Silsesquioxanes as Models of Silica Supported Catalyst I. [3-(Diphenylphosphino)propyl]-hepta[propyl]-[octasilsesquioxane] and [3-Mercapto-propyl]-hepta[propyl]-[octasilsesquioxane] as Ligands for Transition-Metal Ions[*]

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The ligand [3-(diphenylphosphino)propyl]-hepta[propyl]-[octasilsesquioxane] (dpps) can be prepared by reacting [3-chloropropyl]-hepta[propyl]-[octasilsesquioxane] (cs) with $KP(Ph)_2$. The transition-metal complexes $[Rh(CO)(dpps)_2Cl]$, $[Rh(COD)(dpps)Cl]$ and $[Pt(dpps)_2Cl_2]$ are synthesized as models of functionalized silica-gel surfaces. Without destruction of the siloxane cage, the intermediate compounds $Hg(ss)_2$, and $Pb(ss)_2$ are obtained from [3-mercaptopropyl]-hepta[propyl]-[octasilsesquioxane] (ssH). Starting from $Pb(ss)_2$, the transition-metal complexes $[Au(ss)(P(Ph)_3)]$, $[Rh(ss)(CO)_2]_2$ and $[Rh(ss)(COD)]_2$ are accessible. The compounds have been characterized mostly by ^{1}H, ^{13}C, ^{29}Si and 31P NMR spectroscopy. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: octa(organosilsesquioxane); phosphane ligands; thiolate ligands; platinum group metal complexes; models of silica-supported catalysts

INTRODUCTION

Immobilizing transition-metal catalysts by affixing them to a surface-modified silica gel has been studied quite intensively in recent years[1]. The aim was to combine the favorable properties of homogeneous catalysts with the easy separability of heterogeneous ones. For this purpose, solid polysiloxanes containing transition-metal catalysts bound to phosphino $[silica–(CH_2)_n–P(Ph)_2]$ or mercapto groups $[silica-(CH_2)_n-SH]$ were prepared by several routes.[2,3] The characterization of the materials so obtained proved difficult. The number of methods available for studying amorphous solids is limited, but does include MAS NMR,[4] IR spectroscopy,[6] elemental analysis and kinetics.[7] The cause of the sometimes diminished activity of silica-gel-affixed catalysts or leaching problems cannot be assessed easily using these analytical methods. However, the synthesis of soluble model compounds can be used as an alternative. Thus, Marciniec *et al.* used rhodium(I)complexes with cyclo-octadiene (COD) and disiloxydiphosphine, $[(Ph)_2P(CH_2)_nSi(CH_3)_2]_2O$ ($n = 1–3$) or the trisiloxyphosphine, $(Ph)_2P(CH_2)_2(CH_3)Si[O-Si(CH_3)_2(CH_2)_2P(Ph)_2]_2$ as ligands.[8] Imaki *et al.* described the synthesis of multidentate phosphine ligands connected to cyclotetrasiloxane.[9] Both systems have flexible siloxane skeletons whose mobility will influence their complexing properties. Feher *et al.* and other groups use partially condensed organosilsesquioxanes to simulate the direct attachment of metal complexes to silica surfaces.[10–12] Dittmar suggested the use of functionalized octa(organosilsesquioxanes) for simulating the rigid surfaces of modified silica gel.[13] The use
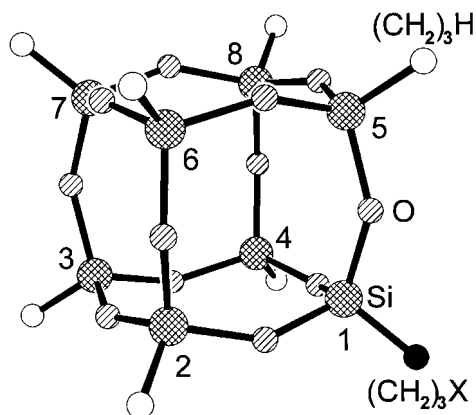
Figure 1 Sketch of the structure of the silsesquioxane ligands with X = Cl (cs), X = P(Ph)$_2$ (dpps) and X = SH (ssH).

of fully functionalized octa(organosilsesquioxanes) did not prove useful for modeling because their multidentate behavior prevents the formation of easily defined products. Therefore, transition-metal complexes with monofunctional octa(organosilsesquioxane) ligands will be presented in this paper.

RESULTS

General spectroscopic features of the compounds

The substitution patterns of mixed substituted octa(organosilsesquioxanes) (Fig. 1) give rise to clearly distinguishable ^{29}Si NMR spectra.[14] The assignment is furthered by ^{29}Si 2D INADEQUATE NMR spectroscopy. The ^2J(Si–O–Si) coupling is below 1 Hz.

The monosubstituted octa(organosilsesquioxanes) give a pattern of three lines with intensities of 3:1:3 for the H(CH$_2$)$_3$Si part of the molecule. For most of the compounds studied here, a greater shift to lower fields is observed for the 2-, 4- and 5-positions than that for silicon in the 7- or 3-, 6- and 8-positions respectively. The latter resonances were often so close that they could not be resolved at 7.046 T. The ^{13}C NMR and ^{1}H NMR spectra of the n-propyl groups follow the same patterns as the silicon atoms to which they are attached.

The ^{29}Si signal from the X(CH$_2$)$_3$Si segment (intensity = 1) is found most often upfield of the H(CH$_2$)$_3$Si groups. The ^{29}Si NMR data for the cages are collected in Table 1.

[3-(Diphenylphosphino)propyl]-hepta(propyl)-octa(silsesquioxane) (dpps), and derivatives

dpps
The synthesis of dpps using cs and KP(Ph)$_2$ follows the normal procedure[15] except that an excess of KP(Ph)$_2$ was removed by a phosphate buffer to avoid the formation of KOH leading to the destruction of the siloxane cage. The compound proved to be stable towards water and air. The ^{31}P NMR spectrum shows a line at $\delta = -18.6$ ppm, as expected for such a compound.[3,8] The ^{29}Si signal of

Table 1. ^{29}Si NMR data

Compound	1-Si—(CH$_2$)$_3$X (ppm)	^4J(Si,P) (Hz)	2,4,5-Si—(CH$_2$)$_3$H (ppm)	3,6,8-Si—(CH$_2$)$_3$H (ppm)	7-Si—(CH$_2$)$_3$H (ppm)
dpps	−66.74 d	1.4	−66.14	−66.24	−66.22
[Rh(CO)dpps$_2$Cl]	−66.93 t	1.4	−66.04	−66.20	−66.14
[Rh(COD)dppsCl]	−66.84 d	3.0	−65.96	−66.13	−66.11
[Ptdpps$_2$Cl$_2$]	−68.04 t	2.0	−66.54	−66.63	−66.56
ssH	−66.60		−66.05	−66.13	−66.13
Hg(ss)$_2$	−66.74		−66.04	−66.18	−66.18
Pb(ss)$_2$	−66.49		−65.99	−66.11	−66.08
[Au(PPh$_3$)ss]	−65.54		−66.03	−66.23	−66.17
[Rh(CO)$_2$ss]$_2$	−67.28		−65.97	−66.11	−66.11
[Rh(COD)ss]$_2$	−66.53		−66.02	−66.16	−66.11

the $(Ph)_2P$—$(CH_2)3$—Si group shows a $^4J(Si,P)$ coupling of 1.38 Hz.

trans-[Rh(CO)dpps$_2$Cl]

The fixation of $[Rh(CO)_2Cl]_2$ to a silica surface functionalized with phosphino groups, together with their catalytic properties, was explored by several groups because of the high activity of the homogeneous analogues.[16–18] The reaction of dpps with $[Rh(CO)_2Cl]_2$ in a 4:1 molar ratio gives yellow *trans*-[Rh(CO)dpps$_2$Cl] with release of CO (Eq. 1)

$$[Rh(CO)_2Cl]_2 + 4\ dpps \rightarrow$$
$$2trans\text{-}[Rh(CO)dpps_2Cl] + 2CO \quad [1]$$
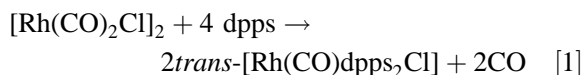
The ^{31}P NMR spectrum of the complex gives a doublet at $\delta = 22.83$ ppm with splitting due to $^1J(Rh,P) = 124.9$ Hz compatible with a *trans* configuration of the phosphine ligands.[19,20] The triplet in the ^{29}Si spectrum can be explained by coupling with both phosphorus atoms. Coupling with the rhodium atom is too small to be observed. Also, the ^{13}C NMR spectrum in the region of the methylene groups consists of triplets. The $\nu(CO)$ band in the IR appears at 1970 cm^{-1} and is characteristic for the kind of compound assumed.[20]

[Rh(COD)dppsCl]

As a model for $[Rh(COD)Cl]_2$ immobilized on siloxanes,[7,21] [Rh(COD)dpps Cl] was synthesized from a reaction of $[Rh(COD)Cl]_2$ and dpps in a molar ratio of 1:2 (Eq. 2)

$$[Rh(COD)Cl]_2 + 2\ dpps \rightarrow$$
$$2[Rh(COD)dppsCl] \quad [2]$$
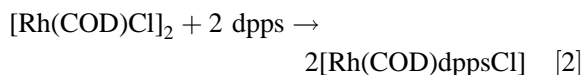
The $^1J(Rh,P)$ coupling of 150.4 Hz of the resonance at $\delta = 25.4$ ppm in the ^{31}P spectrum is in accordance with a literature value of 149 Hz for a comparable compound.[22] The same arguments apply to the ^{13}C resonance. A doublet at $\delta = 69.87$ ppm ($^1J(Rh,C) = 13.7$ Hz) can be assigned to C atoms of the COD ring positioned *trans* to the Cl atom. A doublet of doublets at $\delta = 104.87$ ppm comes from C atoms of the COD ring found at *trans* positions relative to the P atoms with $^1J(Rh,C) = 12.5$ Hz and $^2J(P,C) = 7.0$ Hz. The ^{29}Si spectrum shows a doublet only for the $Si(CH_2)_3X$ part of the molecule due to $^4J(P,Si) = 3.0$ Hz.

cis-[Ptdpps$_2$Cl$_2$]

Fyfe and co-workers, and Jiang *et al.*, describe the ligation of platinum salts at phosphino-functionalized siloxanes.[5,23] Some of them were character-

ized by ^{31}P MAS NMR spectroscopy.[4] As a model, *cis*-[Ptdpps$_2$Cl$_2$] was obtained by reaction of dpps with $[Pt(COD)Cl_2]$ in CH_2Cl_2 (Eq. 3).

$$[Pt(COD)Cl_2] + 2\ dpps \rightarrow$$
$$cis\text{-}[Ptdpps_2Cl_2] + COD \quad [3]$$
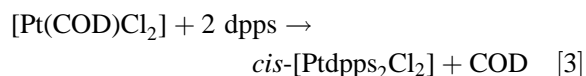
The resulting white solid was insoluble in alkanes and in benzene. NMR measurements had to be run in CDCl$_3$. A value of $^1J(Pt,P) = 3636$ Hz is typical for *cis*-configured platinum complexes of this kind.[5] The ^{29}Si signal for the $Si(CH_2)_3X$ part is a triplet because of coupling with two phosphorus atoms. The signals of the 2-,4- and 5-silicon atoms of the silsesquioxane cage are shifted to higher fields and found at $\delta = -66.63$ ppm, whereas the 3-,6- and 8-silicon atoms resonate at $\delta = -66.54$ ppm and that in the 7-position at $\delta = -66.56$ ppm. The assignment was made using ^{29}Si 2D INADEQUATE NMR.

[3-Mercaptopropyl]-hepta[propyl]-octa[silsesquioxane] derivatives and their complexes

Hg(ss)$_2$

To prepare mercapto complexes from ssH, it is necessary to avoid the formation of strong acids as the siloxane cage is sensitive to them. The product [Hgss$_2$] of the reaction between Hg(CN)$_2$ and ssH (Eq. 4).

$$Hg(CN)_2 + 2\ ssH \rightarrow Hg(ss)_2 + 2HCN \quad [4]$$
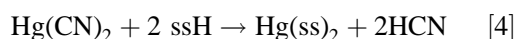
gives the correct signal pattern in the ^{29}Si spectrum to indicate the survival of the octasilsesquioxane cage. However, probably due to fluxionality, neither the ^{13}C nor the ^{29}Si spectra shows ^{199}Hg satellites. ^{199}Hg NMR yields a signal at $\delta = -338$ ppm.

Pb(ss)$_2$

Likewise, the exchange of the proton of ssH by Pb^{2+} to yield Pb(ss)$_2$ (Eq. 5).

$$(CH_3COO)_2Pb + 2\ ssH \rightarrow Pb(ss)_2 +$$
$$2CH_3COOH \quad [5]$$
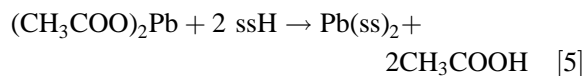
does not affect the siloxane cage. The ^1H and the 13C spectra are somewhat broadened.

[Au(PPh$_3$)ss]

The lead in Pb(ss)$_2$ can be substituted by a number of transition metals, as was observed by Delgado *et al.* for similar compounds.[24] For instance,

Figure 2 Variable-temperature of the COD part the ^{13}C NMR spectra of [Rh(COD)ss]$_2$.

[Au(PPh$_3$)ss] can be obtained this way (Eq. 6).
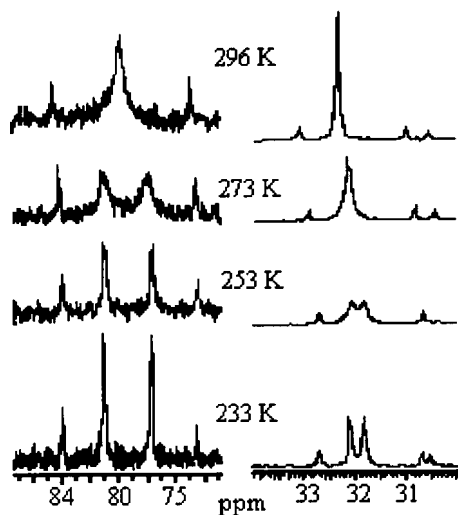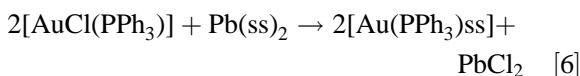
$$2[AuCl(PPh_3)] + Pb(ss)_2 \rightarrow 2[Au(PPh_3)ss]+ \qquad PbCl_2 \quad [6]$$

The product shows a ^{29}Si resonance for S(CH$_2$)$_3$Si at $\delta = -65.54$ ppm downfield relative to that of the H(CH$_2$)$_3$Si groups ($\delta = -66.17$ ppm for the 7-, $\delta = -66.23$ ppm for the 3-,6-,8-, and $\delta = -66.03$ ppm for the 2-,4-,5-positions of the siloxane cage) of the molecule. The ^{31}P NMR signal at $\delta = 35.89$ ppm is comparable with those found by Delgado.

[Rh(CO)$_2$ss]$_2$

Howell and co-workers describe the immobilization of [Rh(CO)$_2$Cl]$_2$ on silica-gel surfaces covered with mercaptopropyl groups.[25] There the μ-Cl bridge atoms were substituted by μ-S(CH$_2$)$_3$–silica gel units. However, no uniform products could be obtained by this method as it was not in all [Rh(CO)$_2$Cl]$_2$ molecules that both μ-Cl bridges were exchanged. A complete reaction was observed by Bolton *et al.*[26] and Kalck *et al.*[27] by using reactions with HSR where R = CH$_3$, C$_6$H$_5$, *p*-FC$_6$H$_4$, C$_6$F$_5$, CH$_2$C$_6$H$_5$ and t-C$_4$H$_9$. Using a similar procedure, the functionalized silsequioxane could be transferred from Pb(ss)$_2$ to [Rh(CO)$_2$ss]$_2$ (Eq. 7).

$$[Rh(CO)_2Cl]_2 + Pb(ss)_2 \rightarrow [Rh(CO)_2ss]_2+ \qquad PbCl_2 \quad [7]$$
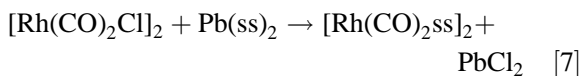
In the IR, v (CO) = 2072, 2049, 2006 cm^{-1} for

[Rh(CO)$_2$ss]$_2$, which corresponds closely to the values found for compounds prepared by Bolton. The ^{29}Si NMR spectrum follows the same general features. While the CO groups show splitting due to ^1J(Rh,C) in the ^{13}C NMR spectrum, no sign of an interaction is observed for the C atoms and protons of the S(CH$_2$)$_3$Si segments.

[Rh(COD)ss]$_2$

The dynamics of a ligand sphere of sulfur and cyclo-octadiene around a rhodium center of the type [Rh(COD)(SR)]$_2$ (with R = CH$_3$, C$_2$H$_5$, i-C$_3$H$_7$, t-C$_4$H$_9$ and C$_6$H$_5$) were studied by Woodward with the help of ^{1}H NMR spectroscopy.[28] A single-crystal X-ray diffraction analysis of [Rh(COD)(SCH$_3$)]$_2$ was published by Wark and Stephan.[29] By using Pb(ss)$_2$, a rhodium complex containing COD and the functionalized silsesquioxane could be obtained (Eq. 8).

$$[Rh(COD)Cl]_2 + Pb(ss)_2 \rightarrow [Rh(COD)ss]_2+ \qquad PbCl_2 \quad [8]$$
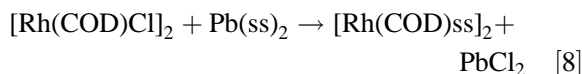
The ^{29}Si NMR spectrum does not show any peculiarities. The ^{1}H and ^{13}C resonance signals of the μ-ss-bridges are not temperature-dependent, but the signals of the COD ligand are, as shown in Fig. 2. The ^{13}C NMR spectrum indicates the presence of two isomers distinguished by the freedom of rotation of the COD ring. The major isomer with the rotating ring gives a broad band at 79.6 ppm for the vinyl C atoms and a sharp line at 32.2 ppm for the CH$_2$ groups of the COD at 298 K. At low temperatures (below -233 K) rotation ceases and the resonances split into doublets of equal intensities ($\delta = 77.6$, 80.9 ppm; ^1J(Rh,C) = 11 Hz) and two singlets ($\delta = 31.6$, 31.9 ppm) due to the unsaturated and saturated parts of the ring. The minor isomer with the COD ring-locked displays two sharp doublets ($\delta = 74.6$ ppm, ^1J(Rh,C) = 15 Hz; $\delta = 84.3$ ppm, ^1J(Rh,C) = 10 Hz) and two singlets ($\delta = 30.9$, 33.0 ppm). The chemical shifts and the carbon–rhodium couplings are as expected from literature data.[22] The existence of two isomers can be explained by a slow inversion around the sulfur atoms of the Rh$_2$S$_2$ ring.[28] Of the three possible configurations of the ring, the one with the two siloxane cages on the sulfur in the axial position can be excluded from consideration by the size of the cage. Of the other two, the one with the siloxane cages in both the axial and the equatorial position seems to leave the most room for a free rotation of the COD ring about the rhodium. Two structure determinations of complexes having a

Rh_2S_2 ring core showed both ligands on the sulfur on the equatorial side of the ring.[28,29]

The compounds presented in this work will be used as soluble models of silica-fixed transition-metal catalysts to study the kinetics of catalysis. We also plan to study the influence of neighboring functional groups on the stability and activity of transition-metal catalysts by using di-, tri- and tetra-functionalized octa(propylsilsesquioxanes).

EXPERIMENTAL

Reactions with air-sensitive compounds were carried out under argon. Solvents were purified and dried by standard methods. cs and ssH were prepared and isolated as described previously[14] and all other reagents were commercially available.

Characterization of ligands and complexes

NMR
Bruker AX300 (^1H, 300 MHz; $^{13}C\{^1H\}$, 75.43 MHz; $^{29}Si\{^1H\}$, 59.60 MHz; $^{31}P\{^1H\}$, 121.44 MHz); Bruker WM250 ($^{31}P\{^1H\}$, 101.20 MHz; $^{199}Hg\{^1H\}$, 44.57 MHz); solvent, C_6D_6 (cis-[Ptdpps$_2$Cl$_2$], CDCl$_3$), T = 296 K.

IR
Nicolet FT-IR spectrophotometer 510Pspectra (KBr disk).

Carbon and hydrogen analyses
Perkin-Elmer Universalverbrennungsautomat PE 2400.

Syntheses

[3-(Diphenylphosphino)propyl]-hepta[propyl]-[octasilsesquioxane] (dpps)
A solution of cs (2 g, 2.45 mmol) in 20 ml THF was titrated with KP(Ph)$_2$ (0.1 mol^{-1} in THF) until the change from white to red color was permanent. n-Hexane (100 ml) was added and the solution was extracted twice with 100 ml KH$_2$PO$_4$/Na$_2$HPO$_4$ buffer (pH = 6.8) and twice with water. After the organic phase had been dried with MgSO$_4$ and the n-hexane had been removed, a white oil was obtained which was recrystallized from methanol and purified by flash chromatography with a silica column and CH$_2$Cl$_2$ as mobile phase. Yield 785 mg (32.7%); m.p. 71.5 °C.

IR (KBr): v = 3074 cm^{-1} w, 3056 w [v(CH), aromatic]; 2959 m, 2930 m, 2870 m [v(CH), aliphatic]; 1588 w, 1482 w, 1464 m, 1435 w, 1410 w, 1379 w, 1341 m, 1302 sh, 1221 sh; 1103 vs [v_{asym}(SiOSi)]; 899 m, 793 m; 739 m, 694 s, 550 m; 475 s, 416 s.

^1H NMR (C_6D_6): δ = 0.74 (m, 14H, Si—C$\underline{H}_2$—CH$_2$—CH$_3$), 0.84 (m, 2H, Si—C$\underline{H}_2$—CH$_2$—CH$_2$—P), 0.96 (m, 21H, Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 1.56 (m, 14H, Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 1.76 (m, 2H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$—P), 2.06 (m, 2H, Si—CH$_2$—CH$_2$—C$\underline{H}_2$—P), 7.07–7.77 (m, 10H, aromatic H).

^{13}C NMR (C_6D_6): δ = 14.4 [d, ^3J(C,P) = 12.7 Hz, Si—C$\underline{H}_2$—CH$_2$—CH$_2$—P], 14.98, 15.03 (Si—C$\underline{H}_2$—CH$_2$—CH$_3$), 17.0 (Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 17.7 (Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 20.2 [d, ^2J(C,P) = 18.2 Hz, Si—C$\underline{H}_2$—CH$_2$—CH$_2$—P], 31.9 [d, ^3J(C,P) = 12.5 Hz, Si—CH$_2$—CH$_2$—C$\underline{H}_2$—P]; 128.7 (d), 131.2 (d); 133.3 (d); 139.9 (d) (aromatic C).

^{31}P NMR (C_6D_6): δ = −18.6 ppm.

Analysis $C_{36}H_{65}O_{12}PSi_8$ (945.6): calcd: C 45.73, H 6.93; found: C 46.00, H 7.19%.

Complexes of [3-(diphenylphosphino)propyl]-hepta[propyl]-[octasilsesquioxane]
For trans-[Rh(CO)dpps $_2$Cl], [Rh(COD)(dpps)Cl], cis-[Ptdpps$_2$Cl$_2$], dpps (94.6 mg, 0.10 mmol) and the platinum group metal complex (**M**) were stirred together in 10 ml CH$_2$Cl$_2$ for 2 h at room temperature and then the volatile compounds were removed in vacuo.

trans-[Rh(CO)dpps $_2$Cl]
M: [Rh(CO)$_2$Cl]$_2$ (9.7 mg, 0.025 mmol), yield 98 mg (95.3%) yellow solid, m.p. 86°C.

IR (KBr): v = 3077 cm^{-1} w, 3058 w [v(CH), aromatic]; 2961 m, 2931 m, 2872 m [v(CH), aliphatic]; 1970 s [v(CO)]; 1458 m, 1437 w, 1410 w, 1379 w, 1341 m, 1302 sh, 1221 sh; 1107 vs [v_{asym}(SiOSi)]; 1067 sh, 1029 sh, 934 sh, 897 m, 797 m, 741 m, 693 s, 546 m, 475 s, 412 s.

^1H NMR (C_6D_6): δ = 0.77 (m, 14H, Si—C$\underline{H}_2$—CH$_2$—CH$_3$), 0.89 (m, 2H, Si—C$\underline{H}_2$—CH$_2$—CH$_2$—P), 0.99 (m, 21H, Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 1.60 (m, 14H, Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 1.99 (m, 2H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$—P), 2.79 (m, 2H, Si—CH$_2$—CH$_2$—C$\underline{H}_2$—P), 7.03–7.87 (m, 10H, aromatic H).

^{13}C NMR (C_6D_6): δ = 14.5 [t, ^3J(C,P) = 6.8 Hz, Si—C$\underline{H}_2$—CH$_2$—CH$_2$—P], 14.97, 15.08 (Si—C$\underline{H}_2$—CH$_2$—CH$_3$), 17.1 (Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 17.73, 17.78 (Si—CH$_2$—CH$_2$—C$\underline{H}_3$), 19.0 (s, Si—

CH$_2$—CH$_2$—CH$_2$—P), 30.8 (t, ^{1}J(C,P) = 13.2 Hz, Si—CH$_2$—CH$_2$—CH$_2$—P); 128.5, 128.6 (d), 130.1, 134.0 (t) (aromatic C), 188.4 [d, ^{1}J(C,Rh) = 73 Hz, CO].

^{31}P NMR (C$_6$D$_6$, 101.20 MHz): δ = 22.8 ppm [d, 1J(P,Rh) = 124.9 Hz].

Analysis: C$_{73}$H$_{130}$ClO$_{25}$P$_2$RhSi$_{16}$ (2057.5): calcd: C 42.62; H 6.37; found: C 42.90, H 6.47%.

[Rh(COD)dppsCl]

M: [Rh(COD)Cl]$_2$ (24.7 mg, 0.05 mmol), yield 115 mg (96.5%) yellow solid, m.p. 107.5°C.

IR (KBr): ν = 3077 cm^{-1} w, 3056 w [υ(CH), aromatic]; 2959 m, 2930 m, 2871 m (υ(CH), aliphatic); 1484 w, 1460 m, 1437 w, 1408 w, 1379 w, 1339 m, 1304 sh, 1223 sh; 1109 vs (υ_{asym}(SiOSi));1068 sh, 1028 sh, 933 sh, 895 m, 789 m, 741 m, 694 s, 544 m, 475 s, 413 s.

^{1}H NMR (C$_6$D$_6$): δ = 0.80 (m, 14H, Si—CH$_2$—CH$_2$—CH$_3$), 0.92 (m, 2H, Si—CH$_2$—CH$_2$—CH$_2$—P), 1.00 (m, 21H, Si—CH$_2$—CH$_2$—CH$_3$), 1.61 (m, 14H, Si—CH$_2$—CH$_2$—CH$_3$), 1.91 (dt, 4H, J(H,Rh) = 155 Hz, CH$_2$(COD)], 1.92 [dt, 4H, J(H,Rh) = 149 Hz, CH$_2$(COD)], 2.37 (m, 2H, Si—CH$_2$—CH$_2$—CH$_2$—P), 2.66 (t, 2H, Si—CH$_2$—CH$_2$—CH$_2$—P), 3.08 [s, 2H, CH(COD) *trans* of Cl], 5.81 [s, 2H, CH(COD) *trans* of P], 7.06–7.71 (m, 10H, aromatic H).

^{13}C NMR (C$_6$D$_6$): δ = 14.9 (d, ^{3}J(C,P) = 5.5 Hz, Si—CH$_2$—CH$_2$—CH$_2$—P), 15.1 (Si—CH$_2$—CH$_2$—CH$_3$), 17.03, 17.07 (Si—CH$_2$—CH$_2$—CH$_3$), 17.67, 17.76 (Si—CH$_2$—CH$_2$—CH$_3$), 21.0 (s, Si—CH$_2$—CH$_2$—CH$_2$—P), 31.4 [d, ^{2}J(C,Rh) = 319.2 Hz, CH$_2$(COD)], 31.6 [d, ^{1}J(C,P) = 25.0 Hz, Si—CH$_2$—CH$_2$—CH$_2$—P], 69.9 [d, ^{1}J(C,Rh) = 13.7 Hz, CH(COD) *trans* of Cl], 104.9 [dd, ^{1}J(C,P) = 7.0 Hz, ^{2}J(C,Rh) = 12.5 Hz, CH(COD) *trans* of P], 128.4 (d), 130.1 (d), 134.1 (d) (aromatic C).

^{31}P NMR (C$_6$D$_6$, 101.20 MHz): δ = 25.4 ppm [d,^{1}J(P,Rh) = 150 Hz].

Analysis: C$_{44}$H$_{77}$ClO$_{12}$PRhSi$_8$ (1192.1): calcd: C 44.33, H 6.51; found: C 43.97, H 6.68%.

cis-[Ptdpps$_2$Cl$_2$]

M: Pt(COD)Cl$_2$ (18.7 mg, 0.05 mmol), yield 104.1 mg (96.6%) white solid, m.p. 211.8 °C.

IR (KBr): ν = 3077 cm^{-1} w, 3055 w [υ(CH), aromatic]; 2961 m, 2931 m, 2874 m [υ(CH), aliphatic]; 1483 w, 1460 m, 1439 w, 1408 w, 1379 w, 1339 m, 1302 sh, 1264 sh, 1223 sh; 1105 vs [υ_{asym}(SiOSi)]; 1066 sh, 1029 sh, 939 sh, 895 m, 801 s, 742 m, 694 s, 549 m, 475 s, 413 s.

^{1}H NMR (CDCl$_3$): δ = 0.55 (m, 14H, Si—CH$_2$—

CH$_2$—CH$_3$), (Si—CH$_2$—CH$_2$—CH$_2$—P, super-position with —CH$_3$), 0.93 (m, Si—CH$_2$—CH$_2$—CH$_3$), 1.37 (m, 14H, Si—CH$_2$—CH$_2$—CH$_3$), 1.63 (m, 2H, Si—CH$_2$—CH$_2$—CH$_2$—P), 2.29 (m, 2H, Si—CH$_2$—CH$_2$—CH$_2$—P), 7.21–7.49 (m, 10H, aromatic H).

^{13}C NMR (CDCl$_3$): 13.4 [d, ^{3}J(C,P) = 6.9 Hz, Si—CH$_2$—CH$_2$—CH$_2$—P), 14.06, 14.15 (Si—CH$_2$—CH$_2$—CH$_3$), 16.1 (Si—CH$_2$—CH$_2$—CH$_3$), 17.1 (Si—CH$_2$—CH$_2$—CH$_3$), 18.6 (s, Si—CH$_2$—CH$_2$—CH$_2$—P), 32.5 [d, ^{1}J(C,P) = 41.2 Hz, Si—CH$_2$—CH$_2$—CH$_2$—P]; 127.6 (t), 130.6, 133.2 (t).

^{31}P NMR (C$_6$D$_6$ 101.20 MHz): δ = 5.6 ppm [t, 1J(P,Pt) = 3636.2 Hz].

Analysis: C$_{72}$H$_{130}$Cl$_2$O$_{24}$P$_2$PtSi$_{16}$ (2157.1): calcd: C 40.09, H 6.07; found: C 39.89, H 5.97%.

Complexes of [3-Mercaptopropyl]-hepta[propyl]-(octasilsesquioxane)

Hg(ss)$_2$

ssH (50 mg, 0.063 mmol) dissolved in 20 ml ethanol was added to a stirred solution of Hg(CN)$_2$ (8.0 mg, 0.032 mmol) in 10 ml ethanol. The white precipitate was filtered after 15 min. and dried *in vacuo*. Yield 41 mg, 72.8% white solid.

IR (KBr): ν = 2957 m, 2930 m, 2870 m [υ(CH), aliphatic]; 1464 m, 1435 w, 1408 w, 1377 w, 1339 m, 1302 sh, 1221 sh; 1107 vs [υ_{asym}(SiOSi)]; 1067 sh, 1032 sh, 899 m, 785 m, 694 s, 554 m, 476 s, 411 s.

^{1}H NMR (C$_6$D$_6$): δ = 0.78 (m, 14H, Si–CH$_2$–CH$_2$–CH$_3$), 0.90 (m, 2H, Si–CH$_2$–CH$_2$–CH$_2$–S), 1.00 (m, 21H, Si—CH$_2$—CH$_2$—CH$_3$), 1.59 (m, 14H, Si—CH$_2$—CH$_2$—CH$_3$), 1.89 (m, 2H, Si—CH$_2$—CH$_2$—CH$_2$—S), 2.89 (m, 2H, Si—CH$_2$—CH$_2$—CH$_2$—S).

^{13}C NMR (C$_6$D$_6$): δ = 12.3 (Si—CH$_2$—CH$_2$—CH$_2$—S), 15.01, 15.03 (Si—CH$_2$—CH$_2$—CH$_3$), 17.02, 17.11 (Si—CH$_2$—CH$_2$—CH$_3$), 17.71, 17.81 (Si—CH$_2$—CH$_2$—CH$_3$), 31.3 (Si—CH$_2$—CH$_2$—CH$_2$—S), 32.1 (Si—CH$_2$—CH$_2$—CH$_2$—S).

^{199}Hg NMR (CDCl$_3$): δ = −338 ppm.

Pb(ss)$_2$

ssH (500 mg, 0.66 mmol) dissolved in 10 ml CH$_2$Cl$_2$ was added to a solution of (CH$_3$COO)$_2$Pb·3H$_2$O (120 mg, 0.32 mmol) in 10 ml dimethylformamide (DMF). After being stirred for 1 h at room temperature the solvent was removed *in vacuo*. Yield 552 mg (96.2%) yellow solid, m.p. 198.9°C.

IR (KBr): ν = 2959 cm^{-1} m, 2930 m, 2872 m [υ(CH), aliphatic]; 1545 w, 1464 m, 1408 w, 1379

w, 1339 m, 1302 sh, 1223 sh; 1108 vs [v_{asym}(SiOSi)]; 899 m, 783 m, 739 m, 696 s; 554 m, 476 s.

^{1}H NMR (C_6D_6): δ = 0.83 (m, 14H, Si—C$\underline{H}_2$—CH$_2$—CH$_3$), (Si—C$\underline{H}_2$—CH$_2$—CH$_2$—S, superposition with —CH$_3$), 1.02 (m, Si—CH$_2$—CH$_2$—C$\underline{H}_3$), 1.66 (m, 14H, Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 2.04 (m, 2H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$—S), 3.78 (m, 2H, Si—CH$_2$—CH$_2$—C$\underline{H}_2$—S).

^{13}C NMR (C_6D_6): δ = 12.5 (Si—$\underline{C}$H$_2$—CH$_2$—CH$_2$—S), 15.09, 15.12 (Si—$\underline{C}$H$_2$—CH$_2$—CH$_3$), 17.08, 17.17 (Si—CH$_2$—$\underline{C}$H$_2$—CH$_3$), 17.74, 17.88 (Si—CH$_2$—CH$_2$—$\underline{C}$H$_3$), 30.1 (Si—CH$_2$—$\underline{C}$H$_2$—CH$_2$—S), 32.5 (Si—CH$_2$—CH$_2$—$\underline{C}$H$_2$—S).

Analysis: $C_{48}H_{110}O_{24}PbS_2Si_{16}$ (1767.7): calcd: C 32.62; H 6.22; found: C 32.44; H 6.40%.

For [Au(PPh$_3$)ss], [Rh(CO)$_2$ss]$_2$ and [Rh(COD)ss]$_2$, Pb(ss)$_2$ and the metal complex (**M**) were stirred together in THF (20 ml) at room temperature. After 3 h the PbCl$_2$ was centrifuged off and the solvent removed to dryness *in vacuo*.

[Au(PPh$_3$)ss]

Pb(ss)$_2$ (178.7 mg, 0.100 mmol), **M**: ClAu(PPh$_3$)$_3$ (100.0 mg, 0.202 mmol), yield 225 mg (79.9%) white solid, m.p. 175.0°C.

IR (KBr): v = 3079 cm^{-1} w, 3053w [v(CH), aromatic]; 2959 m, 2928, 2870 m [v(CH), aliphatic]; 1588 w, 1482 w, 1464 m, 1435 w, 1410 w, 1379 w, 1341 m, 1302 sh, 1221 sh; 1109 vs [v_{asym}(SiOSi)]; 896 m, 795 m, 747 m, 695 s, 669m, 542 m, 475 s.

^{1}H NMR (C_6D_6): δ = 0.75 (m, 14H, Si—C$\underline{H}_2$—CH$_2$—CH$_3$), 0.98 (m, 21H, Si—CH$_2$—CH$_2$—C$\underline{H}_3$), 1.24 (m, 2H, Si—C$\underline{H}_2$—CH$_2$—CH$_2$—S), 1.59 (m, 14H, Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 2.28 (m, 2H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$—S), 3.44 (m, 2H, Si—CH$_2$—CH$_2$—C$\underline{H}_2$—S), 6,95 – 7.35 (m, 5H, aromatic H).

^{13}C NMR (C_6D_6): δ = 12.6 (Si—$\underline{C}$H$_2$—CH$_2$—CH$_2$—S), 14.97, 15.08, 15.12 (Si—$\underline{C}$H$_2$—CH$_2$—CH$_3$), 17.01, 17.03 (Si—CH$_2$—$\underline{C}$H$_2$—CH$_3$), 17.67, 17.70 (Si—CH$_2$—CH$_2$—$\underline{C}$H$_3$), 31.9 (Si—CH$_2$—$\underline{C}$H$_2$—CH$_2$—S), 32.4 (Si—CH$_2$—CH$_2$—$\underline{C}$H$_2$—S), 129.4 (d), 130.7, 131.4 (d), 134.6 (d) (aromatic C).

^{31}P NMR (CDCl$_3$): δ = 35.9 ppm.

Analysis: $C_{42}H_{70}AuO_{12}PSSi_8$ (1251.7): calcd: C 70.27, H 5.59; found: C 40.42, H 5.85%.

[Rh(CO)$_2$ss]$_2$

Pb({SS})$_2$ (92.9 mg, 0.052 mmol), **M**: [Rh(CO)$_2$Cl]$_2$ (20.0 mg, 0.052 mmol), yield 72 mg (72.7%) brown–red solid, m.p. 177.0°C.

IR (KBr): v = 2959 cm^{-1} m, 2930 m, 2872 m [v (CH), aliphatic]; 2072, 2049, 2006 [v (CO)]; 1464 m, 1406 w, 1377 w, 1339 m, 1302 sh, 1221 sh; 1107 vs [v_{asym} (SiOSi)]; 1069 sh, 1032 sh, 897 m, 789 m, 693 s; 552 m, 476 s, 413 s.

^{1}H NMR (C_6D_6): δ = 0.80 (m, 14H, Si—C$\underline{H}_2$—CH$_2$—CH$_3$), (Si—C$\underline{H}_2$—CH$_2$—CH$_2$—S, superposition with —CH$_3$), 1.02 (m, Si—CH$_2$—CH$_2$—C$\underline{H}_3$), 1.62 (m, 14H, Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 2.02 (m, 2H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$—S), 2.94 (m, 2H, Si—CH$_2$—CH$_2$—C$\underline{H}_2$—S).

^{13}C NMR (C_6D_6): δ = 12.1 (Si—$\underline{C}$H$_2$—CH$_2$—CH$_2$—S), 15.02, 15.04 (Si—$\underline{C}$H$_2$—CH$_2$—CH$_3$), 16.99, 17.06 (Si—CH$_2$—$\underline{C}$H$_2$—CH$_3$), 17.64, 17.75 (Si—CH$_2$—CH$_2$—$\underline{C}$H$_3$), 28.0 (Si—CH$_2$—$\underline{C}$H$_2$—CH$_2$—S), 38.8 (Si—CH$_2$—CH$_2$—$\underline{C}$H$_2$—S), 185.8 [d, ^{1}J(C,Rh) = 70 Hz, CO].

Analysis: $C_{52}H_{110}O_{28}Rh_2S_2Si_{16}$ (1902.7): calcd: C 32.80, H 5.78; found: C 32.63 H 6.01%.

[Rh(COD)ss]$_2$

Pb(ss)$_2$ (71.7 mg, 0.037 mmol), **M**: [Rh(COD)Cl]$_2$ (30.0 mg, 0.037 mmol), yield 53.7 mg (74.4%) brown–red solid, m.p. 201.4 C°.

IR (KBr): v = 2957 m, 2930 m, 2872 s [v(CH), aliphatic]; 2830 m, 1560 w, 1458 m, 1408 w, 1377 w, 1339 m, 1302 m, 1221 sh; 1105 vs [v_{asym}(SiOSi)]; 1068 sh, 899 m, 785 m, 693 s, 552 m, 476 s, 411 s.

^{1}H NMR (C_6D_6): δ = 0.78 (m, 14H, Si—C$\underline{H}_2$—CH$_2$—CH$_3$), 0.90 (m, 2H, Si—C$\underline{H}_2$—C$\underline{H}_2$—CH$_2$—S), 1.02 (m, 21H, Si—CH$_2$—C$\underline{H}_2$—C$\underline{H}_3$), 1.63 (m, 14H, Si—CH$_2$—C$\underline{H}_2$—CH$_3$), 1.95 (m, 2H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$—S), 2.18 (m, 2H, Si—CH$_2$—CH$_2$—C$\underline{H}_2$—S), 2.36 [m, 16H, CH$_2$, (COD)], 4.25 [m, 8H, CH, (COD)].

^{13}C NMR (CD$_2$Cl$_2$): δ = 12.8 (Si—$\underline{C}$H$_2$—CH$_2$—CH$_2$—S), 15.09, 15.12 (Si—$\underline{C}$H$_2$—CH$_2$—CH$_3$), 17.11, 17.17 (Si—CH$_2$—$\underline{C}$H$_2$—CH$_3$), 17.91, 17.98 (Si—CH$_2$—CH$_2$—$\underline{C}$H$_3$), 27.0 (Si—CH$_2$—$\underline{C}$H$_2$—CH$_2$—S), 27.9 (Si—CH$_2$—CH$_2$—$\underline{C}$H$_2$—S), 30.9, 32.2, 33.0 [CH$_2$,(COD)] (296 K); 30.6, 31.6, 31.9, 32.5 [CH$_2$,(COD)] (213 K), 74.7 [d, ^{1}J(C,Rh) = 15 Hz] 79.6, 84.3 [d, ^{1}J(C,Rh) = 10 Hz] CH, (COD)], (296 K); 74.5 [d, ^{1}J(C,Rh) = 11 Hz], 80.9 [d, ^{1}J(C,Rh) = 11 Hz], 83.8 [d, ^{1}J(C,Rh) = 13 Hz], (CH$_2$), (COD), (213 K).

Analysis: $C_{64}H_{134}O_{24}Rh_2S_2Si_{16}$ (1804.0): calcd: C 42.61, H 6.71; found: C 42.31, H 6.70%.

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