did not indicate any marked changes except a moderate broadening of both lines (cf. Figure 3, bottom trace). The spectrum of **4**/TiO_2/dmf displayed two further broad lines of lower intensity at δ = 79.4 and 26.6 ppm. The pairwise appearance of these signals in this and in other spectra suggests that they belong to a single species which must then bear two distinguishable phosphane ligands but further structure assignment is unfeasible.

Both the failure of the cross polarisation scheme and the line narrowing in the static spectra are typical for species undergoing isotropic motion and suggest that the complexes have become detached from the surface and are dissolved in the solvent. This hypothesis is in accord with earlier results indicating that phosphanes immobilised on TiO_2 are highly prone to leaching,[15] an observation that was independently confirmed by the finding that the same signals were observable in ^{31}P NMR spectra of solutions prepared by extracting the immobilised complex with a larger volume of an appropriate solvent and subsequent filtration.

Measurement of ^{31}P NMR spectra of suspensions of **7**/TiO_2 in acetonitrile produced similar results to those obtained in dmf. In contrast, studies of the system **4**/TiO_2/CH_3CN led to the remarkable observation that ^{31}P CP-

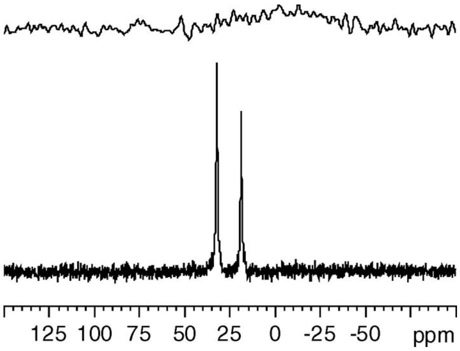


Figure 3. $^{31}P\{^1H\}$ NMR spectra of a nonspinning sample of **7** on TiO_2/dmf recorded with cross polarisation (top trace) and direct excitation of the ^{31}P nuclei (bottom trace).

MAS NMR spectra displayed spinning sideband manifolds similar to those found for **4**/TiO_2/CH_2Cl_2 (cf. Figure 4, upper traces, and Table 1) whereas ^{31}P NMR spectra recorded without cross polarisation showed, at the same time, two narrow isotropic lines (Figure 4, bottom) with similar chemical shifts [$\delta(^{31}P)$ = 32.0, 18.3 ppm] as **4**/TiO_2/dmf. As expected, the spectrum of a nonspinning sample recorded under cross-polarisation displayed a powder lineshape, which is characterised by values of δ_{ii} similar to those of **4**/TiO_2/CH_2Cl_2, whereas the corresponding spectrum recorded with direct ^{31}P excitation remained unchanged apart from an insignificant line broadening.

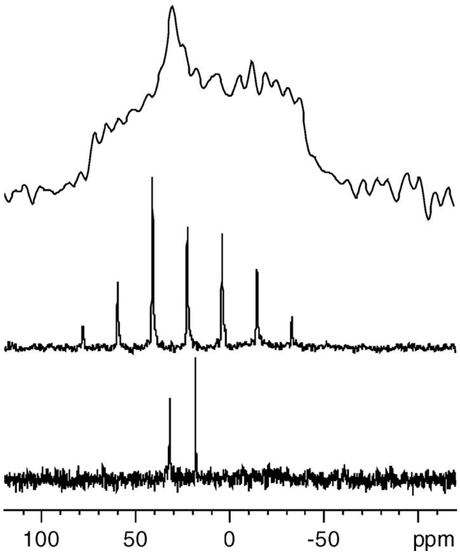
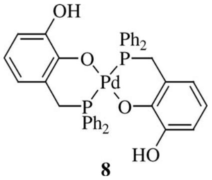


Figure 4. $^{31}P\{^1H\}$ spectra of **4**/TiO_2/CH_3CN recorded (a) under cross-polarisation with a nonspinning sample (top trace), (b) under cross-polarisation and MAS (ν_{rot} = 3000 Hz, middle trace) and (c) with MAS (ν_{rot} = 3000 Hz) and direct excitation of the ^{31}P nuclei (bottom trace).

These findings are in agreement with previously published studies on TiO_2-immobilised phosphane complexes[15] and can be readily explained by assuming that the surface-bound complex **7** completely dissolves in acetonitrile, whereas, in the case of **4**, only partial dissolution occurs and a fraction of the complex remains on the carrier. The fact that the signal of the complexes in solution under cross-polarisation conditions cannot be observed is due to the averaging of the dipolar coupling, whereas the suppression of the signal of the surface-bound species under direct excitation of ^{31}P can be rationalised by assuming effective saturation of this resonance due to a much longer ^{31}P T_1 relaxation time. The validity of this hypothesis was confirmed by the finding that the signals of surface-bound and dissolved species were in fact both visible in a spectrum recorded under direct excitation of ^{31}P with shorter excitation pulses and longer relaxation delays.

As Pd-catalysed reactions are often carried out in the presence of bases,[5,8,11] we extended our NMR spectroscopic studies to suspensions of **4**/TiO_2 and **7**/TiO_2 in CH_2Cl_2 or dmf containing 10 vol.-% of triethylamine. We noted that under these conditions complete detachment of the complexes from the surface took place and that all signals detected were now attributable to species in solution. The observed chemical shifts revealed further that **4** and **7** had been transformed into new products. Samples containing **4** displayed a single sharp line at 61.0 (in CH_2Cl_2/Et_3N) or 56.8 ppm (in dmf/Et_3N) which we assigned, on the basis of the similarity with the data of analogous compounds,[19] to the bis(chelate) complex **8**. This hypothesis is further corroborated by the finding that formation of the same product was likewise observed upon treatment of a solution of **4** with excess triethylamine (Scheme 3).



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Scheme 3.

Samples containing **7** gave complicated spectra indicative of the presence of a mixture of several species which could not be further assigned. As intramolecular dehydrohalogenation and formation of a chelate ring is in this case prevented by the unfavourable positioning of the OH groups, it is likely that an intermolecular condensation pathway leading to the formation of oligonuclear complexes is followed.

Analogous NMR spectroscopic studies of suspensions of **7**/NP-TiO_2 produced spectra showing a single spinning sideband manifold which is characterised by a chemical shift that is identical to that of the dry material, but the signal has a slightly reduced linewidth (see Table 1). In contrast to the previously described results, these findings give no evidence for either detachment of the immobilised complexes from the surface or the occurrence of similar base-induced reactions as had been observed for **4**/TiO_2 or **7**/TiO_2. The line narrowing effects are well known in NMR spectra of suspensions of immobilised phosphane complexes[16–18] and are, in the first place, attributable to the increased librational mobility of surface-bound species that are in contact with the solvent;[15] the rather moderate extent of the line narrowing in this case (in comparison to known cases of precedence[15,16]) is presumably due to the presence of a rather rigid molecular skeleton in the phosphane ligands employed.

Summarising the results of the NMR studies presented, it can be stated that the behaviour of the surface-bound complexes depends on both the molecular structures of the complexes **4** and **7** and, to an even larger extent, the properties of the carrier material. Thus, deposition of both complexes on neutral TiO_2 is feasible but the complexes can be easily eluted by polar solvents. Judging from the different solubilities in acetonitrile, **7** is slightly more mobile than **4**. On the other hand, **4** displays a larger sensitivity of the anisotropic chemical shift data to environmental influences, which correlates with a closer proximity of the catechol OH groups (as potential surface binding sites) to the phosphorus atom and may be indicative of a closer interaction between the phosphane complex and the surface. The reactivity of the surface-bound complexes in the presence of a base reveals that the catechol moieties are available for chemical reactions and led us, in connection with the easy detachment of the surface-bound complexes, to conclude that the surface binding operates presumably by means of adsorptive hydrogen-bonding interactions. This is also in accord with previous findings on the behaviour of TiO_2-tethered phosphane complexes.[15] In contrast, immobilised complexes on slightly acidic TiO_2 nanoparticles (NP-TiO_2) are definitely more tightly bound and gave no spectroscopic evidence for either the occurrence of leaching or of any base-induced dehydrochlorination. Both findings are compatible with the view[12] that the catechol OH groups support an ester-like interaction with metal atoms on the surface which is presumably more covalent in character. Although we cannot yet give a definite explanation for this at first glance surprising behaviour (one would expect that the formation of the surface esters should be more favoured on the more basic surface) several arguments to support the given interpretation can be proposed: in addition to the common place assumption that the surfaces of nanoparticles often exhibit enhanced reactivity due to the larger concentration of defect sites, one can argue that esterification on NP-TiO_2 benefits from acid catalysis. Furthermore, the formation of catecholate esters in a weakly acidic environment is no contradiction in itself as it is well known that chelate formation may increase the acidity of the free OH functions. Regardless of the nature of the interaction, however, the NMR spectroscopic studies indicate that the surface-bound complexes exist in the same manner as the pure crystalline materials i.e. exclusively as *trans* configured complexes whereas in solution an equilibrium mixture of *cis* and *trans* isomers exists.

The persistent attachment of the phosphane complex to the surfaces of TiO_2 nanoparticles stimulated us to explore the catalytic activity of **7**/NP-TiO_2. To this end, we investigated the use of the immobilised complex as a catalyst for the Sonogashira coupling of 4-iodo-nitrobenzene and phenyl acetylene. Combining both components for 24 h at ambient temperature in triethylamine in the presence of copper iodide and 10 mol-% of the immobilised complex **7** on NP-TiO_2 produced, after chromatographic workup, the expected coupling product in 70% yield. Repetition of the reaction using the recovered catalyst produced, in a second run, a yield of 68%, whereas in a third consecutive run the yield dropped to 10%. ICP analysis of the solid recovered after each run revealed that the loading of Pd dropped significantly after the first two runs indicating the occurrence of catalyst leaching during the reactions. However, as the Pd loading in the second and third run was the same, the observed drop in the catalytic performance cannot be attributed to leaching alone. Presumably, chemical degradation of the complex is also of importance.

These results indicate that **7**/NP-TiO_2 can, in principle, be applied as a catalyst although it seems to be less tightly bound to the surface of the support than the related complex **5**[11] and its use seems to offer no advantage when compared with the homogeneous reaction with the related complex **2** as a precatalyst which gave a yield of 90% of the same product in the same reaction time and with a comparable catalyst loading.[8] Moreover, as the possibility of catalyst leaching from the support must be acknowledged, it remains undecided if the product is really formed in a heterogeneous or homogeneous reaction.

Conclusions

It has been demonstrated that catechol phosphane complexes **4** and **7** can be deposited on the surface of both neutral TiO_2 and slightly acidic TiO_2 nanoparticles. Characterisation of both dry specimens and suspensions by ^{31}P HRMAS NMR experiments with or without the use of cross-polarisation revealed that, in the first case, the action of polar solvents is sufficient to accomplish partial or even complete detachment from the surface. This finding is in accord with the assumption that the complexes are predominantly adsorbed by means of hydrogen-bonding interactions. In contrast, complexes deposited on TiO_2 nanoparticles with a slightly acidic surface showed more resistance to leaching and failed to undergo base-induced dehydrochlorination, thus suggesting a tighter bonding mode which is presumably more covalent in nature. The use of the heterogenised complex as catalyst in a carbon–carbon cross coupling reaction was demonstrated.

Experimental Section

General Remarks: All manipulations were carried out under a dry argon atmosphere and solvents were dried by standard procedures unless otherwise mentioned. Phosphanes **1a**,**b**[7] and complex **4**[9] were prepared as reported earlier. The immobilisation experiments were carried out with two different solid phases, viz. neutral titania (Merck, TiO_2 p.a., denoted as TiO_2; pH of 10% dispersion in water ≈ 7) and pyrogenic TiO_2 nanoparticles (Degussa AEROXIDE TiO_2 P25, denoted as NP-TiO_2, pH of 4% dispersion in water ≈ 3.5–4.5, specific surface $50 \pm 15\ m^2 g^{-1}$, medium particle size 21 nm). Both phases are commercially available and were dried by heating to 90 °C in vacuo for 4 h before use. Immobilisation of the complexes was accomplished in the same way as described for **5**[11] by stirring CH_2Cl_2 solutions of **4** or **7** with solid TiO_2 and filtering off the supernatant liquid. The remaining solid was washed with several portions of solvent and dried in vacuo. The loading of the complex on the support was calculated from the results of elemental analyses of the materials obtained (neglecting any decomposition during the immobilisation process) as 60 mg of **4** g^{-1} of TiO_2, 48 mg of **7** g^{-1} of TiO_2 and 45 mg (57 µmol) of **7** g^{-1} of NP-TiO_2, respectively.

NMR Experiments: Solution NMR spectra were recorded with a Bruker AC 250 spectrometer (^{1}H: 250.1 MHz, ^{13}C: 62.8 MHz, ^{31}P: 101.2 MHz) at 303 K. NMR spectra of solids or suspensions were recorded with a Bruker Avance 400 spectrometer (^{13}C: 100.5 MHz, ^{31}P: 161.9 MHz) equipped with a 4 mm MAS probe. Solid samples were prepared in standard ZrO_2 rotors and suspensions in HRMAS rotors equipped with an additional tight PTFE spacer to prevent extrusion of the liquids. MAS experiments were carried out by using spinning speeds between 3 and 10 kHz (solids) or 1.5 to 6 kHz (suspensions). Cross-polarisation was applied using a ramp-shaped contact pulse and a mixing time between 3 and 5 ms if required. Measurements on nonspinning solid samples aiming at the observation of powder lineshapes were made with a Hahn-echo pulse sequence. Experiments aiming at the selective observation of mobile species in suspensions were carried out with the standard pulse sequence used to record X{^{1}H} spectra in solution. It was found that superior lineshapes were in these cases obtained if decoupling of ^{1}H was accomplished by using a WALTZ-sequence rather than the high power CW-decoupling scheme normally applied for solid samples. Chemical shifts are referenced to ext. TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P).

Preparation of Complex 7: To a solution of **1a** (200 mg, 0.64 mmol) in THF (20 mL) was added (cod)$PdCl_2$ (93 mg, 0.32 mmol). The reaction mixture was stirred for 2 h at room temperature and then concentrated under reduced pressure to half the total volume. Storing this solution overnight at +4 °C afforded shining yellow, needle like crystals which were isolated by filtration and dried in vacuo. Yield: 240 mg (95%); m.p. 223 °C. ^{1}H NMR (CD_3CN): δ = 7.30–6.96 (m, 10 H, Ph), 6.90–6.61 (m, 10 H, Ph), 6.38 (d, $^3J_{H,H}$ = 7.93 Hz, C_6H_3), 6.31 (d, $^3J_{H,H}$ = 7.47 Hz, C_6H_3), 6.14 (ddd, $\Sigma^3J_{H,H}$ = 8.24 Hz, C_6H_3), 3.65 (d, $^2J_{P,H}$ = 11.6 Hz, CH_2 of *cis*), 3.50 (t, $\Sigma J_{P,H}$ = 4 Hz, CH2 of *trans* isomer), 3.37 (m, THF), 1.54 (m, THF) ppm. ^{13}C NMR ($CDCl_3$; only data for the more abundant *trans* isomer given): δ = 139.7 (m, C_6H_3), 139.4 (t, $\Sigma J_{C,P}$ = 1.8 Hz, C_6H_3), 129.1 (p, $\Sigma J_{C,P}$ = 5.5 Hz, C_6H_3), 126.2 (t, $J_{C,P}$ = 1.0 Hz, Ph), 125.9 (t, $J_{C,P}$ = 1.2 Hz, Ph), 123.9 (s, Ph), 123.3 (q, $\Sigma J_{C,P}$ = 4.8 Hz, *i*-C), 120.0 (t, $J_{C,P}$ = 3.2 Hz, C_6H_3), 118.5 (t, $J_{C,P}$ = 2.9 Hz, C_6H_3), 112.4 (broad, s, C_6H_3), 62.3 (s, THF), 26.2 (t, $J_{P,C}$ = 13.9 Hz, CH_2), 23.1 (s, THF) ppm. ^{31}P{^{1}H} NMR (CD_3CN): δ = 33.3 (s, *cis* isomer), 20.3 (s, *trans* isomer) ppm.

Sonogashira Coupling of Phenyl Acetylene and 4-Iodo-nitrobenzene Using 7/NP-TiO_2 as a Catalyst: Phenylacetylene (0.15 mL, 1.3 mmol), CuI (10 mg, 0.05 mmol) and **7**/NP-TiO_2 (500 mg, corresponding to approx. 0.03 mmol of **7**) were added to a solution of 4-iodo-nitrobenzene (80 mg, 0.32 mmol) in triethylamine (30 mL). The suspension was stirred for 24 h at room temp. The solids were then filtered and washed with triethylamine (20 mL). The combined filtrates were evaporated to dryness and the resultant residue was chromatographed (silica, CH_2Cl_2/hexane, 3:7) to obtain a pale yellow solid of (4-nitrophenyl)phenylethyne (yield 70% based on 4-iodo-nitrobenzene) which was identified by its ^{1}H NMR spectrum. The experiment was repeated two times with the recycled catalyst under otherwise identical conditions to give yields of 68% and 10% of the coupling product, respectively. ICP analysis of the recovered solid after each catalytic run disclosed Pd loadings of 4.6, 2.6 and 2.6 mg (corresponding to 43, 24 and 24 µmol) of Pd g^{-1}NP-TiO_2.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (Graduate College 448 "Modern NMR Methods in Material Science"; scholarship for S. K. M.) is gratefully acknowledged. We thank Prof. Dr. M. Hunger (Institute of Technical Chemistry, University of Stuttgart) for providing the ICP analyses.

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Received: July 25, 2008