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# POSSphites—monophosphites derived from incompletely condensed silsesquioxanes

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**Abstract**—A straightforward three-step synthetic route is followed to obtain nanostructured silsesquioxane based monophosphite compounds **1**–**3**, which we named POSSphites. These compounds, derived from ($c$-$C_5H_9)_7Si_7O_9(OH)_3$ and commercially available phenol derivatives, differ mainly in the steric bulk around the phosphorus atom. Preliminary results in the rhodium-catalyzed hydroformylation of 1-octene exemplify the use of these ligands for homogeneous catalysis. High activities, with a turnover frequency of up to 5000 $h^{-1}$ were obtained. Ligands **1**–**3** are the first silsesquioxane derived monophosphite ligands to be successfully applied in homogeneous catalysis.

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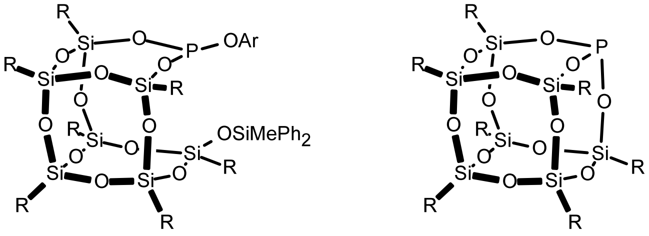
The hydroformylation of alkenes using rhodium complexes is the most prominent example of a homogeneously catalyzed reaction performed on a large industrial scale.[1] Diphosphite ligands have been studied intensively for this reaction,[2] but monophosphites have also received attention.[3] Rhodium complexes with bulky ligands of this latter type have been shown to be highly active catalysts for hydroformylation which in some cases can also convert internal double bonds to the desired linear aldehyde.[4]

Polyhedral oligosilsesquioxanes (POSS) have been studied extensively for a number of years, either as homogeneous models for silica supports,[5] as building blocks for inorganic or hybrid materials[6] or as ligand backbones for (transition) metal complexes.[7] However limited attention has been paid to the synthesis and application of silsesquioxane based phosphorus containing ligands. The few systems reported so far deal with peripheral functionalization of (dendritic) silsesquioxanes with phosphorus moieties, tethered by various (alkyl) spacers.[8]

We were interested to see whether silsesquioxanes could be valuable as a backbone for the synthesis of monodentate phosphorus π-acceptor ligands. We could thereby make use of the fact that silsesquioxanes exhibit electron-withdrawing character, similar to silica.[9] To illustrate the applicability of these ligands in homogeneous catalysis, we have chosen the Rh-catalyzed hydroformylation of 1-octene. We pursued the synthesis of monophosphite compounds **1**–**3**, which we term POSSphites. In these compounds, the phosphorus atom is built into the silsesquioxane framework and the degree of steric bulk can be varied. To establish an initial structure–activity relationship we included compound **4** in the study which was previously reported but without use in catalysis (Fig. 1).[10]

Starting from the incompletely condensed silsesquioxane trisilanol $(R)_7Si_7O_9(OH)_3$[11] ($R = c$-$C_5H_9$), the



**1-3**

**4**

**Figure 1.** Schematic representation of the silsesquioxane compounds used. **1**–**3**: R = cyclopentyl; Ar = phenyl (**1**), 3,5-di-*tert*-butylphenyl (**2**), 1-naphthyl (**3**). **4**: R = cyclohexyl.

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*Keywords*: silsesquioxanes; phosphite; rhodium; phosphorus ligand; homogeneous catalysis; hydroformylation.

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monophosphite compounds **1**–**3** were synthesized in three steps and obtained in good yield. After initial monosilylation of the trisilanol,[12] the resulting disilanol was reacted with $PCl_3$ to generate a phosphorochloridite functionalized silsesquioxane which was converted in situ into the desired monophosphite by reaction with the appropriate phenol under basic conditions (Scheme 1).[13]

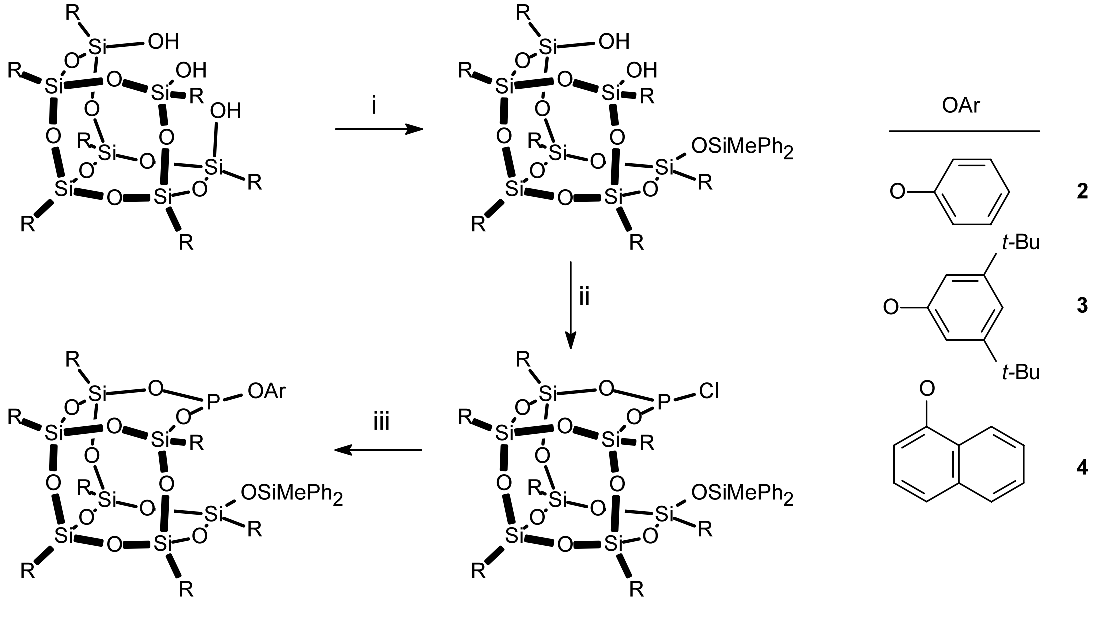
This is different from the synthesis of compound **4**, where the silsesquioxane trisilanol $(R)_7Si_7O_9(OH)_3$ ($R = c\text{-}C_6H_{11}$), is corner-capped with the phosphorus atom by reaction with $PCl_3$. Remarkably, attempts to prepare an analogue of the monophosphites **1**–**3** with $R = c\text{-}C_6H_{11}$ or of **4** with $R = c\text{-}C_5H_9$ met with complications.

The appropriate regions of the $^{13}C$ and $^{29}Si$ NMR spectra of **1**–**3** clearly demonstrate the incorporation of the phosphorus atom into the silsesquioxane skeleton for each of the novel monophosphites. The 2:2:1:1:1 ratio of the signals for the *ipso*-carbons of the organic side group on the silicon corner-atoms remains but with chemical shifts of 0.1–0.5 ppm compared to the monosilylated starting material while the $^{29}Si$ NMR spectrum shows the same pattern, indicative of a structure where the two remaining silanols are attached to a phosphorus atom (Fig. 2).

In an attempt to compare reactivity and electron-withdrawing character of phosphites derived from silsesquioxanes with phosphites based on simple siloxanes, disilanol $(HO)Si(Ph)_2OSi(Ph)_2(OH)$ **5** was selected as the backbone for the preparation of such a compound. Synthesis of the corresponding phosphite, following the same procedure as for **2**, however, failed (Scheme 2). Further investigations and comparison with literature showed that starting compound **A** had a completely different electronic character, resulting in low reactivity.[14] Therefore, the commercially available tris-(*tert*-butyldimethylsilyl)phosphite **5** was chosen as a reference compound.

In order to get a first impression on the behavior of these novel ligands under catalytic conditions we studied the rhodium-catalyzed hydroformylation of 1-octene (Scheme 3). The catalysis was carried out under standard conditions, at 20 bar of syngas (1:1) and a reaction temperature of 80°C.

With monophosphite **1** the catalytic system showed very high activity with a turnover frequency of around 5000 $h^{-1}$ and a conversion of 30% after 15 min (entry 1). Even when increasing the substrate to catalyst ratio, the activity remained nearly constant, indicative of a stable catalytic complex (entry 2). The selectivity to the linear aldehyde nonanal was moderate with a linear to branched ratio of 2.1, as expected for a monophosphite. Both ligands **2** and **3** were applied, to study the effect of steric bulk around the phosphorus center on the catalytic activity. The Rh-complexes of these ligands were less active, as is evidenced by the lower turnover frequencies of 2500 and 2200 $h^{-1}$, respectively (entries 3 and 4). The regioselectivity however did not change. This led us to conclude that no mono-ligated complexes are formed with these ligands. Interestingly, under these conditions the reference material **4** showed no catalytic activity at all, even after 1 h (entry 5). At the moment we have no decisive explanation why this reference compound shows virtually no activity. It might originate from unfavorable coordination to the metal center, arising from constraints in the ligand structure, such as a large Tolman angle.[10] We are currently investigating this in more detail. Also the simple silylphosphite **5** showed little activity under these conditions (entry 6), probably due to the electronic character of the ligand which prevents favourable coordination to the rhodium atom (Table 1).



**Scheme 1.** Synthetic route to compounds **1**–**3**: *Reagents and conditions*: (i) $ClSiMePh_2$, $NEt_3$, THF, 1 h; (ii) $PCl_3$, $NEt_3$, THF, −15°C, 30 min; (iii) desired phenol, THF, −78°C, 15 min, then rt, 16 h.

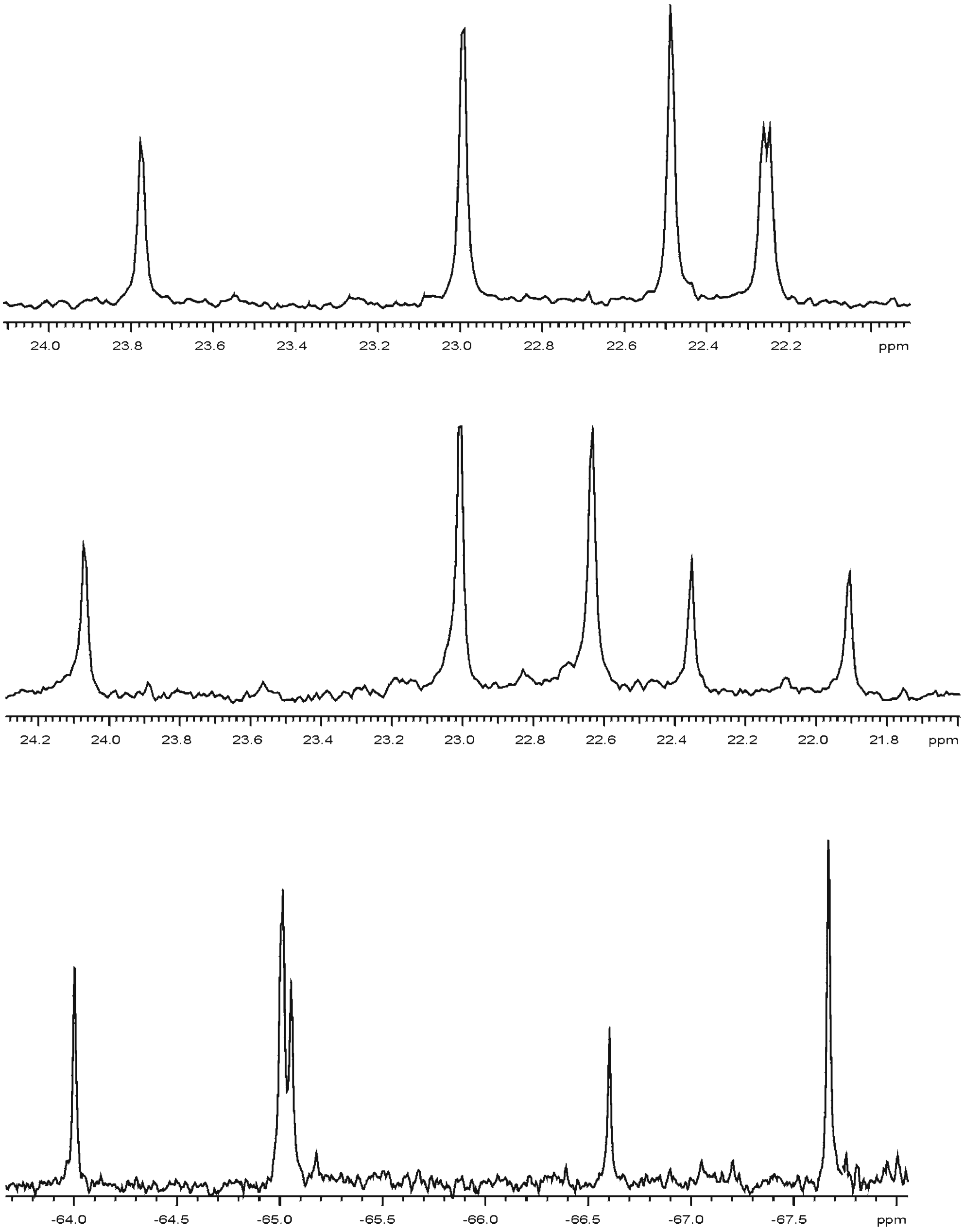
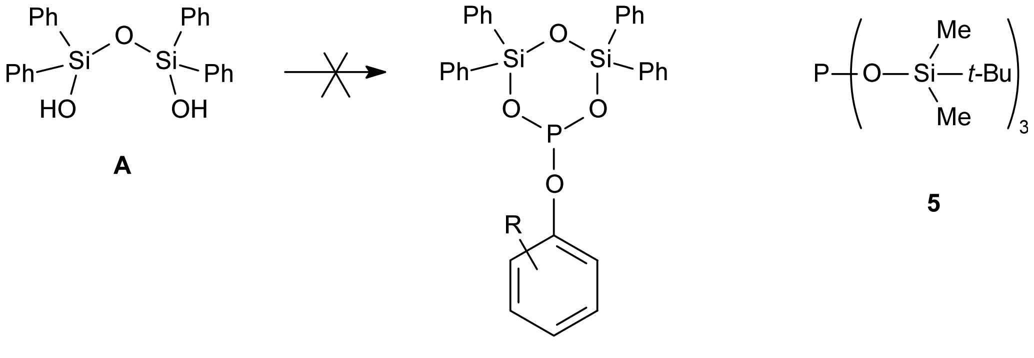
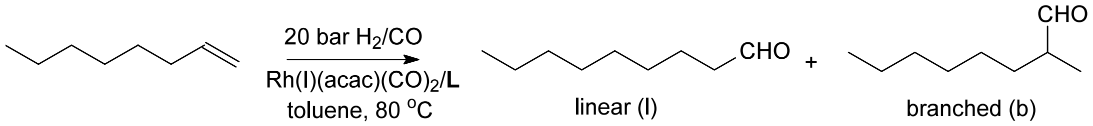


**Figure 2.** $^{13}$C NMR spectra of ($c$-$C_5H_9)_7Si_7O_9(OH)_2(OSiMePh_2)$ (top) and compound **1** (middle); $^{29}$Si NMR spectrum of **1** (bottom).



**Scheme 2.**



**Scheme 3.**

**Table 1.** Rhodium catalyzed hydroformylation of 1-octene using monophosphite ligands **1**–**5**[a]

| Entry | Ligand | Time (min) | S/Rh ratio | Conversion [%][b] | Selectivity aldehydes [%][b] | l/b ratio[b] | TOF[c] |
|---|---|---|---|---|---|---|---|
| 1 | **1** | 15 | 4000 | 31.5 | 94.5 | 2.2 | 5000 |
| 2 | **1** | 15 | 8000[d] | 14.5 | 95.5 | 2.1 | 4500 |
| 3 | **2** | 20 | 4000 | 22.9 | 94.4 | 2.1 | 2500 |
| 4 | **3** | 20 | 4000[e] | 17.8 | 94.8 | 2.1 | 2200 |
| 5 | **4** | 60 | 4000 | <1%[f] | – | – | – |
| 6 | **5** | 20 | 4000 | 2.2 | 31.9 | 2.2 | 260 |

[a] Reaction conditions: 1-octene (31.0 mmol), decane (12.5 mmol), toluene (12.7 mL); $p=20$ bar $CO/H_2$ (1:1); $T=80°C$; $[Rh(acac)(CO)_2]=0.39$ mM; ligand:Rh = 10:1.

[b] Determined by GC analysis.

[c] Turnover frequency, defined as (mol octene converted) (mol rhodium)$^{-1}$ hour$^{-1}$.

[d] $[Rh(acac)(CO)_2]=0.20$ mM.

[e] Ligand:Rh = 5:1.

[f] Below detection limit.

The great potential of phosphites in hydroformylation catalysis is based on the strong π-acceptor character of the phosphorus atoms induced by the surrounding oxygen atoms. From our results we conclude that Rh-catalysts with monophosphite ligands incorporated in a silsesquioxane framework show similar catalytic activities to other monophosphites, although the regioselectivities under non-optimized conditions are somewhat lower.[3,4]

In summary, we have described the synthesis of three new monophosphites **1**–**3** based on an incompletely condensed silsesquioxane framework. Rhodium catalysts containing these ligands show high activities in the hydroformylation of 1-octene, with turnover frequencies up to 5000 h$^{-1}$. The selectivity under non-optimized conditions is moderate at l/b ratios of around 2. We are currently expanding the scope of P-containing ligands based on silsesquioxane backbones, including bulky electron-withdrawing mono- and diphosphites and diphosphinites[15] as well as using dendritic POSS skeletons for continuous catalysis.

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13. Synthesis of compounds **1**–**3**, illustrated for compound **1**: To a solution of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMePh_2)$ (1.76 g, 1.64 mmol) in 25 mL THF was added $NEt_3$ (0.83 g, 8.20 mmol). At −15°C $PCl_3$ (236 mg, 1.72 mmol) was added dropwise by syringe. After stirring for 1 h at rt, the solution was cooled to −78°C and a solution of phenol (162 mg, 1.72 mmol) in 5 mL THF was added dropwise. Subsequently, 5 mL of THF was added via the same syringe and the solution was allowed to warm up to rt overnight. The solvent was removed in vacuo and 10 mL hexanes added to precipitate salts. After filtration the solution was concentrated by removal of solvents to leave 1.74 g (89%, 1.46 mmol) of a turbid colorless oil, that solidified upon standing, of the pure product. $^1$H NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.63 (dd, $J_1=7.3$ Hz, $J_2=2.2$ Hz), 7.31 (m), 7.11 (t), 6.95 (t), 6.80 (d, $J=8.8$ Hz), 1.77 (br m $C_5H_9$), 1.58 (br m $C_5H_9$), 1.28 (br m $C_5H_9$), 0.71 (s, $CH_3$) $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 137.9, 134.2, 129.1, 127.4, 123.0, 121.0, 120.9, 31.7, 27.6, 27.5, 27.4, 27.3, 27.2, 27.1, 27.0, 26.9, 24.1, 23.0, 22.6, 22.4, 21.9 (1:2:2:1:1 for $C_{ipso}H$), −0.6 (Si*Me*$Ph_2$) $^{31}$P NMR (162 MHz, $CDCl_3$, ppm) $\delta$ 122.6 (s) $^{29}$Si NMR (99 MHz, $CDCl_3$, ppm) −10.58 ($SiMePh_2$), −64.01, −65.02, −65.06, −66.60, −67.65 (1:2:1:1:2).
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