

Synthesis, structure, immobilization and solid-state NMR of new dppp- and tripod-type chelate linkers

Mona Bogza, Thomas Oeser, Janet Blümel *

Department of Organic Chemistry, Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received 25 January 2005; revised 8 April 2005; accepted 11 April 2005

Available online 2 June 2005

Abstract

Chelating phosphines incorporating ethoxysilane functions for immobilizations have been synthesized and fully characterized. $(\text{EtO})\text{Si}(\text{CH}_2\text{PPh}_2)_3$, $(\text{EtO})_2\text{Si}(\text{CH}_2\text{PPh}_2)_2$, and $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ could be prepared in high yields from cheap starting materials. The ethoxysilanes, as well as a Pd complex thereof have been characterized by X-ray structures, and immobilized on silica. The success of the immobilization was proved by ^{31}P solid-state NMR of the dry materials and of the suspensions. Two representative chelate metal complexes, $(\text{EtO})_2\text{Si}(\text{CH}_2\text{PPh}_2)_2\text{PdCl}_2$ and $(\text{EtO})\text{Si}(\text{CH}_2\text{PPh}_2)_3\text{W}(\text{CO})_3$ have been synthesized, characterized and immobilized. © 2005 Elsevier B.V. All rights reserved.

Keywords: Ethoxysilanes; Chelating phosphines; Solid-state NMR; Immobilization; Linkers; Pd catalyst

1. Introduction

The success of immobilized species is crucially dependent on the behavior of the linker, no matter whether they are applied for combinatorial chemistry [1], solid-phase synthesis [2], chromatography [3], or catalysis [4]. We, and also many other groups [5] have striven to improve the recyclability and lifetime of immobilized catalysts by anchoring them on oxidic supports via linkers [6–8]. For such surface chemistry solid-state NMR spectroscopy [9] proves to be an indispensable and powerful analytical method. For our systems we recently optimized the cross polarization (CP) process at high magic angle spinning (MAS) frequencies [10] for getting better signal to noise ratios (S/N), and implemented stationary [11a,11b] and HR-MAS suspension NMR spectroscopy [11c] to study the mobilities of surface species,

as well as their reactivity with oxidic surfaces, and their structural nature.

There with we could clarify the reaction of the popular $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ or of chelating phosphines with the silica surface [6–8,12,13]. The solvent turned out to be important for the immobilization process [14], while the strongest bonding takes place with silica [11b]. Furthermore, metal complexes with two monodentate linkers are not necessarily bound in a chelating manner [15], making them vulnerable to leaching [8,11]. This problem can for example be solved by using chelating linkers that prolong the lifetimes of the catalysts substantially [6–8,11c,12]. Surprisingly, chelate phosphine linkers incorporating ethoxysilane groups for immobilizations on silica are still rare [6,7,12,17], and many, e.g. bisphosphinoamine linkers [11c], even decompose during the immobilization process or form phosphonium salts as side-products [11c,16]. In earlier studies on Ni and Rh complexes we showed that dppp-type linkers gave the best immobilized catalysts [6–8], while the length of the spacer did not display a visible effect. However, rigid spacers that reduced the contact of the metal complex

* Corresponding author. Tel.: +49 6221 548470; fax: +49 6221 544904.

E-mail address: J.Blumel@urz.uni-heidelberg.de (J. Blümel).

with the surface led to more active catalysts. Therefore, in this work, we will present a new class of rigid bi- and tridentate dppp-type linkers incorporating the ethoxysilane group in the center of the chelate backbone. These linkers, in contrast to previous ones [12] are symmetric, which is desirable from an analytical point of view, and it will be demonstrated that they can coordinate and anchor metal complexes in a clean and well-defined manner.

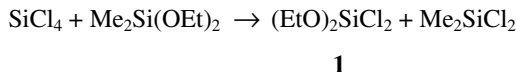
Dppp-type ligands with heteroatoms in the center of the backbone are enjoying growing interest, because they allow the fine-tuning of their electronic properties. In the case of the borate ligands $[\text{Ph}_2\text{B}(\text{CH}_2\text{PPh}_2)_2]^-$ for example, even a negative charge can be introduced [18]. Although dppp-type phosphine chelate ligands with a silicon atom in the center, such as $\text{Ph}_2\text{Si}(\text{CH}_2\text{PPh}_2)_2$ provide useful neutral versions of electron-rich ligands, and are known to produce, e.g., highly active Wilkinson catalysts for hydrogenations [18], to the best of our knowledge there are no versions incorporating ethoxysilane groups for immobilization.

The same accounts for tripodal phosphines. For example, the silicon and tin versions of triphos, $\text{MeSi}(\text{CH}_2\text{PPh}_2)_3$ and $\text{MeSn}(\text{CH}_2\text{PPh}_2)_3$, are known, and their Rh(I) and Ru(II) coordination chemistry has been explored [19]. Recently, in addition the tridentate ligand $t\text{BuSi}(\text{CH}_2\text{PMe}_2)_3$, and the reactivity of vanadium complexes thereof, has been studied [20], but again no alkoxo derivative is known.

For later comparisons of our immobilized catalysts with their homogeneous versions, we also sought to synthesize a dppp-type ligand with Si in the center, but without ethoxy groups, namely $\text{Si}(\text{CH}_2\text{PPh}_2)_4$. The latter can function both as bi- and tridentate ligand, and will later also allow the study of cooperative effects. Furthermore, it might be useful as a building block for dendrimers, as the known $\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_4$ already is [21,22].

2. Results and discussion

The starting material for our synthesis, $(\text{EtO})_2\text{SiCl}_2$, (**1**), could not be obtained by comproportionation of $(\text{EtO})_4\text{Si}$ with SiCl_4 , because the resulting mixture, due to similar boiling points of the products, turned out to be inseparable. Therefore, we synthesized **1** by stirring equimolar amounts of SiCl_4 and $\text{Me}_2\text{Si}(\text{OEt})_2$ in a sealed tube for 5 h at 165 °C (Scheme 1). The resulting mixture of **1**, EtOSiCl_3 , and Me_2SiCl_2 , in a typical ratio of



Scheme 1. Synthesis of $(\text{EtO})_2\text{SiCl}_2$.

1.0:0.2:1.1, with traces of $(\text{EtO})_3\text{SiCl}$, could easily be separated by distillation with a vigreux column at ambient pressure. So, **1** has been obtained in analytically pure form in about 61% yield with respect to SiCl_4 (Scheme 1).

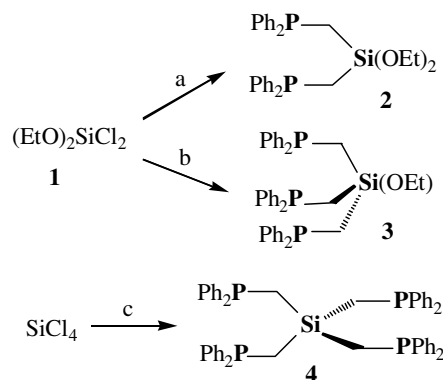
The new ligands, with the names we suggest to be Si-bisphos (**2**), Si-triphos (**3**) and Si-quadruphos (**4**), were synthesized according to the route given in Scheme 2, with typical, unoptimized yields of 84%, 82%, and 66%, respectively. The lithium salt $\text{Ph}_2\text{PCH}_2\text{Li}(\text{TMEDA})$ (**5**) was obtained as described in the literature [23]. It should be mentioned that an attempt to obtain **2** along with $\text{Si}(\text{OEt})_4$ by disproportionation of $\text{Ph}_2\text{PCH}_2\text{Si}(\text{OEt})_3$ [17] using CsF, as successfully applied to $\text{HSi}(\text{OEt})_3$ [24], unfortunately did not work.

The NMR signal assignments of all the compounds in this work have been done by standard 1D and 2D techniques, and by comparison with previously described linkers with Ph_2PR moieties [6a,11c,12,17]. The triplet and quartet of the ^{29}Si NMR signals of **2** and **3**, respectively, are in nice agreement with the multiplicities expected for two and three equivalent ^{31}P nuclei in the alpha position to silicon. Taking a look at the ^{13}C NMR spectra of **2–4**, **6**, and **7**, the most interesting feature is found for the aryl carbon signals, many of which display “virtual ^{31}P couplings” [25]. This is confirmed by various ^1H and ^{31}P decoupling experiments, in which the corresponding aryl carbon signals appear equally coupled to all phosphorus nuclei within the molecules [25].

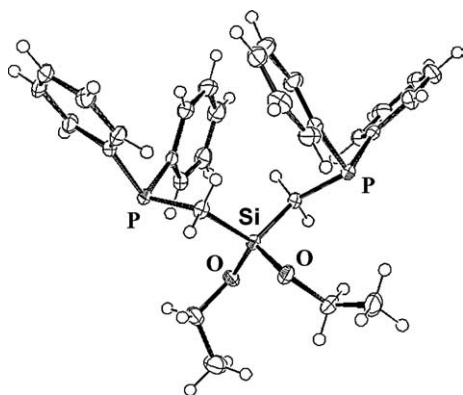
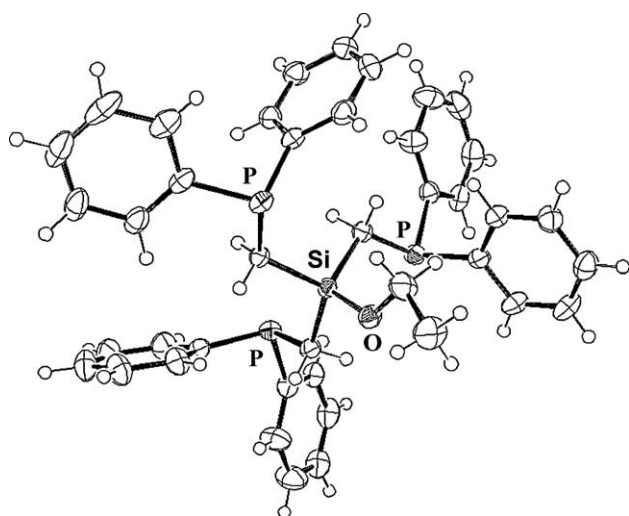
Although linkers incorporating ethoxysilane groups are usually viscous liquids and thus hard to crystallize, compounds **2** and **3** do so readily, and they could be subjected to X-ray analyses (Figs. 1 and 2).

In both cases, as expected, the substituents at the Si center are arranged in a tetrahedral manner, and the diphenylphosphine moieties assume the positions imposed on them by the packing demands in the crystals.

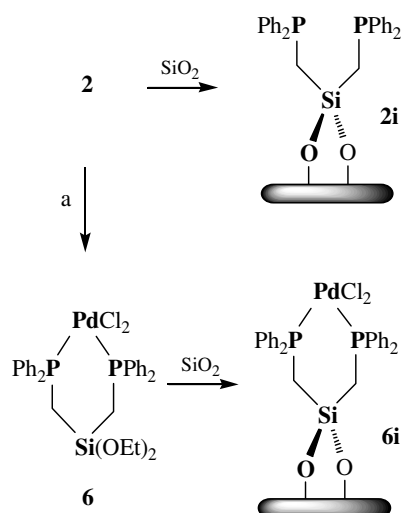
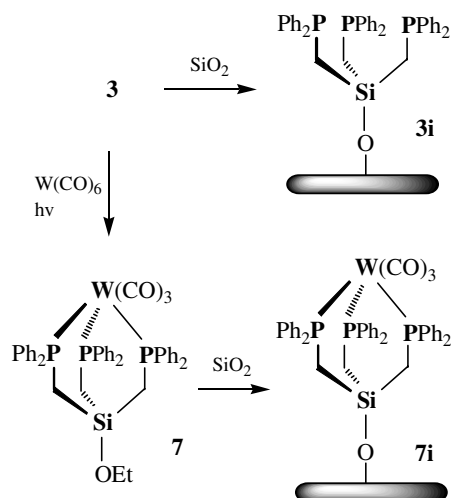
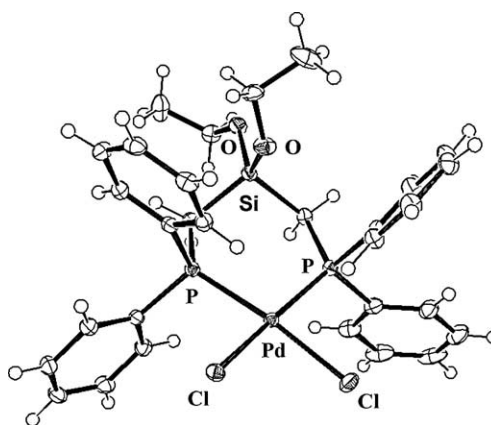
Although the ligands, out of the ensembles of conformation that one would expect to be populated in solu-



Scheme 2. Synthesis of the phosphine ligands **2**, **3**, and **4** (pentane, RT): a: 2 equivalents of $\text{Ph}_2\text{PCH}_2\text{Li}(\text{TMEDA})$ (**5**) [23], 1 h; b: 3 equivalents of **5**, 4 h; c: 4 equivalents of **5**, 1 h, pentane.

Fig. 1. Crystal structure of **2**.Fig. 2. Crystal structure of **3**.

tion, crystallize in forms that are not preorganized for coordination, they readily bind in a chelating, not in a bridging manner, and provide only well-defined mononuclear complexes. This coordination preference of ligands **2** and **3** could be demonstrated by transforming them into the Pd and W complexes **6** and **7** (Schemes 3 and 4). The complexation proceeds smoothly, and the ligands do not have to be recrystallized prior to reacting them with the proper metal precursors. As their data show, both ligands coordinate in the desired bi- and tridentate manner without forming dinuclear bridged species or involving the ethoxysilane groups. For **6** this is additionally proven by an X-ray analysis (Fig. 3), which shows that ligand **2** readily accommodates the square planar coordination at the Pd center. The phenyl groups are arranged in a way to make space for the Cl atoms, while the Si atom deviates about 0.89 Å perpendicular out of the least squares plane defined by the Pd(PC)₂ fragment. Secondary interactions of the ethoxy oxygen atoms with the metal center obviously do not take place.

Scheme 3. Synthesis of the molecular and immobilized species **2i**, **6** and **6i**. a: PdCl₂(NCPh)₂.Scheme 4. Synthesis of the molecular and immobilized species **3i**, **7** and **7i**.Fig. 3. Crystal structure of the palladium complex **6**. The cocrystallized acetone solvent molecule is not shown for clarity.

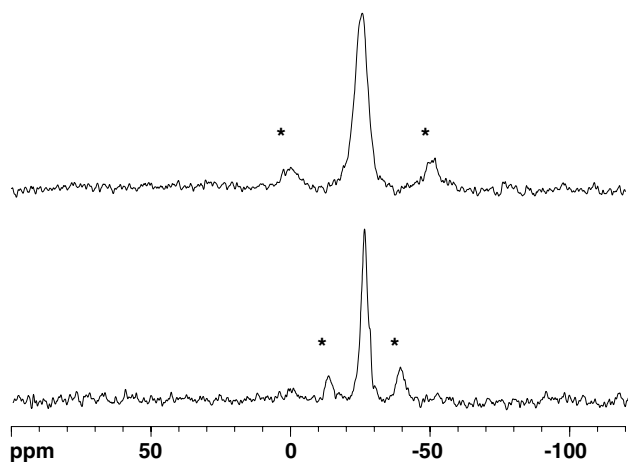


Fig. 4. ^{31}P CP/MAS (top, 4 kHz) and ^{31}P suspension HR MAS (bottom, 2 kHz, in toluene as the suspension medium) spectra of **3i** on silica. Asterisks denote rotational sidebands. For details of the measurements see [10] and [11c].

The linkers **2** and **3** can be immobilized on silica in a clean and well-defined manner, giving **2i** and **3i**. The surface coverages are in the typical range [6–8,10–14], for example 63 mg (0.092 mmol) of **3** are immobilized on 1 g of silica. The ^{31}P CP/MAS spectra show no signals of ligand destruction [11c], phosphine oxide [16a] or phosphonium salts [16b], which often occur as side products in the cases of other linkers. Furthermore, they are strongly bound in a covalent manner, and after thorough washing do not show leaching from the support. Fig. 4, for example, shows the ^{31}P CP/MAS spectrum of **3i** on silica at 4 kHz rotational speed (top spectrum). The halfwidth of the CP/MAS signal is about 800 Hz. The suspension HR MAS spectrum of **3i** in toluene gives a much narrower line with a halfwidth of merely 335 Hz even at the low spinning frequency of 2 kHz [11c]. Thus, any phosphonium- or phosphine oxide-type side-products from the immobilization would not escape our attention.

Since the ethoxysilane groups are not involved in the coordination of the metal complexes **6** and **7**, they can function as the usual anchors when immobilizing these on silica as **6i** and **7i** (Scheme 3 and 4). The clean and well-defined immobilization is again proven by ^{31}P CP/MAS NMR, which demonstrates the absence of any uncomplexed phosphines, as well as other unwanted species (see above). Therefore, we conclude that the linkers **2** and **3** are ready to be applied for example as metal scavengers, or linkers for immobilized catalysts.

3. Conclusion

A new type of linker for immobilization of metal complexes on oxidic supports has been described and fully characterized, including their X-ray structures.

Due to the rigid geometry of the linkers, as well as the steric demand of the phenyl substituents at the phosphine moieties the ligands should protect immobilized metal complexes from each other, as well as from the silica surface, thus preventing their premature deactivation and leading to recyclable catalysts with longer lifetimes. This option will be explored in our future work, along with potential cooperative effects in homogeneous catalysts derived from **4**.

4. Experimental

All reactions were carried out in Schlenk flasks under purified nitrogen. The solvents were dried and distilled according to standard procedures prior to use. Support material: Silica gel 40 (Merck, specific surface area 750 m²/g, average pore diameter 40 Å, particle size 0.063–0.2 mm). The solution NMR spectra were recorded on routine Bruker spectrometers at field strengths corresponding to 250, 300, and 500 MHz. The solid-state NMR spectra were recorded on a fully digital Bruker Avance 400 NMR spectrometer equipped with a 4 mm MAS probehead. This probehead was used for both, classical and suspension MAS measurements. For CP/MAS parameters see [10], for suspension HR-MAS measurement conditions see [11c]. The signal assignments are based on comparisons with previous phosphine linkers [6a,12], ^{31}P -decoupled, and 2D correlation spectra.

4.1. $(\text{EtO})_2\text{SiCl}_2$ (**1**)

SiCl_4 (8.00 g, 47.09 mmol) was combined with 6.98 g (47.09 mmol) of $(\text{CH}_3)_2\text{Si}(\text{OEt})_2$, and stirred in a sealed tube for 5 h at 165 °C. After distillation with a standard vigreux column (length 16 cm, diameter 1 cm) at ambient pressure, 5.4 g (28.55 mmol) of **1** could be collected at a bath temperature range of 150–160 °C, corresponding to a yield of 60.6%. As a minor impurity $(\text{EtO})_3\text{SiCl}$ could occur in up to 5%.

4.2. $(\text{EtO})_2\text{Si}(\text{CH}_2\text{PPh}_2)_2$ (**2**)

$\text{Ph}_2\text{PCH}_2\text{Li}(\text{TMEDA})$ (**5**) (2.34 g, 7.26 mmol) was suspended in 20 ml of pentane and combined with 0.64 g (3.39 mmol) of $(\text{EtO})_2\text{SiCl}_2$ (**1**) dissolved in 10 ml of pentane. After stirring the reaction mixture for 1 h, it was filtered, and the solvent was partially removed in vacuo. Ligand **2** was obtained in 84.4% yield (1.48 g, 2.86 mmol) as a colorless powder that could be recrystallized from hot pentane. Mp 69 °C. ^1H NMR (acetone-*d*₆, 500.1 MHz): δ 7.43 (t, broad, $^3J(\text{P},\text{H}) = 7.4$ Hz, $^3J(\text{H},\text{H}) = 7.4$ Hz, 8H, H_o), 7.32–7.28 (m, 12H, H_m , H_p), 3.63 (q, 4H, $^3J(\text{H},\text{H}) = 7.0$ Hz, OCH_2), 1.36 (s, broad, 4H, PCH_2), 1.01 (t,

$^3J(\text{H,H}) = 7.0$ Hz, 6H, CH_3). ^{13}C NMR (acetone- d_6 , 125.8 MHz): δ 142.71 (dd, $^1J(\text{P,C}) = 17.0$ Hz, $^5J(\text{P,C}) = 1.7$ Hz, C_i), 134.02 (dd, $^2J(\text{P,C}) = 20.8$ Hz, $^6J(\text{P,C}) = 0.6$ Hz, C_o), 129.80 (s, C_p), 129.69 (virtual m, distance of outer lines: $J(\text{P,C}) = 10.7$ Hz, C_m), 59.72 (t, $^4J(\text{P,C}) = 1.9$ Hz, OCH_2), 19.11 (s, CH_3), 13.76 (dd, $^1J(\text{P,C}) = 31.6$ Hz, $^3J(\text{P,C}) = 3.2$ Hz, PCH_2). ^{31}P NMR (acetone- d_6 , 202.5 MHz) δ -23.29. ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ -15.46 (t, $^2J(\text{P,Si}) = 15.4$ Hz). HR-MS (FAB) m/z (%): 517.1855 ($[\text{M} + \text{H}]^+$, 19.5), calc. 517.1882; 471.1486 ($[\text{M} - \text{OEt}]^+$, 4.16), calc. 471.1463. Elemental Anal. Calc.: C, 69.75; H, 6.63; P, 11.99. Found: C, 69.78; H, 6.71; P, 11.92. ^{31}P CP/MAS of polycrystalline **2**: -22.9/-24.1. ^{31}P CP/MAS of **2i**: δ -25.38.

X-ray data for **2**: $\text{C}_{30}\text{H}_{34}\text{O}_2\text{P}_2\text{Si}$, colorless crystal (irregular plate), dimensions $0.28 \times 0.20 \times 0.05$ mm³, crystal system monoclinic, space group $P2_1/n$, $Z = 4$, $a = 14.572(1)$ Å, $b = 12.183(1)$ Å, $c = 15.963(2)$ Å, $\beta = 104.353(2)^\circ$, $V = 2745.5(5)$ Å³, $\rho = 1.250$ g/cm³, $T = 100(2)$ K, $\theta_{\text{max}} = 26.37^\circ$, radiation Mo $\text{K}\alpha$, $\lambda = 0.71073$ Å, 0.3° ω -scans with CCD area detector, covering a whole sphere in reciprocal space, 24093 reflections measured, 5581 unique ($R_{\text{int}} = 0.055$), 4630 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS [26] based on the Laue symmetry of the reciprocal space, $\mu = 0.23$ mm⁻¹, $T_{\text{min}} = 0.94$, $T_{\text{max}} = 0.99$, structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL (6.12) software package [27], 452 parameters refined, all hydrogen atoms were refined isotropically, goodness-of-fit 1.09 for observed reflections, final residual values $R_1(F) = 0.050$, $wR(F^2) = 0.106$ for observed reflections, residual electron density -0.30 to 0.58 eÅ⁻³.

4.3. (EtO)Si(CH₂PPh₂)₃ (**3**)

$\text{Ph}_2\text{PCH}_2\text{Li}(\text{TMEDA})$ (**5**) (3.02 g, 9.37 mmol) was suspended in 20 ml of pentane and combined with 0.56 g (2.98 mmol) of $(\text{EtO})_2\text{SiCl}_2$ (**1**), dissolved in 10 ml of pentane. After stirring the reaction mixture for 4 h, the colorless precipitate was collected on a frit, and 1.65 g (2.45 mmol) of **3** could be extracted in 82.2% yield as a colorless powder with toluene, and subsequently dried in vacuo. Mp 99 °C. ^1H NMR (acetone- d_6 , 500.1 MHz): δ 7.36–7.32 (m, broad, 12H, H_o), 7.31–7.28 (m, 18H, H_m , H_p), 3.42 (q, $^3J(\text{H,H}) = 7.0$ Hz, 2H, OCH_2), 1.28 (s, broad, 6H, PCH_2), 0.82 (t, $^3J(\text{H,H}) = 7.0$ Hz, 3H, CH_3). ^{13}C NMR (acetone- d_6 , 125.8 MHz): δ 142.57 (d, $^1J(\text{P,C}) = 17.3$ Hz, C_i), 133.97 (virtual dd, distance of outer lines: $J(\text{P,C}) = 23.2$ Hz, C_o), 129.82 (s, C_p), 129.71 (virtual m, distance of outer lines: $J(\text{P,C}) = 14.5$ Hz, C_m), 60.20 (q, $^4J(\text{P,C}) =$

2.3 Hz, OCH_2), 18.95 (s, CH_3), 15.35 (dt, $^1J(\text{P,C}) = 32.2$ Hz, $^3J(\text{P,C}) = 4.0$ Hz, PCH_2). ^{31}P NMR (acetone- d_6 , 121.5 MHz) δ -23.49. ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ 7.29 (q, $^2J(\text{P,Si}) = 15.3$ Hz). HR-MS (FAB) m/z (%): 671.2217 ($[\text{M} + \text{H}]^+$, 33.8), calc. 671.2212; 593.1703 ($[\text{M} + \text{H} - \text{C}_6\text{H}_5]^+$, 49.2), calc. 593.1742. Elemental Anal. Calc.: C, 73.41; H, 6.16; P, 13.85. Found: C, 73.53; H, 6.19; P, 13.76. ^{31}P CP/MAS of polycrystalline **3**: -15.3/-26.9/-46.2. ^{31}P CP/MAS of **3i**: δ -25.04.

X-ray data for **3**: $\text{C}_{41}\text{H}_{41}\text{OP}_3\text{Si}$, colorless crystal (irregular), dimensions $0.26 \times 0.22 \times 0.08$ mm³, crystal system triclinic, space group $P\bar{1}$, $Z = 2$, $a = 11.2457(8)$ Å, $b = 12.1789(9)$ Å, $c = 14.528(1)$ Å, $\alpha = 81.112(2)^\circ$, $\beta = 80.782(1)^\circ$, $\gamma = 67.705(1)^\circ$, $V = 1807.7(2)$ Å³, $\rho = 1.232$ g/cm³, $T = 200(2)$ K, $\theta_{\text{max}} = 28.31^\circ$, radiation Mo $\text{K}\alpha$, $\lambda = 0.71073$ Å, 0.3° ω -scans with CCD area detector, 18531 reflections measured, 8765 unique ($R_{\text{int}} = 0.029$), 6989 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS [26] based on the Laue symmetry of the reciprocal space, $\mu = 0.23$ mm⁻¹, $T_{\text{min}} = 0.94$, $T_{\text{max}} = 0.98$, structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL (6.12) software package [27], 570 parameters refined, the terminal carbon atom at the ethoxy group is disordered over two positions (55:45%), hydrogen atoms at disorder and neighbouring positions were treated using appropriate riding models all other H's were refined isotropically, goodness-of-fit 1.10 for observed reflections, final residual values $R_1(F) = 0.056$, $wR(F^2) = 0.125$ for observed reflections, residual electron density -0.33 to 0.55 eÅ⁻³.

4.4. Si(CH₂PPh₂)₄ (**4**)

$\text{Ph}_2\text{PCH}_2\text{Li}(\text{TMEDA})$ (1.76 g, 5.44 mmol) was dissolved in a mixture of 10 ml pentane and 5 ml THF, and subsequently treated with SiCl_4 (0.23 g, 1.36 mmol). After stirring the reaction mixture for 2 h at RT, the resulting colorless precipitate was filtered, washed with pentane, and dried in vacuo. Compound **4** was thus obtained as a colorless powder in a yield of 64.5% (0.74 g, 0.89 mmol). Mp 157 °C. ^1H NMR (CDCl_3 , 300.1 MHz): δ 7.23 (m, broad, 40H, phenyl-H), 1.01 (s, 8H). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 140.78 (d, broad, $^1J(\text{P,C}) = 14.2$ Hz, C_i), 132.62 (d, $^2J(\text{P,C}) = 20.9$ Hz, C_o), 128.34 (s, C_p), 128.20 (virtual t, distance of outer lines: $J(\text{P,C}) = 6.9$ Hz, C_m), 12.26 (d, broad, $^1J(\text{P,C}) = 32.6$ Hz, PCH_2). ^{31}P NMR (CDCl_3 , 121.5 MHz) δ -23.96. ^{29}Si NMR (CDCl_3 , 99.3 MHz): δ 2.68 (quin, $^2J(\text{P,Si}) = 15.8$ Hz). HR-MS (FAB) m/z (%): 825.2585 ($[\text{M} + \text{H}]^+$, 54.8), calc. 825.2549; 747.2132 ($[\text{M} - \text{C}_6\text{H}_5]^+$, 100.0), calc. 747.2084. ^{31}P CP/MAS of polycrystalline **4**: -29.6.

4.5. $[(EtO)_2Si(CH_2PPh_2)_2]PdCl_2$ (**6**)

To a solution of $(PhCN)_2PdCl_2$ (60 mg, 0.16 mmol) in toluene (8 ml), 82 mg (0.16 mmol) of **2** was added in a dropwise manner. After stirring the mixture for 3 h at RT, about 80% of the solvent was removed and 20 ml of pentane was added. Complex **6** precipitated as a colorless powder, which was collected on a frit, washed with pentane and dried in vacuo to give 94 mg (0.14 mmol) of material, corresponding to a yield of 85.3%. 1H NMR (acetone- d_6 , 300.1 MHz): δ 7.84 (dd, $^3J(P,H) = 12.0$ Hz, $^3J(H,H) = 6.0$ Hz, 8H, H_o), 7.51–7.48 (m, 12H, H_m , H_p), 3.49 (q, 4H, $^3J(H,H) = 7.0$ Hz, OCH_2), 1.87 (dd, $^2J(P,H) = 15.6$ Hz, $^4J(P,H) = 5.7$ Hz, 4H, PCH_2), 0.94 (t, $^3J(H,H) = 7.0$ Hz, 6H, CH_3). ^{13}C NMR (acetone- d_6 , 75.5 MHz): δ 135.36 (virtual m, distance of outer lines: $J(P,C) = 14.4$ Hz, C_o), 134.37 (d, $^1J(P,C) = 57.6$ Hz, C_i), 132.44 (virtual t, distance of outer lines: $J(P,C) = 2.6$ Hz, C_p), 129.61 (virtual m, distance of outer lines: $J(P,C) = 14.6$ Hz, C_m), 59.92 (s, OCH_2), 18.87 (s, CH_3), 13.64 (d, $^1J(P,C) = 24.5$ Hz, PCH_2). ^{31}P NMR (acetone- d_6 , 121.5 MHz) δ 23.40. HR-MS (FAB) m/z (%): 692.0245 ($[M]^+$, 2.0), calc. 692.0215; 659.0538 ($[M - Cl]^+$, 100.0), calc. 659.0531. ^{31}P CP/MAS of **6i**: δ 24.86.

X-ray data for **6**: $C_{30}H_{34}Cl_2O_2P_2PdSi + C_3H_6O$, colorless crystal (prism), dimensions $0.24 \times 0.12 \times 0.08$ mm³, crystal system monoclinic, space group $P2_1/n$, $Z = 4$, $a = 10.515(1)$ Å, $b = 20.817(2)$ Å, $c = 15.597(2)$ Å, $\beta = 96.813(2)^\circ$, $V = 3390.0(6)$ Å³, $\rho = 1.473$ g/cm³, $T = 100(2)$ K, $\theta_{max} = 28.34^\circ$, radiation Mo $K\alpha$, $\lambda = 0.71073$ Å, 0.3° ω -scans with CCD area detector, covering a whole sphere in reciprocal space, 34582 reflections measured, 8391 unique ($R_{int} = 0.036$), 7303 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS [26] based on the Laue symmetry of the reciprocal space $\mu = 0.87$ mm⁻¹, $T_{min} = 0.82$, $T_{max} = 0.93$, structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL (6.12) software package [27], 539 parameters refined, the carbon atoms of one ethoxy group are disordered over two positions (60:40%), hydrogen atoms at disordered groups were treated using appropriate riding models, all other were refined isotropically, goodness-of-fit 1.02 for observed reflections, final residual values $R_1(F) = 0.025$, $wR(F^2) = 0.059$ for observed reflections, residual electron density -0.26 to 0.66 e/Å³.

4.6. $[(EtO)Si(CH_2PPh_2)_3]W(CO)_3$ (**7**)

Ligand **3** (215 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (10 ml) and combined with a suspension of $W(CO)_6$ (112 mg, 0.32 mmol) in CH_2Cl_2 (10 ml). This mixture was irradiated with a UV lamp for 5 h at RT,

and then filtered to remove residual $W(CO)_6$. After removal of the solvent in vacuo 20 ml of toluene was added. Complex **7** could be obtained in 63.8% yield (192 mg, 0.20 mmol) as a pale yellow powder after adding 30 ml of pentane, washing the precipitate with pentane, and drying it in vacuo. 1H NMR ($CDCl_3$, 500.1 MHz): δ 7.42 (t, broad, $^3J(P,H) = ^3J(H,H) = 7.5$ Hz, 12H, H_o), 7.25 (t, $^3J(H,H) = 7.0$ Hz, 6H, H_p), 7.16 (t, $^3J(H,H) = 7.0$ Hz, 12H, H_m), 3.70 (q, $^3J(H,H) = 7.0$ Hz, 2H, OCH_2), 1.78 (d, $^2J(P,H) = 7.0$ Hz, 6H, PCH_2), 1.20 (t, $^3J(H,H) = 7.0$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 211.50 (s, CO), 139.21 (d, $^1J(P,C) = 40.2$ Hz, C_i), 131.77 (virtual m, distance of outer lines: $J(P,C) = 13.0$ Hz, C_o), 129.06 (s, C_p), 128.19 (virtual m, distance of outer lines: $J(P,C) = 9.5$ Hz, C_m), 59.97 (s, OCH_2), 18.18 (s, CH_3), 11.89 (s, broad, PCH_2). ^{31}P NMR ($CDCl_3$, 202.5 MHz) δ -4.59 (s with satellites, $^1J(W,C) = 219.3$ Hz). HR-MS (FAB) m/z (%): 938.1448 ($[M]^+$, 100.0), calc. 938.1496; 910.1398 ($[M - CO]^+$, 36.1), calc. 910.1547; 833.1011 ($[M - CO - C_6H_5]^+$, 16.51), calc. 833.1156. IR (KBr): $\tilde{\nu}$ 1929, 1833 cm⁻¹. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) 256 nm (14682), 282 (11011), 404 (8768). ^{31}P CP/MAS of **7i**: δ -2.9 , -8.4 (4 kHz).

5. Supporting information

Crystallographic data for the structural analyses of **2**, **3**, and **6** has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 260233 for **2**, No. 260234 for **3**, and No. 260235 for **6**.

Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, fax: (int code) +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk, or on the web <http://www.ccdc.cam.ac.uk>.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (SFB 623) and INSTRUCTION AG for financial support, F. Piester for the results of one experiment, and Dr. J. Furrer for valuable advice on suspension NMR spectroscopy.

References

- [1] (a) K.C. Nicolaou, R. Hanko, W. Hartwig (Eds.), Handbook of Combinatorial Chemistry, vols. 1, 2, Wiley-VCH, Weinheim, 2002; (b) S.R. Wilson, A.W. Czarnik (Eds.), Combinatorial Chemistry, John Wiley & Sons, New York, 1997; (c) W. Bannworth, E. Felder (Eds.), Combinatorial Chemistry, Wiley-VCH, Weinheim, 2000;

- (d) G. Jung, *Combinatorial Chemistry*, Wiley-VCH, Weinheim, 1999.
- [2] (a) P. Seneci, *Solid-Phase Synthesis and Combinatorial Technologies*, John Wiley & Sons, New York, 2000;
(b) F. Zaragoza Dörwald, *Organic Synthesis on Solid Phase*, Wiley-VCH, Weinheim, 2000.
- [3] (a) E.F. Vansant, P. VanDer Voort, K.C. Vrancken, *Characterization and Chemical Modification of the Silica Surface*, Elsevier, Amsterdam, 1995;
(b) R.P.W. Scott, *Silica Gel and Bonded Phases*, John Wiley and Sons, New York, 1993;
(c) G.A. Subramanian, *Practical Approach to Chiral Separations by Liquid Chromatography*, VCH, Weinheim, 1994;
(d) R.K. Iler, *The Chemistry of Silica*, John Wiley, New York, 1979.
- [4] (a) F.R. Hartley, *Supported Metal Complexes*, D. Reidel Publishing Co., Dordrecht, Holland, 1985, and literature cited therein;
(b) J.H. Clark, *Supported Reagents in Organic Reactions*, VCH, Weinheim, 1994;
(c) J.A. Gladysz (ed.), *Special Issue on Recoverable Catalysts and Reagents*, *Chem. Rev.*, 2002, 102, No. 10;
(d) D.E. DeVos, I.F.J. Vankelecom, P.A. Jacobs (Eds.), *Chiral Catalyst Immobilization and Recycling*, Wiley, VCH, Weinheim, 2000.
- [5] For some representative examples see:
(a) H. Gao, R.J. Angelici, *Organometallics* 18 (1999) 989;
(b) M. Jia, W.R. Thiel, *Chem. Commun.* (2002) 2392;
(c) Z. Lu, E. Lindner, H.A. Mayer, *Chem. Rev.* 102 (2002) 3543;
(d) H. Gao, R.J. Angelici, *J. Am. Chem. Soc.* 119 (1997) 6937;
(e) P. McMorn, G.J. Hutchings, *Chem. Soc. Rev.* 33 (2004) 108.
- [6] (a) C. Merckle, S. Haubrich, J. Blümel, *J. Organomet. Chem.* 627 (2001) 44;
(b) C. Merckle, J. Blümel, *Adv. Synth. Catal.* 345 (2003) 584;
(c) C. Merckle, J. Blümel, *Top. Catal.* 34 (2005) 5.
- [7] (a) K.D. Behringer, J. Blümel, *Inorg. Chem.* 35 (1996) 1814;
(b) S. Reinhard, P. Šoba, F. Rominger, J. Blümel, *Adv. Synth. Catal.* 345 (2003) 589.
- [8] S. Reinhard, K.D. Behringer, J. Blümel, *New J. Chem.* 27 (2003) 776.
- [9] (a) A.T. Bell, A. Pines (Eds.), *NMR Techniques in Catalysis*, Marcel Dekker, Inc., New York, 1994;
(b) G. Engelhardt, D. Michel, *High-Resolution solid-state NMR of silicates and zeolites*, John Wiley & Sons, New York, 1987;
(c) C.A. Fyfe, *Solid-State NMR for Chemists*, C.F.C. Press, Guelph, Canada, 1983;
- (d) E.O. Stejskal, J.D. Memory, *High resolution NMR in the solid state*, Oxford University Press, New York, 1994;
(e) J.J. Fitzgerald (Ed.), *Solid-State NMR spectroscopy of inorganic materials*, American Chemical Society, Washington, DC, 1999;
(f) M.J. Duer, *Introduction to Solid-State NMR Spectroscopy*, Blackwell Publishing, Oxford, 2004.
- [10] S. Reinhard, J. Blümel, *Magn. Reson. Chem.* 41 (2003) 406.
- [11] (a) K.D. Behringer, J. Blümel, *Z. Naturforsch.* 50b (1995) 1723;
(b) C. Merckle, J. Blümel, *Chem. Mater.* 13 (2001) 3617;
(c) T. Posset, F. Rominger, J. Blümel, *Chem. Mater.* 17 (2005) 586.
- [12] G. Tsiavaliaris, S. Haubrich, C. Merckle, J. Blümel, *Synlett* (2001) 391.
- [13] J. Blümel, *J. Am. Chem. Soc.* 117 (1995) 2112.
- [14] K.D. Behringer, J. Blümel, *J. Liquid Chromatogr.* 19 (1996) 2753.
- [15] K.D. Behringer, J. Blümel, *J. Chem. Soc., Chem. Commun.* (1996) 653.
- [16] (a) J. Blümel, *Inorg. Chem.* 33 (1994) 5050;
(b) J. Sommer, Y. Yang, D. Rambow, J. Blümel, *Inorg. Chem.* 43 (2004) 7561.
- [17] F. Piester, R. Fetouaki, M. Bogza, T. Oeser, J. Blümel, *Chem. Commun.* (2005) 1481.
- [18] (a) T.A. Betley, J.C. Peters, *Angew. Chem.* 115 (2003) 2487;
(b) J.C. Thomas, J.C. Peters, *Inorg. Chem.* 42 (2003) 5055.
- [19] S. Herold, A. Mezzetti, L.M. Venanzi, A. Albinati, F. Lianza, T. Gerfin, V. Gramlich, *Inorg. Chim. Acta* 235 (1995) 215.
- [20] T.W. Hayton, B.O. Patrick, P. Legzdins, *Organometallics* 23 (2004) 657.
- [21] L. Ropartz, K.J. Haxton, D.F. Foster, R.E. Morris, A.M.Z. Slawin, D.J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.* (2002) 4323.
- [22] D.E. Hendriksen, A.A. Oswald, G.B. Ansell, S. Leta, R.V. Kastrup, *Organometallics* 8 (1989) 1153.
- [23] D.J. Peterson, *J. Organomet. Chem.* 8 (1967) 199.
- [24] L.N. Parshina, L.A. Oparina, M.Y. Khil'ko, B.A. Trofimov, *J. Organomet. Chem.* 665 (2003) 246.
- [25] (a) R.K. Harris, *Can. J. Chem.* 42 (1964) 2275;
(b) W.H. Hersh, P. Xu, B. Wang, J.W. Yom, C.K. Simpson, *Inorg. Chem.* 35 (1996) 5453;
(c) W.H. Hersh, *J. Chem. Educ.* 74 (1997) 1485.
- [26] G.M. Sheldrick, *Program SADABS V2.03 for Absorption Correction*, Bruker Analytical X-ray Division, Madison, WI, 2001.
- [27] G.M. Sheldrick, *Software Package SHELXTL V6.12 for Structure Solution and Refinement*, Bruker Analytical X-ray Division, Madison, WI, 2001.