

New Bifunctional Chelating Phosphine Ligands for Immobilization of Metal Complexes on Oxidic Supports

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Abstract: The immobilization of transition metal complexes by bifunctional phosphines containing ethoxysilane groups is of widespread interest. Especially desirable are chelating phosphines, since they can reduce leaching of the metal complexes. Easy syntheses of the bifunctional chelating ethoxysilane phosphines $\text{Ph}_2\text{PCH}_2\text{CH}[\text{OSi}(\text{OEt})_3]\text{CH}_2\text{PPh}_2$, and $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{P}(\text{CH}_2)_y\text{Si}(\text{OEt})_3$ ($x = 2, 3$; $y = 2, 3$), and the nickel derivative $(\text{CO})_2\text{Ni}[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{Si}(\text{OEt})_3]$ are reported. The ethoxysilane groups present convenient handles for immobilization on oxidic supports.

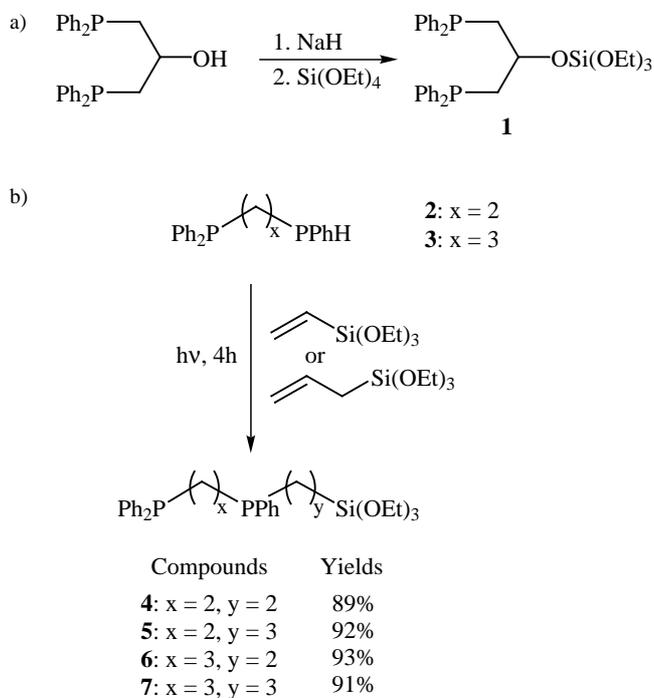
Key words: immobilized catalysts, bifunctional ligands, chelating ligands, silica support, solid-state NMR

Immobilized molecular catalysts are of growing commercial and academic interest, because they can combine the advantages of heterogeneous and homogeneous catalysts.^{1,2} They are easy to separate from the reaction mixtures, and recycle, are much easier to tailor and fine tune than heterogeneous catalysts, and remain as active and selective as their homogeneous analogs.

For some time our group, like others, has pursued this idea² by immobilizing homogeneous catalysts on silica supports via bifunctional linkers like $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$. Silica is an inexpensive material, and its reaction with ethoxysilane groups has been studied in detail.³ Suspension NMR⁴ and multinuclear solid-state NMR^{2,3} have served as powerful tools for investigating the amorphous solid materials. At the present state we are able to immobilize any arbitrary phosphine complex on the silica surface via covalent bonding, cleanly and in a well-defined manner.

However, when metal complexes with two bifunctional monodentate phosphines are treated with silica under standard immobilization conditions, only one usually becomes attached. In other words, only a small fraction of the metal is bound in a chelating manner.⁵ This might be one reason for leaching during the catalytic reaction. Furthermore, the metal centers can detach from the phosphine linkers, if the catalyst is recycled.⁶ In order to attach the complexes firmly to the oxidic support, we therefore sought to synthesize chelating phosphine ligands, which still contain the ethoxysilane group. Only few ligands of this type are known,⁷ and their syntheses are mostly very tedious, and need multiple steps.

Our initial attempt to synthesize the ether phosphine $\text{Ph}_2\text{PCH}_2\text{CH}[\text{O}(\text{CH}_2)_3\text{Si}(\text{OEt})_3]\text{CH}_2\text{PPh}_2$ starting from deprotonated $\text{Ph}_2\text{PCH}_2\text{CHOHCH}_2\text{PPh}_2$ and $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ failed, as nucleophilic attack at silicon always took place even under varied reaction conditions, yielding the ill-defined, partly crosslinked $\text{Ph}_2\text{PCH}_2\text{CH}[\text{OSi}(\text{OEt})_2(\text{CH}_2)_3\text{Cl}]\text{CH}_2\text{PPh}_2$. This reaction path could be proved by using $\text{Si}(\text{OEt})_4$ with the alcoholate, which led to our first useful chelating ligand $\text{Ph}_2\text{PCH}_2\text{CH}[\text{OSi}(\text{OEt})_3]\text{CH}_2\text{PPh}_2$ (**1**).⁸

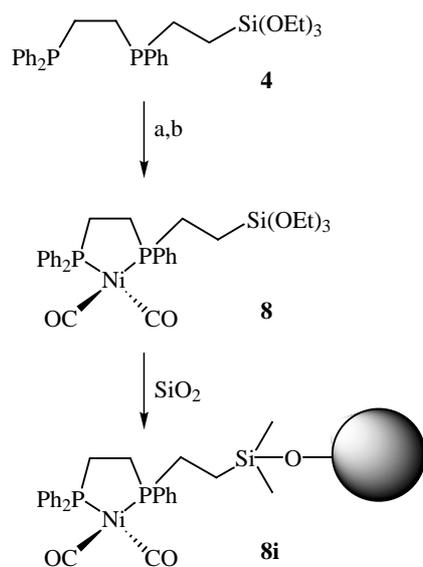


Scheme 1 a) Synthesis of **1** (yield 63%); b) synthesis of ligands **4** to **7** as described in note 8.

However, we were also interested in preparing unsymmetric chelating ligands, because these have displayed interesting features in catalysis, as compared to their symmetric analogs.⁹ Especially Achiwa's important work on highly efficient chiral bisphosphine ligands in rhodium-catalyzed asymmetric hydrogenations has to be mentioned.⁹ As shown in Scheme 1, we applied a strategy used previously,^{2,10} namely the photochemical addition of sec-

ondary phosphines to olefinic substituents in silanes. The raw yields of **4** to **7** were quantitative, and the compounds were obtained analytically pure and in excellent yields of about 90% after Kugelrohr distillation (Scheme 1).⁸ Educts **2** and **3** could conveniently be synthesized in high yields by a literature procedure,¹¹ and distilled in a Kugelrohr oven.

The reaction of Ni(cod)₂ with **4** and CO lead to the successful preparation of the nickel complex **8** (Scheme 2), which shows that the proper diphosphos bite angle¹² is retained. This recipe⁸ is an improvement over earlier routes using toxic Ni(CO)₄.



Scheme 2 Synthesis of nickel complex **8** as described in note 8. a) Ni(cod)₂; b) CO.

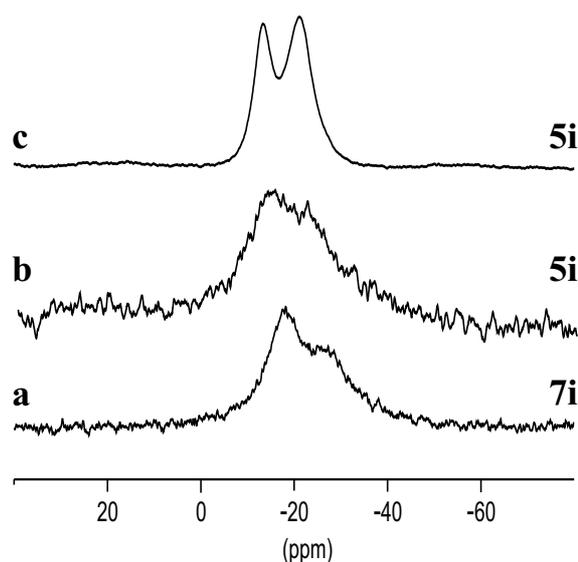


Figure a, b: 121.49 MHz ³¹P suspension NMR⁴ spectra of immobilized ligands **7i** and **5i** in THF. c: 161.97 MHz ³¹P CP/MAS NMR spectrum² of immobilized compound **5i** ($\nu_{\text{rot}} = 8$ kHz).

All compounds **4** to **8** were immobilized on silica to give materials **4i** to **8i**, according to the procedure described earlier.^{2,3} The success of the clean immobilization was proved by the ³¹P CP/MAS NMR spectra shown in the Figure. The ³¹P NMR chemical shifts of **4i** to **8i** are about the same as for **4** to **8**. Especially interesting is the question, whether the two phosphine moieties will display different behavior during catalysis. From an analytical point of view, this should be easy to clarify, because the two phosphine resonances are far enough apart to allow their separation even under the low-resolution conditions of suspension NMR spectroscopy (Figure).⁴ Interestingly, the greater mobility of the Ph₂P group as compared to the PPh moiety, which is closer to the support surface, is already obvious in the spectra. The low-field resonance of the bound ligands, e.g. **5i** and **7i**, is the narrower one due to reduced chemical shift anisotropy. Investigating this effect systematically, and testing the catalytic activity of **8** and its analogs with ligands **5** to **7** as well as their immobilized versions are ongoing research interests in our laboratory.¹³

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- (8) All the compounds **1** to **8** and **4i** to **8i** were fully characterized. The ¹³C and ¹H NMR signal assignments are based upon

former results,^{2,3,13} as well as $^{13}\text{C}\{^{31}\text{P}\}$, ^1H -, ^1H -, ^1H -, and ^1H -COSY spectra. Syntheses and data given for selected compounds:

Compound 1: EA calc. for $\text{C}_{33}\text{H}_{40}\text{P}_2\text{SiO}_4$: 67.10 (C), 6.83 (H), 10.49 (P), found 67.54 (C), 6.79 (H), 10.28 (P); ^{31}P NMR (121.49 MHz, C_6D_6): δ -23.19; ^1H NMR (300.13 MHz, C_6D_6): δ 7.42 - 7.55 (m, 8H, H_o), 7.11 - 6.95 (m, 12H, H_m , H_p), 4.47 (quint., 1H, CHOSi , $^3J_{\text{H,H}}$ 6.5 Hz), 3.82 (quart., 6H, OCH_2 , $^3J_{\text{H,H}}$ 7.0 Hz), 2.80 (d, 4H, PCH_2 , $^3J_{\text{H,H}}$ 6.5 Hz), 1.12 (t, 9H, CH_3 , $^3J_{\text{H,H}}$ 7.0 Hz); ^{13}C NMR (75.47 MHz, C_6D_6): δ 140.38 (d, C_i , $^1J_{\text{P,C}}$ 13.8 Hz), 140.36 (d, C_i , $^1J_{\text{P,C}}$ 14.5 Hz), 134.08 (d, C_o , $^2J_{\text{P,C}}$ 19.4 Hz), 133.87 (d, C_o , $^2J_{\text{P,C}}$ 19.4 Hz), 129.33 (d, C_m , $^3J_{\text{P,C}}$ 6.9 Hz), 129.19 (s, C_p), 70.69 (t, CHO , $^2J_{\text{P,C}}$ 17.6 Hz), 60.10 (s, OCH_2), 39.66 (dd, PCH_2 , $^1J_{\text{P,C}}$ 15.2 Hz, $^3J_{\text{P,C}}$ 9.0 Hz), 19.06 (s, CH_3); HR-MS [EI^+] 590.2184 (calc. 590.2171).

Synthesis of compounds **4** to **7**:

Compounds **4** to **7** have been synthesized by irradiating **2** or **3** together with 1.2 equivalents of vinyl- or allylsilane with UV light in a standard irradiation apparatus with stirring and water cooling. The surplus of starting silane was then removed in a Kugelrohr oven at 120 °C under reduced pressure (0.02 mbar).

Compound 4: EA calc. for $\text{C}_{28}\text{H}_{38}\text{P}_2\text{SiO}_3$: 65.60 (C), 7.47 (H), found 65.79 (C), 7.68 (H); ^{31}P NMR (121.49 MHz, C_6D_6): δ -11.90 (d, PPh_2 , $^3J_{\text{P,P}}$ 27.8 Hz), -12.80 (d, PPh , $^3J_{\text{P,P}}$ 27.8 Hz); ^1H NMR (300.13 MHz, C_6D_6): δ 7.44 - 7.41 (m, 2H, H_o , PPh), 7.36-7.29 (m, 4H, H_o , PPh_2), 7.06 - 7.03 (m, 3H, H_m , H_p , PPh), 7.00 - 6.98 (m, 6H, H_m , H_p , PPh_2), 3.69 (quart., 6H, OCH_2 , $^3J_{\text{H,H}}$ 7.0 Hz), 2.23 - 2.04 (m, 2H, Ph_2PCH_2), 1.93 - 1.81 (m, 4H, $\text{CH}_2\text{PPhCH}_2$), 1.09 (t, 9H, CH_3 , $^3J_{\text{H,H}}$ 7.0 Hz), 0.87 - 0.71 (m, 2H, CH_2Si); ^{13}C NMR (125.77 MHz, C_6D_6): δ 139.44 (d, C_i , PPh_2 , $^1J_{\text{P,C}}$ 15.1 Hz)*, 139.13 (d, C_i , PPh_2 , $^1J_{\text{P,C}}$ 15.1 Hz)*, 138.80 (d, C_i , PPh , $^1J_{\text{P,C}}$ 17.9 Hz)*, 133.19 (d, C_o , PPh_2 , $^2J_{\text{P,C}}$ 18.8 Hz)^o, 132.98 (d, C_o , PPh_2 , $^2J_{\text{P,C}}$ 18.8 Hz)^o, 132.91 (d, C_o , PPh , $^2J_{\text{P,C}}$ 17.9 Hz)^o, 128.90 (s, C_p , PPh)', 128.68 (d, C_m , PPh_2 , PPh , $^3J_{\text{P,C}}$ 6.6 Hz), 128.56 (s, C_p , PPh_2)', 58.49 (s, OCH_2), 24.48 (t, PPh_2CH_2 , $^1J_{\text{P,C}} = ^2J_{\text{P,C}}$ 14.6 Hz)"', 24.07 (t, CH_2PPh , $^1J_{\text{P,C}} = ^2J_{\text{P,C}}$ 16.0 Hz)"', 21.10 (d, $\text{CH}_2\text{CH}_2\text{Si}$, $^1J_{\text{P,C}}$ 15.1 Hz), 18.52 (s, CH_3), 6.57 (d, CH_2Si , $^2J_{\text{P,C}}$ 10.4 Hz); *,^o,',",[#], interchangeable assignments. MS [Cl^+] M^+ 513.3.

Synthesis of compound **8**:

$\text{Ni}(\text{cod})_2$ (124 mg, 0.45 mmol) was dissolved in 10 mL of dry and oxygen free toluene, and cooled to -30 °C. Ligand **4** (214 mg, 0.42 mmol) was dissolved in 5 mL of toluene and added slowly via syringe to the $\text{Ni}(\text{cod})_2$ solution. While stirring for 30 min. at -30 °C, the color of the solution changed from yellow to orange. Then, CO was bubbled into the reaction mixture for 2 h, and the solution turned yellow again. After the cooling bath was removed and all volatile substances were distilled off in vacuo, compound **8** was obtained in nearly quantitative yield (96%, 272 mg, 0.43 mmol).

Compound 8: EA calc. for $\text{C}_{30}\text{H}_{38}\text{P}_2\text{SiO}_3\text{Ni}$: 57.44 (C), 6.11 (H), 9.87 (P), found 57.68 (C), 6.38 (H), 9.05 (P); ^{31}P NMR (121.49 MHz, C_6D_6): δ 52.02 (d, PPh , $^3J_{\text{P,P}}$ 37.9 Hz), 47.56 (d,

PPh_2 , $^3J_{\text{P,P}}$ 37.9 Hz); ^1H NMR (300.13 MHz, C_6D_6): δ 7.72 (m, 2H, H_o , PPh), 7.64 (m, H_o , PPh_2), 7.51 (m, H_o , PPh_2), 7.05 - 6.95 (m, 9H, H_m , H_p), 3.73 (quart., 6H, OCH_2 , $^3J_{\text{H,H}}$ 7.0 Hz), 2.23 (m, 2H, $\text{PPh}_2\text{CH}_2\text{CH}_2$), 1.90 (m, 2H, PPh_2CH_2), 1.61 (m, 2H, $\text{CH}_2\text{CH}_2\text{Si}$), 1.11 (t, 9H, CH_3 , $^3J_{\text{H,H}}$ 7.0 Hz), 0.86 (m, 2H, CH_2Si); ^{13}C NMR (125.77 MHz, C_6D_6): δ 202.30 (t, CO , $^2J_{\text{P,C}}$ 3.5 Hz), 202.18 (t, CO , $^2J_{\text{P,C}}$ 5.2 Hz), 137.94 (dd, C_i , PPh , $^1J_{\text{P,C}}$ 26.0 Hz, $^3J_{\text{P,C}}$ 5.2 Hz)*, 137.67 (dd, C_i , PPh_2 , $^1J_{\text{P,C}}$ 25.3 Hz, $^3J_{\text{P,C}}$ 5.2 Hz)*, 136.61 (dd, C_i , PPh_2 , $^1J_{\text{P,C}}$ 21.8 Hz, $^3J_{\text{P,C}}$ 5.9 Hz)*, 132.53 (d, C_o , PPh , $^2J_{\text{P,C}}$ 14.5 Hz)^o, 132.50 (d, C_o , PPh_2 , $^2J_{\text{P,C}}$ 12.5 Hz)^o, 132.14 (d, C_o , PPh_2 , $^2J_{\text{P,C}}$ 13.8 Hz)^o, 129.96 (d, C_p , PPh , $^4J_{\text{P,C}}$ 2.1 Hz)', 129.59 (d, C_p , PPh_2 , $^4J_{\text{P,C}}$ 2.1 Hz)', 129.37 (d, C_p , PPh_2 , $^4J_{\text{P,C}}$ 2.1 Hz)', 128.81 (d, C_m , PPh_2 , $^3J_{\text{P,C}}$ 6.2 Hz)"', 128.73 (d, C_m , PPh_2 , $^3J_{\text{P,C}}$ 6.2 Hz)"', 128.65 (d, C_m , PPh , $^3J_{\text{P,C}}$ 9.0 Hz)"', 58.65 (s, OCH_2), 29.78 (dd, PPh_2CH_2 , $^1J_{\text{P,C}}$ 26.0 Hz, $^2J_{\text{P,C}}$ 21.1 Hz)[#], 28.10 (t, CH_2PPh , $^1J_{\text{P,C}} = ^2J_{\text{P,C}}$ 22.1 Hz)[#], 25.50 (dd, $\text{CH}_2\text{CH}_2\text{Si}$, $^1J_{\text{P,C}}$ 15.22 Hz, $^3J_{\text{P,C}}$ 4.8 Hz), 18.55 (s, CH_3), 5.87 (d, CH_2Si , $^2J_{\text{P,C}}$ 1.4 Hz); *,^o,',",[#], interchangeable assignments; IR (KBr): $\nu(\text{CO})$ 1998, 1942 cm^{-1} .

Immobilization Procedure:

All the ligands **4** to **7** and the nickel complex **8** have been immobilized on silica (Merck silica 40, specific surface area 750 m^2/g , particle size 70 to 230 mesh, average pore diameter 40 Å, predried at 600 °C in vacuo) to give **4i** to **8i** by stirring an excess of the molecular compounds with the support material in toluene at 60 °C for about 5 hours.² After washing twice with toluene, and twice with THF, the surface coverages were determined by weighing back the molecular compounds after removing the solvents from the supernatant solutions.³ For suspension NMR the THF slurries were used directly, for solid-state NMR the material was dried in vacuo at room temperature. All immobilized species were checked by solid-state NMR and IR spectroscopy. E.g.: IR of **8i** (KBr): $\nu(\text{CO}) = 2007$ and 1951 cm^{-1} .

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