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The immobilisation of phenoxaphosphine-modified xanthene-type ligand on polysiloxane support and application thereof in the hydroformylation reaction

R.P.J. Bronger[a], J.P. Bermon[a], J.N.H. Reek[a], P.C.J. Kamer[a], P.W.N.M. van Leeuwen[a,*], D.N. Carter[b], P. Licence[b], M. Poliakoff[b]

[a] *Department of Inorganic Chemistry, Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*
[b] *The School of Chemistry, University Park, Nottingham NG72RD, UK*

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Abstract

For the first time a phenoxaphosphino-modified Xantphos-type ligand (**1**) has been covalently anchored to polysiloxane support (silica-**1** and sol–gel-**1**). The use of these heterogenised ligands in the rhodium catalysed hydroformylation of 1-octene gives a system that is competitive with systems employing Xantphos (**9**) as ligand, but with the added advantages of immobilised systems, like facile catalyst recycling and facile product–catalyst separation. During the recycle experiments no rhodium leaching was detected by ICP analysis (<00.2% Rh-leaching of initial intake) when either silica-**1** or sol–gel-**1** were used.

The application of sol–gel-**1** for the hydroformylation of *trans*-2-octene resulted in an active and regio-selective catalyst, but under forced reaction conditions ($T = 393$ K, $p(CO/H_2) = 3.6$ bar) significant catalyst deterioration was detected.

The use of supercritical carbon dioxide as reaction medium in a continuous-flow set-up resulted in similar activities, but slightly lower regio-selectivities compared to batch-wise hydroformylation reactions in toluene.

Keywords: Xantphos; Support; Supercritical carbon dioxide; Hydroformylation

1. Introduction

Many industrial processes apply homogeneous catalysts for the production of bulk chemicals, e.g. hydroformylation, the Monsanto and BP acetic acid processes, Wacker oxidation process, terephthalic acid process [1], and for the production of many important fine chemicals and pharmaceuticals, e.g. Ibuprofen and Naproxen [2]. A key issue in these processes remains the separation of the catalyst from the products, especially for the fine chemical industry; important factors to consider are catalyst costs, added value, and toxicity of the metal. Thus in the past decades intensive research has been devoted to facilitate product–catalyst separation for a number of catalytic reactions [3]. Distillation, liquid–liquid separation or extraction, catalyst destruction and crystallisation are all applied in bulk chemical industry. Often the catalyst cannot be reused easily and therefore many different methods for catalyst recycling have been studied [4]. Successful approaches in the laboratory include the attachment of homogeneous catalysts to polymeric or dendrimeric support [5–9], aqueous biphasic catalysis [10,11], fluorous catalysis [12–15], the use of supercritical fluids [16,17] and ionic liquids [18–22] or combinations thereof [23–26]. Unfortunately there is no general methodology that overcomes all the problems often encountered with these systems, like loss of activity, catalyst instability, metal leaching and problems concerning the solubility of the different components. For

* Corresponding author. Tel.: +31 20 525 5419; fax: +31 20 525 6456.
E-mail address: pwnm@science.uva.nl (P.W.N.M.v. Leeuwen).

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example inorganic materials such as silica are particularly suited for the preparation of heterogenised homogeneous catalysts because of their high physical strength and chemical inertness, but the activity is in general lower compared to the homogeneous system. One of the problems of immobilisation on soluble polymers is caused by the limited availability of proper membrane materials that are compatible with the reaction conditions, while aqueous phase catalysis is limited to substrates that are soluble in water.

Previous studies in which Nixantphos was heterogenised on silica support (silica-**6** [27] and sol–gel-**6** [28]) showed that high regio-selectivities, moderate activities and highly stable catalysts for the rhodium catalysed hydroformylation can be obtained. Substitution of the diphenylphosphino-moieties by phenoxaphosphino-moieties could give some additional advantages, like improved activity and the possibility of selective hydroformylation of internal olefins, while a high regio-selectivity and good recyclability are retained [29–32].

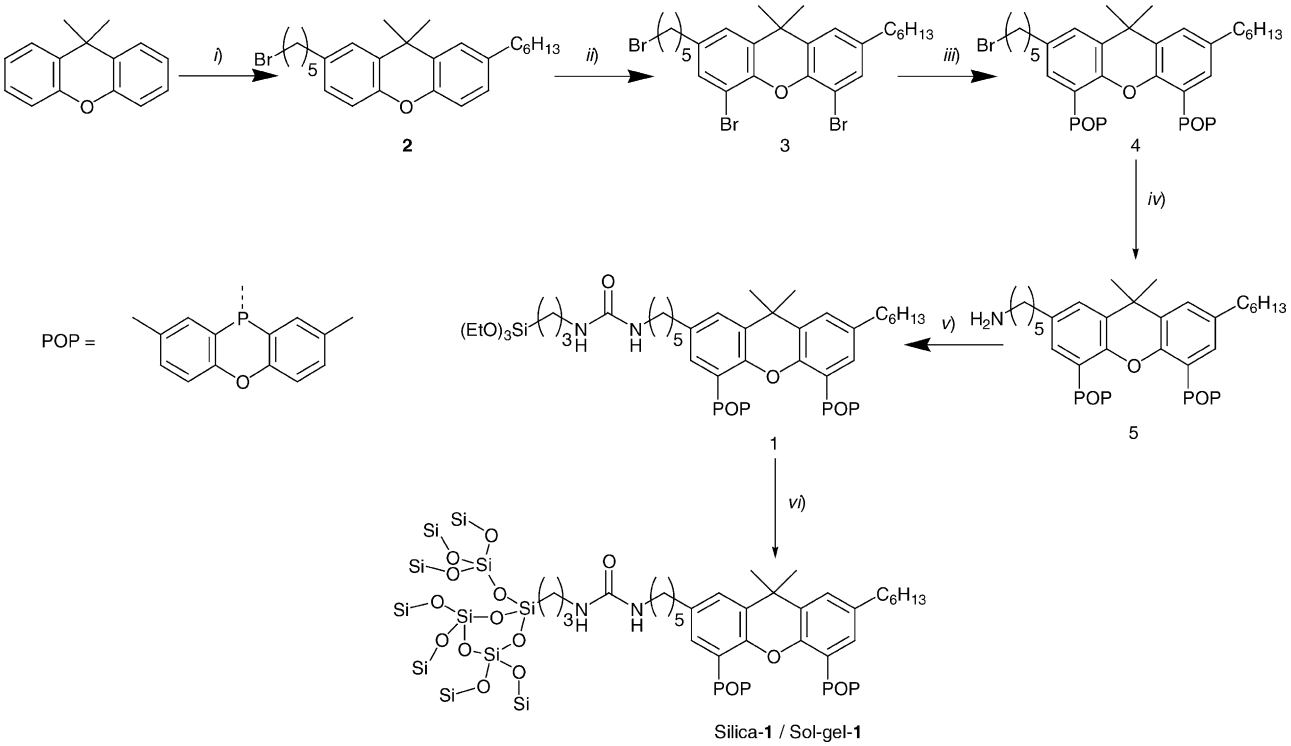
Here we report the synthesis of a new phenoxaphosphino-modified ligand (**1**), prepared via a route comparable to the synthesis of a dicationic ligand employed in the hydroformylation of 1-octene in ionic liquids [33], and recyclable non-covalently bound ligands (silica-**7**) [34]. Thus, small and facile modifications in the generic backbone (**4**) allow a rapid screening of this type of ligand under many different reaction conditions.

Herein we describe the application of this type of ligand by covalently anchoring the ligand on a polysiloxane support for the use in the rhodium catalysed hydroformylation of 1-octene in toluene and in supercritical carbon dioxide ($scCO_2$).

2. Results and discussion

2.1. Synthesis

Ligand **1** was prepared via a multistep procedure (Scheme 1). Friedel–Crafts acylation of 9,9-dimethylxanthene with 5-bromovaleryl chloride and hexanoylchloride followed by an indium(III) chloride catalysed reduction [35] gives **2** in a good yield (∼86% with respect to 9,9-dimethylxanthene). Selective mono-functionalisation of the 9,9-dimethylxanthene backbone is possible since the introduction of the first acyl-group deactivates 9,9-dimethylxanthene for electrophilic substitution to such an extent that only after complete mono-substitution of 9,9-dimethylxanthene a second electrophilic attack takes place and only on the aromatic ring that is non-substituted. We chose to put only one single functional group on the backbone in order to retain optimal fluxional structure and contact to the solution. Effectively, the ligand can move from the polysiloxane support and thereby the final catalyst will resemble more the homogeneous analogue. Next the 4 and 5



Scheme 1. Synthesis of silica-**1** and sol–gel-**1** (yields between parenthesis): (i) (a) 1 equiv. hexanoyl chloride/1 equiv. $AlCl_3$, (b) 1 equiv. 5-bromovalericacid chloride/1 equiv. $AlCl_3$ (86%), (c) $InCl_3$/chlorodimethylsilane (86%); (ii) Br_2 (83%); (iii) (a) *n*-BuLi, −80 °C, 30 min, (b) 10-chloro-2,8-dimethylphenoxaphosphine (POP-Cl) (53%); (iv) NH_3 (l), 70 °C (89%); (v) 1.1 equiv. triethoxysilane-*n*-propylisocyanate (95%); (vi) silica-**1**: silica, 70 °C; sol–gel-**1**: TMOS/H_2O/THF, $Rh(CO)_2(acac)$.

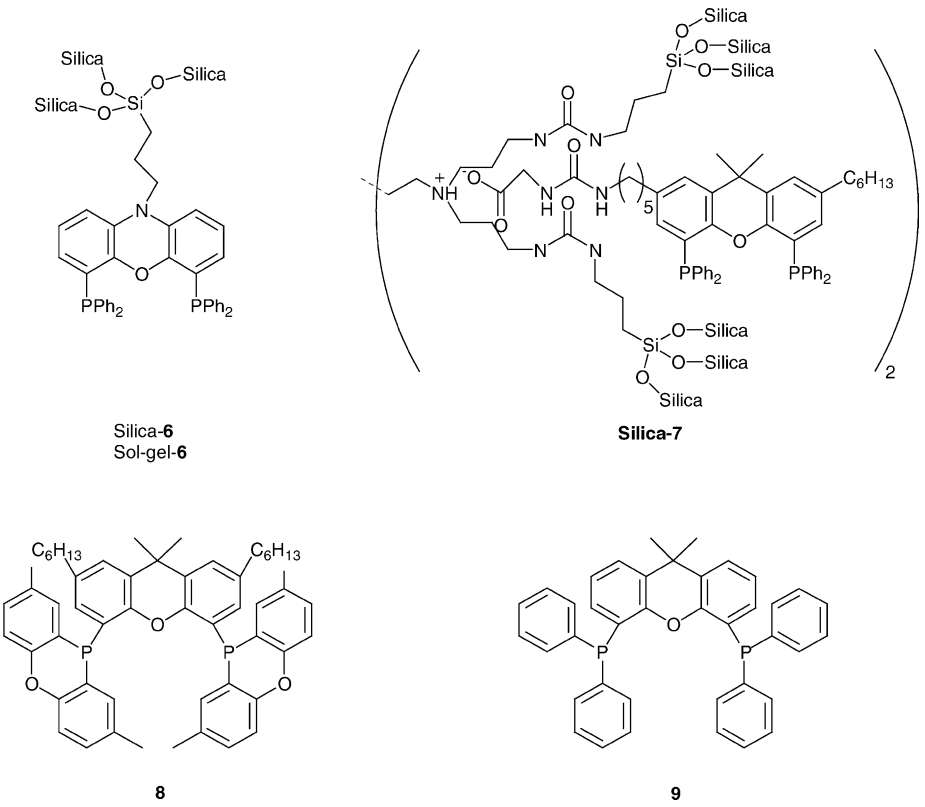


Fig. 1. Xantphos-type ligands used for comparison with Silica-**1** and Sol-gel-**1**.

positions of the xanthene backbone were brominated. Subsequent lithiation with *n*-butyllithium at −80 °C and reaction with 2,8-dimethyl-10-chlorophenoxaphosphine yielded **4**. Compound **5** was obtained by the reaction of **4** with ammonia at 70 °C. Next the amine was reacted with triethoxysilane-*n*-propylisocyanate to give **1** in a moderate overall yield (32%, based on 9,9-dimethylxanthene). Anchoring of **1** on commercially available silica (particle size 200–500 μm) took place by the condensation reaction between the tri-ethoxysilane groups of the ligand and free silanol groups of silica at 70 °C to yield silica-**1**. The catalyst precursor was prepared by adding 0.1 equiv. of $Rh(CO)_2(acac)$ to a mechanically stirred suspension of silica-**1** in a 5:1 THF:Et_3N mixture [27].

The sol–gel procedure involved the immobilisation of a 10:1 mixture of **1** and $Rh(CO)_2(acac)$ in THF using tetramethylorthosilicate (TMOS), MeOH and H_2O [28]. Gelation started after a few hours and was continued for 36 h. The resulting gel was carefully dried and crushed into free flowing silica to yield the pink-red sol–gel-**1**.

2.2. Batch-wise hydroformylation recycling experiments

The catalytic performance and recyclability of silica-**1** and sol–gel-**1** in the hydroformylation of 1-octene was studied by performing a series of consecutive catalytic experiments in a batch-wise process. The results are compared with silica-**6** [27], sol–gel-**6** [28], silica-**7** [34], **8** [29] and Xantphos (**9**) [36,37] (Fig. 1 and Tables 1 and 2).

Table 1
Results of the hydroformylation of trans 1-octene in subsequent cycles[a]

Ligand	Cycle	Conversion (%)	Isomerisation (%)	TOF[b]	*l*/*b*[c]
Silica-**6**	1	20	0.2	8.7	37
Sol–gel-**6**	1	20	2.0	35	35
Silica-**7**	1	40	9.0	17	25
8	1	20	9.0	1700	27
Xantphos	1	20	3.7	187	52
Sol–gel-**1**	1	12	22.2	111	33
	2	16	21.3	76	41
	3	88	16.4	28	27
	4	25	19.7	99	35
	5	20	17.7	84	32
	6[d]	7	–	9	7.6
	7	28	46.9	115	2.7
	8	22	14.4	34	5.9
Silica-**1**	1	37.9	7.4	232	30
	3	22.6	7.2	133	25
	5	33.3	9.8	119	29
	7	22.2	8.3	143	25

[a] Conditions: $p(CO/H_2)$ (1:1) = 20 bar, ligand/Rh = 10, substrate/Rh = 640, T = 80 °C, initial TOF determined and averaged over indicated conversion.

[b] Average turn over frequencies were calculated as (mol aldehyde) (mol catalyst)$^{-1}$ h^{-1} at indicated conversion. For the immobilised systems much scatter was observed, but with different catalyst batches gave TOF-values within the same range.

[c] Linear to branched ratio.

[d] Substrate = *trans*-2-octene, $p(CO/H_2)$ (1:1) = 3.2 bar, T = 120 °C.

Table 2
Results from hydroformylation of 1-octene using silica-**1**, values shown are average numbers over a period of 1.5–5 h[a]

Entry	p_{CO_2} (bar)	CO_2-flowrate[b] (L min^{-1})	1-Octene-flowrate[b] (mL min^{-1})	Conversion (%)	TOF[c]	*l*/*b*[d]
1	80	0.65	0.05	1.02	44.1	19.6
2	120	0.65	0.05	2.94	126.6	12.5
3	160	0.65	0.05	0.99	54.0	12.3
4	120	0.33	0.05	2.60	111.8	10.7
5	120	1.40	0.05	1.23	52.7	18.7
6	120	0.65	0.03	2.57	66.5	22.6
7	120	0.65	0.10	0.32	27.3	19.0

[a] Ligand:Rh ratio is 10:1, catalysis performed at 80 °C, substrate:syngas = 1:5. No accurate data on the extent of isomerisation can be provided due to the low conversions.
[b] Flowrates at 20 °C, 1 atm.
[c] Average turn over frequencies were calculated as (mol aldehyde) (mol catalyst)$^{-1}$ h^{-1} at indicated conversion.
[d] Linear to branched ratio.

Compared to silica-**6**, sol–gel-**6** and silica-**7**, both silica-**1** and sol–gel-**1** show a higher activity under similar reaction conditions. In addition, sol–gel-**1** shows a slight increase in regio-selectivity compared to the homogeneous system (**8**), but with more isomerisation, and silica-**1** shows a similar regio-selectivity, while immobilisation of the diphenylphosphino-modified ligands [28,29,34] resulted in a decrease in regio-selectivity. It has been observed before that changes in catalyst environment have less effect on regio-selectivity when phenoxaphosphino-modified ligands are used [33]. The increase in regio-selectivity for sol–gel-**1** compared to **8** is in part attributed to an increase in isomerisation activity as isomerisation offers an 'escape route' of the branched alkyl rhodium species, but the overall selectivity toward the linear aldehyde has decreased. Compared to catalysis in presence of **8** a large decrease in hydroformylation activity was observed, which is commonly encountered for heterogenised systems. On the other hand both activity and selectivity with silica-**1** and sol–gel-**1** are very competitive with the results obtained for Xantphos (**9**) under identical reaction conditions. It must be noted, though, that the amount of isomerisation is much higher in the immobilised systems and therefore the selectivity toward the linear aldehyde is much lower.

In contrast to the system where silica-**6** and sol–gel-**6** were employed no hydrogenation activity was observed when silica-**1** or sol–gel-**1** were used. The hydrogenation activity in presence of silica-**6** and sol–gel-**6** were attributed to the formation of [Rh(diphosphine)(CO)]$^+$ species having a siloxate as its counterion [27]. The absence of any hydrogenation activity gives a strong indication that a similar cationic species is not formed when phenoxaphosphino-substituted ligands are used. The steric shielding of the phenoxaphosphino-moieties might hamper the formation of such a species under the applied catalysis conditions.

The high isomerisation activity and the high regio-selectivity obtained with sol–gel-**1**, prompted us to test this system for the hydroformylation of *trans*-2-octene. Despite the promising initial results, the catalyst was not stable under typical hydroformylation conditions for internal alkenes (high temperature, $T = 120$ °C; low pressure, $p(CO/H_2) = 3.2$ bar). Severe catalyst deterioration was observed in consecutive recycling experiments using 1-octene as substrate (Table 1, sol–gel-**1**, cycle 7 and 8).

2.3. Continuous hydroformylation in $scCO_2$

An elegant approach toward catalyst recycling involves the use of supercritical carbon dioxide ($scCO_2$; $T_c = 31$ °C, $p_c = 73.75$ bar, $\rho_c = 0.468$ g mL^{-1}). This environmentally benign medium has a number of advantages over conventional solvents: it is highly miscible with gases, there exists no liquid-gas boundary, and it has a high compressibility. Previous studies using silica-**6** in $scCO_2$ resulted in a large increase in hydroformylation activity [16]. This effect was mainly attributed to increased mass-transfer. Therefore, silica-**1** was tested in $scCO_2$ using a continuous-flow reactor. In addition we tested the influence of various reaction parameters on catalytic performance (Table 2).

In contrast to our expectations, the use of silica-**1** did not show an improvement in hydroformylation activity. Thus, silica-**1** behaves differently in $scCO_2$ than silica-**6**. Additionally, the regio-selectivity decreased compared to the results obtained in toluene. This drop in regio-selectivity is ascribed to an enhanced rate of CO-insertion in the secondary alkyl rhodium intermediate. This should be reflected in the amount of isomerisation, but since we operated under very low conversion levels, no accurate measurement of the amount of isomerisation could be accomplished. Nevertheless, it is assumed that the rate of isomerisation is suppressed considerably taking into consideration the results during the hydroformylation of *trans*-2-octene (vide infra).

Variation of the CO_2 pressure between 80 and 160 bar showed optimum conditions around 120 bar (Table 2, compare entries 1–3). At lower CO_2 pressures (80 bar) increased regio-selectivity was observed, similar to those found in traditional homogeneous systems. Decreased activity (>120 bar) was also observed by Cole-Hamilton and coworkers [38], but they could not provide a satisfactorily explanation, we also cannot explain this observation. Plausible explanations range from problems of reaction engineering i.e. controlling

the reactant/catalyst contact time or bed to more fundamental questions including the effect of changes in the density of the reaction mixture require further investigation. Future studies including an appraisal of the phase behaviour of this particular reaction system must be conducted.

The CO_2 flowrate effectively influences the residence time of the substrate in the medium. A decrease in CO_2 flowrate leads to an increased contact time of the substrate with the catalyst, and could in theory lead to a higher conversion compared to catalysis at higher CO_2 flowrates. Surprisingly, decreasing the CO_2 flowrate from 0.65 to 0.33 L min^{-1} did not lead to an increase in conversion, but to a slight decrease in conversion. Increasing the flowrate to 1.4 L min^{-1} did show the expected effect as the conversion dropped. The regio-selectivity increased by decreasing the CO_2 flowrate (Table 2, compare entries 2, 4, and 5). Similar effects were expected and observed by changing the substrate flowrate. For the regio-selectivity, however, a minimum was found at a substrate flowrate of 0.05 mL min^{-1} at a CO_2 flowrate of 0.65 L min^{-1} ($p_{CO_2} = 120$ bar) (Table 2, compare entries 2, 6 and 7).

When *trans*-2-octene was used as substrate (at an increased temperature of 120 °C and syngas/substrate = 2.5) no hydroformylation took place, which is potentially the result of decreased rate of isomerisation. However, under these conditions the catalyst remains stable as no rhodium leaching (<0.2% of initial Rh-intake as determined by ICP analysis) was detected and the activity was restored when the initial reaction conditions were applied (substrate = 1-octene, $T = 80$ °C, syngas/substrate = 5).

3. Conclusions

In conclusion we have prepared a new highly stable heterogenised catalyst that shows enhanced activities when used for the hydroformylation of terminal olefins. Although the catalyst obtained from sol–gel-**1** and $Rh(CO)_2(acac)$ is very selective and moderately active for the hydroformylation of internal olefins, with regard to stability the system has to be improved considerably.

Although the use of $scCO_2$ does not lead to improved activity, it does offer a more facile separation of substrate from the reaction medium. Additionally the stability is enhanced considerably since under forced reaction conditions the catalyst retained its activity and selectivity. The influence of most reaction parameters is still unclear and needs further exploration.

4. Experimental

4.1. General procedure

All air or moisture sensitive reactions were performed using standard Schlenk techniques under an inert atmosphere of purified argon. Toluene was distilled from sodium, THF from sodium/benzophenone, and hexanes from sodium/benzophenone/triglyme. Isopropanol and dichloromethane were distilled from CaH_2. Chemicals were purchased from Acros Chimica, and Aldrich Chemical Co. All Alkenes were filtered through neutral, activated alumina to remove peroxide impurities before reaction. Synthesis gas (CO/H_2, 1:1, 99.9%) was purchased from Air Liquide. Silica gel 60 (230–400 mesh) for column chromatography was purchased from Merck. Silica 100 (0.2–0.5 mm), BET: 300–400 $m^2\ g^{-1}$, porevolume 0.9–1.2 mL g^{-1} (N_2-isotherm) was also purchased from Merck. Melting points were determined on a Gallenkamp MFB-595 melting point apparatus in open capillaries and are reported uncorrected. NMR spectra were recorded on a Varian Mercury 300 or Inova 500 spectrometer. ^{31}P and ^{13}C spectra were measured ^{1}H decoupled. TMS was used as a standard for ^{1}H and ^{13}C NMR and 85% of H_3PO_4 in H_2O for ^{31}P NMR. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. Gas chromatographic analysis were run on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J&W Scientific, DB-130 m column, film thickness 3.0 mm, carrier gas 70 kPa He, FID detector) equipped with a Hewlett Packard Data system (Chrom-Card) using decane as an internal standard.

Batch-wise hydroformylation reactions were carried out in a 200 mL homemade stainless steel autoclave. Continuous hydroformylation experiments were carried out in a flow-reactor system the details of which are almost identical to the hydrogenation apparatus described elsewhere [39] but with pressurised synthesis gas ($CO:H_2$, 1:1) used in place of H_2.

4.2. 2-Hexanoyl-9,9-dimethylxanthene

At 0 °C 8.32 g of $AlCl_3$ (62.4 mmol) was added slowly to a stirred solution of 13.1 g of 9,9-dimethylxanthene (62.4 mmol) and 8.8 mL of hexanoylchloride (62.4 mmol) in 200 mL of CH_2Cl_2. The mixture was warmed to room temperature and was stirred overnight. Next, the mixture was poured on 300 mL ice and extracted with 3×100 mL CH_2Cl_2. The combined extracts were washed with 150 mL of a 10% $NaHCO_3$ solution and washed with dichloromethane. The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. Crude yield: 17.6 g (57 mmol, 91%) of a yellow/brown solid that was used without any further purification. ^{1}H NMR ($CDCl_3$): $\delta = 8.10$ (d, $^{4}J(H, H) = 2.1$ Hz, 1H), 7.81 (dd, $^{3}J(H, H) = 8.7$ Hz, $^{4}J(H, H) = 2.4$ Hz, 1H), 7.42 (dd, $^{3}J(H, H) = 5.7$, $^{4}J(H, H) = 1.5$ Hz, 1H), 7.22 (td, $^{4}J(H, H) = 7.8$ Hz, $^{4}J(H, H) = 1.5$ Hz, 1H), 7.14 (td, $^{3}J(H, H) = 7.5$, $^{4}J(H, H) = 1.5$ Hz, 1H), 7.08 (d, $^{3}J(H, H) = 8.5$, 1H), 7.05 (dd, $^{3}J(H, H) = 7.5$, $^{4}J(H, H) = 1.5$ Hz, 1H), 2.94 (t, $^{3}J(H, H) = 7.8$ Hz, 2H), 1.66 (m, 8H), 1.37 (m, 4H), 0.92 ppm (t, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 199.46$ (s), 154.21 (s), 149.88 (s), 132.58 (s), 130.45 (s), 129.82 (s), 128.22 (s), 127.81 (s), 127.27 (s), 126.44 (s), 123.98 (s), 116.60 (s), 116.66 (s),

38.55 (s), 34.24 (s), 32.85 (s), 31.83 (s), 24.50 (s), 22.76 (s), 14.18 ppm (s).

4.3. 2-(5-Bromopentanoyl)-7-hexanoyl-9,9-dimethylxanthene

At 0 °C 9.1 g of $AlCl_3$ (68 mmol) was added slowly to a stirred solution of 17.6 g of 2-hexanoyl-9,9-dimethylxanthene (57 mmol) and 9.1 mL of 5-bromovaleryl chloride (68 mmol) in 200 mL of CH_2Cl_2. The mixture was warmed to room temperature and was stirred overnight. Next, the mixture was poured on 300 mL ice and extracted with 3×100 mL CH_2Cl_2. The combined extracts were washed with 150 mL of a 10% $NaHCO_3$ solution and extracted with CH_2Cl_2 (3×100 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. Crude yield: 25 g (53.3 mmol, 94%) of a yellow/brown solid that was used without any further purification. ^{1}H NMR ($CDCl_3$): $\delta = 8.10$ (d, ^4J(H, H) = 1.8 Hz, 2H), 7.83 (d, ^3J(H, H) = 8.4 Hz, 2H), 7.10 (d, ^3J(H, H) = 8.4 Hz, 2H), 3.46 (t, ^3J(H, H) = 6.3 Hz, 4H), 3.00 (t, ^3J(H, H) = 6.8 Hz, 2H), 2.93 (t, ^3J(H, H) = 7.5 Hz, 2H), 1.9 (m, 4H), 1.8–1.6 (m, 2H), 1.69 (s, 6H), 1.4–1.3 (m, 4H), 0.91 ppm (t, ^3J(H, H) = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 199.41$ (s), 198.57 (s), 153.54 (s), 153.32 (s), 133.25 (s), 132.93 (s), 130.20 (s), 130.02 (s), 128.30 (s), 128.33 (s), 127.33 (s), 127.32 (s), 116.87 (s), 116.78 (s), 38.58 (s), 37.43 (s), 33.52 (s), 33.05 (s), 32.41 (s), 32.04 (s), 24.43 (s), 23.11 (s), 22.73 (s), 14.15 ppm (s).

4.4. 2-(5-Bromopentyl)-7-hexyl-9,9-dimethylxanthene (**2**)

To a stirred suspension of 470 mg of $InCl_3$ (2.1 mmol) and 11.2 mL of chlorodimethylsilane (4.8 equiv., 102.7 mmol) in 80 mL of CH_2Cl_2 was added 10.0 g of 2-(5-bromopentanoyl)-7-hexanoyl-9,9-dimethylxanthene (20 mmol) in 80 mL of CH_2Cl_2. The reaction was quenched after complete reduction of the ketone functionalities by addition of 100 mL of water (~4 h reaction time). Next, the mixture was extracted with 3×80 mL of CH_2Cl_2. Subsequently the organic layer was dried over $MgSO_4$. The solvents were removed in vacuo and the resulting solid was purified by flash column chromatography (eluent: hexanes). Yield: 7.6 g (17 mmol, 86%) of a slightly yellow compound that was used without further purification. ^{1}H NMR ($CDCl_3$): $\delta = 7.20$ (s, 2H), 7.01 (d, ^3J(H, H) = 8.1 Hz, 2H), 6.96 (d, ^3J(H, H) = 8.7 Hz, 2H), 3.55 (t, ^3J(H, H) = 6.6 Hz, 0.9H) 3.42 (t, ^3J(H, H) = 6.6 Hz, 1.1H), 2.62 (t, ^3J(H, H) = 6.9 Hz, 2H), 2.60 (t, ^3J(H, H) = 7.2 Hz, 2H), 1.9–1.1 (m, 14H), 1.64 (s, 6H), 1.0–0.8 ppm (m, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$): $\delta = 149.01$ (s), 148.82 (s), 137.51 (s), 136.79 (s), 130.06 (s), 129.85 (s), 127.47 (s), 127.41 (s), 126.03 (s), 126.01 (s), 116.34 (s), 116.23 (s), 35.82 (s), 35.57 (s), 34.28 (s), 34.06 (s), 32.95 (s), 32.60 (s), 31.99 (s), 31.97 (s), 31.10 (s), 29.25 (s), 28.07 (s), 22.90 (s), 14.37 ppm. GC–MS (*m*/*z*, rel. intensity): 444/446 (M+, 6), 429/431 (100), 349 (29), 307 (7), 294 (10), 236 (7), 223 (13), 207 (10).

4.5. 4,5-Dibromo-2-(5-bromopentyl)-7-hexyl-9,9-dimethylxanthene (**3**)

To an ice-cooled solution of 1.97 g 2-(5-bromopentyl)-7-hexyl-9,9-dimethylxanthene (4.4 mmol) in 30 mL of CH_2Cl_2 was added dropwise 0.81 mL of Br_2 (3.6 equiv., 16.7 mmol) in 2 mL of hexanes. The reaction mixture was warmed to room temperature and stirred overnight. Excess Br_2 was quenched with 20 mL of an aqueous $NaSO_3$ solution and the mixture was extracted with 3×20 mL of CH_2Cl_2. Subsequently, the organic layer was dried over $MgSO_4$. The solvents were removed in vacuo and the resulting solid was purified by flash column chromatography (eluent: CH_2Cl_2). Yield: 2.2 g (3.7 mmol, 83%) of a yellow solid that was used without further purification. ^{1}H NMR ($CDCl_3$): $\delta = 7.29$ (d, ^4J(H, H) = 1.5 Hz, 2H), 7.11 (d, ^4J(H, H) = 1.8 Hz, 2H), 3.55 (t, ^3J(H, H) = 6.3 Hz, 0.9H), 3.40 (t, ^3J(H, H) = 6.3 Hz, 1.1H), 2.58 (t, ^3J(H, H) = 7.5 Hz, 2H), 2.55 (t, ^3J(H, H) = 7.8 Hz, 2H), 1.93 (quintet, ^3J(H, H) = 7.1 Hz, 2H), 1.7–1.55 (m, 4H), 1.59 (s, 6H), 1.6–1.4 (m, 2H), 1.4–1.25 (m, 6H), 0.88 ppm (t, ^3J(H, H) = 6.6 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$): $\delta = 145.92$ (s), 145.71 (s), 139.27 (s), 138.54 (s), 131.86 (s), 131.66 (s), 131.28 (s), 131.22 (s), 124.92 (s), 124.91 (s), 110.92 (s), 110.80 (s), 35.66 (s), 35.54 (s), 35.29 (s), 33.99 (s), 32.82 (s), 32.04 (s), 31.91 (s), 31.70 (s), 30.84 (s), 29.11 (s), 27.94 (s), 22.85 (s), 14.34 ppm (s).

4.6. 2-(5-Bromopentyl)-7-hexyl-9,9-dimethyl-4,5-bis(2,8-dimethyl-10-phenoxaphosphino)xanthene (**4**)

At −78 °C 3.2 mL of *n*-butyllithium (2.5 M in hexanes, 7.9 mmol) was added to a stirred solution of 2.2 g 4,5-dibromo-2-(5-bromopentyl)-7-hexyl-9,9-dimethylxanthene (3.6 mmol) in 75 mL of Et_2O. The resulting solution was stirred for 30 min at −78 °C. Subsequently, a suspension of 2.4 g of 2,8-dimethyl-10-chloro-phenoxaphosphine (9.3 mmol) in 20 mL of toluene was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred overnight. Next the diethylether was removed in vacuo and the mixture was diluted with 50 mL of CH_2Cl_2 and hydrolyzed with 50 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over $MgSO_4$. The solvents were removed in vacuo and the resulting yellow/white solid was crystallized from 2-propanol/toluene. Yield: 1.7 g of white crystals (1.9 mmol, 53%). ^{1}H NMR ($CDCl_3$): $\delta = 7.93$ (d, ^3J(P, H) = 6 Hz, 4H), 7.16 (m, 4H), 7.11 (m, 4H), 7.06 (m, 2H), 6.50 (m, 2H), 3.34 (t, ^3J(H, H) = 7.0 Hz, 2 H), 2.4–2.3 (m, 4H), 2.34 (s, 12H), 1.79 (quintet, ^3J(H, H) = 7.0 Hz, 1.1 H), 1.70 (quintet, ^3J(H, H) = 7.5 Hz, 0.9 H), 1.50 (s, 6H), 1.4 (m, 4H), 1.31 (t, ^3J(H, H) = 7.0 Hz, 2H), 1.2 (m, 8H), 0,87 ppm (t, ^3J(H, H) = 7.5 Hz, 3H). ^{13}C {^{1}H} NMR

($CDCl_3$): δ = 154.36 (s), 154.29 (s), 150.82 (t, 17.6 Hz), 137.58 (s), 136.86 (s), 136.83 (s), 135.90 (t, 8.7 Hz), 135.62 (t, 8.7 Hz), 132.90 (d, 6.3 Hz), 132.82 (d, 6.3 Hz), 131.81 (s), 131.64 (s), 131.58 (s), 130.09 (s), 129.86 (s), 127.19 (vt, unresolved), 127.08 (s), 35.41 (s), 35.12 (s), 34.66 (s), 33.92 (s), 32.83 (s), 32.57 (s), 31.84 (s), 31.19 (s), 30.27 (s), 28.86 (s), 28.06 (s), 22.76 (s), 20.82 (s), 14.31 ppm (s). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ = −70.38 ppm (s). Anal. Calcd. for $C_{54}H_{57}BrO_3P_2$: C, 72.40; H, 6.41. Found: C, 72.42; H, 6.44.

4.7. 2-(5-Aminopentyl)-7-hexyl-9,9-dimethyl-4,5-bis(2,8-dimethyl-10-phenoxaphosphino)xanthene (**5**)

A homemade 100 mL hastelloy autoclave was equipped with a stirring bean and filled with approximately 60 mL of NH_3(l). To this was added a solution of 420 mg of 2-(5-bromopentyl)-7-hexyl-9,9-dimethyl-4,5-bis(2,8-dimethyl-10-phenoxaphosphino)-xanthene in 10 mL of THF, that was cooled down to −80 °C. The autoclave was closed and stirred at 70 °C overnight. During heating the pressure increased to approximately 20 bar. Next, the autoclave was cooled to room temperature and slowly depressurised. The autoclave was washed several times with dichloromethane and the solvents were removed in vacuo. The solid was dissolved in dichloromethane and washed with water (3 × 20 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. Yield: 0.35 g (89%) of a pure white solid. ^1H NMR ($CDCl_3$): δ = 7.94 (bs, 4H), 7.16 (d, ^3J(H, H) = 8.5 Hz, 4H), 7.10 (d, ^3J(H, H) = 8.5 Hz, 4H), 7.05 (s, 2H), 6.49 (d, ^4J(H, H) = 2 Hz, 2H), 5.30 (s, 2H), 2.67 (t, ^3J(H, H) = 7.0 Hz, 2H), 2.37 (t, ^3J(H, H) = 7 Hz, 4H), 2.33 (s, 12H), 1.53 (s, 6H), 1.41 (m, 6H), 1.22 (m, 8H), 0.86 ppm (t, ^3J(H, H) = 7.0 Hz, 3H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ = 154.14 (s), 154.08 (m), 150.55 (t, unresolved), 137.33 (s), 136.89 (s), 135.54 (m),132.65 (d, 10.6 Hz), 132.61 (d, 11.06 Hz), 131.60 (s), 131.50 (s), 131.40 (s), 131.36 (s), 129.80 (s), 129.64 (s), 126.97 (vt, unresolved), 126.86 (s), 118.17 (t, 5.5 Hz), 117.31 (s), 41.81 (s), 35.19 (s), 35.10 (s), 34.43 (s), 32.73 (s), 31.62 (s), 30.97 (s), 30.75 (s), 28.63 (s), 26.13 (s), 22.55 (s), 20.61 (s), 14.09 ppm (s). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ = −70.46 ppm (s). Anal. Calcd. for $C_{54}H_{59}NO_3P_2$: C, 77.95; H, 7.15; N, 1.68. Found: C, 77.76; H, 7.21; N, 1.61.

4.8. 2-(5-(3-(Triethoxysilyl)propylurea)pentyl)-7-hexyl-9,9-dimethyl-4,5-bis(2,8-dimethyl-10-phenoxaphosphino)xanthene (**1**)

A mixture of 720 mg of 2-(5-amino-pentyl)-7-hexyl-9,9-dimethyl-4,5-bis(2,8-dimethyl-10-phenoxaphosphino)xanthene (0.9 mmol) and 270 μL of triethoxysilane-*n*-propylisocyanate (1.1 mmol) in 15 mL of CH_2Cl_2 were stirred overnight. The resulting mixture was evaporated in vacuo to yield pure 2-(5-(3-(triethoxysilyl)propylurea)pentyl)-7-hexyl-9,9-dimethyl-4,5-bis(2,8-dimethyl-10-phenoxaphosphino)-xanthene (**1**). Yield: 890 mg (0.8 mmol, 95%). ^1H NMR ($CDCl_3$): δ = 7.96 (d, J = 9 Hz, 2H), 7.95 (d, J = 7.5 Hz, 2H), 7.16 (d, ^3J(H, H) = 8.5 Hz, 4H), 7.13 (d, ^3J(H, H) = 8.0 Hz, 4H), 7.06 (d, ^4J(H, H) = 3 Hz, 2H), 6.50 (d, ^4J(H, H) = 5.7 Hz, 2H), 4.42 (t, ^3J(H, H) = 5.5 Hz, 1H), 4.24 (t, ^3J(H, H) = 5.5 Hz, 1H), 3.83 (q, ^3J(H, H) = 7.0 Hz, 6H), 3.18 (q, ^3J(H, H) = 6.5 Hz, 2H), 3.11 (q, ^3J(H, H) = 6.5 Hz, 2H), 2.39–2.32 (m, 4H), 2.33 (s, 12H), 1.64 (quintet, ^3J(H, H) = 8.0 Hz, 2H), 1.55 (s, 6H), 1.53 (m, 2H), 1.44–1.37 (m, 6H), 1.24 (t, ^3J(H, H) = 7.2 Hz, 9H), 1.21 (m, 6H), 0.88 (t, ^3J(H, H) = 7.0 Hz, 3H), 0.66 ppm (t, ^3J(H, H) = 8.0 Hz, 2H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ = 158.32 (s), 154.38 (s), 154.29 (s), 150.68 (m, unresolved), 137.37 (s), 137.04 (s), 135.89 (t, 14.6 Hz), 135.67 (t, 14.6 Hz), 132.87 (t, 10.9 Hz), 131.82 (s), 131.64 (s), 131.59 (s), 130.06 (s), 129.86 (s), 127.09 (s), 118.41 (t, 8.7 Hz), 118.34 (t, 8.7 Hz), 117.54 (s), 117.51 (s), 58.67 (s), 43.19 (s), 40.82 (s), 35.41 (s), 35.32 (s), 34.66 (s), 32.59 (s), 31.83 (s), 31.19 (s), 30.93 (s), 30.27 (s), 28.85 (s), 26.50 (s), 23.82 (s), 22.76 (s), 20.82 (s), 18.53 (s), 14.31 (s), 7.83 ppm (s). Anal. Calcd. for $C_{64}H_{80}N_2O_7P_2Si$: C, 71.22; H, 7.47; N, 2.60. Found: C, 71.29; H, 7.41; N, 2.48.

4.9. Synthesis of silica bound 1 (silica-**1**)

To a mechanically stirred slurry of 3.2 g of pre-dried silica (at T = 180 °C, under reduced pressure) in 40 mL of toluene was added 320 mg of **1** (0.30 mmol). The reaction mixture was stirred at 70 °C overnight. Subsequently, the silica was washed with toluene, dried under reduced pressure and stored under an inert atmosphere.

The catalyst pre-cursor (silica-**1**)Rh(acac) was prepared by stirring a suspension of 2.6 mg of $Rh(CO)_2$(acac) and 1 g silica-**1** in 5 mL of THF and 1 mL of Et_3N for 30 min. Next, the solvent was removed and the pink-red silica was washed with toluene (3 × 10 mL) and dried in vacuo. Rhodium content: 1×10^{-5} mol g^{-1}.

4.10. Synthesis of sol–gel bound **1** (sol–gel-**1**)

To a mixture of 129 mg of **1** (0.12 mmol) and 3.2 mg of $Rh(CO)_2$(acac) (0.1 equiv., 0.012 mmol) in 6 mL of THF was added 2 mL of H_2O and 2 mL of tetramethylorthosilicate. After 1.5 h, 0.2 mL of MeOH was added and the mixture was allowed to stand for 36 h. The resulting gel was carefully dried and crushed into free flowing silica to yield the pink-red sol–gel-**1**. This was subsequently washed with MeOH, THF and Et_2O. Yield: 0.98 g of a pink-red silica. That was either used directly or stored under an inert atmosphere at −20 °C. Rhodium content: 1.3×10^{-5} mol g^{-1}.

4.11. Batch-wise hydroformylation

In a typical experiment a homemade 200 mL autoclave was charged with a 1 g of silica-**1** or sol–gel-**1**. Next 8.5 mL

of toluene was added. The reactor was purged and pressurised to 16 bar of syngas ($CO:H_2$, 1:1) and heated to 80 °C. After 1 h the substrate was introduced by overpressure of 20 bar of CO/H_2. The reactions were stopped by cooling on ice and venting the gases. The reaction mixture was removed from the silica by syringe and analysed by GC. Next, the silica was washed with toluene (2×5 mL), and prepared for the next hydroformylation cycle. The top-layer was removed for analysis. New substrate was added, the reactor was pressurised and heated for the next hydroformylation cycle.

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