Water-Soluble Tripodal Phosphane Ligands and Their Rhodium Complexes

Philipp Stößel, Hermann A. Mayer*, and Friedrich Auer

Institut für Anorganische Chemie,
Auf der Morgenstelle 18, D-72076 Tübingen, Germany
Fax: (internat.) +49 (0)7071/295306
E-mail: hermann.mayer@uni-tuebingen.de

Received July 24, 1997

Keywords: Tripodal P ligands / Rhodium / Water-soluble complexes / Immobilization / Biphasic hydroformylation

The synthesis of the water-soluble tripodal phosphane ligand *cis,cis*-1,3,5-$(PPh_2)_3$-1,3,5-$[CH_2(OCH_2CH_2)_xOCH_3]C_6H_6$ (x = 30−160) (**5**) has been achieved in a four-step reaction sequence. The alcohol $Mo(CO)_3$[*cis,cis*-1,3,5-$(PPh_2)_3$-1,3,5-$(CH_2OH)_3C_6H_6$] (**1**) is converted to the corresponding alcoholate **2**, which forms the polyethylene glycol derivative **3** in a polyaddition reaction with oxirane. After methylation of the end groups of **3**, the ligand **5** is obtained by a combined photochemical/oxidative demolybdenation reaction. The water-soluble tripodal phosphane **5** and the methoxymethyl functionalized tripodal ligand **6** react with $Rh(PPh_3)_3(CO)H$ to form the water-soluble and water-insoluble rhodium carbonyl hydrido complexes **5a** and **6a**, respectively. The catalytic activity of the rhodium complex **5a** in the hydroformylation of 1-hexene was found to be comparable in a single-phase system (1-hexene/methanol) with that in the biphasic system (1-hexene/water). Only traces of alcohol were found, which demonstrates that the catalyst **5a** displays higher selectivity in hydroformylation than in hydrogenation.

Simplification of process engineering in the field of biphasic homogeneous catalysts has spurred the successful industrial application of these systems.[1] For example, in aqueous biphasic oxo-catalysis, the reactants and the products stay in the organic phase while the catalyst remains in the aqueous phase.[1][2] Such a two-phase system exhibits low catalytic activity in the hydroformylation of higher olefins because of mass transfer limitations that result from the lower solubility of such longer-chain derivatives in water. Water solubility of transition metal complexes is generally achieved by using phosphane ligands that bear polar substituents such as $-SO_3Na$[1b][1f][3] or $-NR_3^+$.[4] It has been suggested that the problems encountered due to mass transfer limitations may be overcome by using phosphane ligands derivatized with polyalkylene glycol ether groups.[5] The inverse temperature dependence of the solubility of polyalkylene oxide oligomers in water[6] leads to a single-phase system at higher temperatures. In this way, at elevated temperature, the catalyst migrates from the aqueous phase into the organic phase and is available to perform homogeneous catalysis. Upon cooling the system, the catalyst migrates back into the aqueous phase and can be recovered by simple phase separation. Ethylene glycol moieties with various chain lengths have been introduced into several phosphane ligand systems.[5][7][8] Polyethylene glycol has also been used as a hydrophilic film in which water-soluble rhodium complexes were dissolved to act as immobilized homogeneous catalysts.[9]

Herein, we report on the synthesis of water-soluble tripodal phosphanes and their rhodium complexes, and present preliminary results of investigations into the catalytic activity of these complexes in the hydroformylation of 1-hexene. Our goal was to functionalize the cyclohexane backbone of the tripodal phosphane ligand *cis,cis*-1,3,5-$(PPh_2)_3C_6H_9$ (tdppcy)[10] with polyethylene glycol groups, in order to solubilize tdppcy-type ligands and their metal complexes in water.

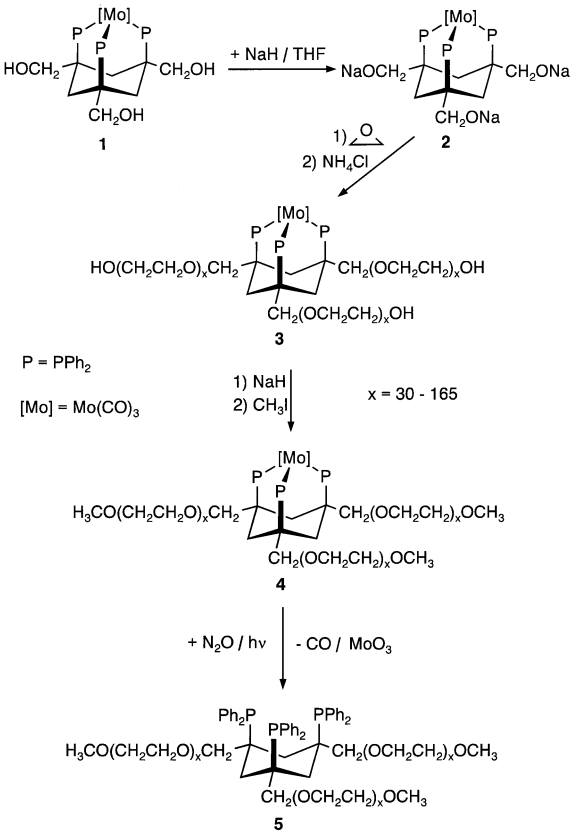
Results and Discussion

In recent studies, it was demonstrated that the $Mo(CO)_3$ fragment serves as an excellent protecting group when modifying tripodal phosphane ligand systems with a cyclohexane backbone.[11] Thus, the thermally stable tris(hydroxymethyl) complex **1**[11] (Scheme 1) is an ideal starting material for the functionalization of the cyclohexane backbone with polyethylene glycol groups under the rather severe conditions of a base-catalyzed oxirane polyaddition reaction. In the first step, the triol **1** is converted into its corresponding trialcoholate **2** with stoichiometric amounts of NaH in hot THF.

Treatment of a solution of in situ generated **2** with oxirane at 170−185°C leads in a polyaddition reaction to the polymer trisodium alcoholate, which is then converted into the alcohol **3** with anhydrous NH_4Cl. The degree of polymerization can be controlled by adjusting the stoichiometric ratio of oxirane to **1** in the range 90:1 and 500:1. In Table 1, the stoichiometric ratios of oxirane to **1** used in typical polyaddition reactions are listed, together with the properties of the resulting homologous polymers of **3**, the calculated average molecular weights M_p, and degrees of polymerization P.

The parameters M_p and P were calculated independently from the mass balance of the reaction, as well as from the relative integrals of the ethoxy and the phenyl proton sig-

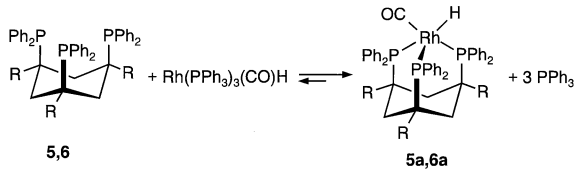
  1434−1948/98/0101−0037 $ 17.50+.50/0



nals in the ^{1}H-NMR spectra.[12] According to Flory, the distribution of the molecular weight of polyethylene glycol ethers follows a Poisson distribution if (i) all the initiating groups are accessible at the beginning of the reaction, (ii) only the reaction of a polymer with a monomer occurs, and (iii) all the reaction steps are kinetically identical.[13] It has been shown that these criteria are met in the case of addition reactions of oxirane to monofunctional alcohols under the conditions of a stoichiometric polyaddition reaction used here.[14] When it is further assumed that the three chains in each molecule grow independently from one another, this leads to a Poisson distribution with an expectation value P for the degree of polymerization of the homologous polymers of **3**. The relation of the degree of polymerization P to the degree of polymerization X of a single chain attached to the cyclohexane backbone is then given by the equation $P = 3\ X$.

The hydroxylic end groups of the homologous polymers of **3** react smoothly with methyl iodide under Williamson ether synthesis conditions to form the corresponding triether complexes **4** (Scheme 1). Polymers **3** and **4** are miscible with water in any ratio when the degree of polymerization is approximately 90 or greater. They are also soluble in polar organic solvents such as THF, CD_2Cl_2, and $CDCl_3$, and swell in diethyl ether. Their properties are comparable with those of polyethylene glycols with similar degrees of polymerization. The local C_{3v} symmetry at the molybdenum centres of **3** and **4** is confirmed by spectroscopic data of the complexes, which are comparable with those of their monomeric counterparts.[11] The IR spectra display two sharp ν(CO) absorptions at 1936 and 1844 cm^{-1} for the $Mo(CO)_3$ fragment besides intense absorptions due to the polyethylene glycol ether chains. The ^{31}P{^{1}H}-NMR spectra show singlets at δ = 46.2 (**3**) and δ = 46.1 (**4**), respectively. In the ^{13}C{^{1}H}-NMR spectra, the ring methylene and the quaternary carbon atoms display complex multiplet patterns as a result of interactions with the phosphorus nuclei. Two multiplets are observed for the axial and equatorial cyclohexane ring protons in the ^{1}H-NMR spectra. Besides the intense absorptions attributable to the ethoxy protons, the hydroxylic end groups of **3** and the methyl end groups of **4** give rise to singlets in the ^{1}H-NMR spectra.

Liberation of the polyethylene glycol functionalized tripodal phosphane ligands **5** can be achieved by irradiating solutions of **4** in the presence of the mild oxidizing agent N_2O (Scheme 2).[11]



R = $CH_2(OCH_2CH_2)_xOCH_3$ (**5**), CH_2OCH_3 (**6**)

The solubility of **4** allows the reaction to be carried out in a mixture of THF and aqueous K_2CO_3, under which conditions the in-situ generated MoO_3 is converted into soluble molybdate, thereby facilitating easy separation. The homologous tripodal phosphane ligands **5** are obtained in high yields as colorless to off-white waxy materials. Their

Table 1. Average molecular weight (M_P), degree of polymerization (P) and properties of **3**[12]

1:C_2H_4O[a]	T[b] [°]	t[c] [h]	M_P[d]	P[d]	M_P[d]	P[e]	consistency	color	melting range [°C]
1:102.9	180	14	4919	91.2	5078	94.8	highly viscous	pale-yellow, clear	–
1:218.4	170	18	8893	181.5	8985	183.6	waxy	yellow, transparent	52–55
1:223.5	170	18	10255	209.1	10355	211.6	brittle	yellow, transparent	54–57
1:267.6	180	14	12206	256.8	12219	257.1	brittle	yellow, transparent	57–61
1:582.9	175	18	22621	493.5	–[f]	–[f]	brittle	pale-brown, transparent	62–65

[a] Ratio of **1** to oxirane. – [b] Reaction temperature. – [c] Reaction time. – [d] Average molecular weight (M_P), degree of polymerization (P), calculated from the mass balance of the reaction. – [e] Average molecular weight (M_P), degree of polymerization (P), calculated from the relative ^{1}H-NMR integrals of ethoxy and phenyl protons. – [f] Average molecular weight (M_P), degree of polymerization (P) cannot be calculated.

solubilities are comparable to those found for the molybdenum complexes **3** and **4**. The singlets in the $^{31}P\{^1H\}$-NMR spectra of the homologous polymers of **5** are shifted 15.5 ppm further upfield compared to those of the molybdenum complexes. The alkane regions of the $^{13}C\{^1H\}$-NMR spectra display triplets ($\delta = 34.18$, $^2J_{PC} = 18.07$ Hz) and doublets of triplets ($\delta = 42.06$, $^1J_{PC} = 21.57$, $^3J_{PC} = 9.35$ Hz), which result from interaction of the three methylene and the three quaternary carbon atoms with the phosphorus nuclei. In addition, the carbon atoms of the methyl end groups, the ethoxy carbon atoms and the exocyclic methylene carbon atoms attached to the cyclohexane ring are each observed as singlets. In contrast to the spectra of the molybdenum complexes **3** and **4**, the *ipso*, *ortho*, and *meta* carbon atoms of the phenyl rings of **5** are resolved into doublets. The non-equivalent ring methylene hydrogen atoms in the ^{1}H-NMR spectra of **5** give rise to doublets of triplets ($\delta = 1.93$, $^2J_{HH} = 13.61$, $^3J_{PH} = 10.13$ Hz) and broad doublets ($\delta = 2.26$, $^2J_{HH} = 13.61$, $^3J_{PH} < 5.0$ Hz).

When $Rh(PPh_3)_3(CO)H$ is treated with equimolar amounts of the tripodal ligands **5** or **6** at elevated temperatures in DMSO, the solutions become deep-red or orange in color, respectively. ^{31}P-NMR spectroscopic investigations confirm that an equilibrium is set up between the tripod ligands **5**, **6**, the complex $Rh(PPh_3)_3(CO)H$, and free PPh_3, leading to carbonyl hydrido species of the general composition $[Rh(\eta^{n,n+1}\text{tripod})(PPh_3)_{2-n}(CO)H]$, $n = 0-2$. The equilibrium can be shifted in favor of the carbonyl hydrido complexes **5a**, **6a** (Scheme 2) by continuously removing PPh_3 in a liquid-liquid extractor using *n*-hexane as the extracting solvent and DMSO as the reaction medium.[15] However, this reaction procedure has the disadvantage that the high boiling point of DMSO does not allow the complete removal of the solvent from the polyethylene glycol functionalized product **5a**. If, on the other hand, stoichiometric amounts of **5** are treated with $Rh(PPh_3)_3(CO)H$ in a melt at 80°C in vacuo, in the absence of solvent, the PPh_3 is removed by sublimation thereby affording **5a** quantitatively. The red-brown homologous polymers of the carbonyl-hydrido complexes **5a** are obtained as water-soluble waxy solids, while the yellow-orange methoxymethyl functionalized complex **6a** is soluble in polar organic solvents.

Apart from the IR spectroscopic data, which are very sensitive to changes in the functional groups at the *ipso*-position of the cyclohexane ring[16], the spectroscopic data of compound **6a** correspond to those of the polyethylene glycol functionalized complex **5a**. Two absorptions [1973, 1902 cm^{-1} (**5a**) and 1950, 1911 cm^{-1} (**6a**)] are observed in the IR spectra of the carbonyl hydrido complexes **5a**, **6a**, which are characteristic of metal hydride and carbonyl groups, respectively. Doublets in the $^{31}P\{^1H\}$-NMR spectra [$\delta = 40.3$, $^1J_{RhP} = 118.4$ Hz (**5a**), $\delta = 43.3$ $^1J_{RhP} = 117.3$ Hz (**6a**)] and doublets of quartets at $\delta = -8.97$ ($^2J_{PH} = 34.7$, $^1J_{RhH} = 12.9$ Hz) and $\delta = -8.28$ ($^2J_{PH} = 34.5$, $^1J_{RhH} = 12.9$ Hz) in the ^{1}H-NMR spectra of **5a** and **6a**, respectively, are what one would expect for dynamic pentacoordinate rhodium complexes (Scheme 2). Thus, only one set of resonances for the ring methylene and quaternary carbon atoms is observed in the $^{13}C\{^1H\}$-NMR spectra of both complexes. In addition, characteristic signals in the expected regions are found for the polyethylene glycol functions and the methoxymethyl groups.

Preliminary studies aimed at demonstrating the catalytic activity of complex **5a** have been conducted. The results are summarized in Table 2. The hydroformylation of 1-hexene catalyzed by **5a** ($P = 209.1$) was performed either in a single homogeneous phase with methanol as solvent, or in a biphasic system (water/1-hexene).

Table 2. Hydroformylation of 1-hexene with complex **5a** ($P = 91$) as catalyst[a]

product	single phase[b] amount [%]	biphase[c] amount [%]
n-hexane	–	–
1-hexene	4.3	3.5
2- and 3-hexene	26.5	20.5
2-methylhexanal	21.8	29.2
n-heptanal	47.3	46.4
2-methylhexanol	0.1	0.1
n-heptanol	–	0.3

[a] Conditions: 119°C, 2 h, 15 bar of CO, 15 bar of H_2, 1:5000 catalyst to substrate ratio. – [b] 1-Hexene/methanol, 10:3 (v/v). – [c] 1-Hexene/water, 10:3 (v/v).

The pressure of the synthesis gas (15 bar of CO, 15 bar of H_2) and the temperature (119°C) were kept constant during the whole reaction period. The organic products were separated from the catalyst by distillation (single phase) or by decantation of the clear, colorless organic phase from the clear, red-brown aqueous phase (biphase). The hydrocarbon- and aqueous phases were analyzed by $^{31}P\{^1H\}$-NMR spectroscopy. No detectable amounts of **5a** were found in the organic phase, whereas the aqueous phase contained **5a** and decomposition products. Both systems showed high activity, since only minor amounts of 1-hexene remained after a reaction time of 2 h. Catalyst **5a** displayed higher selectivities towards hydroformylation than hydrogenation. In neither medium was any hexane detected, and traces of heptanol were only observed in the biphasic system. The degree of conversion to *n*-heptanal was comparable in both systems, while the extent of hydroformylation of the isomerized hexenes was greater in the biphasic medium.

This work was supported by the *Fonds der Chemischen Industrie*, Frankfurt/Main, Germany, and the *University of Tübingen*. We thank *BASF AG* and *DEGUSSA AG* for loans of $Mo(CO)_6$ and $RhCl_3 \cdot 3\ H_2O$, respectively.

Experimental Section

General: All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried under argon; THF was distilled from Na/Ph_2CO; dichloromethane was distilled from CaH_2; methanol was distilled from Mg; water was degassed by the freeze-pump-thaw technique. Oxirane and N_2O were commercial and medical grade, respectively, and were used without further purification. The molybdenum complex **1**[11], the ligand **6**[11] and $Rh(PPh_3)_3(CO)H$[17] were prepared as described

in the literature. – ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker DRX250 spectrometer operating at 250.13, 62.90, and 101.26 MHz, respectively. ^{1}H chemical shifts were referenced to the residual proton peaks of the solvents and are quoted in ppm downfield from TMS. ^{13}C chemical shifts were calibrated against the deuterated solvent multiplet are referenced to TMS. ^{31}P chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. In addition to a ^{13}C{^{1}H}-NMR spectrum, a ^{13}C-DEPT experiment was routinely performed for each compound. Infrared spectra were recorded on a Bruker ISF 48.

Tricarbonyl[cis,cis-1,3,5-tris(diphenylphosphanyl)-1,3,5-tris(hydroxypolyethoxymethyl)cyclohexane]molybdenum (**3**): A steel autoclave fitted with a Teflon inlet was charged with a suspension of 907 mg (1.0 mmol) of **1** and 72 mg (3.0 mmol) of NaH in 120 ml of THF. The suspension was heated to 100°C for 2 h, and then cooled to −20°C, whereupon the desired amount of oxirane was condensed into the autoclave. The reaction mixture was heated at 170°C for 18 h, and was then allowed to cool to room temp. The pale-yellow solution was transferred to a Schlenk tube and the autoclave was rinsed with two 25-ml portions of THF. The combined organic phases were reduced to a volume of 100 ml under reduced pressure so as to remove remaining traces of oxirane. Then, 177 mg (3.3 mmol) of anhydrous NH_4Cl was added. The resulting mixture was heated at 80°C for 2 h, the solvent was removed under reduced pressure at 50−60°C, and the remaining pale-yellow, viscous oil was dissolved in 100 ml of dichloromethane. The salts (NaCl and residual NH_4Cl) were filtered off by passage through a short column of SiO_2 (1 cm) and washed once with 25 ml of dichloromethane. The dichloromethane was removed from the combined solutions under reduced pressure and the pale-yellow residue was dried in vacuo (12 h at 60°C). Yield quantitative. – IR (KBr): $\tilde{\nu}$ = 3487 cm^{-1} ν(OH), 2883 ν(CH_2), 1936, 1844 ν(CO), 1113 ν(OCH_2). – ^{31}P{^{1}H} NMR (CD_3OD): δ = 46.2 (s). – ^{1}H NMR (CD_3OD): δ = 1.77−1.95 (m, 3 H, CHH_e), 2.48−2.81 (m, 3 H, CHH_a), 3.44−3.70 [m, 6 + 4×(*P* − 1) + 12 H, CH_2O(CH_2CH_2O)$_{P-1}$CH_2CH_2OH], 4.56 [br. s, 3 H, $CH_2O(CH_2CH_2O)_{P-1}CH_2CH_2O$*H*], 6.91−7.30 (m, 30 H, C_6H_5). – ^{13}C{^{1}H} NMR (CD_3OD): δ = 30.18−30.82 (m, CH_2), 39.85−40.00 (m, CP), 62.77 [s, $CH_2O(CH_2CH_2O)_{P-1}CH_2$*C*H$_2$OH], 71.29 [s, CH_2O(*C*H$_2$*C*H$_2$O)$_{P-1}$*C*H$_2$CH$_2$OH], 73.45 [s, *C*H$_2$O(CH$_2$CH$_2$O)$_{P-1}$CH$_2$CH$_2$OH], 128.41 (br. s, *meta*-C_6H_5), 129.79 (s, *para*-C_6H_5), 136.85 (br. s, *ortho*-C_6H_5), 138.00−138.51 (m, *ipso*-C_6H_5), 220.66−221.67 (m, CO).

Tricarbonyl[cis,cis-1,3,5-tris(diphenylphosphanyl)-1,3,5-tris(methoxypolyethoxymethyl)cyclohexane]molybdenum (**4**): A mixture of 1.0 mmol of a homologous polymer of **3** and 216 mg (9.0 mmol) of NaH in 150 ml of THF was heated in a sealed Schlenk tube at 80°C for 2 h. After cooling to room temp., 1.1 ml (18.0 mmol) of iodine-free methyl iodide was added dropwise via a syringe. The mixture was heated at 60°C for 16 h under exclusion of light, and was then reduced to a volume of 100 ml under reduced pressure. Subsequently, 481 mg (9.0 mmol) of anhydrous NH_4Cl was added. The resulting mixture was heated at 80°C for 2 h, the solvent was removed under reduced pressure at 50−60°C, and the remaining pale-yellow, viscous oil was dissolved in 100 ml of dichloromethane. The salts (NaCl and residual NH_4Cl) were filtered off by passage through a short column of SiO_2 (1 cm) and washed once with 25 ml of dichloromethane. The dichloromethane was removed from the combined solutions under reduced pressure and the pale-yellow residue was dried in vacuo (16 h at 60°C). Yield 98−100%. – IR (KBr): $\tilde{\nu}$ = 2883 cm^{-1} ν(CH_2), 1936, 1844 ν(CO), 1113 ν(OCH_2). – ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 46.1 (s). – ^{1}H NMR (CD_2Cl_2): δ = 1.77−1.93 (m, 3 H, CHH_e), 2.48−2.81 (m, 3 H, CHH_a), 3.31 [s, 9 H, $CH_2O(CH_2CH_2O)_{P-1}CH_2CH_2OCH_3$], 3.40−3.66 [m, 6 + 4×(*P* − 1) + 12 H, CH_2O(CH_2CH_2O)$_{P-1}$CH_2-CH_2OCH$_3$], 7.04−7.31 (m, 30 H, C_6H_5). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 29.15−29.73 (m, CH_2), 38.85−39.00 (m, CP), 58.77 [s, $CH_2O(CH_2CH_2O)_{P-1}CH_2CH_2OCH_3$], 69.86 [s, CH_2O(*C*H$_2$-*C*H$_2$O)$_{P-1}$*C*H$_2$*C*H$_2OCH_3$], 71.53 [s, *C*H$_2$O(CH$_2CH_2$O)$_{P-1}CH_2$-CH$_2OCH_3$], 127.34 (br. s, *meta*-C_6H_5), 128.84 (s, *para*-C_6H_5), 135.83 (br. m, *ortho*-C_6H_5), 136.84−137.33 (m, *ipso*-C_6H_5).

cis,cis-1,3,5-Tris(diphenylphosphanyl)-1,3,5-tris(methoxypolyethoxymethyl)cyclohexane (**5**): A solution of 0.5 mmol of **4** in 150 ml of THF and 5 ml of an aqueous solution of K_2CO_3 (2.0 M) were placed in a double-walled Duran Schlenk tube and the mixture was degassed by using the freeze-pump-thaw technique. The vigorously stirred solution was cooled to 15°C (cooling solvent: water) and dinitrogen monoxide (N_2O) was added (1.0−1.3 bar). Then, the reaction mixture was irradiated for 1.5 h with light from a TQ 150 W (Original Hanau) high-pressure mercury lamp, which was positioned 5 cm from the Schlenk tube. After 1.5 h, the progress of the reaction was monitored by ^{31}P{^{1}H}-NMR spectroscopy. If small amounts of the starting material were still present, irradiation was continued. After complete conversion, the brown solution was concentrated to a volume of 10 ml under reduced pressure. The brown, viscous residue was dissolved in 100 ml of dichloromethane, the aqueous layer was removed, and the organic layer was dried over 5 g of CaO (2 h). The CaO was then filtered off and washed with two 25-ml portions of dichloromethane. The solvent was removed under reduced pressure and the colorless to off-white, viscous oil was dried in vacuo (12 h at 60°C). Yield 88−92%. – ^{31}P{^{1}H} NMR (CD_3OD): δ = 30.8 (s). – ^{1}H NMR (CD_3OD): δ = 1.93 (dt, $^2J_{HH}$ = 13.61, $^3J_{PH}$ = 10.13 Hz, 3 H, CHH_a), 2.26 (br. d, $^2J_{HH}$ = 13.61, $^3J_{PH}$ < 5.0 Hz, CHH_e), 3.35−3.80 [m, 6 + 4×(*P* − 1) + 12 H, CH_2O(CH_2CH_2O)$_{P-1}$CH_2CH_2OCH$_3$], 3.41 [s, 9 H, $CH_2O(CH_2CH_2O)_{P-1}CH_2CH_2OCH_3$], 7.37−7.54 (m, 30 H, C_6H_5). – ^{13}C{^{1}H} NMR (CD_3OD): δ = 34.18 (t, $^2J_{PC}$ = 18.07 Hz, CH_2), 42.06 (dt, $^1J_{PC}$ = 21.57, $^3J_{PC}$ = 9.35 Hz, CP), 59.08 [s, $CH_2O(CH_2$-$CH_2O)_{P-1}CH_2CH_2OCH_3$], 71.21 [s, CH_2O(*C*H$_2$*C*H$_2$O)$_{P-1}$*C*H$_2$-*C*H$_2OCH_3$], 72.77 [br. s, *C*H$_2$O(CH$_2CH_2$O)$_{P-1}CH_2CH_2OCH_3$], 129.17 (d, $^3J_{PC}$ = 6.73 Hz, *meta*-C_6H_5), 129.90 (br. s, *para*-C_6H_5), 135.68 (d, $^1J_{PC}$ = 21.57 Hz, *ipso*-C_6H_5), 135.76 (d, $^2J_{PC}$ = 21.57 Hz, *ortho*-C_6H_5).

Carbonylhydrido[cis,cis-1,3,5-tris(diphenylphosphanyl)-1,3,5-tris(methoxypolyethoxymethyl)cyclohexane]rhodium(I) (**5a**): A stirred mixture of a homologous polymer of **5** (0.5 mmol) and 459 mg (0.5 mmol) of $Rh(PPh_3)_3(CO)H$ was heated at 90°C for 24 h under reduced pressure (0.1−0.5 mbar). The PPh_3 sublimed during the course of the reaction. The viscous, deep-red to brown, clear reaction mixture was then allowed to cool to room temp. to furnish a quantitative yield of **5a**. – IR (KBr): $\tilde{\nu}$ = 1973 cm^{-1} ν(RhH), 1902 ν(CO). – ^{31}P{^{1}H }NMR ([D$_8$]THF): δ = 40.3 (d, $^2J_{RhP}$ = 118.4 Hz). – ^{1}H NMR ([D$_8$]THF): δ = −8.97 (dq, $^2J_{PH}$ = 34.69 Hz, $^1J_{RhH}$ = 12.87, 1 H, RhH), 1.82−1.96 (m, 3 H, CHH_e), 2.29−3.18 (m, 3 H, CHH_a), 3.29 [s, 9 H, $CH_2O(CH_2CH_2O)_{P-1}$-$CH_2CH_2OCH_3$], 3.35−3.73 [m, 6 + 4×(*P* − 1) + 12 H, CH_2O-(CH_2CH_2O)$_{P-1}$CH_2CH_2OCH$_3$], 6.96−7.47 (m, 30 H, C_6H_5). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 31.54−31.84 (m, CH_2), 40.68 (d, $^2J_{PC}$ = 13.51 Hz, CP), 58.92 [s, $CH_2O(CH_2CH_2O)_{P-1}CH_2CH_2$-$OCH_3$], 71.17 [s, CH_2O(*C*H$_2$*C*H$_2$O)$_{P-1}$*C*H$_2$*C*H$_2OCH_3$], 72.73 [s, *C*H$_2$O(CH$_2CH_2$O)$_{P-1}CH_2CH_2OCH_3$], 127.59−127.72 (m, *meta*-C_6H_5), 129.81 (br. s, *para*-C_6H_5), 136.12−136.36 (m, *ortho*-C_6H_5), 134.38−140.92 (m, *ipso*-C_6H_5).

Carbonylhydrido[cis,cis-1,3,5-tris(diphenylphosphanyl)-1,3,5-tris(methoxymethyl)cyclohexane]rhodium(I) (**6a**): 385 mg (0.5 mmol)

of **6** and 459 mg (0.5 mmol) of $Rh(PPh_3)_3(CO)H$ were dissolved in 100 ml of DMSO at 100°C. After the reaction mixture had cooled to 60°C, it was extracted with *n*-hexane for 4 h in a liquid-liquid extractor. The reaction mixture was maintained at 60°C throughout the course of the extraction. DMSO was removed from the orange reaction mixture under reduced pressure at 60°C. The remaining orange solid was suspended in 100 ml diethyl ether, the orange solid was filtered off (P3), washed with five 25-ml portions of diethyl ether, and dried in vacuo. Yield 401 mg (89%), m.p. 221°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1950 cm^{-1} ν(RhH), 1911 ν(CO). – $^{31}P\{^1H\}$ NMR ([D$_5$]pyridine): δ = 43.3 (d, $^2J_{RhP}$ = 117.3 Hz). – ^1H NMR ([D$_5$]pyridine): δ = −8.28 (dq, $^2J_{PH}$ = 34.53 Hz, $^1J_{RhH}$ = 12.85, 1 H, RhH), 2.07−2.22 (m, 3 H, CH_eH), 2.47−3.28 (m, 3 H, CH_aH), 3.17 (s, 9 H, CH_2OCH_3), 3.86 (br. s, 6 H, CH_2OCH_3), 7.02−7.76 (m, 30 H, C_6H_5). – $^{13}C\{^1H\}$ NMR ([D$_5$]pyridine): δ = 31.08−31.39 (m, CH_2), 40.08−40.29 (m, CP), 58.44 (s, CH_2OCH_3), 77.32−77.48 (m, CH_2OCH_3), 127.63−127.71 (m, *meta*-C_6H_5), 128.44 (br. s, *para*-C_6H_5), 135.81−135.97 (m, *ortho*-C_6H_5), 139.92−140.43 (m, *ipso*-C_6H_5). – MS (FAB), *m/z*: 899.1 [M^+ − H], 871.2 [M^+ − H − CO]. – $C_{49}H_{52}RhO_4P_3$ (900.77): calcd. C 65.34, H 5.82; found C 65.13, H 5.58.

Hydroformylation: The hydroformylation of 1-hexene with **5a** as catalyst was performed in a 100-ml steel autoclave. During the reaction, the temperature and pressure were monitored electronically and were kept constant. The catalyst and the substrate were transferred into the autoclave under an argon atmosphere. After heating the autoclave to the reaction temperature, the gases CO and H_2 were introduced. After separation, the products were analyzed by gas chromatography and the catalyst residues by $^{31}P\{^1H\}$-NMR spectroscopy.

1-Hexene/Methanol (Single Phase): A mixture of 152.8 mg (0.015 mmol, P = 209.1) of **5a**, 9.4 ml (75 mmol) of 1-hexene, and 2.8 ml of methanol was pressurized with 15 bar of CO and 15 bar of H_2 at 119°C. After 2 h, the autoclave was allowed to cool to room temperature. The organic products were separated by vacuum distillation and analyzed by gas chromatography.

1-Hexene/Water (Biphase): A mixture of 152.8 mg (0.015 mmol, P = 209.1) of **5a**, 2.8 ml of water, and 9.4 ml (75 mmol) of 1-hexene was pressurized with 15 bar of CO and 15 bar of H_2 at 119°C. After 2 h, the autoclave was allowed to cool to room temperature. The clear, colorless organic solution was separated by decantation and distilled prior to gas chromatographic analysis.

[1] [1a] J. A. Moulijin, P. W. N. M. van Leeuwen, R. A. van Santen, in *Catalysis*, Elsevier, Amsterdam, **1993**. – [1b] W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem.* **1993**, *105*, 1588−1609; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524−1544. – [1c] B. Cornils, *Angew. Chem.* **1995**, *107*, 1709−1711; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1575−1577. – [1d] G. Papadogianakis, R. A. Sheldon, *New. J. Chem.* **1996**, *20*, 175−185. – [1e] B. Cornils, W. A. Herrmann, R. W. Eckl, *J. Mol. Catal. A.* **1997**, *116*, 27−33. – [1f] F. Joó, A. Kathó, *J. Mol. Catal. A.* **1997**, *116*, 3−26.

[2] M. Beller, B. Cornils, C. D. Frohning, C. W. Kohlpaintner, *J. Mol. Catal. A.* **1995**, *104*, 17−85.

[3] F. Bitterer, O. Herd, A. Heßler, M. Kühnel, K. Rettig, O. Stelzer, W. S. Sheldrick, S. Nagel, N. Rösch, *Inorg. Chem.* **1996**, *35*, 4103−4113.

[4] [4a] A. Heßler, S. Kucken, O. Stelzer, J. Blotevogel-Baltronat, W. S. Sheldrick, *J. Organomet. Chem.* **1995**, *501*, 293−302. – [4b] F. Bitterer, S. Kucken, O. Stelzer, *Chem. Ber.* **1995**, *128*, 275−279.

[5] [5a] Z. Jin, Y. Yan, H. Zuo, B. Fell, *J. Prakt. Chem./Chem. Ztg.* **1996**, *338*, 124−128. – [5b] Z. Jin, X. Zheng, B. Fell, *J. Mol. Catal. A.* **1997**, *116*, 55−58.

[6] H. L. Greenwald, G. L. Brown, *J. Phys. Chem.* **1954**, *58*, 825−828.

[7] [7a] T. Okano, M. Yamamoto, T. Noguchi, H. Konishi, J. Kiji, *Chem. Lett.* **1982**, 977−980. – [7b] Y. Amrani, D. Sinou, *J. Mol. Catal.* **1984**, *24*, 231−233.

[8] T. C. Mitchell, K. Heesche-Wagner, *J. Organomet. Chem.* **1992**, *436*, 43−53.

[9] M. J. Naughton, R. S. Drago, *J. Catal.* **1995**, *155*, 383−389.

[10] H. A. Mayer, H. Otto, H. Kühbauch, R. Fawzi, M. Steimann, *J. Organomet. Chem.* **1994**, *472*, 347−354.

[11] P. Stößel, H. A. Mayer, C. Maichle-Mössmer, R. Fawzi, M. Steimann, *Inorg. Chem.* **1996**, *35*, 5860−5867.

[12] Calculation of M_p and P from: the mass balance of the reaction: $M_p = (W_e \times M_e) / W_e$; $P = M_e \times (W_p - W_e) / M_o \times W_e$ and the relative integrals of the ethoxy and phenyl protons: $M_p = P \times M_o + M_e$; $P = (30\ I_{ethoxy}/4\ I_{phenyl}) - 3/2$; M_p = average of molecular weight [g/mol], P = degree of polymerization, W_e = weight of **1** used [g], W_p = weight of **3** recovered [g], M_e = molecular weight of **1** [g/mol], M_o = molecular weight of oxirane [g/mol], I_{ethoxy} = integral of the ethoxy protons, I_{phenyl} = integral of the phenyl protons.

[13] J. P. Flory, *J. Am. Chem. Soc.* **1940**, *62*, 1561−1565.

[14] J. Gaube, *Chem.-Ing.-Techn.* **1973**, *45*, 979−983.

[15] H. A. Mayer, P. Stößel, R. Fawzi, M. Steimann, *Chem. Ber.* **1995**, *128*, 719−723.

[16] [16a] P. Stößel, W. Heins, H. A. Mayer, R. Fawzi, M. Steimann, *Organometallics* **1996**, *15*, 3393−3403. – [16b] P. Stößel, W. Heins, H. A. Mayer, W. Hörner, T. S. Ertel, H. Bertagnolli, *J. Organomet. Chem.* in press.

[17] N. Ahmad, S. D. Robinson, M. F. Uttley, *J. Chem. Soc., Dalton Trans.* **1972**, 843−847

[97174]