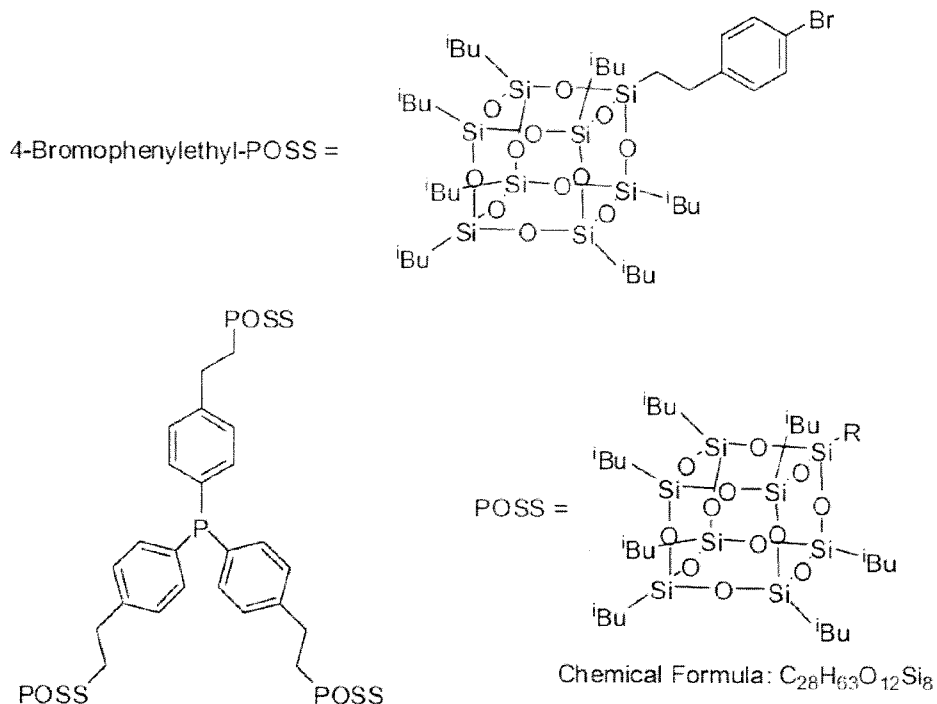


**Polyhedral oligomeric silsesquioxane (POSS) bonded
ligands and the use thereof**

5 The hydroformylation of olefins and olefin-containing mixtures are a subject of research in the chemical industry. An ongoing objective in catalytic hydroformylation is retention of the activity and selectivity of the catalytically active compositions used in respect of the olefins and olefin-containing
10 mixtures to be hydroformylated under the reaction conditions. In particular, in the case of transition metal-containing, catalytically active compositions, it is an object of research to prevent or at least significantly decrease the inhibition of the catalytic
15 effect, the formation of transition metal clusters and the precipitation of the transition metal itself. The present invention makes a contribution to this objective by showing a way of, in a simple way, separating the desired target products from the
20 catalytically active composition while retaining the catalytic activity of the latter and avoiding thermal stress on the reaction mixture.

The present invention provides POSS-modified ligands,
25 where POSSs are polyhedral oligomeric silsesquioxane derivatives. The polyhedral oligomeric silsesquioxane derivatives used are reacted with ligand precursors known per se. The resulting POSS-modified ligands have a greatly increased molecular weight compared to
30 unmodified ligands. In an embodiment of the invention, an alkylphenyl-substituted, in particular an ethylphenyl-substituted, POSS-substituted triphenylphosphine derivative is prepared from triorganophosphines such as triphenylphosphine:



Preparation of POSS-substituted triphenylphosphine

- 5 4-Bromophenylethyl-POSS (11 g, 10.92 mmol) is dissolved in 100 ml of THF and cooled to -78°C . n-BuLi (2.5 M in hexane, 4.8 ml, 12 mmol) is added dropwise and the reaction mixture is stirred at this temperature for 1 hour. PCl_3 (0.5 g, 3.64 mmol) is added dropwise. The
- 10 reaction mixture is allowed to warm to room temperature and is stirred overnight. The solvent is removed under reduced pressure. The reaction product is extracted from the remaining solid with toluene-hexane (1:1, 150 ml) and washed with degassed water. The organic
- 15 phase is dried over MgSO_4 . The solvents are removed under reduced pressure. The product is obtained as a white solid in a yield of 78% (8 g, 2.84 mmol).
- ^1H NMR δ (ppm): 7.24 (dd, $J = 12.4$ Hz, $J = 14.4$ Hz, 12H), 2.69 (m, 6H), 1.87 (sept, $J = 6.7$ Hz, 7H), 0.97 (d, $J = 6.6$ Hz, 42H), 0.62 (d, $J = 7$ Hz, 14H)
- 20 ^{13}C NMR δ (ppm): 145.15, 133.83, 127.94, 125.61, 28.97, 25.70, 23.88, 22.53, 14.07

^{31}P NMR δ (ppm): -7.76 (s)

Maldi-Tof: m/z = 2809.07 (M+Na)

Elemental analysis: calculated (found): C 46.45
5 (46.54), H 7.69 (7.77)

The present invention further provides transition metal-containing compositions which can be obtained by reaction of the POSS-modified ligands with suitable transition metal precursors and are catalytically active in the hydroformylation of olefins and olefin-containing mixtures. A characteristic of these novel transition metal complexes prepared using POSS-modified ligands in the catalytically active compositions is that the activity and selectivity are maintained compared to the transition metal complexes which have not been modified with POSS. At the same time, the catalytically active compositions according to the invention can be separated off completely from the reaction mixture by means of organic nanofiltration and can be recirculated to the hydroformylation reaction. In one embodiment of the invention, the above-described POSS-substituted triphenylphosphine is reacted with a rhodium-containing, suitable transition metal precursor, e.g. $[\text{Rh}(\text{acac})(\text{CO})_2]$, to form the catalytically active composition.

The present invention further provides for the use of POSS-modified ligands in catalytically active compositions in the hydroformylation of olefins and olefin-containing mixtures. In an embodiment of the invention, the above-described POSS-substituted triphenylphosphine is reacted with a rhodium-containing, suitable transition metal precursor, e.g. $[\text{Rh}(\text{acac})(\text{CO})_2]$, to form the catalytically active composition which is used in the hydroformylation of olefins such as 1-octene:

Example 1: Hydroformylation of 1-octene in a continuously operated membrane reactor

The hydroformylation experiments were carried out in a continuously operated experimental plant; see sketch of plant. This experimental plant consisted of a reaction part and a membrane part. The reaction part comprised a 100 ml autoclave **b** with a circulation pump **c**. The autoclave **b** was equipped with a pressure regulator **A** for the synthesis gas. By means of this pressure regulator **A**, the synthesis gas pressure was kept constant in the entire system during the reaction. The synthesis gas uptake of the system was determined by means of a flow meter **C**. For the introduction of feed and catalyst solutions before the start of the reaction, the reactor was equipped with a pressure burette **a** which could be supplied with synthesis gas and thus allowed introduction of the feed and catalyst solutions under reaction conditions. The autoclave **b** was additionally equipped with a level regulator **B**. The feed pump **e** was controlled by this level regulator **B** and then pumped feed solution comprising the olefin-containing mixture, optionally solvent, from a reservoir **h** into the autoclave **b** so as to keep the level in the autoclave constant. This feed reservoir **h** was blanketed with argon to avoid contact with air. The necessary turbulence in the autoclave was generated by the circulation pump **c** which itself was constructed for this purpose. The pump **c** built up circulation of the reaction solution via a nozzle in the top of the autoclave **b** and thus ensured appropriate gas/liquid exchange. The synthesis gas and the feed were likewise fed into the nozzle.

A crossflow chamber **f** was likewise installed in this circuit. The crossflow chamber **f** separates the reaction part from the membrane part of the plant. The crossflow chamber **f** brings about mixing of the membrane circulation with the reactor output and

ensured that the free gas in the outlet from the reactor could not get into the membrane part but instead was recirculated to the reaction circuit.

The membrane part comprised a pressure tube which
5 contained a ceramic membrane **j** having a length of 200 mm and a specific filter area of 0.0217 m²/m and a cutoff of 450 D and a circulation pump **g** which generated circulation over the membrane. The connection to the reaction part was effected via the above-
10 described crossflow chamber **f**.

The permeate flow through the membrane **j** was brought about by a pressure regulator **F** on the permeate side. This regulator made it possible to build up a pressure difference over the membrane area and thus produce a
15 product flow **i** of aldehydes.

Before the start, the reaction system was pressurized five times with 2.0 MPa of synthesis gas CO/H₂ (1:1) and depressurized each time. The feed solution (1.9 M 1-octene in toluene) was then transferred by means of an
20 HPLC pump from the above-described feed reservoir **h** into the experimental plant **b** to 90% of the desired fill level. After start-up of the reactor circuit, the reaction part was heated to 80°C and a pressure of 2.0 MPa of CO/H₂ (1:1) was set. The reaction system was
25 equilibrated for 1 hour before the catalytically active composition containing 15 mg (58 µmol) of Rh(acac)(CO)₂ and 815 mg (290 µmol) of the POSS-substituted PPh₃ according to the invention, corresponding to an L:Rh ratio of 5:1, in 14 ml of toluene was introduced via
30 the above-described pressure burette **a** (t = 0) under the reaction pressure. The catalyst solution was made up under an argon atmosphere. A differential pressure TMP of 0.35 MPa was subsequently set at the membrane **j** by means of the permeate pressure regulator **F** in order
35 to remove the product **i**, aldehydes, formed from the system. The amount of product **i** discharged was then replaced by feed solution from the reservoir **h** by means of the above-described level regulator **B** on the

autoclave and the fill level in the reaction system was thus kept constant. The reaction was carried out for a period of 14 days; during this time, samples were taken and analyzed at regular intervals. The conversion of 1-octene and the regioselectivity (1/b ratio) were determined by means of GC analysis. Rh and P retentions by the membrane were determined by ICP-OES analysis of the permeate. Both the Rh losses and the P losses were very small. Based on the total amount of rhodium and phosphorus, these losses were 0.07% (Rh) and 0.97% (P).

Continuous hydroformylation of 1-octene; specifications

Reaction volume	220 ml
Reaction temperature	80°C
Reaction pressure	2.0 MPa CO/H ₂ (1/1)
[Rh]	0.26 mM
[1-Octene]	1.9 M
Solvent	Toluene
L:Rh	5:1
Reactor circulation	0.45 l/min
Membrane circulation	2.27 l/min
Membrane	Manufacturer = Inopor Material = TiO ₂ Length = 200 mm di = 7 mm da = 10 mm Pore size = 0.9 nm Filtration area = 0.0217 m ² /m cutoff = 450 D
TMP	0.35 MPa
Permeate flow	10 g/h

Continuous hydroformylation of 1-octene using POSS-substituted PPh₃/Rh

Sample	Time (min)	Yield (%)	l/b
1	0	0	
2	10	0.0	
3	20	1.3	
4	30	4.0	2.8
5	40	6.9	2.8
6	50	10.3	2.8
7	60	13.6	2.8
8	70	17.3	2.8
9	80	20.8	2.8
10	90	23.5	2.8
11	100	27.4	2.8
12	110	30.5	2.8
13	120	34.2	2.8
14	140	40.7	2.8
15	160	46.8	2.8
16	180	52.1	2.8
17	240	67.6	2.8
18	300	79.9	2.8
19	360	89.7	2.8
20	420	90.3	2.8
21	1020	95.8	2.5
22	1080	95.7	2.5
23	1140	95.6	2.5
24	1200	95.7	2.5
25	1260	95.8	2.5
26	1620	96.0	2.5
27	2490	96.3	2.4
28	3030	96.1	2.3
29	3930	96.2	2.3
30	5650	96.4	2.3
31	7050	96.5	2.3
32	8680	96.7	2.3
33	11590	96.4	2.4

Sample	Time (min)	Yield (%)	l/b
34	14260	95.2	2.3
35	17450	93.5	2.3
36	19620	90.5	2.3

Example 2: Hydroformylation of 1-butene in a continuously operated membrane reactor

5 The hydroformylation experiments were carried out in a continuously operated experimental plant; see sketch of plant. This experimental plant consisted of a reaction part and a membrane part. The reaction part comprised a 100 ml autoclave **b** with a circulation pump **c**. The
10 autoclave **b** was equipped with a pressure regulator **A** for the synthesis gas. By means of this pressure regulator **A**, the synthesis gas pressure was kept constant in the entire system during the reaction. The synthesis gas uptake of the system was determined by
15 means of a flow meter **C**. For the introduction of feed and catalyst solutions before the start of the reaction, the reactor was equipped with a pressure burette **a** which could be supplied with synthesis gas and thus allowed introduction of the feed and catalyst
20 solutions under reaction conditions. The autoclave **b** was additionally equipped with a level regulator **B**. The feed pump **e** was controlled by this level regulator **B** and then pumped feed solution comprising the olefin-containing mixture, optionally solvent, from a
25 reservoir **h** into the autoclave **b** so as to keep the level in the autoclave constant. This feed reservoir **h** was blanketed with argon to avoid contact with air. The necessary turbulence in the autoclave was generated by the circulation pump **c** which itself was constructed for
30 this purpose. The pump **c** built up circulation of the

reaction solution via a nozzle in the top of the autoclave **b** and thus ensured appropriate gas/liquid exchange. The synthesis gas and the feed were likewise fed into the nozzle.

5 A crossflow chamber **f** was likewise installed in this circuit. The crossflow chamber **f** separates the reaction part from the membrane part of the plant.

The crossflow chamber **f** brings about mixing of the membrane circulation with the reactor output and
10 ensured that the free gas in the outlet from the reactor could not get into the membrane part but instead was recirculated to the reaction circuit.

The membrane part comprised a pressure tube which contained a ceramic membrane **j** having a length of
15 200 mm and a specific filter area of 0.0217 m²/m and a cutoff of 450 D and a circulation pump **g** which generated circulation over the membrane. The connection to the reaction part was effected via the above-described crossflow chamber **f**.

20 The permeate flow through the membrane **j** was brought about by a pressure regulator **F** on the permeate side. This regulator made it possible to build up a pressure difference over the membrane area and thus produce a product flow **i** of aldehydes.

25 Before the start, the reaction system was pressurized five times with 2.0 MPa of synthesis gas CO/H₂ (1:1) and depressurized each time. The feed solution (1.9 M 1-butene in toluene) was then transferred by means of an HPLC pump from the above-described feed reservoir **h**

30 into the experimental plant to 90% of the desired fill level. After start-up of the reactor circuit, the reaction part was heated to 80°C and a pressure of 20 bar of CO/H₂ (1:1) was set. The reaction system was equilibrated for 1 hour before the catalytically active
35 composition containing 15 mg (58 µmol) of Rh(acac)(CO)₂ and 815 mg (290 µmol) of the POSS-substituted PPh₃ according to the invention, corresponding to an L:Rh ratio of 5:1, in 14 ml of toluene was introduced via

the above-described pressure burette **a** ($t = 0$) under the reaction pressure. The catalyst solution was made up under an argon atmosphere. A differential pressure of 0.30 MPa was subsequently set at the membrane **j** by means of the permeate pressure regulator **F** in order to remove the product **i**, aldehydes, formed from the system. The amount of product **i** discharged was then replaced by feed solution from the reservoir **h** by means of the above-described level regulator **B** on the autoclave and the fill level in the reaction system was thus kept constant. The reaction was carried out for a period of 14 days; during this time, samples were taken and analyzed at regular intervals. The conversion of 1-octene and the regioselectivity (l/b ratio) were determined by means of GC analysis. Rh and P retentions by the membrane were determined by ICP-OES analysis of the permeate. Both the Rh losses and the P losses were very small. Based on the total amount of rhodium and phosphorus, these losses were 0.08% (Rh) and 0.95% (P).

20

Continuous	hydroformylation	experiment;
reactor/reaction specifications		

Reaction volume	220 ml
Reaction temperature	80°C
Reaction pressure	2.0 MPa CO/H ₂ (1/1)
[Rh]	0.28 mM
[1-Butene]	1.9 M
Solvent	Toluene
L:Rh	5:1
Reactor circulation	0.45 l/min
Membrane circulation	2.27 l/min

**Continuous hydroformylation experiment;
reactor/reaction specifications**

Membrane	Manufacturer = Inopor
	Material = TiO ₂
	Length = 200 mm
	di = 7 mm
	da = 10 mm
	Pore size = 0.9 nm
	Filtration area = 0.0217 m ² /m
	cutoff = 450 D
TMP	0.3 MPa
Permeate flow	10 g/h

Continuous hydroformylation of 1-Butene using POSS-substituted PPh₃/Rh

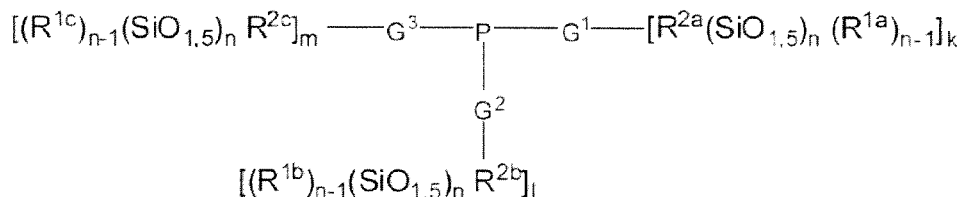
Sample	Time (min)	Yield (%)	l/b
1	0	0	
2	10	0.5	
3	20	1.8	
4	30	6.1	2.9
5	40	9.4	3.0
6	50	13.5	3.1
7	60	17.8	3.0
8	90	27.8	3.0
9	120	38.1	2.9
10	180	58.4	3.0
11	240	70.7	2.9
12	300	82.4	2.9
13	360	85.9	2.9
14	720	92.0	2.8
15	1080	94.3	2.7
16	1200	94.3	2.8
17	1440	94.5	2.7
18	2880	95.6	2.6

Sample	Time (min)	Yield (%)	l/b
19	4320	95.7	2.3
20	5760	95.4	2.4
21	8640	95.3	2.3
22	11520	95.8	2.3
23	14400	95.7	2.2
24	17280	95.0	2.4
25	20160	93.7	2.3
26	23040	92.8	2.3
27	25920	91.8	2.3
28	28800	89.4	2.3

In further embodiments of the invention relating to the use of POSS-modified ligands in catalytically active compositions in hydroformylation, use was made of, inter alia, raffinates such as raffinate I, raffinate II and also mixtures containing olefins having from 3 to 20 carbon atoms as olefin-containing mixtures.

Claims:

1. An organic phosphorus-containing compound covalently bound to polyhedral oligomeric silsesquioxane derivatives of the formula 1



wherein $(R^{1a,b,c})_{n-1}(SiO_{1.5})_n R^{2a,b,c}$ are polyhedral oligomeric silsesquioxane derivatives in which $n \geq 4$;

where R^{1a} , R^{1b} , R^{1c} are each selected independently from the group consisting of identical or different, branched or linear C_1 - C_{20} -alkyl chains, cycloalkyl, C_1 - C_{20} -alkoxy, aryl, aryloxy, heteroaryl and arylalkyl groups,

where k , l , m are each 0 or 1, with the proviso that $k + l + m \geq 1$,

where R^{2a} , R^{2b} , R^{2c} are each the linkage between polyhedral oligomeric silsesquioxane derivatives and G^1 , G^2 and/or G^3 ,

where R^{2a} , R^{2b} , R^{2c} are each selected independently from the group consisting of linear or branched C_1 - C_{20} -alkyl chains, C_3 - C_{10} -cycloalkyl, C_1 - C_{20} -alkoxy, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkenyloxy, aryloxy, C_1 - C_{20} -alkylthio, C_1 - C_{20} -carboxylate, aryl or heteroaryl, C_1 - C_{20} -alkyl halide, fused aryl or heteroaryl, C_3 - C_{10} -cycloalkyl groups, ethers, polyethers, polythioethers, amines, amides, carboxylates, aryl-bridged alkyl chains in which the aryl structure can have further substituents;

- where G1, G2 and G3 are each identical or different units which are monovalently bound to phosphorus and are selected from the group consisting of unsubstituted and/or substituted aliphatic, cycloaliphatic, heterocycloaliphatic, perfluoroalkylated, aromatic, heteroaromatic, fused aromatic, fused heteroaromatic units.
- 5
2. The organic phosphorus-containing compound as claimed in claim 1, wherein n is from 6 to 12, where R^{1a} , R^{1b} , R^{1c} are identical and are each C₁-C₈-alkyl chains or phenyl groups and G1, G2 and/or G3 are identical or different units which are monovalently bound to phosphorus and are selected from the group consisting of acyl, alkyl, aryl, heteroaryl, cycloalkyl.
- 10
- 15
3. The organic phosphorus-containing compound as claimed in claim 2, wherein n = 8 and R^{1a} , R^{1b} , R^{1c} are identical and are each C₄-alkyl chains, where R^{2a} , R^{2b} , R^{2c} are identical and are each C₂-alkyl chains, where G1, G2 and G3 are identical and are each phenyl groups which are monovalently bound to phosphorus.
- 20
- 25
4. A catalytically active composition containing at least one organic phosphorus-containing compound as claimed in any of claims 1-3 and at least one metal selected from group 8, 9 or 10 of the Periodic Table of the Elements.
- 30
5. The catalytically active composition as claimed in claim 4, characterized in that the metal is selected from group 9 of the Periodic Table of the Elements.
- 35

6. The catalytically active composition as claimed in claim 5, characterized in that the metal is rhodium.
- 5
7. A process for the hydroformylation of olefin-containing mixtures, which contains a catalytically active mixture as claimed in any of claims 4-6.
- 10
8. The process for the hydroformylation of olefin-containing mixtures as claimed in claim 7, characterized in that the olefin-containing mixture contains olefins having from 3 to 20 carbon atoms.
- 15
9. The process for the hydroformylation of olefin-containing mixtures as claimed in claim 8, characterized in that the olefin-containing mixture is selected from the group consisting of propene, raffinate I, raffinate II, raffinate III.
- 20
10. The process for the hydroformylation of olefin-containing mixtures as claimed in claim 8, characterized in that the olefin-containing mixture contains 1-butene.
- 25
11. The process for the hydroformylation of olefin-containing mixtures as claimed in claim 8, characterized in that the olefin-containing mixture contains 1-octene.
- 30
12. The process for the hydroformylation of olefin-containing mixtures as claimed in any of claims 7 to 11, characterized in that the catalytically active composition is separated off from a stream containing the product by means of organic
- 35

nanofiltration without the use of thermal separation processes.

13. A multiphase reaction mixture comprising:
- a) an olefin-containing mixture as claimed in any
5 of claims 8-11,
 - b) a gas mixture containing carbon monoxide,
hydrogen and
 - c) aldehydes,
- 10 characterized by the presence of a catalytically active composition as claimed in any of claims 4-6.