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On the Immobilization of a Monophosphaferrocene on a Silica Support

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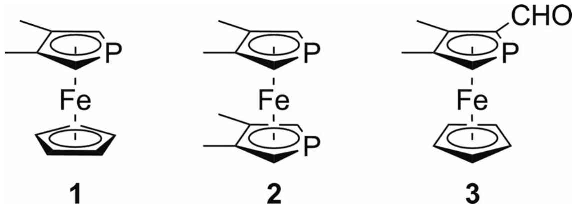
Abstract. Reactions of 2-formyl-3,4-dimethyl-1-phosphaferrocene with aminopropyl (AP) functionalized hexagonal mesoporous silica (HMS) were studied in the absence and presence of an excess of the mild reducing agent Na[BH_3CN]. Starting material and reaction products were characterized by analytical and multinuclear (^{13}C, ^{29}Si, ^{31}P) MAS NMR spectroscopic data. Both reactions proceeded by partial derivatization of surface-bound NH_2 groups to yield products with tethered phosphaferrocene units. Evaluation of spectroscopic data and the results of homogeneous model reactions confirmed that condensation of both components gives imines, which are obviously kinetically labile and allow leakage of the tethered phosphaferrocene into solution. Reactions carried out in the presence of Na[BH_3CN] proceed as reductive amination to yield secondary amines with enhanced kinetic stability. The reductive amination is accompanied by formation of minor amounts of phosphorus-containing by-products as well as the hydrolysis of surface bound ethoxy groups present in the starting material.

Introduction

Phosphaferrocenes like compounds **1** and **2** (Scheme 1) were first prepared in the late 1970ies,[1,2] and the elaboration of their chemistry has since then received continuing interest.[3] An interesting aspect of these compounds is that the phosphorus atom is on one hand sufficiently nucleophilic to support the formation of metal complexes, whereas the ring system allows on the other hand easy derivatization by electrophilic substitution.[2,3] This reactivity permits introduction of extra functionality into the phospholyl moiety, and the combination of both factors makes phosphaferrocenes an ideal platform for the construction of planar chiral ligands.[4]



Scheme 1.

Starting with the first discovery of the catalytic activity of a phosphaferrocene complex,[5] these ligands have now found a variety of applications in catalysis.[6] To the best of our knowledge, all catalytic transformations studied so far are based on homogeneous reactions, and although attempts to immobilize catalysts in order to improve their separation and recycling receive currently some attention,[7,8] no such attempts with phosphaferrocenes or their complexes seem to have been reported. Considering that phosphaferrocenes exhibit reasonable stability and can tolerate a wide range of experimental conditions, we set out to perform a model study in order to evaluate the prospect of anchoring a functionalized monophosphaferrocene to the surface of a modified silica material.

Results and Discussion

Even though pure phosphaferrocenes are air-stable species [1,2] they resemble other types of low-coordinate phosphorus compounds since reactions must usually be performed under exclusion of air and moisture in order to prevent degradation. Having recently found that even chemically quite stable phosphinines (phospha-benzenes) may undergo extensive decomposition during attempts to link them to the surfaces of functionalized silica [9] or gold nanoparticles,[10] we reckoned that the choice of a proper carrier material and coupling reaction might also be a critical prerequisite for the successful surface anchoring of phosphaferrocenes.

Mesoporous silicas seemed a suitable material as their surface was proven to display a certain tolerance toward low-coordinate phosphorus compounds,[9] and can easily be functionalized by coupling with trialkoxysilanes bearing various functional groups, including phosphines and their complexes.[7] Hexagonal mesoporous silicas (HMS),[11] although having a less ordered structure than MCM-41 or SBA-15 materials, are further very easily accessible, and their preparation does not require strongly acidic conditions. Last, but not least, aminopropyl (AP) functionalized HMS[12,13] were shown to react under particularly mild conditions with aldehydes to give materials with covalently tethered imine functions.[14] In view of these aspects, we decided to explore the prospect of linking

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formyl phosphaferrocene (**3**)[2] to aminopropyl moieties grafted to the surface of HMS.

The preparation of hexagonal mesoporous silica[11] and its functionalization with 3-aminopropyl-triethoxysilane[13] was carried out as described. The material was characterized by elemental analysis, nitrogen adsorption/desorption studies, and ^{13}C and ^{29}Si CP MAS NMR spectroscopic data. The loading of amine functionalities (elemental analysis revealed the presence of 1.7 mmol$\cdot$g^{-1} nitrogen, corresponding to an anchoring efficiency of 58 %) and the reduction of the BET surface area (811 m$^2\cdot$g^{-1} before and 536 m$^2\cdot$g^{-1} after amine functionalization) are similar to previously reported data.[13] A ^{13}C CP-MAS NMR spectrum (Figure 1) shows three signals at 6.5, 22.8, and 40.7 ppm attributable to propyl carbon atoms and two further, less intense lines at δ = 13.5 and 56.6 ppm that we assign to residual ethoxy groups. The observed chemical shifts and the asymmetry of the signal at δ = 22.8 ppm match previously reported values for functionalized silica produced by gas-phase deposition of aminopropyl-triethoxysilane.[15] The ^{29}Si MAS and ^{29}Si CP-MAS NMR spectra (Figure 2) show signals arising from Q^4 and Q^3 units [$Q_n = Si(OSi)_n(OH)_{4-n}$] of the silica framework[16] at –111.0 and –104.0 ppm, whereas the signal of Q^2 groups that had still been observable in the ^{29}Si NMR spectrum of HMS disappeared. Two additional signals at –68.5 and –61.5 ppm with intensity ratios of approx. 55:45 (Figure 3) are attributed to T^3 and T^2 groups [$T^m = RSi(OSi)_m(OR)_{3-m}$, R = Et, H] of grafted organosilane moieties.[16] The presence of two distinguishable T^n species is in accord with the different relative intensities of the ^{13}C NMR signals of ethoxy and propylidene moieties and the atomic ratio of C:N = 4.2:1 calculated from the analytical data. All findings together suggest that the sample contains comparable amounts of surface bound $RSi(OSi)_3$ (R = 3-aminopropyl, Si = silicon atom in the silica network; calculated C:N ratio = 3:1) and $R(EtO)Si(OSi)_2$ units (calculated C:N ratio = 5:1).

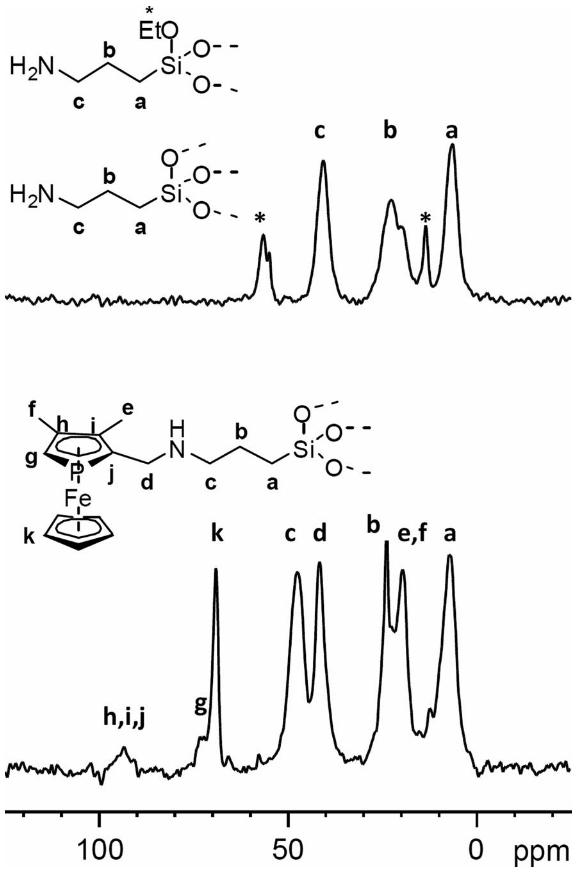


Figure 1. Solid state ^{13}C CP-MAS NMR spectra of AP-functionalized HMS before (top; ν_{rot} 8 kHz, recycle delay 5 s, contact time 3 ms, 4096 transients) and after (bottom; ν_{rot} 8 kHz, recycle delay 5 s, contact time 1.8 ms, 12288 transients) reaction with **3**/Na[BH$_3$CN]. The sketches illustrate the assignment of the signals to the different carbon sites.

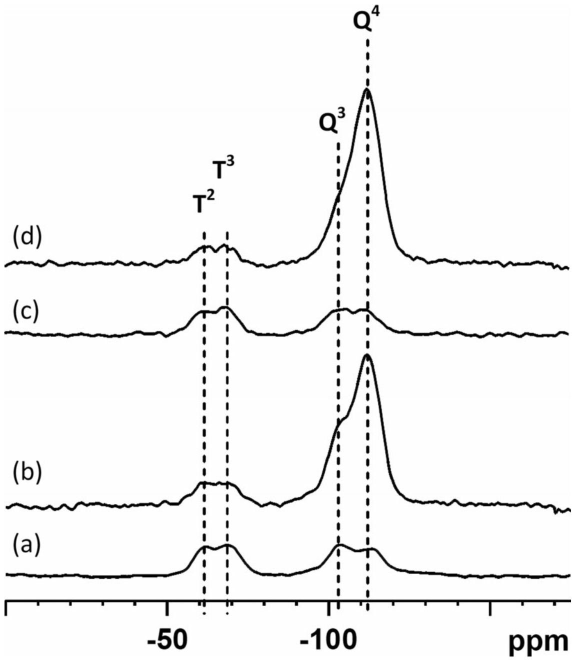


Figure 2. Solid state 79.49 MHz ^{29}Si NMR spectra of AP-functionalized HMS before (traces a, b) and after reaction with **3**/Na[BH$_3$CN] (traces c, d). The labels indicate the assignment of the signals to T^n and Q^n groups (see text). Conditions: trace (a): CP-MAS spectrum, ν_{rot} 8 kHz, recycle delay 7.5 s, contact time 1.4 ms, 3072 transients; trace (b): MAS spectrum, ν_{rot} 8 kHz, recycle delay 120 s, 1536 transients; trace (c): CP-MAS spectrum, ν_{rot} 8 kHz, recycle delay 7.5 s, contact time 1.8 ms, 2048 transients; trace (d): MAS spectrum, ν_{rot} 8 kHz, recycle delay 240 s, 768 transients).

In order to graft phosphaferrocene **3** to the surface of AP-functionalized HMS, both components were reacted for three days in anhydrous methanol at 55 °C. Elemental analysis of the solid residue obtained after decantation of the supernatant liquid and repeated washing with methanol revealed a significant change in the atomic composition (atomic ratio C:N = 7.0:1), which indicated that anchoring of the phosphaferrocene to the surface had indeed taken place. This assumption was confirmed by the observation of a signal at –76 ppm in a ^{31}P MAS NMR spectrum, which compares well with the signals of **3** (δ^{31}P –62[2]), and of the single product observed upon reaction of **3** with an equimolar quantity of *n*-propylamine in methanol (δ^{31}P –75[17]). However, when ^{31}P NMR spectra of washing liquids continued to show – even after repeated wash-

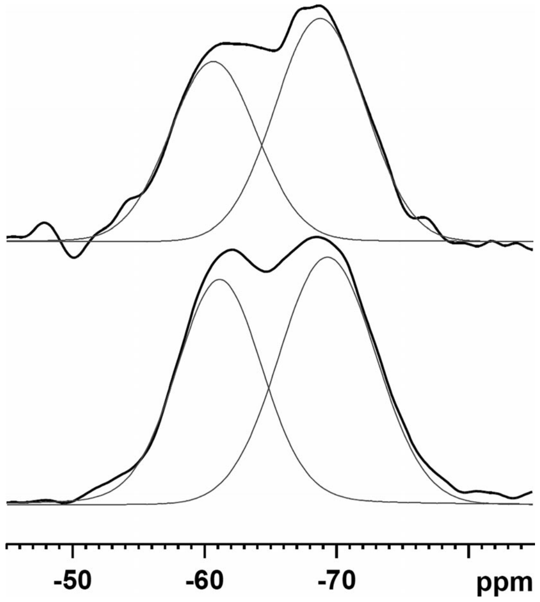
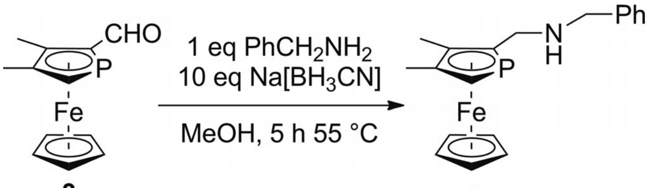


Figure 3. Expansion of the solid state 79.49 MHz ^{29}Si CP-MAS NMR spectra of AP-functionalized HMS before (top trace) and after (bottom trace) reaction with **3**/Na[BH$_3$CN]. The grey lines show the results of fits of the experimental lineshapes to a sum of two mixed Gaussian/Lorentzian lines representing distinguishable T^2/T^3 environments. Computation of the integrated relative intensities yielded in both cases a ratio of n(T^3):n(T^2) = 55:45.

ings – a signal attributable to **3**, we concluded that the imine formation is reversible, and the chemical tether is too labile to prevent leaking of immobilized phosphaferrocene into solution.

Since it is well known that cleavage of labile aldimines may be suppressed by their reduction to kinetically inert amines, we sought a way to improve our immobilization protocol by employing this strategy. After some testing we found that reductive amination of **3** is feasible if the coupling with a primary amine is carried out in the presence of a large excess of the mild reducing agent Na[BH$_3$CN].[18] Thus, phosphaferrocenylamine (**4**) (Scheme 2) was obtained in a single step from **3** and benzylamine as red oil that was characterized by spectroscopic data, and formation of an analogous coupling product was confirmed by ^{31}P NMR spectroscopic monitoring of the reaction of **3** and 3-aminopropyl-triethoxysilane.[19]



Scheme 2.

Coupling of **3** to the surface of AP-modified HMS was carried out using the same protocol as in the synthesis of **4**, and the resulting brownish material was characterized by elemental analysis, nitrogen adsorption/desorption, and CP MAS NMR spectroscopic data. The different atomic composition (the analytical data reveal a ratio C:N of 5.8:1) and the still lower BET surface area (397 m^2•g^{-1}) as compared to AP-modified HMS give strong evidence that anchoring of phosphaferrocene has taken place, and the failure to observe spectroscopically detectable amounts of **3** in washing liquids (after any unreacted starting material was removed) suggest that the immobilized material is indeed connected to the surface by a stable covalent tether. However, the observation of a smaller C:N ratio than in the previously described imine coupling product also indicates that the presence of the reducing agent has an adverse effect on the phosphaferrocene loading.

The presence of grafted phosphaferrocene moieties on the surface is confirmed by the MAS NMR spectroscopic data. A ^{31}P NMR spectrum recorded with direct excitation of ^{31}P and high power ^{1}H decoupling displays a signal around –75 ppm with a shoulder on the left side and indicates the presence of two phosphaferrocene species with slightly different chemical environment (spectral deconvolution gave chemical shifts of –76.1 and –70.3 with relative intensities of 77:13). A further weak resonance at δ = +42 ppm (10 % of total spectral intensity) reveals a minor amount of decomposition products (arising presumably from nucleophilic attack at the phosphorus atom and subsequent decomplexation of the phosphole ring[21]). A ^{31}P CP-MAS NMR spectrum showed the same signals but with much lower intensity. This effect reflects presumably the known reduction of CP-efficiency at high spinning speeds, which is due to the splitting of the Hartmann-Hahn matching profile into separated sidebands and has previously been observed in CP-MAS NMR spectra of other surface bound phosphorus compounds;[20] since the spectrum recorded without CP

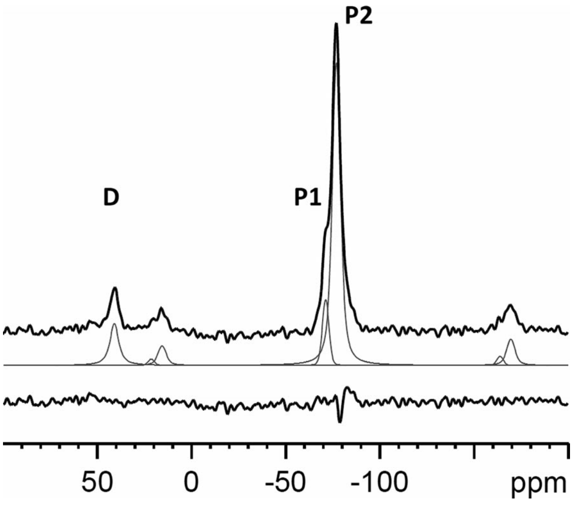


Figure 4. Solid state 161.9 MHz ^{31}P MAS NMR spectrum of AP-functionalized HMS after reaction with **3**/Na[BH$_3$CN] (ν_{rot} = 14 kHz, 1024 transients, relaxation delay 5 s) The top trace shows the experimental spectrum, the middle trace the result of a simulation of the experimental lineshape as the sum of three spinning sideband manifolds, and the bottom trace the difference between experiment and fit. The labels indicate the assignment of the isotropic lines to an unknown decomposition product (D) and two distinguishable phosphaferrocene sites (P1, P2). The integrated intensities indicate a molar ratio of D:P1:P2 = 10:13:77.

was of sufficient quality, we did not optimize the Hartmann–Hahn match (Figure 4<yigr4 pos="x22">).

The tethering of intact phosphaferrocene is also evident from the ^{13}C CP-MAS NMR spectrum (Figure 1). Comparison with the spectrum of **4** allows assigning all carbon sites in the phosphaferrocene moiety. Four additional signals are attributable to the carbon atoms in the propylidene spacer and the methylene group linking the amine and phosphaferrocene functionalities. Resonances of ethoxy units, which had been present in the AP-modified silica, are no longer visible. Similar findings had previously been noted during the post-functionalization of similar modified silicas[22] and indicate that these groups hydrolyze during the grafting process. Comparison of relative signal intensities reveals that the resonances of the carbon atoms in the propylidene spacer are much stronger than those in the phosphaferrocene moiety. Even though no quantitative evaluation was feasible, this finding supports the earlier mentioned hypothesis that only incomplete functionalization of the anchoring groups had been accomplished.

The ^{29}Si MAS and CP-MAS NMR spectra resemble closely those of the AP-functionalized silica before treatment with phosphaferrocene and indicate that the silica framework has not undergone any structural changes during the grafting process. In particular, the ratio of T^2 and T^3 sites is essentially unaffected (Figure 3), which suggests that the observed loss of ethoxy groups does not turn the former $RSi(OEt)(OSi)_2$ into $RSi(OSi)_3$ groups as had previously been proposed,[22] but may possibly produce $RSi(OH)(OSi)_2$ units with a further free silanol function. The coexistence of such T^2 and T^3 sites on the silica surface implies that tethered phosphaferrocene moieties may exhibit different chemical environments, and suffices to explain the shoulder on the ^{31}P NMR signal of surface bound phosphaferrocenes.

Additional experiments revealed that although the amount of side products (as indicated by the observation of a minor ^{31}P NMR signal around 40 ppm) varied somewhat between different reactions, their formation could not be completely avoided. Pre-treatment of the functionalized silica with $HN(SiMe_3)_2$ (in order to deactivate silanol functions on the surface) did not lead to a significant improvement, thus suggesting that the observed side products might arise from side-reactions during the reductive amination step.

Conclusions

It was shown that persistent grafting of phosphaferrocene aldehyde **3** to the surface of AP-functionalized silica may be accomplished by coupling both components in the presence of the mild reducing agent $Na[BH_3CN]$. Solid-state NMR studies and model reactions carried out in solution suggest assigning the formed product the structure of an aminomethylated phosphaferrocene. The NMR studies indicate further that only partial derivatization of the surface functionalities was achieved, and that the grafting process is accompanied by hydrolytic cleavage of surface bound ethoxy functions. Although formation of phosphorus-containing by-products could not completely be avoided, the amount of these species was found to be much lower than in attempts to immobilize other types of low-coordinate phosphorus compounds,[9] and the phosphaferrocene core remained largely intact. These findings led us to conclude that (i) the phosphaferrocene moiety is obviously less susceptible towards side-reactions during functionalization and seems therefore more suitable for immobilization than other types of low-coordinate phosphorus compounds, (ii) the application of as mild reaction conditions as possible is apparently a crucial prerequisite for the immobilization of any type of low-coordinate phosphorus compounds, and (iii) still further efforts are required to prepare well defined materials that contain no decomposition products and allow to exploit the full potential of phosphaferrocenes in heterogeneous catalysis.

Experimental Section

General Remarks: All manipulations were carried out in an argon atmosphere using Schlenk techniques. Solvents were dried prior to use by common procedures. Preparation of phosphaferrocene aldehyde **3**,[4] HMS,[11] and functionalization of the latter with 3-aminopropyltriethoxysilane [13] were carried out as described. Solution NMR spectra were recorded with a Bruker Avance 250 spectrometer (^1H: 250.1 MHz, ^{13}C: 62.8 MHz, ^{31}P: 101.2 MHz) at 303 K and solid-state NMR spectra with a Bruker Avance 400 spectrometer (^{13}C: 100.5 MHz, ^{29}Si: 79.49 MHz, ^{31}P: 161.9 MHz) equipped with a 4 mm MAS probe. MAS experiments were performed using standard ZrO_2 rotors and spinning speeds between 8 and 9 kHz for ^{13}C and ^{29}Si NMR spectra and 14 kHz for ^{31}P NMR spectra. Cross polarization was applied using a ramp-shaped contact pulse and mixing times between 0.8 and 5 ms unless noted. Chemical shifts were referenced to ext. TMS (^1H,^{13}C) or 85 % H_3PO_4 (Ξ = 40.480747, ^{31}P). EI-MS: Varian MAT 711, 70eV. Elemental analysis: Perkin–Elmer 24000 CHN/O Analyser. Nitrogen adsorption-desorption experiments were carried out with a Micromeritics ASAP 2000 particle size analyzer.

2-(Benzylamino)methyl-3,4-dimethyl-phosphaferrocene (4): Benzylamine (295 mg, 2.76 mmol) was added to 2-formyl-3,4-dimethyl-1-phosphaferrocene (720 mg, 2.76 mmol) in MeOH (20 mL). Solid $NaBH_3CN$ (1.70 g, 27.6 mmol) was added, and the mixture was heated at 55 °C for 5 h. Deoxygenated water (20 mL) was added. The organic phase was separated and filtered through a short plug of neutral alumina. The solvent was removed under vacuum to obtain an orange oil. Yield 720 mg, 74 %. **$^{31}P\{^1H\}$ NMR** (CD_3OD): δ = –76.5 ppm. **^1H NMR** (CD_3OD): δ = 2.10 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 3.16 (dd, $^3J_{PH}$ = 13.5 Hz, 2 H, CH_2N), 3.32 (s, 2 H, CH_2N), 3.63 (d, $^2J_{PH}$ = 37.0 Hz, 1 H, PCH), 4.06 (s, 5 H, Cp), 7.21–7.35 (m, 5 H, C_6H_5) ppm. **$^{13}C\{^1H\}$ NMR** (CD_3OD): δ = 13.8 (s, CH_3), 17.3 (s, CH_3), 53.73 (d, $^2J_{PC}$ = 1.7 Hz, CH_2N), 54.76 (s, CH_2N), 73.01 (s, Cp), 76.70 (d, $^1J_{PC}$ = 58.3 Hz, α-CH), 94.64 (d, $^2J_{PC}$ = 4.9 Hz, β-C), 96.26 (d, $^1J_{PC}$ = 58.9 Hz, α-C), 97.43 (d, $^2J_{PC}$ = 6.8 Hz, β-C), 123.75, 129.47, 130.72, 140.5 (C_6H_5) ppm. **MS** (EI = 70 eV): *m/e* (%) = 351.1 (100) $[M]^+$, 244.0 (44) $[M - NHCH_2C_6H_5 + H]^+$.

Immobilization of 3 on AP-functionalized HMS: (a) With Imine Coupling: Compound **3** (400 mg, 1.52 mmol) was stirred with AP-functionalized HMS (2.00 g) in anhydrous MeOH (15 mL) at 55 °C for 3 d. The material was filtered, washed with methanol (3 × 50 mL), and dried in vacuo for 8 h. Analytical data: found C 13.49 H 2.67 N 2.22 %. **MAS $^{31}P\{^1H\}$ NMR:** δ = –76 ppm. Repeated washings with MeOH produced washing liquids, whose ^{31}P NMR spectra continuously displayed a signal attributable to **3**.

(b) With Reductive Amination: Compound **3** (400 mg, 1.52 mmol) was added to AP-functionalized HMS (2.00 g) in anhydrous MeOH (15 mL). Solid Na[BH_3CN] (470 mg, 7.6 mmol) was added and the reaction mixture was heated to 50 °C for 3 d. The suspension was filtered, the residue was washed with MeOH (3 × 50 mL), and dried in vacuo for 8 h. Analytical data: found C 11.69 H 2.94 N 2.34 %. MAS NMR spectra are displayed in Figures 1–4. **^{13}C CP-MAS NMR** (assignments refer to the labels shown in Figure 1): δ = 95 (h, i, j), 72.9 (g), 70.1 (k), 47.6 (c), 41.6 (d), 23.8 (b), 19.6 (e,f), 7.1 (a) ppm.

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[17] Although the occurrence of hydrolytic cleavage of the imine moiety during work-up prevented isolation of the product, the expected constitution was further confirmed by ^{1}H NMR spectroscopic data obtained directly from the reaction mixture: δ^{1}H = 8.17 (d, $^{3}J_{HP}$ = 8.8 Hz, C*H* = N), 3.95 (d, $^{2}J_{HP}$ = 37.4 Hz, PCH), 4.20 (s, Cp), 3.12 (m, NCH_2) 2.31 (s, CH_3), 2.21 (s, CH_3), 1.57 (m, CH_2), 0.89 (t, CH_3).

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[19] The ^{31}P NMR spectrum showed the signals of two products at –75.4 ppm (major product) and 76.1 ppm (minor product). As the specific reactivity of the Si(OEt)$_3$ moiety made chromatographic separation unfeasible, the nature of the by-product remains in the dark.

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