Tripodal Phosphane Ligands with Novel Linker Units and Their Rhodium Complexes as Building Blocks for Dendrimer Catalysts

Ralf A. Findeis[a] and Lutz H. Gade*[a]

Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

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An efficient strategy for the backbone functionalization of a tripodal phosphane ligand which allows its attachment to solid supports and polymers has been developed. Using pentaerythrol (**1**) as the starting material, the functionalized phosphane tripod $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (**9**) was obtained in good yield in a four-step synthesis. Reaction of **9** with $[Mo(CO)_3(MeCN)_3]$ and $[Rh(COD)_2][A]$ gave the complexes $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (**10**) and $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Rh(COD)][A]$ (A = BF_4: **11a**, PF_6: **11b**), respectively, two of which were characterised by X-ray diffraction. The carbosilane dendrimer $Si\{(CH_2)_3SiMe_2Cl\}_4$ "G[0]-[Cl]$_4$" (**12**) and its first generation analogue $Si[(CH_2)_3SiMe\{(CH_2)_3SiMe_2Cl\}_2]_4$ "G[1]-[Cl]$_8$" (**15**) were reacted with, respectively, four and eight molar equivalents of the lithium alkoxy derivative of **9** giving the two functionalized dendrimers G[0]-$[OCH_2CH_2Otriphos]_4$ (**13**) and G[1]-$[OCH_2CH_2Otriphos]_8$ (**16**). These were metallated with four and eight molar equivalents of $[Rh(COD)_2][BF_4]$ in CH_2Cl_2, selectively yielding the metallated dendrimers G[0]-$[OCH_2CH_2OtriphosRh(COD)BF_4]_4$ (**14**) and G[1]-$[OCH_2CH_2OtriphosRh(COD)BF_4]_8$ (**17**). Comparative catalytic hydrogenation of styrene and 1-hexene using $[Rh(triphos)(COD)][BF_4]$ (**11a)** and the metallodendrimers **14** and **17** showed that the fixation to the low generation dendrimers did not alter the catalytic hydrogenation properties of the catalysts.

Introduction

The immobilization of molecular catalysts may lead to catalytic phases which combine the virtues of homogeneous catalysis (high activity and selectivity, directed catalyst design) with those of heterogeneous catalysts (e.g. facile catalyst separation and recycling).[1] However, leaching of the metal is a major practical problem, regardless of the method of catalyst fixation and the nature of the support material.[2] This may be suppressed to various degrees by using polydentate ligands which form thermally and kinetically stable complexes with the catalyst metal. Polydentate phosphanes have been widely employed in this context and tripodal systems, such as the "triphos" ligand $MeC(CH_2PPh_2)_3$, are good examples of this capacity.[3] Their use as ligands in heterogenized metal catalysts requires the functionalization of their backbone structure, preferentially in the apical position. Modified triphos ligands have been employed for the physisorption of Ru and Rh complexes on oxidic supports[4] and the covalent fixation of such catalyst precursors to polystyrene.[5] Immobilized triphos-based catalysts have been studied in catalytic hydrogenation and hydroformylation as well as the isomerization of allylic alcohols.[6] Additionally, backbone-functionalized triphos complexes have been employed in two-phase catalysis.[7]

Since the first reports of the dendrimer fixation of molecular catalysts,[8] a variety of ligands and catalytically active complexes has been immobilized on the inside and outside of dendritic polymers.[9] Due to the importance of phosphanes in homogeneous catalysis, the immobilization of both chiral and achiral phosphane ligands has been studied in a range of such systems.[10] However, there is as yet no report of the fixation of triphos derivatives to dendrimers. To this end, efficient preparative methods for the synthesis of functionalized triphos ligands were required. Important contributions to this field have been reported by Bianchini and Huttner and their co-workers in recent years.[3–7,11–16]

Previously published syntheses of such derivatives partially suffer from the nontolerance of certain functional groups (e.g. C-C multiple bonds)[11] or the fact that the phosphanyl groups are introduced at a very early stage of the reaction sequence, making subsequent work up more difficult.[12–16] Moreover, if expensive (chiral) phosphanyl functions are to be introduced in an early reaction step of the synthetic pathway[17] the loss of phosphane during the overall sequence may be considerable. A strategy in which the phosphane is introduced in the final step of the ligand-linker synthesis, was therefore an important objective of our work. In this paper

[a] Laboratoire de Chimie Organométallique et de Catalyse, CNRS UMR 7513, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg, France

we report the efficient synthesis of triphos derivatives containing an ether-alcohol function in the apical position of the ligand backbone, their fixation to zeroth- and first-generation carbosilane dendrimers and their metallation to give cationic rhodium complexes. These were then employed in a comparative study as hydrogenation catalysts.

Results and Discussion

Synthesis of the Tripodal Phosphane $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (9)

We chose pentaerythol (**1**) as the starting material for the synthesis of an apically functionalized *triphos* ligand. This tetraalcohol is a cheap basic chemical which possesses a functionalized neopentane structure and thus appears to be well suited for the synthetic objective. There are several reports in the literature, namely from Huttner and coworkers, of the use of this starting material in *triphos* chemistry; however, these workers decided to functionalize the apical position after introduction of the phosphane groups.[13−16] As stated above, this sequence will reduce the overall yields based upon the phosphane starting material. Since the diphenylphosphanyl groups referred to in this work are model systems for more complex tridentate P-donor ligands, this point was of particular importance to us.

The four hydroxyl functions in **1** are chemically equivalent, and in order to attach a linker group to only one of these it had to be differentiated with respect to the others. This is readily achieved by reaction of **1** with triethyl orthoacetate in toluene to give the known methyl trioxabicyclooctane derivative **2** (Scheme 1).[18] The unchanged "apical" OH-function was then coupled with benzyl-protected 2-chloroethanol[19] as a linker unit to give $BzOCH_2CH_2OCH_2C(CH_2O)_3CCH_3$ (**3**), which, in turn, was hydrolysed yielding the triol $BzOCH_2CH_2OCH_2C(CH_2OH)_3$ (**4**). After functional group interconversion with $SOCl_2$ in dry pyridine, giving the trichloride **5**, and hydrogenolytic deprotection, compound **6** was reacted with Ph_2PH under strongly basic reaction conditions to yield the target phosphane $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (**9**) in good yield.

The differentiation of the OH groups by orthoester protection requires the multistep sequence in the synthesis of **9** as discussed above. This leads to moderate overall yields of the triphos derivative in spite of the relatively high yields in each individual reaction step. It was therefore desirable to devise a shorter route to compound **9**. This was possible via the 3-chloro-2,2-bis(chloromethyl)propan-1-ol (**7**), which is directly accessible from pentaerythrol (Scheme 1).[20] Reaction of **7** with THP-protected 2-bromoethanol gave $THPOCH_2CH_2OCH_2C(CH_2Cl)_3$ (**8**), which was converted into compound **6** by hydrolytic deprotection. This strategy provided a facile access to large quantities of the key intermediate **6**.

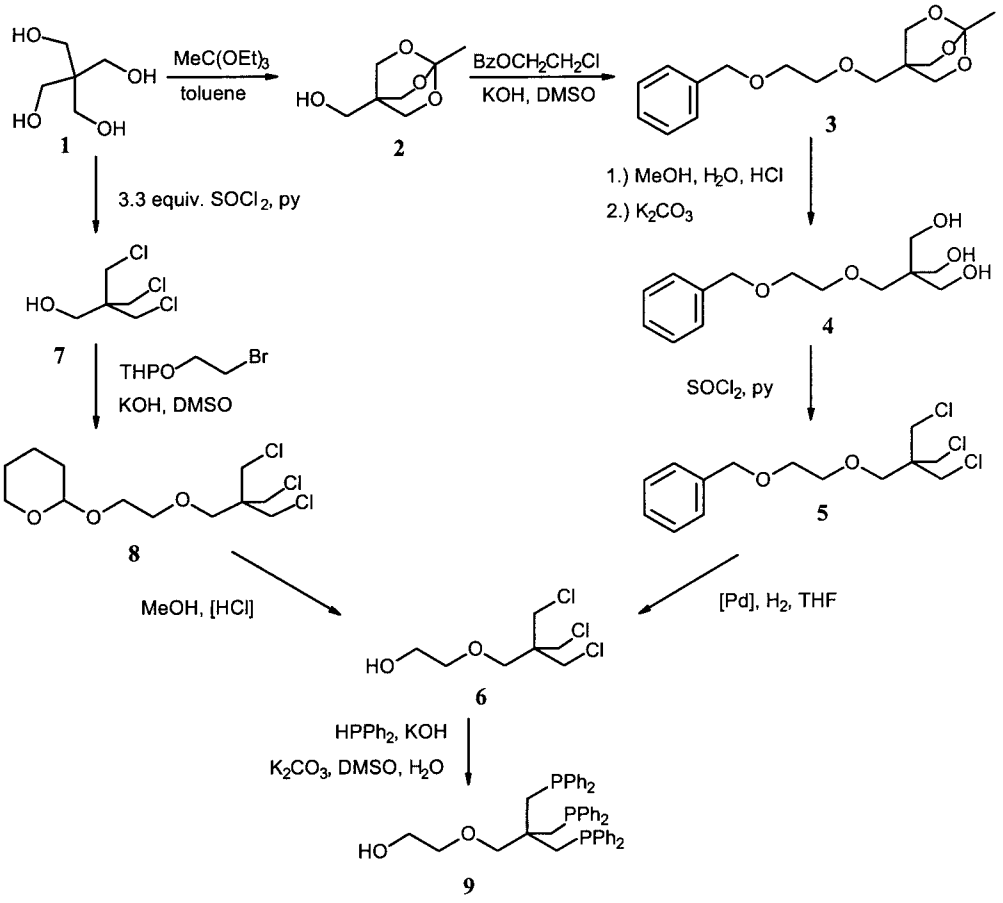
Synthesis and Structural Characterization of the Tripod-Metal Complexes $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (10) and $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Rh(COD)][A]$ ($A^- = BF_4^-$: 11a; $A^- = PF_6^-$: 11b).

In order to assess the structural details and the ligand properties of the triphosphane $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (**9**), it was reacted with one molar equivalent of $[Mo(CO)_3(MeCN)_3]$ to yield the yellow, air stable triphosphane-molybdenum complex $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (**10**; Scheme 2). The ^{31}P NMR resonance of the coordinated phosphane ligand is observed at $\delta = 15.6$ ppm (**9**: $\delta = -25.8$ ppm) and the ν(CO) bands appear in the IR spectrum at 1929 and 1834 cm^{-1}. The molecular ion peak at $m/z = 866$ in the mass spectrum confirms the formulation of the complex.

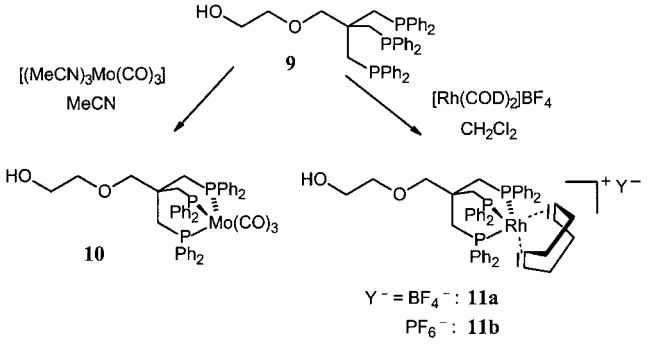
Single crystals of complex **10**, which were suitable for an X-ray diffraction study, were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compound. The molecular structure of **10** is displayed in Figure 1a along with its principal bond lengths and angles. The phosphane ligand adopts the expected facial coordination mode in a molybdenum complex having a slightly distorted octahedral coordination geometry. The Mo−P distances of 2.5242(9) to 2.5302(8) Å and the M−CO bond lengths of 1.965(3) to 1.968(3) Å are within the expected range. Both the P−Mo−P and the C−Mo−C angles, which lie in the ranges of 81.11(3) to 84.67(3)° and 84.4(1) to 86.8(1)°, respectively, are below 90° defining a slightly elongated trigonal antiprismatic first coordination sphere (Figure 1b).

In view of the principal objective of this work, the synthesis of cationic triphos-rhodium hydrogenation catalysts attached to dendritic supports, the ligand-linker unit **9** was reacted with $[Rh(COD)_2]BF_4$ to give the Rh^I complex $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Rh(COD)][BF_4]$ (**11a**; Scheme 2) which was characterised by elemental analysis and ^1H, ^{13}C and ^{31}P NMR spectroscopy. The most characteristic spectroscopic feature is the doublet at $\delta = 4.3$ ppm in the ^{31}P NMR spectrum ($^1J_{Rh,P} = 106.8$ Hz) indicating the equivalence of all three phosphorus nuclei on the NMR time scale at 293 K. The observation of an essentially unchanged single phosphorus resonance even at −80 °C is consistent with a rapid dynamic exchange, probably according to a turnstile mechanism, as was previously observed for $[Rh(triphos)(COD)]PF_6$ and $[Ir(triphos)(COD)]PF_6$.[21] We were unable to obtain single crystals of compound **11a** which were suitable for X-ray diffraction. This was achieved, however, after anion exchange with $NH_4[PF_6]$ giving the yellow crystalline complex $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Rh(COD)][PF_6]$ (**11b**; Scheme 2). A single crystal X-ray structure analysis of complex **11b** established its molecular structure, which is displayed in Figure 2a, while the inner coordination environment of the rhodium atom is highlighted in Figure 2b.

The coordination geometry of the complex displayed in Figure 2b is a distorted trigonal bipyramid, the apical position being occupied by the phosphorus atom P(1) and the centroid of the olefinic double bond C(5)−C(6). Whereas



Scheme 1. The two synthetic strategies for the preparation of the ligand-linker **9**



Scheme 2. Synthesis of the tripod-metal complexes **10** and **11a/b**

the Rh−P bond length to the apical phosphane unit [Rh−P(1) 2.303(2) Å] is significantly shorter than for those of the two equatorial phosphanes [Rh−P(2) 2.405(2), Rh−P(3) 2.406(2) Å], the Rh−C distances to the apical olefin carbon atoms [Rh−C(5) 2.264(6), Rh−C(6) 2.327(6) Å] are significantly greater than for the equatorial π-olefin ligands [Rh−C(1) 2.180(6), Rh−C(2) 2.155(6) Å]. The P(1)−Rh−centroid{C(5)/C(6)} angle of 170.13(4) deviates slightly from the ideal of 180°, while the P(1)−Rh−P(2/3) and P(1)−Rh−centroid{C(1)/C(2)} angles are close to 90°. As observed in the crystal structure of the molybdenum complex **10**, the oxygen atoms in the $HOCH_2CH_2O$- spacer in **11b** adopt a gauche conformation.

The packing of the molecules of **11b** in the unit cell is displayed in Figure 2c. For the sake of clarity, the phenyl groups of the diphenylphosphane units, and the lattice solvent molecules (CH_2Cl_2), have been omitted. The molecules are arranged in such a way that the apical alcohol units of the tripod ligands face each other forming intermolecular hydrogen bonds while the PF_6 anions are arranged along channels in the crystal near to the positively charged rhodium complex units.

Fixation of [{$HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$}-Rh(COD)][$BF_4$] (11a) to Zeroth and First Generation Carbosilane Dendrimers

In order to asses the suitability of the apically derivatized *triphos* ligand **9** for the fixation of rhodium hydrogenation catalysts to carbosilane dendrimers, the known zeroth generation dendrimer $Si\{(CH_2)_3SiMe_2Cl\}_4$, "G[0]-$[Cl]_4$" (**12**) and its first generation analogue $Si[(CH_2)_3SiMe\{(CH_2)_3SiMe_2Cl\}_2]_4$, "G[1]-$[Cl]_8$" (**15**) [22] were reacted with, respectively, four and eight molar equivalents of the lithium alkoxy derivative of **9**. After work up the two func-

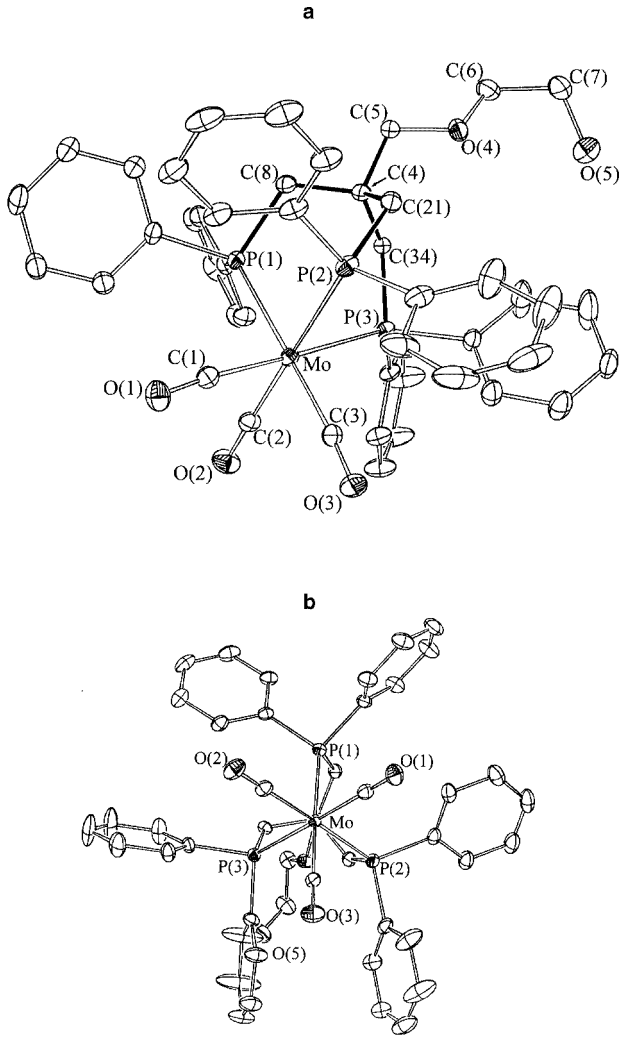


Figure 1. a) Molecular structure of complex **10**; principal bond lengths (Å) and angles (°): Mo−P(1) 2.5292(7), Mo−C(3) 1.966(3), O(4)−C(6) 1.427(4), Mo−P(2) 2.5242(9), C(1)−O(1) 1.165(3), C(6)−C(7) 1.497(5), Mo−P(3) 2.5302(8), C(2)−O(2), 1.164(4), C(7)−O(5) 1.423(4), Mo−C(1) 1.968(3), C(3)−O(3) 1.155(3), O(4)−O(5) 2.751(3), Mo−C(2) 1.965(3), C(5)−O(4) 1.403(4); P(1)−Mo−P(2) 84.67(3), C(1)−Mo−C(2) 84.4(1), C(4)−C(8)−P(1) 116.4(4), P(1)−Mo−P(3) 84.49(2), C(1)−Mo−C(3) 84.9(1), C(4)−C(21)−P(2) 117.3(2), P(2)−Mo−P(3) 81.11(3), C(2)−Mo−C(3) 86.8(1), C(4)−C(34)−P(3) 116.7(2); b) view along the virtual threefold molecular axis of the tripohos-$Mo(CO)_3$ unit

tionalized dendrimers G[0]-[OCH_2CH_2Otriphos]$_4$ (**13**) and G[1]-[OCH_2CH_2Otriphos]$_8$ (**16**) were isolated in high yield (Scheme 3 and 4).

The dendrimer phosphanes **13** and **16** were characterised by elemental analysis, ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectroscopy as well as FAB (**13**) and MALDI-TOF (**16**) mass spectrometry. Stirring of **13** and **16** with, respectively, four and eight molar equivalents of [$Rh(COD)_2$][BF_4] in CH_2Cl_2 selectively gave the metallated dendrimers G[0]-[OCH_2CH_2OtriphosRh(COD)BF_4]$_4$ (**14**) (Scheme 3) and G[1]-[OCH_2CH_2OtriphosRh(COD)BF_4]$_8$ (**17**) (Figure 3). These were characterised by the analytical and NMR spectroscopic techniques applied to the phosphane precursors as well as

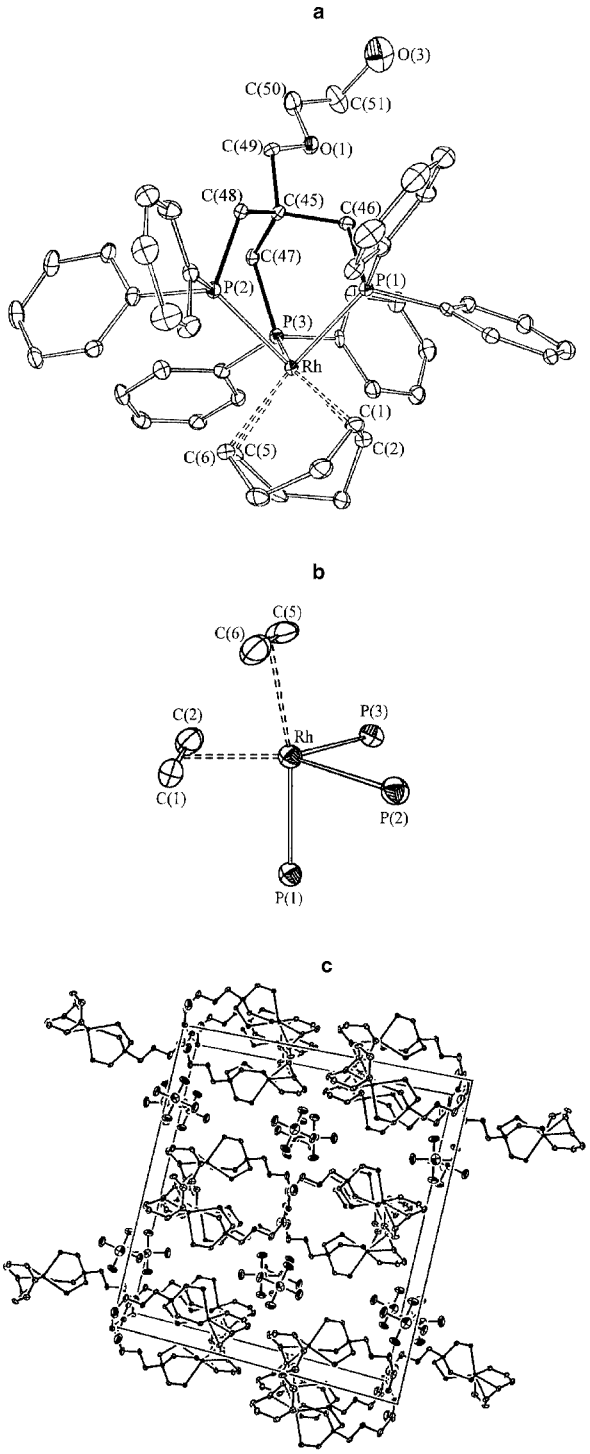
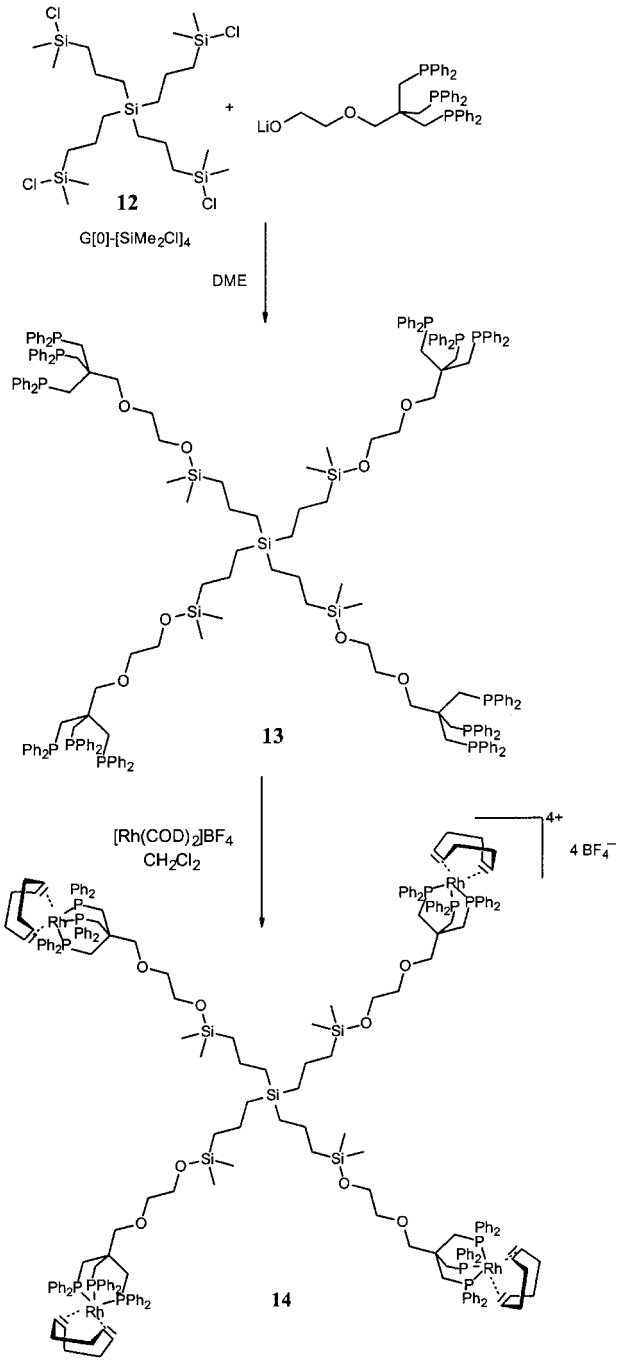


Figure 2. a) Molecular structure of complex **11b**; principal bond lengths (Å) and angles (°):Rh−P(1) 2.303(2), Rh−C(5) 2.264(6), O(1)−C(49) 1.411(7), Rh−P(2) 2.405(2), Rh−C(6) 2.327(6), O(1)−C(50) 1.412(7), Rh−P(3) 2.406(2), P(1)−C(46) 1.851(5), C(50)−C(51) 1.53(1), Rh−C(1) 2.180(6), P(2)−C(48) 1.843(6), O(2)−C(51) 1.55(2), Rh−C(2) 2.155(6), P(3)−C(47) 1.849(6); P(1)−Rh−P(2) 87.56(6), P(1)−C(46)−C(45) 115.0(4), C(49)−O(1)−C(50) 112.9(5), P(1)−Rh−P(3) 87.11(5), P(2)−C(48)−C(45) 116.8(4), O(1)−C(50)−C(51) 109.5(6), P(2)−Rh−P(3) 89.52(5), P(3)−C(47)−C(45) 117.4(4), C(50)−C(51)−O(2) 100.8(9); b) ligand arrangement in the first coordination sphere of complex **11b**; c) the packing of the molecules of **11b** in the unit cell; for the sake of clarity, the phenyl groups of the diphenylphosphane units, and the lattice solvent molecules (CH_2Cl_2) have been omitted



Scheme 3. Fixation of **9** to the end groups of the zeroth generation dendrimer G[0]-[$SiMe_2Cl$]$_4$ (**12**) to give G[0]-[OCH_2CH_2Otriphos]$_4$ (**13**) and subsequent metallation yielding G[0]-[OCH_2CH_2OtriphosRh(COD)BF_4]$_4$ (**14**)

by electrospray mass spectrometry, which confirmed the uniformity of the products. The molecular ion peaks were observed at m/z = 1002.2 for compound **14**, corresponding to the $[(M - 4BF_4)/4]^+$ ion, and at m/z = 1041.3 for the octametallated dendrimer **17**, corresponding to the $[(M - 8BF_4)/8]^+$ ion.

Comparison of the Catalytic Behavior of the Rhodium Complexes [Rh(triphos)(COD)][BF_4], 11a, 14 and 16 (cat1−4) in the Hydrogenation of Styrene and 1-Hexene

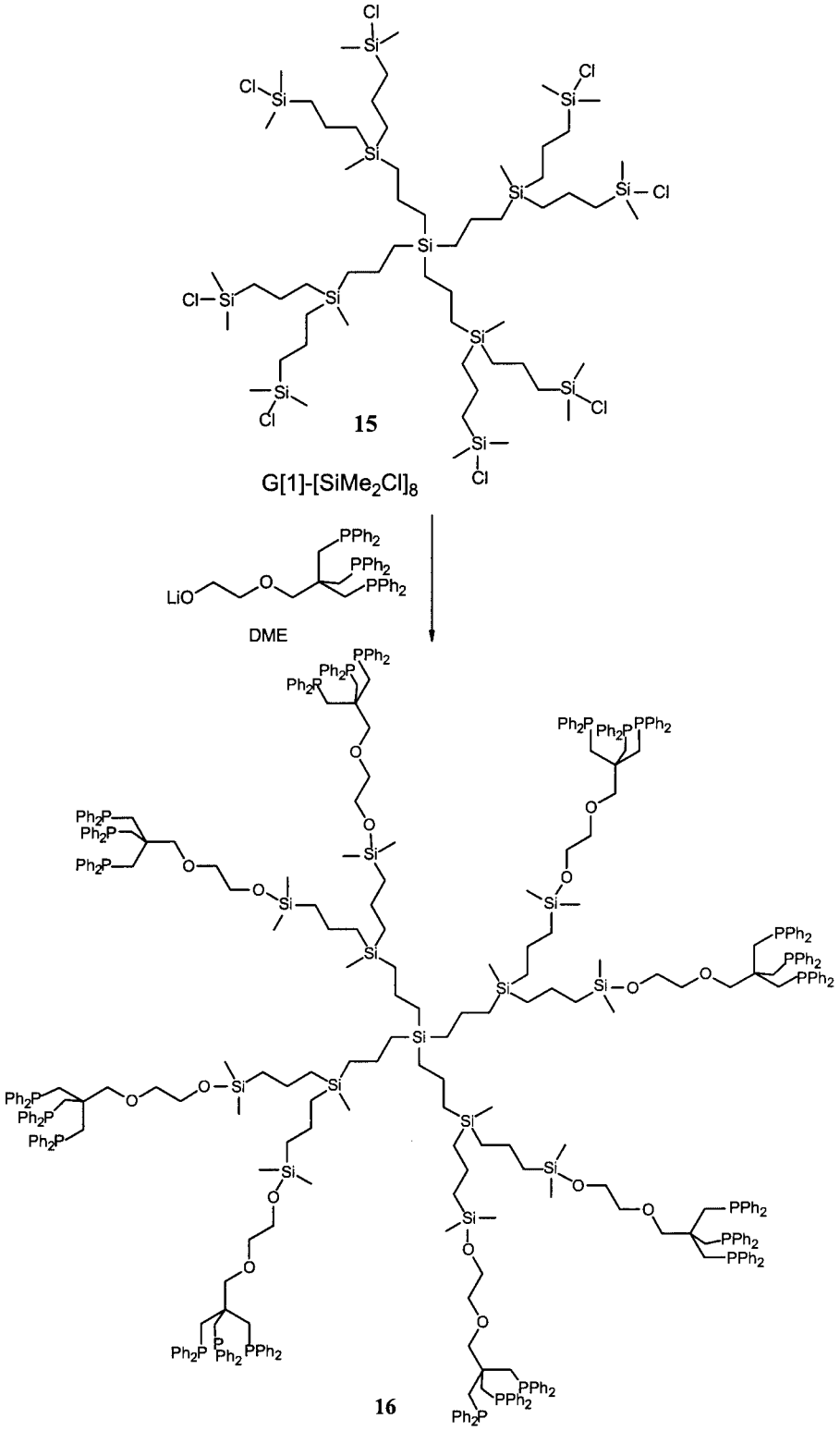
As outlined in the introduction, the hydrogenation of olefins was to be investigated in a comparative study of the catalytic properties of the mononuclear *triphos*-rhodium complexes [Rh(triphos)(COD)][BF_4] (**cat1**) and **11a** (**cat2**) as well as their dendrimer-linked derivatives **14** (**cat3**) and **16** (**cat4**). Mononuclear triphos-rhodium catalysts have been studied previously and were found to be active hydrogenation catalysts for simple nonfunctionalized alkenes.[17,21a,23,24] All catalytic tests were carried out at 1 bar of H_2 pressure and 20 ± 1 °C with an equivalent amount of catalyst (1 mol %), i.e. a constant number of catalytic sites in the system.

As simple substrates for catalytic hydrogenations styrene and 1-hexene are frequently chosen, the latter in order to assess the competition between hydrogenation and alkene isomerization within the coordination sphere of the catalyst.[25] After an initial induction period, during which the COD ligand is reduced, the hydrogenation of the styrene occurs at a constant rate until an almost quantitative conversion of the substrate. The catalytic activities of the catalysts **cat1** − **cat4** did not vary significantly and were found to be at TOF = 10 h^{-1} under the standard conditions cited above.

As has been shown by van Leeuwen and co-workers, carbosilane metallodendrimer catalysts of the first and second generation may possess the required molecular dimensions to allow recycling by membrane filtration.[11] If performed in batch reactors, this requires catalysts which retain their original activity after separation and reintroduction to a catalytic conversion. The dendrimer catalysts **cat3** and **cat4** were found to be isolable (removal of the solvent and reaction product under vacuum) after a complete conversion and re-usable for a subsequent cycle without significant decrease in activity during the first three cycles of catalyst isolation and reintroduction to a new batch of substrates.

In order to test the activity of the new dendritic catalysts towards a second standard substrate employed in hydrogenation tests, the hydrogenation at 1 bar H_2 pressure was carried out using 1-hexene. A competing reaction in this transformation is the isomerization of the alkene to a mixture of (*E*)- and (*Z*)-2-hexene. The typical course of this reaction, as followed by GC-MS, is again represented for **cat4** in Figure 4.

After an induction period, during which the catalytically active species is generated, the conversion of 1-hexene sets in, giving hexane, (*Z*)-2-hexene and (*E*)-2-hexene with a turnover frequency of 30 h^{-1} based on the 1-hexene consumed. After the complete consumption of 1-hexene, the hydrogenation of (*Z*)-2-hexene leads to the further production of hexane, albeit at a lower rate. The curve representing the generation of hexane levels off when the concentration of the *Z*-isomer has dropped to about 30% of its maximum value. As observed for practically all cationic rhodium hydrogenation catalysts, the conversion of the *E*-isomer is



Scheme 4. Fixation of **9** to the end groups of the first generation dendrimer G[1]-[$SiMe_2Cl$]$_8$ (**15**) to give G[1]-[OCH_2CH_2Otriphos]$_8$ (**16**)

much slower and essentially insignificant on the chosen time scale.[25] Comparison of **cat1** − **cat4** showed an overall identical catalytic behaviour.

Conclusions

In this paper we have presented an efficient strategy for the backbone functionalization of the *triphos* ligand which

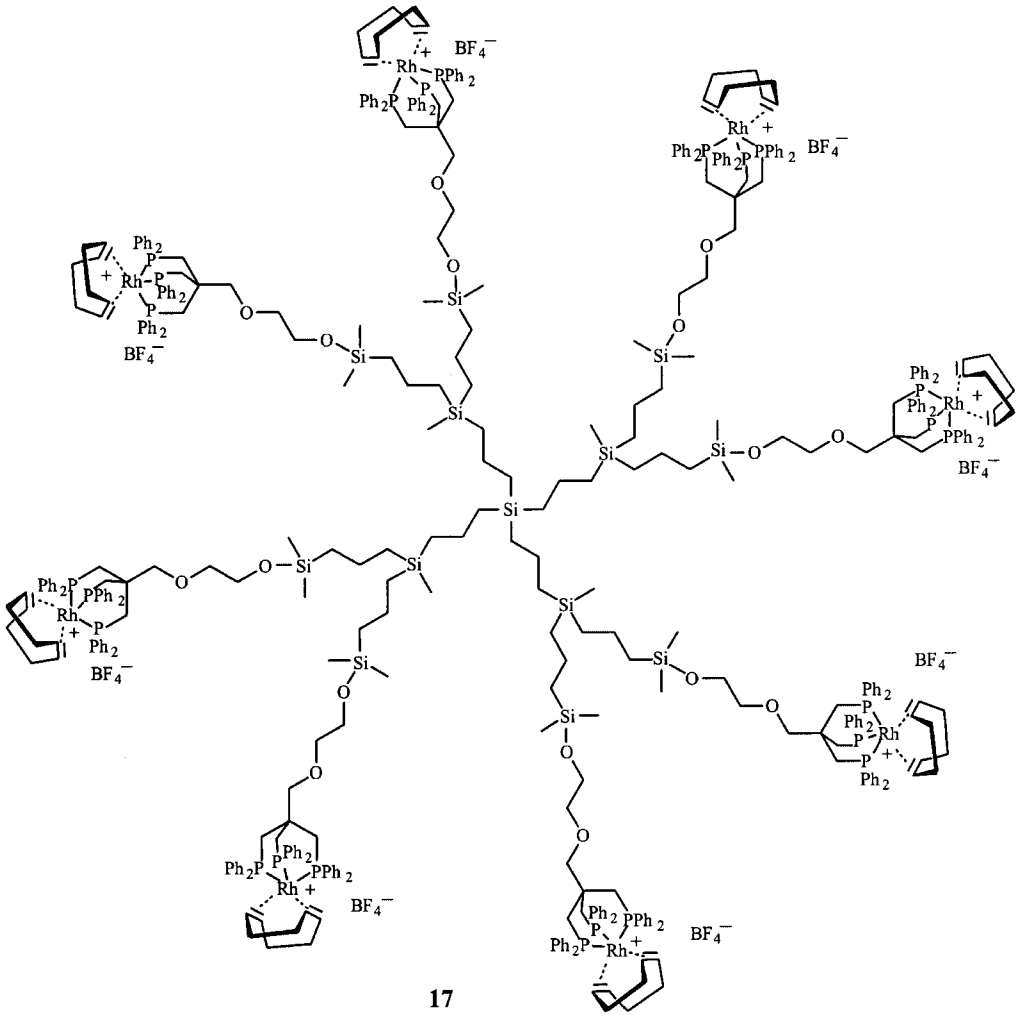


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Figure 3. First generation rhododendrimer G[1]-[OCH_2CH_2OtriphosRh(COD)BF_4]$_8$ (**17**)

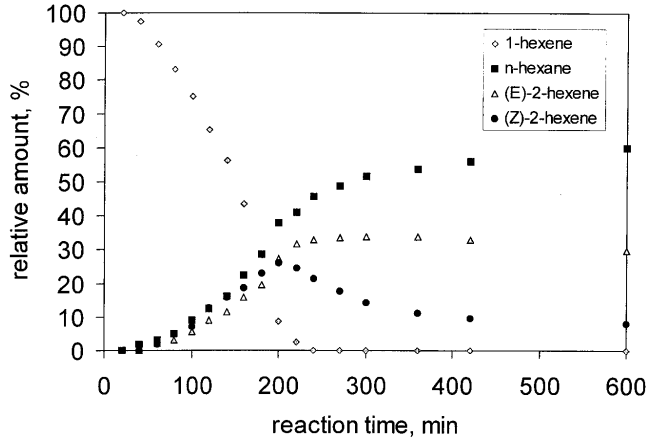


Figure 4. A typical conversion diagram for the hydrogenation of 1-hexene, represented here for the rhododendrimer **16** (**cat4**)

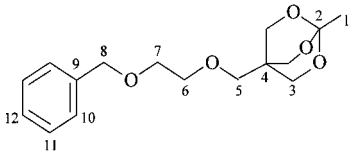
allows its attachment to solid supports and polymers. We have also been able to completely characterise two carbosilane dendrimer derivatives and found them to be sufficiently robust to allow for several recycling steps. Fixation to the low-generation dendrimers did not alter the catalytic hydrogenation properties of the triphos-rhodium catalyst. This constitutes the basis for the extension of this work to higher dendrimer generations which is currently under way.

Experimental Section

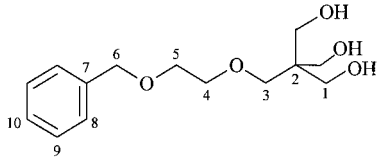
All manipulations were performed under nitrogen (desiccant P_4O_{10}, Granusic®, J. T. Baker) on a high vacuum line using standard Schlenk techniques, or in a glovebox. All reaction flasks were heated prior to use by means of three evacuation-refill cycles. Solvents and solutions were transferred by needle-septa techniques. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and stored over 4 Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite or by centrifugation. The ^1H, ^{13}C, ^{19}F, ^{29}Si and ^{31}P NMR spectra were recorded on Bruker AC 200, Bruker Avance 250 and Bruker AMX 400 FT NMR spectrometers. ^1H and ^{13}C data are listed in parts per million [ppm] relative to tetramethylsilane and were refer-

enced using the residual protonated solvent peak (^{1}H) or the carbon resonance (^{13}C). ^{29}Si, ^{19}F and ^{31}P NMR spectroscopic data are listed in ppm relative to, respectively, tetramethylsilane, $FCCl_3$ and 85% H_3PO_4 as external standards. Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out by the microanalytical service at the chemistry department at Strasbourg. 4-(Hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (**2**),[18] benzyl 2-chloroethyl ether,[19] diphenylphosphane,[26] 3-chloro-(2,2-chloromethyl)-propan-1-ol (**7**),[20] 2-(2-Bromoethoxy)tetrahydropyran,[27] $[(MeCN)_3Mo(CO)_3]$,[28] $[Rh(COD)_2]BF_4$,[29] G[0]-$[Cl]_4$ (**12**),[30] G[1]-$[Cl]_8$ (**15**) [31] and $[CH_3C(CH_2PPh_2)_3Rh(COD)]BF_4$ [21] were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially and used without further purification.

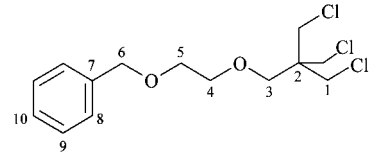
Preparation of $BzOCH_2CH_2OCH_2C(CH_2O)_3CCH_3$ (3): 4-(Hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (**2**; 14.3 g, 89.0 mmol) was added to a stirred suspension of finely powdered KOH (11.2 g, 200 mmol) and benzyl 2-chloroethyl ether (30.9 g, 181 mmol) in 150 mL of DMSO. The reaction mixture was stirred at 60 °C for 2 h and then cooled to room temperature. Water (500 mL) was then added and the solution thus obtained was extracted with three portions of Et_2O (200 mL). The combined organic extracts were washed with 100 mL of a saturated aqueous solution of NaCl, then with 100 mL of water and subsequently dried over Na_2SO_4. After removal of the solvent by distillation, the yellow oily residue was purified by column chromatography to yield $BzOCH_2CH_2OCH_2C(CH_2O)_3CCH_3$ (**3**) as a colourless, viscous liquid. Yield: 20.5 g (70.2 mmol, 79%). R_f (Al_2O_3 60 neutral, EtOAc/*n*-hexane = 2:8): 0.49. ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 1.42 (s, 3 H, H-1), 3.23 (s, 2 H, H-5), 3.54−3.60 (m, 4 H, H-6,7), 4.00 (s, 6 H, H-3), 4.54 (s, 2 H, H-8), 7.25−7.35 (m, 5 H, H-10,11,12) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 23.2 (CH_3, C-1), 34.6 (C, C-4), 69.0 (CH_2, C-3), 69.1(CH_2, C-6/7), 69.3 (CH_2, C-6/7), 70.9 (CH_2, C-8), 72.8 (CH_2, C-5), 108.1 (C, C-2), 127.2 (CH, C-12), 127.3 (CH, C-11), 128.1 (CH, C-10), 137.9 (C, C-9) ppm. IR (film): $\tilde{\nu}$ = 3007 (w), 2876 (m), 1485 (m), 1453 (m), 1401 (s) 1354 (m), 1296 (m), 1209 (m), 1165 (m), 1127 (s), 1055 (s), 989 (m), 930 (m), 864 (s), 739 (m), 698 (m), 617 (m) cm^{-1}. $C_{16}H_{22}O_5$ (294.35) calcd. C 65.29. H 7.53: found C 65.41. H 7.62.



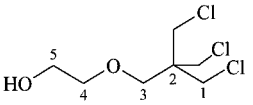
Preparation of $BzOCH_2CH_2OCH_2C(CH_2OH)_3$ (4): A solution of (18.2 g, 61.8 mmol) of $BzOCH_2CH_2OCH_2C(CH_2O)_3CCH_3$ (**3**) in 40 mL of methanol and 50 mL of 2 N HCl was stirred at room temperature for 6 h. Solid Na_2CO_3 (7.51 g, 71.3 mmol) was carefully added to the reaction mixture in small portions and the solution was subsequently stirred for another 18 h at ambient temperature. The solvents were removed by distillation, the residue was extracted with methanol and the solution was evaporated to dryness to yield pure $BzOCH_2CH_2OCH_2C(CH_2OH)_3$ (**4**) as a soft amorphous solid. Yield: 14.4 g (53.1 mmol, 86%). ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 3.53 (s, 2 H, H-3), 3.60 (br. s, 4 H, H-4,5), 3.65 (s, 6 H, H-1), 4.54 (s, 2 H, H-6), 7.25−7.35 (m, 5 H, H-8,9,10) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 45.0 (C, C-2), 64.5 (CH_2, C-4/5), 69.0 (CH_2, C-4/5), 70.8 (CH_2, C-6), 72.8 (CH_2, C-3), 73.2 (CH_2, C-1) 127.7 (CH, C-10), 127.8 (CH, C-9), 128.4 (CH, C-8), 137.6 (C, C-7) ppm. IR (film): $\tilde{\nu}$ = 3413 (vs), 2931 (s), 2878 (s), 1448 (s), 1410 (s), 1094 (s), 1040 (s), 837 (m), 746 (m), 699 (s) cm^{-1}. $C_{14}H_{22}O_5$ (270.33) calcd. C 62.20, H 8.20: found C 61.88. H 8.03.



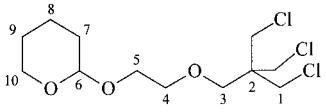
Preparation of $BzOCH_2CH_2OCH_2C(CH_2Cl)_3$ (5): $SOCl_2$ (20.5 g, 172 mmol) was added dropwise to a stirred mixture of $BzOCH_2CH_2OCH_2C(CH_2OH)_3$ (**4**; 14.1 g, 52.2 mmol) and dry pyridine (13.6 g, 172 mmol) at 0 °C. After complete addition, the reaction mixture was stirred for 30 min at 0 °C, then for 30 min at room temperature, and finally at 110−120 °C for 2.5 h. After cooling to 0 °C 150 mL of iced water was added and the aqueous phase thus obtained was twice extracted with 50 mL of CH_2Cl_2. The combined organic layers were treated with 100 mL of dilute HCl and with 2 × 100 mL of water and were then dried over Na_2SO_4. The solvent was removed by distillation at normal pressure, and the residue was purified by column chromatography to give $BzOCH_2CH_2OCH_2C(CH_2Cl)_3$ (**5**) as a colourless liquid. Yield: 9.52 g (29.2 mmol, 56%). R_f (Kieselgel, EtOAc/*n*-hexane = 1:9) = 0.34. ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 3.53 (s, 2 H, H-3), 3.59−3.67 (m, 4 H, H-4,5), 3.64 (s, 6 H, H-1), 4.54 (s, 2 H, H-6), 7.25−7.34 (m, 5 H, H-8,9,10) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 44.3 (CH_2, C-1), 46.3 (C, C-2), 68.6 (CH_2, C-4/5), 69.3 (CH_2, C-4/5), 71.0 (CH_2, C-6), 73.2 (CH_2, C-3), 127.6 (CH, C-10), 127.7 (CH, C-9), 128.4 (CH, C-8), 138.2 (C, C-7) ppm. IR (film): $\tilde{\nu}$ = 3029 (w), 2920 (m), 1495 (w), 1453 (m), 1434 (m), 1354 (m), 1307 (m), 1267 (m), 1104 (s), 871 (m), 798 (m), 741 (m), 698 (s), 616 (w) cm^{-1}. $C_{14}H_{19}Cl_3O_2$ (325.66): calcd. C 51.63. H 5.88: found C 51.89. H 5.74.



Preparation of $HOCH_2CH_2OCH_2C(CH_2Cl)_3$ (6) by Deprotection of $BzOCH_2CH_2OCH_2C(CH_2Cl)_3$ (5): A mixture of $BzOCH_2CH_2OCH_2C(CH_2Cl)_3$ (**5**; (8.32 mg 25.5 mmol) and 310 mg of Pd/C was stirred in THF at room temp under 1 bar of H_2 for 12 h. The reaction mixture was then filtered through celite, the solvent removed by distillation at normal pressure and the oily residue purified by fractional distillation at reduced pressure giving compound $HOCH_2CH_2OCH_2C(CH_2Cl)_3$ (**6**) as a colourless liquid. Yield: 4.88 g (20.7 mmol, 81%). B.p.: 97−99 °C/0.64 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 3.48 (s, 2 H, H-3), 3.54 (t, $^3J_{H,H}$ = 4.3 Hz, 2 H, H-4/5), 3.59 (s, 6 H, H-1), 3.68 (t, $^3J_{H,H}$ = 4.3 Hz, 2 H, H-4/5) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 44.5 (CH_2, C-1), 46.5 (C, C-2), 62.0 (CH_2, C-5), 68.8 (CH_2, C-4), 73.0 (CH_2, C-3) ppm. IR (film): $\tilde{\nu}$ = 3373 (br), 2962 (s), 2877 (s), 1476 (m), 1434 (s), 1360 (m), 1308 (m), 1126 (s), 1062 (s), 871 (s), 806 (m), 759 (m), 742 (m), 701 (m) cm^{-1}. $C_7H_{13}Cl_3O_2$ (235.54): calcd. C 35.69, H 5.56; found C 35.23, H 5.50.

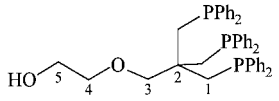


Preparation of $THPOCH_2CH_2OCH_2C(CH_2Cl)_3$ (8): Finely powdered KOH (9.45 g, 168 mmol) was added at room temperature to a vigorously stirred solution of 3-chloro-2,2-bis(chloromethyl)propan-1-ol (**7**; 8.02 g, 41.9 mmol) and (2-bromoethoxy)tetrahydropyran (26.2 g, 125 mmol) in 40 mL of DMSO. There was a strong evolution of heat during the addition and the temperature was controlled by occasional cooling with an ice bath. After complete addition of the solid KOH the reaction mixture was stirred at 60 °C for another 2 h and then cooled to room temperature. Water (180 mL) was added, and the aqueous phase was extracted with 3 × 50 mL of CH_2Cl_2. The combined organic extracts were washed with 3 × 50 mL H_2O and then dried over Na_2SO_4. After removal of the solvent by distillation the residue was subjected to fractional distillation under reduced pressure to give $THPOCH_2CH_2OCH_2C(CH_2Cl)_3$ (**10**) as a colourless liquid. Yield: 9.78 g (30.6 mmol, 73%). B.p.: 115 °C/0.19 Torr. ^1H NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.43−1.57 (m, 6 H, H-7,8,9), 3.44 (s, 2 H, H-3), 3.46−3.62 (m, 4 H, H-4,5), 3.59 (s, 6 H, H-1), 3.77−3.85 (m, 2 H, H-10), 4.69 (t, $^3J_{H,H}$ = 3.3 Hz, 1 H, H-6) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 19.5 (CH_2, C-7/8/9), 25.6 (CH_2, C-7/8/9), 30.8 (CH_2, C-7/8/9), 44.5 (CH_2, C-1), 46.5 (C, C-2), 62.3 (CH_2, C-5), 66.7 (CH_2, C-10), 68.8 (CH_2, C-4), 70.8 (CH_2, C-3), 99.1 (CH, C-6) ppm. IR (film): $\tilde{\nu}$ =2942 (s), 2871 (m), 1440 (m), 1352 (m), 1260 (m), 1201 (m), 1128 (s), 1076 (s), 1036 (s), 1020 (m), 986 (m), 871 (m), 814 (w), 742 (w), 702 (w) cm^{-1}. $C_{15}H_{27}Cl_3O_3$ (319.66): calcd. C 45.09, H 6.62; found C 45.39, H 6.38.

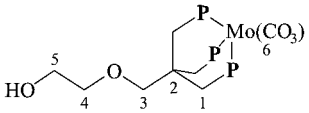


Preparation of $HOCH_2CH_2OCH_2C(CH_2Cl)_3$ (6) by Deprotection of $THPOCH_2CH_2OCH_2C(CH_2Cl)_3$ (8): Solid *p*-toluenesulfonic acid (220 mg) was added to a solution of $THPOCH_2CH_2OCH_2C(CH_2Cl)_3$ (**10**; 11.2 g, 35.1 mmol) in 50 mL of methanol. The reaction mixture was stirred at room temperature for 15 h, neutralised with solid K_2CO_3 and the solvent removed by distillation. The remaining residue was subjected to a fractional distillation as described above to give **6**. Yield: 7.78 g (32.9 mmol, 93%).

Preparation of $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (9): A solution of $HPPh_2$ (7.80 g, 41.9 mmol) in 10 mL of DMSO was added to a vigorously stirred suspension of K_2CO_3 (32.1 g, 233 mmol) in 45 mL of DMSO and this was followed by the addition of KOH (3.95 g, 70.4 mmol) in 3.0 mL of degassed water. The deep-red suspension thus obtained was stirred for 30 min at room temperature and then a solution of of $HOCH_2CH_2OCH_2C(CH_2Cl)_3$ (**6**; 3.14 g, 13.3 mmol) in 15 mL of DMSO was added with a syringe. The reaction mixture was stirred at 90 °C for 2 h and then at 110 °C for another hour. After cooling, 250 mL of water was added, the aqueous phase separated and the volatile organic components removed in vacuo. The residue was extracted with 2 × 20 mL of toluene, the solution treated with 2 × 10 mL of degassed water and then dried over Na_2SO_4. After removal of the solvent the residue was extracted with methanol and the target compound $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (**9**) was obtained as a colourless solid directly from the extract. Yield: 6.64 g (9.71 mmol, 73%). M.p.: 138 °C. ^1H NMR (400.14 MHz, $CDCl_3$, 295 K): δ = 2.38 (d, $^1J_{P,H}$ = 2.9 Hz, 6 H, H-1), 2.81 (t, $^3J_{H,H}$ = 4.4 Hz, 2 H, H-4/5), 3.24 (s, 2 H, H-3), 3.27 (t, $^3J_{H,H}$ = 4.4 Hz, 2 H, H-4/5), 7.16−7.25 (m, 30 H, aromat. H) ppm. $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$, 295 K): δ = 37.5−37.9 (m, CH_2, C-1), 41.7 (q, C, $^2J_{PC}$ = 11.4 Hz, C-2), 60.0 (s, CH_2, C-5), 70.5 (s, CH_2, C-4), 76.5 (q, CH_2, $^3J_{PC}$ = 7.6 Hz, C-3), 127.2−127.5 (m, CH, aromat. C), 131.8−132.1 (m, CH, aromat. C), 138.3 (m, C, aromat. C) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 295 K): δ = −25.8 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3395 (br), 3072 (m), 2864 (m), 1585 (w), 1481 (m), 1434 (s), 1405 (m), 1307 (w), 1259 (m), 1120 (s), 1061 (s), 1026 (m), 999 (m), 869 (m), 831 (m), 693 (m) cm^{-1}. $C_{43}H_{43}O_2P_3$ (684.73): calcd. C 75.43, H 6.33; found C 75.26, H 6.42.

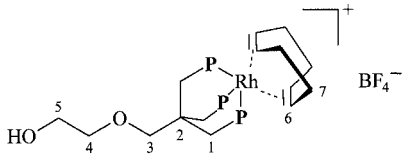


Preparation of $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (10): A solution of $[(MeCN)_3Mo(CO)_3]$ (368 mg, 1.21 mmol) in 5 mL of acetonitrile was slowly added to a stirred suspension of $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (**9**; 831 mg, 1.21 mmol) in 10 mL of acetonitrile. The reaction mixture was stirred at ambient temperature for 16 h and the product was then precipitated by addition of Et_2O. The light brown solid was isolated by filtration, washed with Et_2O and dried under vacuum. Complex $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (**10**) was obtained as an ochre microcrystalline solid after recrystallisation from acetonitrile/Et_2O. Yield: 963 mg (1.11 mmol, 92%). M.p.: 293 °C (dec.). ^1H NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 2.36 (m, 6 H, H-1), 3.43 (s, 2 H, H-3), 3.69 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, H-4/5), 3.81 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, H-4/5), 7.08−7.39 (m, 30 H, aromat. H) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = 31.2 (m, CH_2, C-1), 41.7 (q, C, $^2J_{PC}$ = 7.1 Hz, C-2), 62.4 (s, CH_2, C-5), 73.3 (s, CH_2, C-4), 84.4 (q, CH_2, $^3J_{PC}$ = 9.8 Hz, C-3), 128.4−129.3 (m, aromat. C), 132.0−132.2 (m, aromat. C), 138.8−139.2 (m, aromat. C), 221.3 (m, CO, C-6) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, 295 K): δ = 15.6 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3444 (br), 3057 (w), 2901 (w), 1929 (vs), 1834 (vs), 1481 (m), 1433 (s), 1118 (m), 1082 (m), 999 (w), 831 (m), 737 (m), 697 (s), 623 (m) cm^{-1}. MS (FAB): *m/z* = 866.0 $[M + H]^+$. $C_{46}H_{43}MoO_5P_3$ (864.71): calcd. C 63.90, H 5.01; found C 63.72, H 4.88.



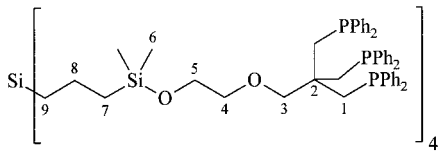
Preparation of $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Rh(COD)]BF_4$ (11a) and of $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3\}Rh(COD)]PF_6$ (11b): A solution of $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (**9**; 766.9 mg, 1.12 mmol) in 15 mL of CH_2Cl_2 was slowly added to a stirred solution of $[Rh(COD)_2]BF_4$ (454.8 mg, 1.12 mmol) in 15 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 14 h, accompanied by a change of colour from red-brown to orange and the product was then precipitated by addition of pentane. The yellow, microcrystalline solid obtained after washing with *n*-pentane and drying in vacuo was the pure complex $[\{HOCH_2CH_2OCH_2C(CH_2PPh_2)_3Rh(COD)\}]BF_4$ (**11a**).

11a: Yield: 1.03 g (1.05 mmol, 94%). M.p.: 165 °C (dec.). ^{1}H NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 2.41−2.46 (m, 4 H, H-7$_{exo}$), 2.60 (s, 6 H, H-1), 2.76−2.82 (m, 4 H, H-7$_{endo}$), 3.65 (s, 2 H, H-3), 3.75 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, H-4/5), 3.84 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, H-4/5), 4.08 (s, 4 H, H-6), 7.10−7.39 (m, 30 H, aromat. H) ppm. ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = 30.8 (m, CH_2, C-1), 33.6 (s, CH_2, C-6), 41.0 (m, C, C-2), 62.3 (s, CH_2, C-5), 73.6 (s, CH_2, C-4), 83.3 (q, CH_2, $^3J_{PC}$ = 11.0 Hz C-3), 84.8 (m, CH, C-7), 128−135 (m, aromat. C) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 295 K): δ = 4.3 (d, $^1J_{RhP}$ = 106.8 Hz) ppm. IR (film): $\tilde{\nu}$ = 3418 (br), 3051 (w), 2933 (w), 2870 (w), 1483 (m), 1433 (s), 1083 (vs), 1054 (s), 830 (m), 744 (m), 696 (s) cm^{-1}. $C_{51}H_{55}BF_4O_2P_3Rh$ (982.63): calcd. C 62.34, H 5.64; found C 62.11, H 5.75.

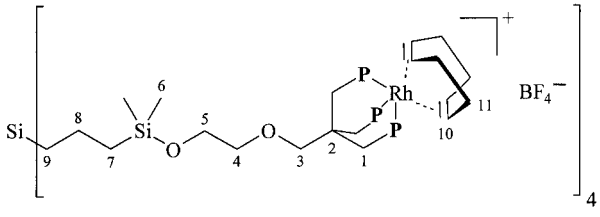


Complex **11b** was obtained by addition of NH_4PF_6 (163 mg, 3.46 mmol) in 5 mL of methanol to a solution of [{$HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$}Rh(COD)]$BF_4$ (**11a**; 170 mg, 0.173 mmol) in 5 mL of methanol. The reaction mixture was stirred at room temperature for 15 h, the precipitate separated by filtration, washed with 2 × 3 mL of methanol and 2 × 5 mL of *n*-pentane and then dried in vacuo. The complex [{$HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$}Rh(COD)]$PF_6$ (**11b**) was isolated as a yellow microcrystalline solid. Yield: 160.3 mg (0.153 mmol, 89%). M.p.: 185 °C (dec.). ^{1}H NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 2.43−2.49 (m, 4 H, H-7$_{exo}$), 2.63 (s, 6 H, H-1), 2.78−2.85 (m, 4 H, H-7$_{endo}$), 3.67 (s, 2 H, H-3), 3.78 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, H-4/5), 3.85 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, H-4/5), 4.11 (s, 4 H, H-6), 7.11−7.42 (m, 30 H, aromat. H) ppm. ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = 31.2 (m, CH_2, C-1), 33.2 (CH_2, C-6), 41.1 (m, C, C-2), 62.5 (CH_2, C-5), 73.7 (CH_2, C-4), 83.5 (q, CH_2, $^3J_{PC}$ = 10.9 Hz C-3), 85.0 (m, CH, C-7), 128−135 (m, aromat. C) ppm. ^{19}F{^{1}H} NMR (376.47 MHz, CD_2Cl_2, 295 K): δ = −73.8 (d, $^1J_{P,F}$ = 715 Hz) ppm. ^{31}P{^{1}H} NMR (121.51 MHz, CD_2Cl_2, 295 K): δ = −143.2 (sept), 5.5 (d, $^1J_{Rh,P}$ = 104.4 Hz) ppm. IR (film): $\tilde{\nu}$ = 3419 (br), 2929 (w), 2862 (w), 2815 (w), 1482 (m), 1434 (s), 1122 (m), 1085 (m), 844 (s), 745 (m), 697 (m) cm^{-1}. $C_{51}H_{55}F_6O_2P_4Rh$ (1040.79): calcd. C 58.86, H 5.33; found C 59.10, H 5.21.

Preparation of G[0]-[OCH_2CH_2Otriphos]$_4$ (13): A 1.6 M solution of *n*BuLi in hexanes (1.40 mL, 2.23 mmol) was added to a stirred solution of $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (**9**; 1.53 mg, 2.23 mmol) in 15 mL of DME at −78 °C. The reaction mixture was warmed to ambient temperature and then stirred for another 30 min. After re-cooling to −78 °C a solution of G[0]-[Cl]$_4$ (**12**; 318.9 mg, 559 μmol) in 10 mL of DME was added dropwise and the reaction mixture was then stirred at ambient temperature for 36 h. After removal of the volatiles, the residue was extracted with toluene and the extract filtered through Celite. Compound G[0]-[OCH_2CH_2Otriphos]$_4$ (**13**) was obtained as a soft amorphous solid after removal of the solvent and drying under vacuum. Yield: 1.66 g (525 μmol, 94%). ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 0.04 (s, 24 H, H-6), 0.50−0.61 (m, 16 H, H-7, 9), 1.22−1.35 (m, 8 H, H-8), 2.55 (s, 24 H, H-1), 2.76 (t, $^3J_{H,H}$ = 4.3 Hz, 8 H, H-4/5), 3.15 (s, 8 H, H-3), 3.21 (t, $^3J_{H,H}$ = 4.3 Hz, 8 H, H-4/5), 7.21−7.36 (m, 120 H, aromat. H) ppm. ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, 295 K): δ = −0.1 (s, CH_3, C-6), 19.3 (s, CH_2, C-7/8/9), 20.0 (s, CH_2, C-7/8/9), 27.3 (s, CH_2, C-7/8/9), 40.4 (m, CH_2, C-1), 44.9 (q, CH_2, $^2J_{PC}$ = 12.4 Hz, C-2), 63.2 (s, CH_2, C-4/5), 73.5 (s, CH_2, C-4/5), 79.5 (q, CH_2, $^3J_{PC}$ = 17.0 Hz, C-3), 129.8−135.2 (m, aromat. C) ppm. ^{29}Si{^{1}H} NMR (79.49 MHz, CD_2Cl_2, 295 K): δ = 0.4 (s, *Si*), 18.7 (s, *Si*−O) ppm. ^{31}P{^{1}H} NMR (121.51 MHz, CD_2Cl_2, 295 K): δ = −26.9 (s) ppm. MS (FAB): *m*/*z* = 3164.3 [M + H]$^+$. $C_{192}H_{216}O_8P_{12}Si_5$ (3163.93): calcd. C 72.89, H 6.88; found C 72.41, H 6.76.

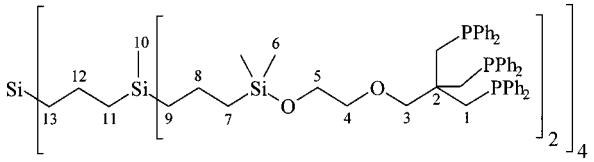


Preparation of G[0]-[OCH_2CH_2OtriphosRh(COD)BF_4]$_4$ (14): A solution of G[0]-[OCH_2CH_2Otriphos]$_4$ (**13**; 305 mg, 96.3 μmol) in 15 mL of CH_2Cl_2 was slowly added with a cannula to a stirred solution of [Rh(COD)$_2$]BF_4 (385 mg, 949 μmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 24 h and the product was then precipitated by addition of *n*-pentane. The precipitate was separated by filtration, washed with 3 × 10 mL of *n*-pentane and then dried in vacuo. The reaction product G[0]-[OCH_2CH_2OtriphosRh(COD)BF_4]$_4$ (**14**) was obtained as a yellow solid. Yield: 369 mg (84.7 μmol, 88%). M.p.: 161 °C (dec.). ^{1}H NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 0.01 (s, 24 H, H-6), 0.49−0.55 (m, 8 H, H-9), 0.60−0.66 (m, 8 H, H-8), 0.86−0.91 (m, 8 H, H-7), 2.43 (br. s, 16 H, H-11$_{exo}$), 2.58 (s, 24 H, H-1), 2.77 (br. s, 16 H, H-11$_{endo}$), 3.61 (s, 8 H, H-3), 3.69 (t, $^3J_{H,H}$ = 4.9 Hz, 8 H, H-4/5), 3.82 (t, $^3J_{H,H}$ = 4.9 Hz, 8 H, H-4/5), 4.09 (br. s, 16 H, H-10), 7.09−7.37 (m, 120 H, aromat. H) ppm. ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = −2.0 (s, CH_3, C-6), 17.3 (s, CH_2, C-7/8/9), 17.9 (s, CH_2, C-7/8/9), 21.1 (s, CH_2, C-7/8/9), 30.8 (m, CH_2, C-1), 33.2 (s, CH_2, C-10), 40.6 (m, C, C-2), 61.9 (s, CH_2, C-5), 73.1 (s, CH_2, C-4), 83.0 (q, $^3J_{P,C}$ = 10.2 Hz, CH_2, C-3), 84.5 (m, CH, C-10), 128.2−135.5 (m, aromat. C) ppm. ^{29}Si{^{1}H} NMR (79.49 MHz, CD_2Cl_2, 295 K): δ = 0.2 (s, *Si*), 17.8 (s, *Si*−O) ppm. ^{31}P{^{1}H} NMR (121.51 MHz, CD_2Cl_2, 295 K): δ = 4.5 (d, $^1J_{Rh,P}$ = 104.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2913 (m), 2870 (m), 1432 (m), 1250 (w), 1084 (s), 1047 (m), 833 (m), 737 (m), 696 (s) cm^{-1}. MS (ESI): *m*/*z* = 1002.2 [(M − 4BF_4)/4]$^+$. $C_{224}H_{264}B_4F_{16}O_8P_{12}Rh_4Si_5$ (4355.50): calcd. C 61.77, H 6.11; found C 61.32, H 6.02.

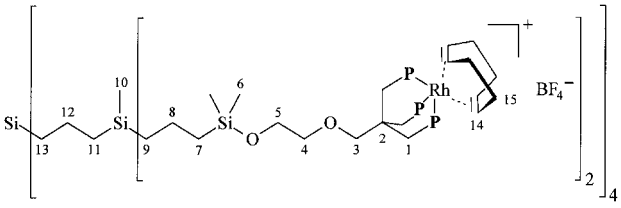


Preparation of G[1]-[OCH_2CH_2Otriphos]$_8$ (16): A 1.6 M solution of *n*BuLi in *n*-hexane (1.77 mL, 2.83 mmol) was added to a solution of $HOCH_2CH_2OCH_2C(CH_2PPh_2)_3$ (**9**; 1.94 g, 2.83 mmol) in 10 mL of DME at −78 °C. The reaction mixture was warmed to room temperature and then subsequently stirred for 30 min. After re-cooling to −78 °C, a solution of G[1]-[Cl]$_8$ (**15**; 514.0 mg, 353 μmol) in 15 mL of DME was added with the aid of a syringe and the reaction mixture was then stirred for 36 h at ambient temperature. After removal of the volatiles, the residue was extracted with toluene and the extract filtered through Celite. After removing the solvent in vacuo, the reaction product G[1]-[OCH_2CH_2Otriphos]$_8$ (**16**) was obtained as an analytically pure soft solid. Yield: 2.13 g (321 μmol, 91%). ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 0.16 (s, 48 H, H-6), 0.20 (s, 12 H, H-10), 0.67−0.77 (m, 48 H, H-7, 9,

11, 13), 1.41−1.51 (m, 24 H, H-8, 12), 2.71 (s, 48 H, H-1), 2.92 (t, $^3J_{H,H}$ = 5.4 Hz, 16 H, H-4/5), 3.29 (s, 16 H, H-3), 3.37 92 (t, $^3J_{H,H}$ = 5.4 Hz, 16 H, H-4/5), 7.33−7.51 (m, 240 H, aromat. H) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 295 K): δ = −1.9 (s, CH_3, C-10), −1.5 (s, CH_3, C-6), 17.7 (s, CH_2, C-7/8/9), 17.8 (s, CH_2, C-11/12/13), 20.8 (s, CH_2, C-7/8/9), 21.8 (s, CH_2, C-7/8/9), 22.3 (s, CH_2, C-11/12/13), 22.9 (s, CH_2, C-11/12/13), 38.1 (m, CH_2, C-1), 42.8 (q, $^2J_{P,C}$ = 12.5 Hz, C, C-2), 61.3 (s, CH_2, C-4/5), 71.5 (s, CH_2, C-4/5), 77.4 (q, $^3J_{P,C}$ = 12.5 Hz, CH_2, C-2), 128.1−140.0 (m, aromat. C) ppm. $^{29}Si\{^1H\}$ NMR (79.49 MHz, CD_2Cl_2, 295 K): δ =0.5 (s, *Si*), 0.9 (s, *Si*Me), 17.6 (s, *Si*Me_2O) ppm. $^{31}P\{^1H\}$ NMR (121.51 MHz, $CDCl_3$, 295 K): δ = −27.3 (s) ppm. MS (MALDI-TOF): *m*/*z* = 6642.9 $[M]^+$. $C_{400}H_{468}O_{16}P_{24}Si_{13}$ (6640.59): calcd. C 72.35, H 7.10; found C 71.83, H 6.93.



Preparation of G[1]-[OCH_2CH_2OtriphosRh(COD)BF_4]$_8$ (17): A solution of G[1]-[OCH_2CH_2Otriphos]$_8$ (**16**; 717.2 mg, 108 μmol) in 15 mL of CH_2Cl_2 was added to a stirred solution of $[Rh(COD)_2]BF_4$ (351 mg, 864 μmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at ambient temperature for 24 h and the product subsequently precipitated by addition of pentane. After centrifugation, the precipitate was washed with 3 × 10 mL of *n*-pentane and then dried in vacuo. The metallodendrimer G[1]-[OCH_2CH_2OtriphosRh(COD)BF_4]$_8$ (**17**) was obtained as a yellow powder. Yield: 945 mg (97.2 μmol, 90%). M.p.: 156C (dec.). ^1H NMR (400.2 MHz, CD_2Cl_2, 295 K): δ = 0.09 (s, 12 H, H-10), 0.20 (s, 48 H, H-6), 0.51−0.67 (m, 48 H, H-7,9,11,13), 1.28−1.38 (m, 24 H, H-8,12), 2.45 (m, 32 H, H-15), 2.60 (s, 48 H, H-1), 2.78 (m, 32 H, H-15), 3.62 (s, 16 H, H-3), 3.70 (m, $^3J_{H,H}$ = 6.1 Hz, 32 H, H-14), 7.08−7.50 (m, 120 H, aromat. H) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = δ = −1.6 (s, CH_3, C-6), 17.9 (s, CH_2, C-7/8/9), 18.2 (s, CH_2, C-11/12/13), 18.6 (s, CH_2, C-7/8/9), 18.6 (s, CH_2, C-11/12/13), 20.9 (s, CH_2, C-7/8/9), 23.2 (s, CH_2, C-11/12/13), 31.2 (m, CH_2, C-1), 33.5 (s, CH_2, C-15), 41.1 (m, C, C-2), 62.3 (s, CH_2, C-5), 73.7 (s, CH_2, C-4), 83.4 (q, $^3J_{P,C}$ = 10.2 Hz, CH_2, C-3), 84.9 (m, CH, C-14), 128.2−135.3 (m, aromat. C) ppm. $^{29}Si\{^1H\}$ NMR (79.49 MHz, CD_2Cl_2, 295 K): δ = 0.5 (s, *Si*Me), 17.6 (s, *Si*Me_2O) ppm. $^{31}P\{^1H\}$ NMR (121.51 MHz, CD_2Cl_2, 295 K): δ = 4.4 (d, $^1J_{Rh,P}$ = 106.8 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2912 (m), 2870 (m), 1482 (m), 1433 (s), 1250 (m), 1084 (s), 1051 (s), 833 (m), 743 (m), 695 (s), cm^{-1}. MS (ESI): *m*/*z* = 1041.3 $[(M - 8\ BF_4)/8]^+$. $C_{464}H_{564}B_8F_{32}O_{16}P_{24}Rh_8Si_{13}$ (9023.73) calcd. C 61.76, H 6.30; found C 61.21, H 6.09.



Catalyst Testing: The catalyst tests were carried out in THF at 1 bar H_2 pressure using 1 mol % of rhodium. The course of the catalytic hydrogenation was monitored by GC/MS spectrometry performed with a Shimadzu GC-17A/GCMS-QP5050A. Column: SGE BPX5, 5% phenyl, polysilyphenylene-siloxane, nonpolar, 30 m, 0.22 mm, carrier gas He. The products were analysed by comparison of the recorded mass spectra and retention times with those of authentic samples. The measured relative ratio of the products was calibrated by comparative measurements with known substance ratios using pure substances.

X-ray Diffraction Study of Compounds 10 and 11b: Suitable crystals of the complexes **10** and **11b** were obtained by layering concentrated solutions of the compounds in dichloromethane with hexanes and allowing slow diffusion at room temperature. The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[32] The structures were solved by direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C−H: 0.95 Å) and isotropic temperature factors [B(H) = 1.3 B_{eqv}(C) Å^2] but not refined. Full least-square refinements on F^2. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were taken from ref.[33] Crystal data and experimental details for the crystals of **10** and **11b** are given in Table 1.

Table 1. X-ray experimental data of compounds **10** and **11b**

	10	**11b**
Formula	$C_{46}H_{43}MoO_5P_3$	$C_{52}H_{57}Cl_2F_6O_2P_4Rh$
Molecular weight	864.7	11125.73
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	11.1938(2)	24.0051(5)
b (Å)	21.3216(4)	23.5811(5)
c (Å)	17.5362(3)	18.9749(5)
β (deg)	97.901(5)	114.302(5)
V (Å^3)	4145.6(1)	9789.3(4)
Z	4	8
$D_{calcd.}$ (g·cm^{-3})	1.39	1.53
*F*000	1784	4624
μ (mm^{-1})	0.477	0.653
Temperature (K)	173	173
Wavelength (Å)	0.71073	0.71073
Radiation	Mo-K_α	Mo-K_α
Theta limits (deg)	2.5/27.50	2.5/27.46
Number of data measd.	17070	18508
Number of data with $I > 3\sigma(I)$	5986	5327
Number of variables	496	614
R	0.036	0.042
Rw	0.046	0.067
GOF	1.058	1.118
Largest peak in final difference (e Å^{-3})	0.743	0.338

CCDC-190059 (**10**) and -190060 (**11b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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